DOCTORAL THESIS

PHENOL OXIDATION CATALYSED BY POLYMER-SUPPORTED METAL COMPLEXES

Presented by:

Ursula Isabel Castro Cevallos

Departament d'Enginyería Química

UNIVERSITAT ROVIRA I VIRGILI

Tarragona, July 2009

Ursula Isabel Castro Cevallos

PHENOL OXIDATION CATALYSED BY POLYMER-SUPPORTED METAL COMPLEXES

DOCTORAL THESIS

Supervised by:

Dr. Christophe Bengoa and
Dr. Azael Fabregat

Departament d'Enginyería Química

UNIVERSITAT ROVIRA I VIRGILI

Tarragona
2009

Universitat Rovira i Virgili
Departament d'Enginyería Química
Escola Técnica Superior d'Enginyería Química

PHENOL OXIDATION CATALYSED BY POLYMER-SUPPORTED METAL COMPLEXES

Presented by:
Ursula Isabel Castro Cevallos

To acquire the grade of:
Doctor

Thesis directed by
Dr. Christophe Bengoa

and co-directed by
Dr. Azael Fabregat

Members of the committee:

Dr. Michele Besson	*Dr. María Eugenia Suárez Ojeda*
Dr. Josep Font	*Dr. Agustí Fortuny*
Dr. Peter A. G. Cormack	*Dr. Jaume Giralt*

Dr. Julián Carrera Muyó

External Reviewers

Dr. Henri Delmas	*Dr. Claude Descorme*

Tarragona, July 2009

UNIVERSITAT
ROVIRA I VIRGILI
ESCOLA TÈCNICA SUPERIOR D'ENGINYERIA QUÍMICA
DEPARTAMENT D'ENGINYERIA QUÍMICA

Avinguda dels Països Catalans, 26
Campus Sescelades 43007
http://www.etseq.urv.es/CREPI

I, Dr. Christophe Bengoa, associate professor in the Department of Chemical Engineering, of the Rovira i Virgili University.

CERTIFY:

That the present study, entitled "Phenol oxidation catalysed by polymer-supported metal complexes", presented by Ursula Isabel Castro Cevallos for the award of the degree of Doctor, has been carried out under my supervision at the Department of Chemical Engineering, and that it fulfils all the requirements to be eligible for the European Doctorate level.

Dr. Christophe Bengoa

Tarragona, July 2009

UNIVERSITAT
ROVIRA I VIRGILI
ESCOLA TÈCNICA SUPERIOR D'ENGINYERIA QUÍMICA
DEPARTAMENT D'ENGINYERIA QUÍMICA

Avinguda dels Països Catalans, 26
Campus Sescelades 43007
Tarragona (Spain)
http://www.etseq.urv.es/CREPI

I, Dr. Azael Fabregat Llangostera, professor in the Department of Chemical Engineering, of the Rovira i Virgili University.

CERTIFY:

That the present study, entitled "Phenol oxidation catalysed by polymer-supported metal complexes", presented by Ursula Isabel Castro Cevallos for the award of the degree of Doctor, has been carried out under my supervision at the Department of Chemical Engineering, and that it fulfils all the requirements to be eligible for the European Doctorate level.

Dr. Azael Fabregat Llangostera

Tarragona, July 2009

To my parents, Elva y Carlos,

to my brother, Carlos,

to my relatives, Ricardo, Lina and Cristina and

to everybody who supported me.

Foreword

The importance of research relies on its concept, which states that research is a human activity based on intellectual application in the investigation of matter. The primary purpose for applied research is discovering, interpreting, and the development of methods and systems for the progress of human knowledge on a wide variety of scientific areas. Moreover the curiosity to know more about something is the human condition that acts as catalyst of the research development.

At undergraduate level, my research experience was limited for economical reasons, however this fact jointly with the continuous pollution increment of my hometown just encouraged my curiosity to know more about the environment, its problems and possible solutions. Then, I found the possibility to develop a research work focused on the treatment of industrial effluents and I knew it would be the best option to fulfil my expectations. After four years, I learned the meaning of the research, the importance of planning and the influence of making decisions. On this way, I believe the research improved my knowledge and strengthened my personality.

Hence I would like to express my thankfulness:

To the Spanish Ministerio de Educación y Ciencia, project “CTM2005-01873” and Ramón y Cajal program of the Spanish Ministerio de Educación y Ciencia, pre-doctoral scholarship, for the financial support.

To the Chemical Reaction Engineering and Process Intensification group members, especially to Dr. Christophe Bengoa and Dr. Josep Font for their constant guidance and help along the progress of this thesis.

To the Department of Pure and Applied Chemistry of the Strathclyde University, Glasgow-Scotland, where I worked out under the supervision of Prof. David C. Sherrington and with the assistance of Dr. Peter Cormack, Rene Mbeleck, Iain Macdonald and Antoni Beltran.

To the Department of Chemical Engineering – INTEMA-CONICET of Universidad Nacional de Mar del Plata, Argentina, where I developed a section of this thesis under the supervision of Dr. Patricia Haure with the help of Dr. Alejandra Ayude, Dr. Paola Massa, Dr. Fernando Ivorra, and a group of technicians.

I would like to thank as well, the people who showed me the importance to work as a group, even more they inspired and encouraged me to continue when things gone wrong, MariE, Alicia, Esther, Ana and Xavier.

On this scientific road I had the opportunity to meet different kind of people with cultural diversity, which highlighted the importance of friendship when you are far from home. Then I would like to thank Marlene, Aurelio and Marelys (Venezuela); Angelica, Tatiana, Eliana and Ronald (Colombia); Iuliana (Romania); Sibel (Turkey); Rita and Filipe (Portugal); Phil and Keilly (England); Daniel (Germany); Santi, Lorena, Amadeu and Juanfran, (Spain); and the ones who were lab, office or university friends.

Isabel Castro Cevallos
Tarragona, July 2009

SUMMARY

The problems of scarcity and the bad use of water have been increased because of the industrial activity, from where effluents with high toxicity and biodegradation difficulties are coming from. For that reason, it is essential to treat these effluents before they are released to the municipal wastewater treatment plants. From the wide variety of chemical processes focussed on the treatment of industrial effluents with high content of organic compounds, it is found the advanced oxidation processes (AOPs), which develop technologies such as the oxidation of organic compounds, e.g. the catalytic wet peroxide oxidation (CWPO). The improvement of this process is based on the variation either of the catalyst or the oxidant source because they directly affect the operational conditions and cost. The use of catalysts in oxidation processes has been extensively studied; moreover, many of these catalysts belong to the oxidant media in liquid phase but they increase the effluent contamination. For this reason the present research work proposes to get advantage of the catalytic activity of homogeneous catalysts, avoiding the metal contamination of the reaction media by the heterogenization of Cu(II) ions over inert matrices, to finally use them as heterogeneous catalysts in the CWPO of phenol. In general, it is recommended to employ the heterogeneous catalysis for the CWPO of phenol because the levels of contamination in the homogeneous catalysis are elevated due to the metal concentration in solution, although in the heterogeneous catalysis the leaching of copper from the polymeric matrix is lower than the previous one but it is an important factor that needs to be controlled. Initially phenol oxidation process was evaluated with the use of a copper salt as homogeneous catalyst, from where it was obtained the highest catalytic capacity of Cu(II) ions at 30ºC and atmospheric pressure. Then, it was studied the catalytic activity of the heterogeneous catalysts with the equivalent Cu(II) content to the homogeneous phase at the same operational conditions. For instance, the polymer-supported-Cu(II) catalysts were employed in the CWPO of phenol, from them it was identified two suitable catalysts: Cu(II) adsorbed onto poly(4-vinylpyridine) with 2% of cross-linking and Cu(II) loaded in poly (DVB-co-VBC) functionalised with imino diacetic acid. Both catalysts demonstrated high catalytic activity without contamination of the effluent by the Cu(II) release. Then, it is concluded that the heterogenization of homogeneous catalysts for the CWPO is an ascertained decision when these catalysts promote high phenol conversion, even more similar to the conversions obtained in homogeneous catalysis.

RESUMEN

Los problemas de escasez y mal uso del agua se han incrementado a causa de la actividad industrial, de la cual provienen los vertidos industriales con alto contenido de compuestos tóxicos y difícilmente biodegradables. Por tanto es indispensable desarrollar el tratamiento de estos efluentes antes de su vertido a las plantas de tratamiento municipal o depuradoras. Dentro de la amplia variedad de procesos químicos para el tratamiento de efluentes industriales con alto contenido de material orgánico, se encuentran los procesos de oxidación avanzada (AOPs), los mismos que desarrollan tecnologías como la oxidación de compuestos orgánicos, e.g. la oxidación húmedo catalítica con peroxido de hidrógeno como oxidante (CWPO). El mejoramiento de éste proceso está basado en la búsqueda de mejores opciones tanto del catalizador como de la fuente oxidante ya que ambos afectan directamente las condiciones y el costo de operación. El uso de catalizadores en procesos de oxidación ha sido extensamente estudiado, mas aún, muchos de estos catalizadores forman parte del medio oxidante en fase liquida pero incrementan la contaminación del efluente. Por lo tanto, el presente trabajo de investigación propone aprovechar la actividad catalítica de catalizadores homogéneos, evitando la contaminación por metal del efluente mediante la heterogeneización de iones de Cu(II) sobre matrices inertes, para luego ser usados como catalizadores heterogéneos en la CWPO del fenol. En general, es recomendable la aplicación de la catálisis heterogénea para este caso porque los niveles de contaminación de la catálisis homogénea son elevados debido al contenido de metal en solución, aunque para la catálisis heterogénea la liberación de cobre de la matriz polimérica es mas baja que el anterior pero es un factor importante que necesita ser controlado. Inicialmente la oxidación del fenol se evaluó con el uso de una sal de cobre como catalizador homogéneo, de donde se obtuvo la máxima capacidad catalítica de los iones de Cu(II) a 30ºC y presión atmosférica. Luego, se evaluó la actividad catalítica de los catalizadores heterogéneos con la carga de Cu(II) equivalente a la evaluación en fase homogénea y a las mismas condiciones operacionales. De hecho, los catalizadores poliméricos soportados con Cu(II) se emplearon en la oxidación húmedo catalítica del fenol, de los cuales se identificaron dos catalizadores: Cu(II) adsorbido sobre poly(4-vinylpyridine) con 2% de entrecruzamiento y Cu(II) soportado en poly (DVB-co-VBC) funcionalizado con ácido aminodiacetico. Ambos catalizadores demostraron alta actividad catalítica sin la adicional contaminación del efluente por liberación de Cu(II). Luego, se

concluye que la heterogeneización de catalizadores homogéneos para la CWPO es una decisión acertada cuando estos catalizadores promueven altas conversiones de fenol, inclusive similares a las conversiones obtenidas en la catálisis homogénea.

INDEX

FIGURE INDEX

TABLE INDEX

CHAPTER I

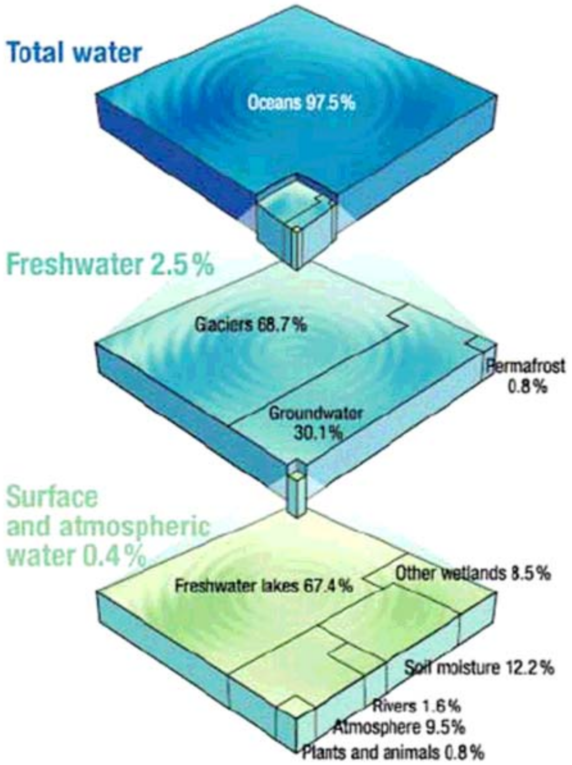
INTRODUCTION

1.1. WATER – IN SILENT CRISIS

Since ancient times, the human beings always had to adapt their lives and activities to the capacity limits of natural sources. The natural and renewable energy sources can be divided into sun, wind, water, minerals and plants. Moreover, about the three-fourths of the earth is water, and its natural cycle is needed to sustain life on earth. Nowadays the water resources are under pressure because of major population change and increased demand. So that, access to reliable data on water availability is extremely important in order to match demand and supply of the water resources, therefore to protect the available sources.

1.1.1. Water availability

The world's water exists normally in different forms and places: in the air, on the surface, below the ground and in the oceans. Earth's approximate water volume is 1 360 000 000 km^3. It can be observed on Figure 1.1 that from a global volume of fresh water about 97,5% of it belongs to the oceans and only 2,5% is fresh water. Then, fresh water is distributed in glaciers 68,2%, ground water 30,1%, permafrost 0,8% and just 0,4% is available on surface and atmospheric water. Moreover, from this 0,4% of fresh water, it exists the distribution in lakes (67,4%), soil moisture (12,2%), atmosphere (9,5%), other wetlands (8,5%), rivers (1,6%) and plants and animals (0,8%), (UNESCO, 2006). In addition, the actual world volume of fresh water in use is 3830 km^3/year, 418 km^3/year of them are in Europe, with 9100 m^3/year per capita (FAO, 2005). Thus, available fresh water sources must be preserved from pollution, as there is already a deficit on water, which can stress the future sustainable development.



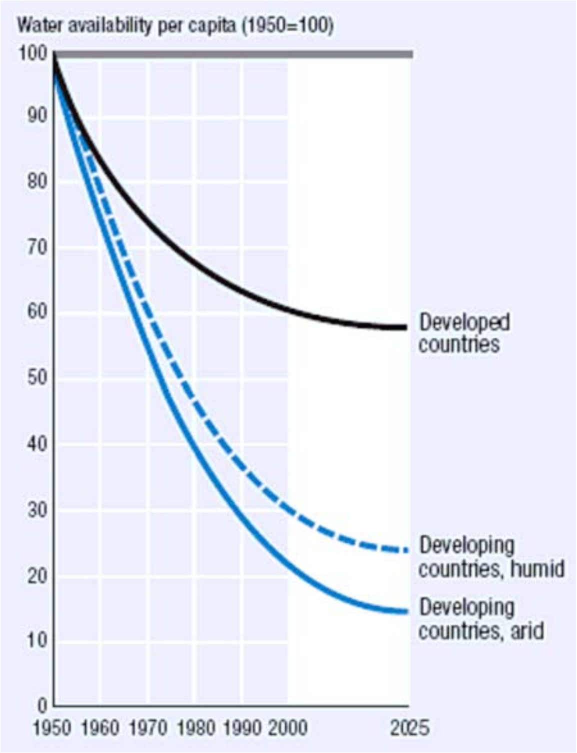
Source: 2nd World Water Development Report

Figure 1.1. Global distribution of the world's water

The nature, variability and availability of water are represented by the earth's hydrological cycle. This cycle is the global mechanism that transfers water from the oceans to the surface, and from the surface, or subsurface environments, and plants to the atmosphere that surrounds our planet. The principal natural component processes of the hydrological cycle are: precipitation, infiltration, runoff, transpiration and evaporation.

Human activities (settlements, industry and agricultural activities) can disturb the components of the natural cycle.

According to the Human Development Report (2006), Figure 1.2, water availability stabilised in developed countries in 1970s, the decline continued in developing countries, especially in arid developing countries. Just how rapid the decline has been becomes apparent when current trends are projected into the future. By 2025 more than 3 milliard people could be living in water-stressed countries and 14 countries will slip from water stress to water scarcity.



Source: Human Developing Report 2006

Figure 1.2. Water availability in decline

1.1.2. Water scarcity

Yet we are far from achieving the sustainable use of water and in many places of the world, people start to face a water crisis. That is, on December 10, 2007 in Oslo-Norway, Al Gore and the Intergovernmental Panel on Climate Change, comprising around 3000 experts, jointly won the Nobel Peace prize for their roles in highlighting climate change (IPCC, 2007). For instance, Thomas Malthus visualised a bleak future for the humanity in 1798. He stated that "population increases in geometric ratio, while the means of subsistence increases in an arithmetic ratio" (Malthus, 1970), however Malthus failed since he did not consider the industrial evolution or the death rate reduction on his projected population explosion. However this essay vision resonates some of the more pessimistic assessments of future scenarios for water availability.

The World Commission on Water has identified the gloomy arithmetic of water as one of the foremost threats to humanity. Therefore, water scarcity defined and will continue promoting life conditions in this century.

Water scarcity can be physical, economic or institutional, and like water itself, it can fluctuate over time and space. But scarcity is both a distorting and limiting lens for viewing water insecurity. It is distorting because much of what passes for scarcity is a policy-induced consequence of mismanaging water resources. And it is limiting because physical availability is only one dimension of water insecurity (Watkins, 2006).

Hydrologists typically assess scarcity by looking at the population-water relation. As noted, the convention is to treat 1700 cubic metres per person per year as the national threshold for meeting water requirements for agriculture, industry, energy and the environment. Availability below 1000 cubic metres is held to represent a state of water scarcity and below 500 cubic metres is absolute scarcity (FAO, 2006).

A lack of water to meet daily needs is a reality for many people around the world and has serious health consequences. Globally, water scarcity already affects four out of every 10 people. The situation is getting worse due to population growth, urbanization and increased domestic and industrial water use. Then, the World Health Organisation (WHO) presents facts about water scarcity that highlight the health consequences of water scarcity, (WHO, 2008). These facts describe that:

- Even in areas with plenty of rainfall or freshwater, water scarcity occurs. Because of the ways in which water is used and distributed, there is not always enough water to fully meet the demands of households, farms, industry, and the environment.
- Water scarcity already affects every continent and four out of every ten people in the world. The situation is getting worse due to population growth, urbanization and the increase in domestic and industrial water use.

- By 2025, nearly 2 billion people will be living in countries or regions with absolute water shortage, where water resources per person fall below the recommended level of 500 cubic metres per year. This is the amount of water a person needs for a healthy and hygienic living.
- Water scarcity forces people to rely on unsafe sources of drinking water. It also means they cannot bathe or clean their clothes or homes properly, increasing in this way the risk of diseases.

1.1.3. Global warming

The combination of both naturally occurring conditions and humanity's actions creates pressure on water resources. Some of the driving forces, which affect water resources, are (UNESCO, 2006):

- Population growth, especially in water-short regions.
- Major demographic changes as people move from rural to urban environments.
- Higher demands for food security and socio-economic well-being.
- Increase competition between users and usages.
- Pollutions from industrial, municipal and agricultural sources.

The Global warming may already be with us, but the much greater warming forecast for the 21st century will produce vast changes in evaporation and precipitation, allied to a more unpredictable hydrological cycle (Watkins, 2006).

1.1.4. Human Impact

As described above, the water resources are in danger, because of human activities. Many of the driving forces, which enhance the global warming, are primarily the results of human actions and include ecosystem and landscape changes, sedimentation, pollution, over-abstraction and climate change. It is important to recognise that each type of landscape change will have their own specific impact, normally directly on ecosystems, then consequently on water resources.

A constantly increased landscape is the pollution, which is caused by humans who have long used air, land and water as sinks into which it is disposed the waste that we generate. Then, these disposal practices leave most wastes inadequately treated, thereby causing pollution. This in turn affects precipitation, surface water and groundwater, as well as degrading ecosystems.

Climate change and hydrological variability of water's distribution and occurrence are natural driving forces that, when combined with the pressures from economic growth and mayor population change, make the sustainable development of the water resources a challenge. For this reason it is important to know the state of the water resources, recognise the impacts and establish a response with strategies and new technologies capable to protect water sources.

1.1.5. Water pollution

The decreasing availability of water and the human impact impulse human beings to control pollutants and contamination of water resources. Sources of water pollution can be found on stationary sources such as sewage treatment plants, factories and ships and non-point sources, more diffusive, includes agricultural run-off, mining activities and paved roads. That is why, the European Pollutant Emission Register (EPER) was established to control and prevent integrated pollution. According to EPER decision, every Member State should report every three years the industrial emissions into air and water. This report should include 50 pollutants with their respective values and comparison with the permissible levels of the EPER decision. Moreover, the threshold values were selected in order to include about the 90% of the emissions of the industries facilities looked at.

The first report was published in 2001, the second reporting year was 2004 and data was provided in June 2006, besides instead to being the third EPER reporting 2007, it was replaced by the European Pollutant Release and Transfer Register (European PRTR). Therefore, the updated and available data is still being 2004 EPER report.

From 50 pollutants considered at the EPER decision, 26 concerned to water. An overview provides the organisation of these pollutants in five groups. The threshold values for each pollutant are defined. If emissions exceed these values, such emissions must be reported.

There are a variety of pollutants on EPER list, although Phenols are taken as representative pollutants of industrial wastewaters because the removal of pollutants from industrial wastewater is one of the most important issues nowadays.

The International Programme in Chemical Safety (IPCS) provides reports called Environmental health criteria documents (EHC). Each EHC makes critical reviews on the chemicals or the combinations of chemicals and physical and biological agents on human health and the environment. Each EHC follows a standard outline, so it is expected to find all the necessary information of pollutants.

1.1.6. Industrial wastewaters

Industrial wastewater has a wide range of pollutant concentrations. These wastes are high in biochemical oxygen demand (BOD), dissolved salts, odour, phenol, and sulphur compounds. For instance, food processing industries, distilleries, and soft drink industries are characterised by very high BOD concentration, suspended solids, dissolved solids, variable pH, and a high level of organic matter. Even though they have low BOD strength, wastewaters from chemical industries are important because they are frequently toxic to aquatic organisms at very low concentrations.

In addition, the biodegradability assessment of industrial wastewater is used on treatment processes to optimise the maximum pollutant removal efficiency. This efficiency is represented by the ration of BOD and chemical oxygen demand (COD), which is widely used to determine the degradability of contaminated water. For instance a BOD/COD ratio of 0,4 is generally considered the cut-off point between biodegradable and difficult to biodegrade waste.

In order to know the levels of possible contamination the United Nations Environment programme on its division of technology, industry and economics reported the typical industrial wastewater pollutant characteristics, Table 1.1 (IETC-UNEP, 2000).

Table 1.1. Typical industrial wastewater pollutant characteristics

Industry	**[BOD] g·L^{-1}**	**[TSS] g·L^{-1}**	**[Oil and Grease] g·L^{-1}**	**Metals present (g·L^{-1})**	**Volatile compounds present (g·L^{-1})**	**Refractory Organics g·L^{-1}**
Oil refinery	0,1-0,3	0,10-0,25	0,2-3,0	Arsenic, Iron	Sulphides	Phenols 0,0-0,27
Tanneries	1-3	4-6	0,05-0,85	Chromium 0,3-1,0	Sulphides, ammonia 0,1-0,2	
Bottling Plant	0,2-6,0	0,0-3,5				
Distillery or sugar factory	0,6-32	0,2-30,0			Ammonia 0,005-0,400	
Food Processing	0,1-7,0	0,03-7,00				Phenols 4-13
Paper factory	0,25-15,00	0,5-100,0		Selenium, Zinc		Phenols 0-0,8
Chemical plant	0,5-2,0	1-170	0-2	Arsenic, Barium, Cadmium		Phenols 0-5

Source: CEP report No. 40, 1998, p9.

1.1.7. Pollutants

The continuous industrial development and the characterisation of the effluents coming from industries highlight the production of refractory compounds like phenols. So that, it is our commitment to evaluate the treatment of refractory compounds to propose feasible technologies and reduce the contamination caused by industrial activity.

1.1.7.1. Refractory compounds – phenols

In accordance with organic chemistry, phenols also called phenolics are a class of chemical compounds consisting of a hydroxyl group (-OH) attached to an aromatic hydrocarbon group. The simplest or representative compound of this group is phenol (C_6H_5OH). Although similar to alcohols, phenols have unique properties and they are not classified as alcohols (since the hydroxyl group is not bonded to a saturated carbon atom). They have relatively higher acidities because the aromatic ring's tight coupling with the oxygen and a relatively loose bond between the oxygen and hydrogen. The polar nature of O-H bond (due to the electronegativity difference of the atoms) results in the formation of hydrogen bonds with other phenol molecules or other H- bonding systems (e.g. water).

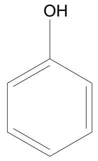
Therefore, phenolic compounds show high melting and boiling points with high solubility in aqueous media.

The abatement of water pollutants like phenols has several alternatives for its treatment. So, a lot of research works have been made due to phenol is strong bactericide even at mild concentrations and frequently is selected as a model compound (Carey, 2001). The election of a specific wastewater treatment will be based on the characteristics of the treated effluent and the expected product. Moreover, phenol-contaminated wastewaters attract particular interest because, aside from being, phenol confers a particularly disagreeable taste and odour to water, even at concentrations below 0,001 mg·L^{-1} (Fortuny et al. 1999). Then the main reason to concern is that prolonged exposures to phenol may be genotoxic for humans and animals. Finally, the necessity to reduce the level of pollutants discharged by industry into municipal sewer systems is urgent because into general pre-treatment regulations phenols are listed within several of the categorical standards.

1.1.7.2. Phenol – As a model compound

Phenol is formed during the natural decomposition of organic materials, although the major part of phenol present in the environment comes from anthropogenic origin. So, in order to identify this model compound, in Table 1.2 is presented the physical and chemical properties of phenol.

Table 1.2. Identity, physical and chemical properties of phenol (WHO, 2008)

Phenol	
Molecular formula	C_6H_5OH
Molar mass	94,11 g·mol^{-1}
Density	1,07 g·cm^{3}
Melting point	40,5 ºC
Boiling point	181,7 ºC
Solubility in water	8,3 g·100 mL^{-1} (20 ºC)

Statistic information according to the Environmental health criteria (EHC), no data are available on atmospheric phenol levels. Background levels are expected to be less than 1 μg·m^3. Either urban or suburban levels vary from 0.1 to 8 μg·m^3, while concentrations in source-dominated areas (industry) were reported to be up to two orders of magnitude higher. Phenol has been detected in rain, surface water and ground water, but data are very scarce. Elevated phenol levels have been reported in sediments and ground waters due to industrial pollution. Occupational exposure to phenol may occur during the production of phenol and its products, during the application of phenolic resins (wood and iron or steel industry) and during a number of other industrial activities. The highest concentration (up to 88 mg·m^3) was reported for workers in the ex-USSR quenching coke with phenol-containing wastewater. Most other reported concentrations did not exceed 19 mg·m^3 (Law 10/1993-Spain and IPCS, 1994).

Additionally, the EPER reports the amounts of Phenol emissions to air, water or WWTP, showing the high quantities of phenol and its compounds to treat. Due to industrial activity increment, it is possible to notice in Table 1.3 that Coke ovens, metal industry and basic organic chemicals are main wastewater producers.

Table 1.3. EPER-report of phenols emission indirect to water.

Emissions direct to WWTP, per industrial activity	Tons /year	%
Coke ovens	823,00	38
Metal industry, Installations for the production of ferrous and nonferrous metals	637,61	29
Basic organic chemicals	510,02	23
Mineral oil and gas refineries	85,45	4
Pharmaceutical products	83,15	4
Others	37,54	2

Then, if high levels of phenols emission continuously increment and treatment in between industrial releases and wastewater treatment plants does not exist, the world will be seriously aware of an imminent environmental contamination because industrial activity will increase pollution, then water resources will be totally cut-off as consequence and human beings will have health problems.

For instance, on Figure 1.3 from data obtained in the UE-EPER-report and its classification per European union countries, Spain directs around 46 tons per year of phenols to water, while has less than 1 ton per year directed to waste water treatment plants. Then with these values, Spain apparently becomes the highest producer of phenols, which are directed to water.

On the other hand, Germany has a high production of phenol as well, but around 38 tons per year are directed to WWTP, giving a possibility to the contaminants to be degraded. Besides, Czech Republic and Austria have high level of phenols production but they direct their phenols wastes to WWTP.

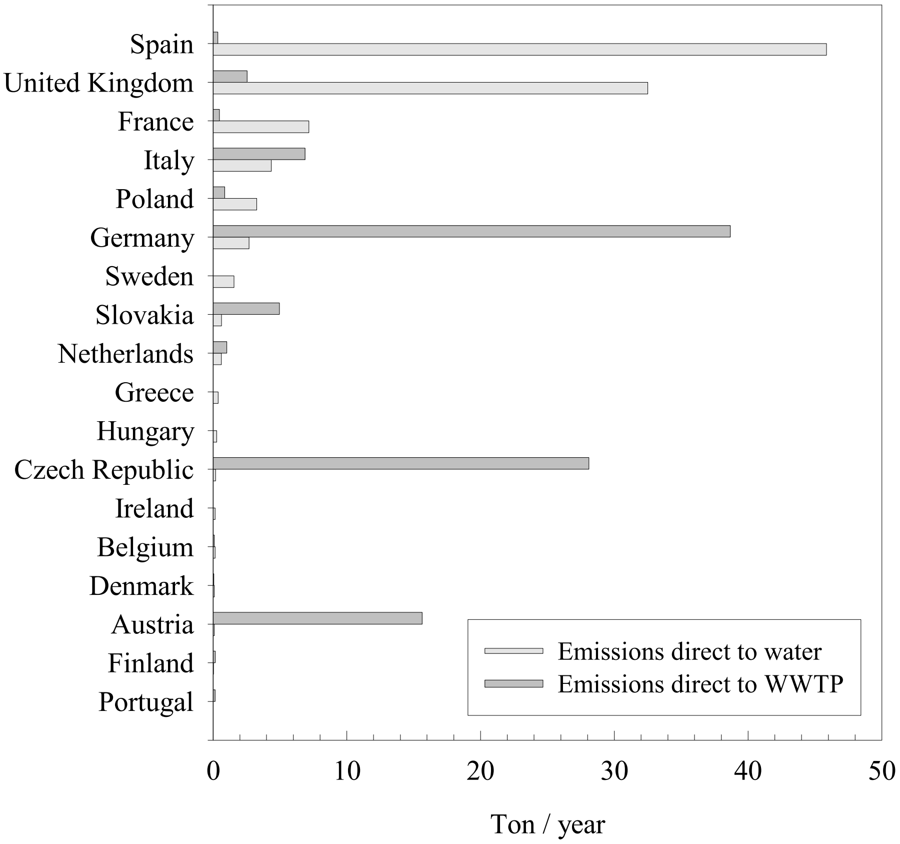


Figure 1.3. EPER-report 2006 of phenols and its emissions direct and indirect to water

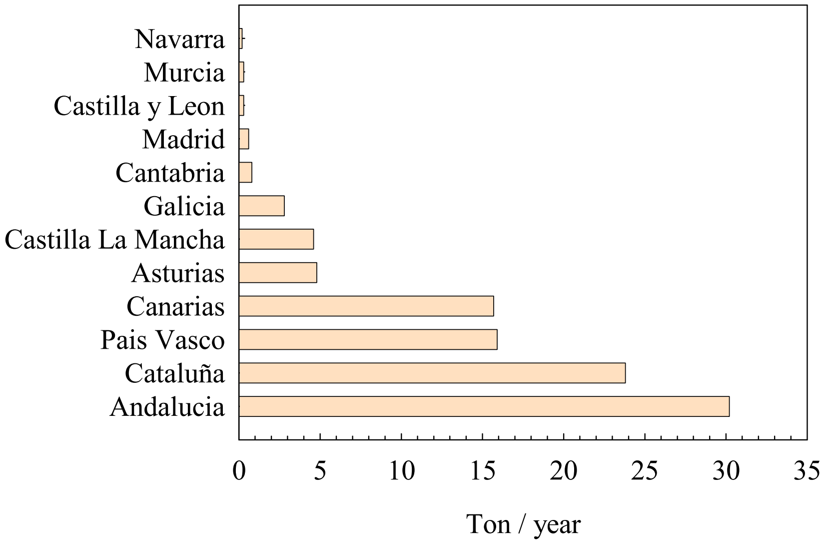


Figure 1.4. Total emissions of phenols and its compounds (Total carbon): Spain communities or regions

Looking deeply, on Figure 1.4 it is shown that Catalonia community has the second highest production of phenols emissions in Spain, around 24 tons per year. So, if it is added to the fact that these emissions are mostly directed to water, it is drawn a critical point of contamination at European levels.

Due to the toxic nature of this compound the Environmental Protection Agency has set a water purification standard of less than 1 part per billion (ppb) of phenol in surface waters. In Italy, in agreement with the recommendations of the European Union, the limit for phenols in potable and mineral waters is 0,5 $\mu g \cdot L^{-1}$ (500 ppb), while the limits for wastewater emissions are 0,5 $mg \cdot L^{-1}$ (0,5 ppm) for surface waters and 1 ppm for the sewerage system (Busca et al., 2008).

The concentration of pollutants on industrial wastewater depends on the industrial source, because when exists high concentration of toxic materials, it is necessary to apply specific processes for their separation, transformation, and further decomposition. Different processes based on biological, physical, chemical and their combinations are available to achieve this goal, however each technique has limitations and different applicability, effectiveness and cost.

1.1.8. Wastewater treatments

Phenols are present in wastewater of various industries such as refineries (6-500 $mg \cdot L^{-1}$), coking operations (28-3900 $mg \cdot L^{-1}$), coal processing (9-6800 $mg \cdot L^{-1}$) and manufacture of petrochemicals 3-1220 $mg \cdot L^{-1}$). Besides, phenols are the main organic constituents present in condensate streams in coal gasification and liquefaction processes. Moreover, other sources of wastes containing phenols are pharmaceutical, plastic, wood products, paint and pulp and paper industries (0,1-1600 $mg \cdot L^{-1}$). It can be mentioned that olive oil mill wastewaters present richness in phenol and polyphenol derivatives, causing a significant problem in the Mediterranean area.

Because of the high concentration of toxic materials in industrial wastewaters, it is necessary to apply specific processes for their separation, transformation, and further decomposition. Different processes based on thermal, biological, physical, chemical and their combinations are available to achieve this goal, however each technique has limitations, different applicability, effectiveness and cost. Besides, the wide variety of technologies for phenol degradation from wastewater was compared (Busca et al., 2008), providing evidence for the strong research efforts carried out in recent time to develop new and improved technologies, moreover some phenol intermediates or derivatives are also water pollutants, so that the different technologies applied to phenol can be performed for its derivatives as well.

1.1.8.1. Physical treatments

Once the effluent characteristics are determined, the pollutants can be separated or isolated from the effluent. Some of these treatments are represented by extraction, adsorption, membrane separation and distillation. For instance, Busca et al. (2008) presented on his review the available technologies for the removal of phenol from fluid streams and Robinson et al., (2005) as well, reported a review of treatment technologies for the treatment of textile effluents. However these processes alone are not able to reduce the toxicity of waste streams at acceptable limits (Parazkeva et al., 2006).

1.1.8.2. Biological treatments

Biological treatments are highly effective for the removal of most contaminants. They operate by the use of microorganisms, which degrade polluted water with contaminated charge and are specially used on effluents with organic content, however if phenol concentration is higher than 200 $mg \cdot L^{-1}$, the substrate becomes bactericide for microorganisms (Vicente, 2003). Despite their success and cost effectiveness, biodegradation processes are inherently slow, do not allow for high degrees of removal, and are not suitable for compounds that are toxic for the microorganisms (Matatov et al., 1998). In addition, it has been studied phenol mineralisation (4-12 $g \cdot L^{-1}$ of phenol loading) employing psychrophilic anaerobic digestion at temperature range between 15-20ºC, where biomass acclimation to phenol had vital importance (Collins et al., 2005).

1.1.8.3. Chemical treatments

Between the chemical processes there are two groups, which are incineration and oxidation processes.

Incineration consists on the complete oxidation of the contaminant at elevated temperatures (800-1000ºC). Although this method is used when the pollutant contains low water content, otherwise the operational costs related to the combustible become excessive (Pariente, 2008).

Chemical treatments of industrial wastewaters are mostly represented by the wet oxidation, which is the oxidation in liquid phase of dissolved pollutants using oxygen as the oxidant source (125-350ºC and 70-230 bar). Chemical oxidation is a popular method since the reactants are inexpensive, for this reason the partial oxidation of organic pollutants to intermediate compounds (amenable to biological treatment) is possible and less expensive to complete oxidation (Matatov et al., 1998). Moreover, chemical oxidation and its classification will be described in deep on Chapter III.

REFERENCES

- Busca, G., Berardinelli, S., Resini, C., Arrighi, L., Technologies for the removal of phenol from fluid streams: A short review of recent developments, J. Hazard. Mater. 160 (2008) 265.
- Carey, F.A., Organic Chemistry 4th Ed., Chapter 24, McGraw Hill Editions (2001).
- Collins, G., Foy, C., McHugh, S., Mahony, T., O'Flaherty, V., Anaerobic biological treatment of phenolic wastewater at 15–18 ºC, Water Research 39 (2005) 1614.
- Environment Agency Pollution inventory data report, Trends and analysis 1998-2001, http://www.environment-agency.gov.uk/research/library/data/34219.aspx
- European Pollutant Emission Register review report, years 2001 and 2004 respectively, http://eper.eea.europa.eu/eper/EPERReview.asp?i=
- Food and Agriculture Organisation of the United Nations (FAO), water resources development and management service, The World Bank (2005).
- Fortuny, A., Bengoa, C., Font, J., Fabregat, A., Bimetallic catalysts for continuous wet catalytic wet air oxidation of phenol, J. Hazard. Mater. B64 (1999) 181.
- Human development report, United Nations Development Program (UNDP), (2006).
- Intergovernmental Panel on climate change – IPCC (2007), http://www.ipcc.ch/
- International Source Book On Environmentally Sound Technologies for Wastewater and Stormwater Management. Newsletter and technical publication of the International Environmental Technology Centre (IETC) – UNEP publications, Osaka (2000).
- Ley sobre vertidos industriales al sistema integral de saneamiento, Servicio de coordinación legislativa y relaciones institucionales, Law 10/1993, October 26th, Spain.
- Malthus, T., An essay on the principle of population, Penguin books, Harmondsworth (1970).

- Matatov-Meytal, Y., Sheintuch, M., Catalytic abatement of water pollutants, Ind. Eng. Chem. Res. 36 (1998) 309.
- Paraskeva, P., Diamadopoulos, E., Technologies for olive mill wastewater (OMW) treatment: a review, J. Chem. Technol. Biotechnol. 81 (2006) 1475.
- Pariente, M.I., Tratamiento de aguas residuales industriales de baja biodegradabilidad mediante un proceso continuo de oxidación húmeda catalítica con peróxido de hidrógeno, Doctoral thesis, Universidad Rey Juan Carlos (2008).
- The International Programme on Chemical Safety (IPCS) Nº 161 (1994), ISBN 92 4 157161 6.
- Second UN World Water Development Report: Water and shared responsibility. UNESCO (2006).
- Vicente J., PhD Thesis: “Wet oxidation of phenol and tiocianate”. Oviedo’s university (2003).
- Watkins, K. Beyond scarcity: Power, poverty and the global water crisis. Human Development Report 2006. New York USA (2006).
- World Health Organization, WHO (2008), http://www.who.int/en/

CHAPTER II

HYPOTHESIS AND OBJECTIVES

2.1. HYPOTHESIS

It is expected that the heterogenization of homogeneous catalysts using polymeric matrices will show activity for the wet oxidation of organic compounds as their homologous homogeneous catalysts, keeping similar activity, and then avoiding the need of any subsequent catalyst recovery step.

2.2. OVERALL OBJECTIVE

Taking into account the expertise background about the catalytic oxidation of phenol at different conditions, it is proposed the use of heterogeneous catalysts, of easy preparation, characterisation and usage, for the oxidation of recalcitrant compounds. Then, it is expected that Cu(II) supported catalysts develop the catalytic oxidation of phenol at soft conditions. After all, the treatment is not seen as an ultimate treatment but has to provide the demanded biodegradability of the model compound to be sent to a municipal Waste Water Treatment Process.

2.3. MAIN OBJECTIVES

- Perform, analyse and evaluate the catalytic oxidation of phenol with Cu(II) ions in homogeneous phase at soft conditions.
- Use different techniques to perform the heterogenization of homogeneous catalysts and characterise the final products.
- Perform, analyse and evaluate the catalytic oxidation of phenol with supported Cu(II) ions in heterogeneous phase at soft conditions.

2.4. SPECIFIC OBJECTIVES

The performance, analysis and evaluation of the catalytic oxidation of phenol in homogeneous phase at soft conditions will be developed as follows:

- Evaluate the influence of temperature, pH, type of oxidant and Cu(II) concentration on the catalytic oxidation of phenol and phenol intermediates formation.
- Determine kinetics and mechanisms from the reaction at homogeneous phase.
- Perform and evaluate the tendencies of phenol intermediates along the reaction time.

The synthesis and characterisation of heterogeneous catalysts will be performed using different ways:

- Adsorption, co-precipitation and polymerisation will be the techniques to prepare heterogeneous catalysts.
- The adsorption method will be used for the heterogeneisation onto polymers like poly(D-glucosamine), poly(4-vinyl pyridine) or cationic resins as supports.
- Synthesise and characterise new Cu-Chitosan composite catalysts based on co-precipitating Cu-Chitosan complexes onto γ-alumina in consecutive impregnation steps.

- Synthesise and characterise Mo(VI) and Cu(II) catalysts using either poly benzyl imidazol, poly(styrene-divinylbenzene) functionalised with 2-aminomethyl-pyridine or poly(styrene-divinylbenzene) functionalised with imino diacetic acid as supports.

The performance, analysis and evaluation of the catalytic oxidation of phenol in heterogeneous phase at soft conditions will be developed as follows:

- Evaluate the influence of temperature, pH and type of oxidant on the catalytic oxidation of phenol using poly (4-vinyl pyridine), chitosan or cationic resins Cu(II) complexes as catalysts. Determine kinetics involved while using catalysts synthesised by adsorption. Then, compare a commercial catalyst with some catalysts obtained by adsorption technique.
- Perform and evaluate the heterogeneous catalytic oxidation of phenol using Cu(II)-chitosan co-precipitated onto γ-alumina.
- Perform and evaluate the heterogeneous catalytic oxidation of phenol using supported-Cu(II) complexes. Determine kinetics and describe evolution of phenol intermediates formation.
- Compare the catalytic activity obtained at homogeneous and heterogeneous phases.

CHAPTER III

BACKGROUND - WET PHENOL OXIDATION AND CATALYSIS

3.1. CHEMICAL TREATMENTS – DESTRUCTION OF PHENOL IN WATER SOLUTION

In Chapter I, it was described that the updated water crisis and the industrial development, with continuous generation of wastewater containing toxic and hazardous organic compounds, increase the environmental pollution. Therefore, it was presented the available processes for industrial effluents treatment, from which chemical processes are very attractive, however it is still being a matter of study the better applicability of these group. For this reason it is important to understand the progress of the chemical treatments for the wet oxidation of phenol.

3.1.1. Wet Air Oxidation and Catalytic Wet Air Oxidation

Wet Air Oxidation (WAO) is an established technology that involves the liquid-phase oxidation of dissolved organics or oxidizable inorganic compounds (Matatov et al., 1998; Debellefontaine et al., 2000; Pintar, 2003), which purpose is to enhance the contact between molecular oxygen and the organic matter. Unfortunately air, as oxygen source, is poorly soluble in water, rather un-reactive at low temperatures; therefore, it needs high temperature (200-350ºC) and pressure (70-230 atm) to be effective (Matatov, et al. 1998), becoming an expensive process (Hancock, 1999; Stüber et al., 2005). Therefore, the use of catalysts improved the reaction and decreased the operational conditions.

Then, the efficiency of WAO can improve considerably by the use of catalysts, either in homogeneous or heterogeneous phase. Then, the WAO with the presence or mediation of catalysts is called catalytic wet air oxidation (CWAO), obtaining higher catalytic efficiency and lower energy requirements (120-250ºC, 5-25 atm) (Hocevar et al., 1999; Arena et al., 2003; Wu et al., 2003) and employing materials, as reported on the review of Levec et al. (2007) or like the activated carbon review reported by Stüber et al. (2005).

3.1.2. Advance Oxidation Processes - Wet Peroxide Oxidation and Catalytic Wet Peroxide Oxidation

Advance oxidation processes (AOPs) have been defined as those aqueous phase oxidation processes, which are based primarily on the participation of the hydroxyl radical mechanism(s) resulting in the destruction of the target pollutant or contaminant compound (Esplugas et al., 2002). AOPs include several techniques, some of which are ozonation, fenton or fenton-like, photocatalysis, and wet oxidation (García et al., 2005), from which ozonation and fenton-like are the most used (Busca et al., 2008).

Ozonation consists in molecular ozone acting directly on the nucleophilic sites and unsaturated bonds of the organic compounds. Ozone decomposition in aqueous solution develops through the formation of •OH radicals. Moreover the increase of pH to the aqueous O_3 solution will thus result into higher rates of •OH radical production (Busca et al., 2008). Ozonation has been widely used for drinking water desinfection-bacterial sterilization, odor and algae, but its application to wastewater treatment is limited due to its high-energy demand (Pera et al., 2004).

Wet oxidation is possible with a cheap oxidant like hydrogen peroxide. Once again the use of a catalyst improves the process but decreases the operational total cost. For instance, the use of hydrogen peroxide needs a promoter in order to generate •OH radicals capable to attack the phenolic ring, that is the case of Fenton reagent (H_2O_2/Fe^{+2}) (Stohs et al., 1995; Bigda, 1995 and Bautista et al., 2008) or Fenton-like reactions (Okawa et al., 2005 and Aguiar et al., 2007).

Fenton reaction is a process based on an electron transfer between H_2O_2 and a metal acting as a homogeneous catalyst. Moreover, Fenton and related reactions are viewed as potentially convenient and economical ways to generate oxidizing species for treating chemical wastes. From a group of bulk oxidants, hydrogen peroxide is inexpensive, safe and easy to handle, and posses no lasting environmental threat since it readily decomposes into water and oxygen (Pignatello et al., 2006). Likewise iron is comparatively inexpensive, safe and environmentally friendly. Researches on application of Fenton chemistry to wastewater started its development in 1894, when Henry J. Fenton reported that H_2O_2 could be activated by Fe(II) salts. Nowadays, the number of scientific articles has increased exponentially and the Fenton reagent group can be divided in two groups called Catalytic Wet Peroxide Oxidation (CWPO) using homogeneous and heterogeneous catalysts.

3.1.2.1. Catalytic Wet Peroxide Oxidation (CWPO) - Homogeneous catalysis

From the group of AOPs, the Wet Peroxide Oxidation (WPO) has a special interest since the use of hydrogen peroxide promotes milder operating conditions (Garcia-Molina et al., 2005 and Pera et al., 2005). Therefore, WPO process is an adaptation from Fenton's reaction that operates around 120ºC, besides it was developed in order to decrease the running cost of wet oxidation, using hydrogen peroxide instead of molecular oxygen. For instance, an advantage for using a liquid oxidizing agent (hydrogen peroxide) is the elimination of the mass transfer problems of WAO process when using molecular oxygen (Debellefontaine et al., 1996). This process was successfully operated however the necessity for recovering the catalyst after reaction was controlled by a precipitation of the transition metal (Fe^{+2}) at pH 9 and filtration (Luck, 1999).

The conventional homogeneous Fenton reaction, which is an attractive treatment method for a large number of hazardous and organic materials, uses Iron (II) salt to produce high generation of hydroxyl radicals. In addition, because of the simplicity of equipment and mild operation conditions it has been postulated as the most economic oxidation alternative. The mechanism of hydrogen peroxide generation has been established in the literature (Pignatello et al., 2006), therefore its catalytic decomposition by means of Fe^{2+} at acid pH (Busca et al., 2008) is expressed on Eq. 3.1.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH\bullet \qquad 3.1$$

For instance, several processes based on different variations of Fenton concept have been developed in past decades with the use of metals like copper or manganese to treat refractory compounds (Luck, 1999). Moreover, the reaction efficiency depends on the acidic pH and stoichiometric excess of hydrogen peroxide. It was reported that peroxide-to-iron molar ratios employed in water treatment typically lie in the range of 100 to 1000 (Pignatello et al., 2006).

3.1.2.2. Catalytic Wet Peroxide Oxidation (CWPO) - Heterogeneous catalysis

The application of conventional homogeneous Fenton reaction gets complications by typical problems such as catalytic separation, regeneration, etc. In order to overcome these problems, it was proposed the use of heterogeneous catalysts on Fenton process, which is also called heterogeneous Fenton (Caudo et al., 2006). Thus, catalyst for the heterogeneous Fenton e.g. solids containing transition metal cations have been synthesised and tested. Therefore, interesting results were reported when using transition metals as active phase and zeolites (Fajerwerg et al., 1996), pillared clays (Luo et al., 2009 and Ramirez et al., 2007) or activated carbon (Zazo et al., 2006) as supports. Although, the main problem of these catalysts comes from the leaching of the active phase when oxidation is carried out at low pH, below 3. On the other hand, it was reported that heterogeneous Fenton oxidation is also suitable for adsorption (Dantas et al., 2006). The adsorption occurs when the catalytic support attracts the toxic compounds to its surface (Araña et al., 2007), where the metal cations have been immobilised. Therefore, the catalytic matrix allows the simultaneous sorption and oxidation of soluble contaminants. For this reason, when working with CWPO it is highly important the development of the catalyst.

a. Catalyst - Fenton like oxidation

Catalyst-based technologies present an optimised activity nowadays, because they intend to achieve clean processes without by-products and eliminating the need for waste disposal (Garin, 2004). For instance, various supports have been tried to anchor metal complexes, but polymer supports provided better control on activity and selectivity of metal complexes (Gupta et al., 2008).

Considering that transition metal complexes are frequently used as homogenous catalysts, it was reported that supported metal complexes showed high catalytic activity and selectivity in comparison to unsupported complexes (Gupta et al., 2008). Additionally, researchers explored the use of iron ions immobilised on a solid support as a strategy to avoid sludge formation and to expand the effective pH range of the Fenton reaction (Moura et al., 2006). On the other hand Cu(II) can also be used with hydrogen peroxide for similar applications in a wider pH range. For instance, the catalytic activity of copper ion in peroxide activation to give hydroxyl radicals is dramatically enhanced by complexation with pyridine, organic acids, amino acids and other chelating acids (Lázaro et al., 2008). Therefore Cu(II) was chosen as catalyst for the catalytic wet peroxide oxidation of phenol.

3.2. CATALYTIC HETEROGENIZATION

In 1959, Nobel Laureate Bruce Merrifield developed the idea of heterogenization of materials into polymeric carriers. He got the brilliant idea to synthesis peptide on an insoluble polymer and he called this process as solid-phase peptide synthesis (SPPS), and then in 1984 he was awarded with the Nobel Prize for his development of the methodology for chemical synthesis on a solid matrix (Stewart, 2007).

It is known that the study of metals complexation is increasing (Ngah et al., 2002 and Mocioi et al., 2007). Then, from the evidence that industrial chemical processes need to meet appropriate environmental standards (Chapter I); it has focused attention on the use of heterogenized reactive species as a potentially important technology, which is under developement since about 1945 (Figure 3.1), for achieving the greening of chemistry (Sherrington, 2001). It is important to notice that for industrial application there are several characteristics that catalysts need (Matatov et al., 1998):

- High activity
- Resistance for poisoning and stability in prolonged use at elevated temperatures
- Mechanical stability and resistance to attrition and
- Physical and chemical stability in various conditions

Therefore, among the variety of heterogenization techniques, ion species could be supported onto polymeric matrices by adsorption, co-precipitation and polymer-support development, which are described below.

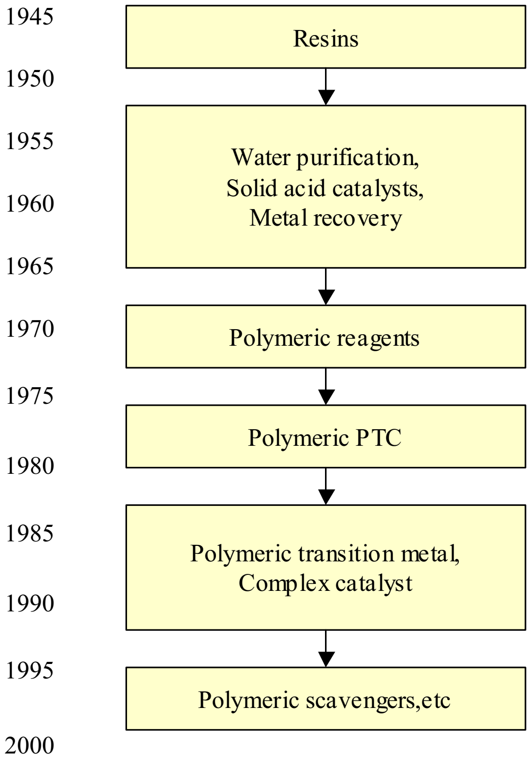


Figure 3.1. Evolutionary use of polymers in supported chemistry

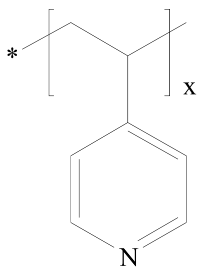
3.2.1. Adsorption

The heterogenisation of homogeneous catalysts by immobilisation improves the easy separation of the catalyst and the simple application on continuous processes (Sheldon et al., 1999 and Barrault et al., 2000). Basically adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid, and becomes bound by physical and/or chemical interactions (Do, 1998). Moreover, the adsorption has become one of the alternative techniques for wastewater treatment laden with Cu(II). Thus, when using heterogeneous catalysts it is important to avoid contamination caused by the catalyst after reaction, therefore the catalytic efficiency will depend on the catalytic activity mostly disturbed by the leaching of the active component (Pestunova et al., 2003). Then, technical adsorption and effectiveness of the process would be the key factor to chose an adsorbent to immobilise Cu(II) ions.

Most of the supports used for the preparation of heterogeneous catalysts are activated carbon, alumina and silica gel (Babel et al., 2003; Pirkanniemi et al., 2002; Wu et al., 2005), however, attention has been paid to the use of polymers as supports because polymers have a rigid and cross-linked polymeric network where catalytic metals can be attached (Saha et al., 2005) preserving their properties as in homogeneous state, thereafter these formed metal-polymers can be in contact with the reaction media without bond brake. For instance, the sorption onto materials of biological origins as synthetic and natural polymers is also recognised as emerging technique (Wan Ngah et al., 2002; Chu, 2002; Li et al., 2003 and Kucherov et al., 2003b). So, Materials like poly (4-vinyl pyridine), poly (D-glucosamine), and cationic resins were chosen as catalytic supports because it is known their adsorption properties, although their application on catalysis have not been totally studied.

3.2.1.1. Poly (4-vinyl pyridine) (PVP)

Immobilisation is often accomplished through the surface modification with functional groups that provides attractive interaction to particles, then functional groups such as pyridyl, amino and carboxyl can be used to immobilise metals. A good example is Poly (4-vinyl pyridine) (PVP) with structural formula presented on Scheme 3.1, which is an attractive polymer for immobilisation of metal ions. This polymer can be very efficient because of the strong affinity of pyridyl group to metals and because of its ability to undergo hydrogen bounding. The three-dimensional and the long chain structure of PVP provide a molecule trap, which is beneficial for maintaining the interaction between Cu(II) and the adsorbent surface (Syukri et al., 2007). Analysis of the behaviour of PVP-Cu(II) complex shows that pyridyl bond group is a function of the metal concentration (Malynych et al., 2002).



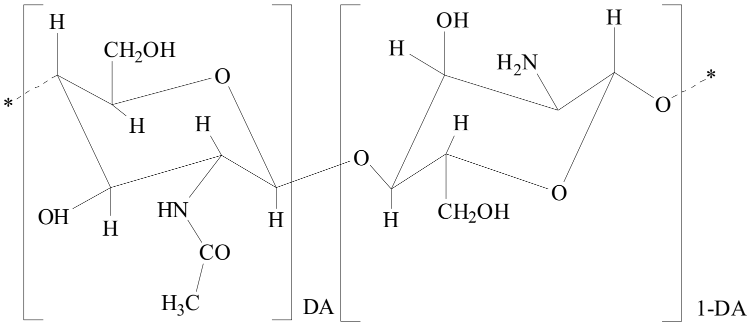
Scheme 3.1. Poly(4-vynilpyridine) structural formula

As reference, PVP has been studied as ligand of metals to form soluble homogeneous complexes (Yamashita et al., 1998), and in 1992, the catalytic facilities of pyridine-metal complexes were reported. The catalytic activity was tested using poly(4-vinyl pyridine-co-N-vinyl pyrrolidone)-Cu(II) complex as catalyst for the catalytic oxidation of hydroquinone, where hydroquinone conversions of 75% were obtained (Yamashita et al., 1993). After all, it is assumed that PVP is a polymer with proved characteristics to become catalyst in coordination with metals, although its adsorption capacity and catalytic activity still being unknown.

3.2.1.2. Poly (D-glucosamine) or Chitosan

Traditionally studies have been used synthetic polymers, but an important effort has been devoted to use biopolymers instead (Dioos et al., 2006). The biopolymer group was based on starch derivatives, gelatin, cellulose, derivatives of chitin and chitosan materials (Guibal, 2005); e.g. it was reported the heterogenization of Fe(II) and Fe(III) ions onto biological origin -crustacean shells- like Chitosan, which is recognised as an emerging technique (Wan Ngah et al., 2002).

Chitosan (Scheme 3.2) is a partially acetylated glucosamine biopolymer resulting from the alkaline deacetylation of Chitin (poly(N-acetyl-β-D-glucosamine)), which is the second most abundant biopolymer in nature close to cellulose. Chitosan is actually a heteropolymer containing both glucosamine and acetylglucosamine units. The presence of amine groups explains its affinity for metal ions.

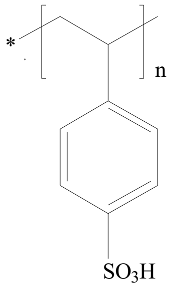


Scheme 3.2. Poly(D-glucosamine) or Chitosan structural formula

In addition, several parameters influence the capacity for adsorbing the metal, such as the source of Chitosan, the degree of Chitosan deacetylation, the nitrogen content of Chitosan, the cross-linking degree, the nature of the metal ion and the solution conditions from the adsorption process (temperature, concentration, pH) (Guibal et al., 1998). The cross-linking occurring on amine groups reduces their pore availability and causes a decrease in the adsorption of the polymer, due to a reduction in the diffusion properties (Dambies et al., 2001). The high proportion of amine functions in this natural polymer promotes binding properties for metal ions such as Cu(II). The porosity of the material has a great relevance and limits the adsorption capacity (Findon et al., 1993). So, based on previous reports (Guibal, 2005), Chitosan has been shown to be a very promising support because it has a strong affinity with metal ions and it does not present diffusion problems while being employed as catalyst.

3.2.1.3. Cationic resins

Once again, the purpose of improving the oxidation efficiency using heterogeneous catalysts can be achieved employing cationic resins, e.g. sulfonic resins (Scheme 3.3). Moreover, the necessity to keep the catalytic metals into the polymeric network after its use in catalytic reactions is still challenging. That is, ion exchange resins are used in many industrial applications involving purification and separations processes where its thermal degradation is a vital characteristic (Simister et al., 2004). For instance, attention was paid to the use of ionic change resins in oxidative pyrolysis, in which several metals including $CuSO_4 \cdot 5H_2O$ were preloaded on the resin, obtaining satisfactory results on the oxidative pyrolysis (Juang et al., 2002). In addition, it was also reported the use of cationic resins with Fe^{+3} for the CWPO of phenol (Liou et al., 2005), Liou et. al. used a macro-porous weak acidic cation exchange resin and after iron adsorption, catalysts presented phenol conversions of 95% at temperatures between 40-80ºC range and atmospheric pressure, further the catalytic activity did not have great changes after use.



Scheme 3.3. Structural formula of sulfonic resins

3.2.2. Co-precipitation technique

For most of the presented studies in the literature (Weng et al., 2007) Chitosan has been used in the form of flakes, powder or hydrogel beads. Although, under reaction conditions like interaction with the oxidant, it has the tendency to agglomerate and become a gel, then it dissolves in acid medium, which is not favourable when the objective is to compare the catalytic activity of metals in homogeneous and heterogeneous phase. To overcome this problem, SiO_2-Chitosan composites have been developed (Kucherov et al., 2003a). However, the catalyst stability will depend on pH and reactants concentration.

Co-precipitation is one of the more successful techniques for synthesising ultra fine ceramic powders. The technique is based on the precipitation of an aqueous solution containing two or more species, which react when putting together and finally precipitate. So, taking into account that transition metal complexes supported on diverse surfaces were used as potentially active catalysts and tested in a variety of reaction systems (Pestunova et al., 2003), an alternative of catalytic heterogenization consists on a continuous precipitation under steady-state conditions, called co-precipitation (Chang et al., 2005). For instance, it was reported similar techniques to prepare heterogeneous catalysts (Massa et al., 2007), where impregnation and precipitation were compared. Additionally, studies of Chitosan as a catalytic support have been published over the last two decades (Guibal, 2004; Guibal, 2005), promoting the idea of a possible use of Chitosan in co-precipitation processes. Therefore, the preparation of catalyst employing the co-precipitation process has been reported and employed on processes like the oxidation of styrene with hydrogen peroxide (Ramanathan et al., 2007). In addition, it was studied the degradation of five model azo textile soluble dyes with hydrogen peroxide in the presence of Cu(II)-Chitosan globules (Sulakova et al., 2007), where the rate of decolourisation was found to be depended on pH, Cu(II) concentration, dye type and hydrogen peroxide concentration.

3.2.3. Polymerisation and metal loading

Taking into account that bonds between support and active component are crucial for the right performance of the catalytic oxidation, so it exists a potential group of catalysts based on polymer-metal complexes, which can develop the catalytic activity. The advantages derived from the use of functionalised macromolecules of easy separation from the oxidation products and possible recycling (Sherrington, 1998; Olason el al., 1999).

The use of polymers such as polybenzimidazole (PBI) resin (Olason et al., 1998) and functionalised poly(styrene-divinylbenzene) resin (Poly(DVB-co-VBC)) (Mbeleck et al., 2007) were studied. In both cases it was demonstrated the effectiveness of each polymer-metal complex as catalysts in different processes. Olason et al. (1998) worked with complexes of Cu, Mn, Fe, Ru and Ti supported on PBI for the heterogeneous catalytic oxidation of cyclohexene. Later, from this group of catalysts PBI-Cu presented conversion of 86% while tert-butylhydroperoxide was the oxidant at inert atmosphere. Moreover, Mbeleck et al. (2007) worked on alkene epoxidation catalysts, such as PBI-Mo and poly(styrene-divinylbenzene) resin functionalised with 2-aminomethyl-pyridine (AMP), followed by Mo(VI) loading (P-AMP-Mo). So that, it was produced a stable and long-live polymer supported complex capable to catalyse up to 10 times an epoxidation reaction, obtaining 100% of conversion at four hours of reaction time.

3.3. LEACHING

One of the problems in heterogeneous catalysis using polymer-metal catalysts is that bonds between metal and ligand are often broken and reformed during catalytic reaction (Cole-Hamilton, 2003). If this happens, the catalyst may break away from the support and become dissolved. This process is called leaching, which leads to loss of activity of the catalyst. In addition, the influence of the organic compounds on copper leaching can be explained considering the radical mechanisms of the oxidation reaction at acid pH. The organic compounds present in the reaction media reduce the copper placed on the polymer. In this step some reduced copper cations can be more easily leached out to the liquid phase. The reduced metal species are quickly oxidised to Cu^{2+} by means of the oxidant source and these cations can rapidly catalyse the oxidation in the liquid phase (Santos et al., 2005), expressed in equations 3.1 and 3.2.

$$RH + Cu^{2+}\text{-Cat} \rightarrow R\bullet + Cu^{+} + Cat + H^{+} \qquad 3.1$$

$$2Cu^{+} + H_2O_2 \rightarrow HO\bullet + OH^{-} + 2Cu^{2+} \qquad 3.2$$

Then, it is important to consider that leaching can be promoted because of the pH decrease due to the acid intermediates formed through the oxidation and because the copper take-off from the surface during the redox reaction of the oxidizable organic compounds. Therefore the use of supported catalysts in the catalytic wet peroxide oxidation has to be considered in order to avoid the deactivation of the catalyst and the transformation of the heterogeneous catalysis into the homogeneous one. Moreover, and increase in wastewater toxicity should be controlled of copper cations concentration in solution. For instance, new technologies have brought metallic pollution levels into the ecosystem, which have been dramatically enlarged since industrial activity has increased. Released industrial wastes with high concentrations of metals like Cu(II) need to be treated by specific and environmentally friendly processes. The elevated metal concentration on industrial effluents represents a green problem because of their high toxicity, separation difficulties and accumulative behaviour in water, e.g. industrial, and mining wastewaters are important sources of metals pollution (Kurniawan et al., 2006).

According the EPER report of 2004, European Union countries inform the state of pollutant emissions. Therefore it is obtained a report with the classification of the activities in which the emission is generated, the amount of pollutant produced and the country in which it is located. For instance the Table 3.1 presents the emissions of copper and its compounds per industrial activity disposed to a wastewater treatment before transferred to the water. It can be appreciated that the installations for the disposal or recovery of industrial waste represent the 7% of copper emissions to wastewater treatment plants.

It is well known that small amounts of copper are essential to many living organisms, including men, however copper has been found to be toxic to certain aquatic organisms at sufficient levels. Besides, excessive exposure to this metal may affect humans, provoking damages on eyes, liver, lungs, digestive system, etc.

Table 3.1. EPER-report of copper emissions indirect to water.

Emissions direct to WWTP, per industrial activity	Tons /year	%
Basic organic chemicals	16,54	46
Others	5,91	17
Metal industry, Installations for the production of ferrous and nonferrous metals	4,84	14
Plants for the pre-treatment of fibres or textiles	3,31	9
Industrial plants for pulp or other fibrous materials and paper	2,61	7
Installation for the disposal or recovery of hazardous waste	2,50	7

Moreover, on Figure 3.2 the data is classified inside Spain area where copper emissions coming from Andalucía and Catalonia communities are the highest. Once again Catalonia, with its continuous industrial increment, becomes an important producer of pollutants like copper.

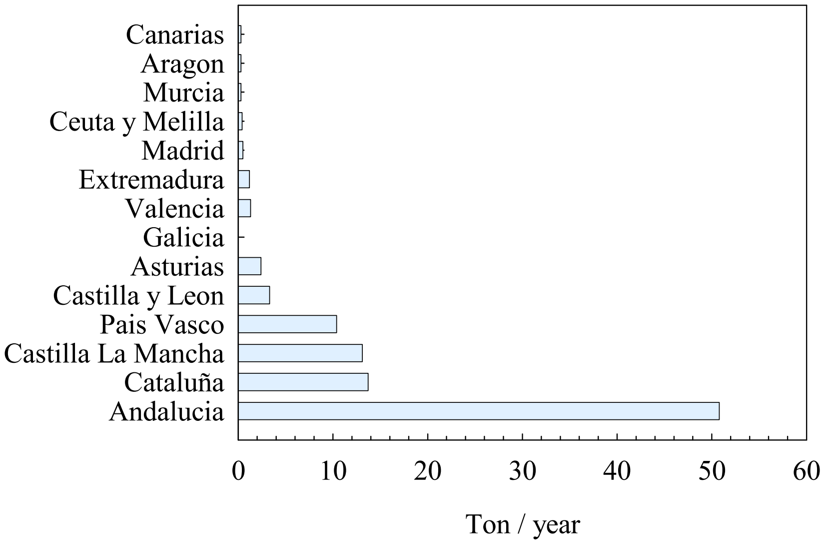


Figure 3.2. Total emissions of copper and its compounds: Spain communities or regions

For this reason, copper is included in surface waters regulations, which implement statutory water quality objectives (EAP, 2001). For this reason it is important to control its use and released. Additionally, average background concentrations of copper in air in rural areas range from 5 to 50 $\mu g \cdot m^3$. Copper levels in seawater of 0.15 $\mu g \cdot L^{-1}$ and in fresh water of 1-20 $\mu g \cdot L^{-1}$ are found in uncontaminated areas. Sediment is an important sink and reservoir for copper (IPCS, 1998). Moreover, Spanish law regulations related to the limits of depuration system inlets allows up to least 5 $mg \cdot L^{-1}$ of copper content (Law 10/1993-Spain), which will limit the permissible metal contamination of the oxidation process. Also, the council of the European communities reported on the directive 76/464EEC the standard regulations related to industrial effluents and they stated that the concentration of copper release by industrial effluents could not exceed 5 $mg \cdot L^{-1}$. Therefore it is necessary to decrease polluted wastewater production by:

(a) the development of new clean technologies,

(b) the improvement on existing technologies performance by new advanced methods for environmental protection and

(c) the building of industrial water-recycling systems without any wastewater discharge. Therefore the improvement of ecologically friendly technologies is pressed by the legislation activity of the governments.

Several methods were developed to remove copper from wastewater such as chemical precipitation, ion exchange, adsorption, electrodeposition or membrane filtration systems (Schmuhl et al., 2001). Although many techniques can be employed for the treatment of wastewater laden with metals, it is important to note that the selection of the most suitable treatment for metal-contaminated wastewater depends on the initial metal concentration, the overall treatment performance compared to other technologies, the plan flexibility and reliability, and the environmental impact as well as economic parameters like operational costs (Kurniawan et al., 2006).

REFERENCES

- Aguiar, A., Ferraz, A., Fe^{3+}- and Cu^{2+}-reduction by phenol derivatives associated with Azure B degradation in Fenton-like reactions, Chemosphere 66 (2007) 947.
- Araña, J., Pulido, E., Rodríguez, V.M., Peña, A., Doña, J.M., Gonzáles, O., Pérez, J., Photocatalytic degradation of phenol and phenolic compounds - Part I. Adsorption and FTIR study, J. Hazard. Mater. 146 (2007) 520.
- Arena, F., Giovenco, R., Torre, T., Venuto, A., Parmaliana A., Activity and resistance to leaching of Cu-based catalysts in the wet oxidation of phenol, Applied catalysis B45 (2003) 51.
- Babel, S., Kurniawan, T.A., Low-cost adsorbents for heavy metals uptake from contaminated water: a review, J. Hazard. Mater. B97 (2003) 219.
- Barrault, J., Abdellaoui, M., Bouchoule, C., Majeste, A., Tatibouet, J.M., Louloudi, A., Papayannakos, N., Gangas, N.H., Catalytic wet peroxide oxidation over mixed (Al–Fe) pillared clays, Appl. Catal. B:27 (2000) L-225.
- Bautista, P., Mohedano, A.F., Casas, J.A., Zazo, J.A., Rodríguez, J.J., An overview of the application of Fenton oxidation to industrial wastewaters treatment, J. Chem. Technol. Biotechnol. 83 (2008) 1323.
- Bigda, R.J., Consider Fenton's chemistry for wastewater treatment, Chem. Eng. Prog. 91 (1995) 62.
- Busca, G., Berardinelli, S., Resini, C., Arrighi, L., Technologies for the removal of phenol from fluid streams: A short review of recent developments, J. Hazard. Mater. 160 (2008) 265.
- Carey, F.A., Organic Chemistry 4th Ed., Chapter 24, McGraw Hill Editions (2001).
- Caudo, S., Centi, G., Genovese, Ch., Perathoner, S., Copper- and iron-pillared clay catalysts for the WHPCO of model and real wastewater streams from olive oil milling production, Top. Catal. 40 (2006) 207.
- Chang, Z., Evans, D.G., Duan, X., Vial, C., Ghanbaja, J., Prevot, V., Roy, M., Forano, C., Synthesis of [$Zn–Al–CO_3$] layered double hydroxides by a coprecipitation method under steady-state conditions, J. Solid State Chem. 178 (2005) 2766.

- Chu, K.H., Removal of copper from aqueous solution by chitosan in prawn shell: adsorption equilibrium and kinetics, J. Hazard. Mater. B90 (2002) 77.
- Cole-Hamilton, D.J., Homogeneous Catalysis—New Approaches to Catalyst Separation, Recovery, and Recycling, Sciencemag 299 (2003) 1702.
- Dantas, T.L.P., Mendoça, V.P., José, H.J., Rodrígues, A.E., Moreira, R.F.P.M., Treatment of textile wastewater by heterogeneous Fenton process using a new composite Fe_2O_3/carbon, Chem. Eng. J. 118 (2006) 78.
- Debellefontaine, H., Chakchouk, M., Foussard, J.N., Tissot, D., Striolo, P., Treatment of organic aqueous wastes: wet air oxidation and wet peroxide oxidation, Environ. Pollution 92 (1996) 155.
- Debellefontaine, H., Foussard J.N., Wet air oxidation for the treatment of industrial wastes. Chemical aspects, reactor design and industrial applications in Europe, Waste management 20 (2000) 15.
- Dioos, B.M.L., Vankelecom, I.F.J., Jacobs, P.A., Aspects of Immobilisation of Catalysts on Polymeric Supports, Adv. Synth. Catal. 348 (2006) 1413.
- Do, D.D., Adsorption analysis: Equilibrium and Kinetics, Vol. 2, Imperial College Press, London 1998.
- Dambies, L., Vincent, T., Domand, A., Guibal, E., Characterization of metal ion interactions with chitosan by X-ray photoelectron spectroscopy, Biomacromolecules 2 (2001) 1198.
- Environment Agency Pollution inventory data report (EAP) , Trends and analysis 1998-2001, http://www.environment-agency.gov.uk/research/library/data
- Esplugas, S., Giménez, J., Contreras, S., Pascual, E., Rodríguez, M., Comparison of different advanced oxidation processes for phenol degradation, Water Research 36 (2002) 1034.
- European Pollutant Emission Register review report (EPER), years 2001 and 2004 respectively, http://eper.eea.europa.eu/eper/EPERReview.asp?i=
- Fajerwerg, K., Debellefontaine, H., Wet oxidation of phenol by hydrogen peroxide using heterogeneous catalysis Fe-ZSM-5: a promising catalyst, Applied Catalysis B: Environ. 10 (1996) L229.

- Findon, A., Mckay, G., Blair, H. S., Transport studies for the sorption of copper ions by chitosan, J. Environ. Sci. Health A28 (1993) 173.
- García-Molina, V., López-Arias, M., Florczyk, M., Chamarro, E., Espulgas, S., Wet peroxide oxidation of chlorophenols, Water Research 39 (2005) 795.
- Garin, F., Environmental Catalysis, Catalysis Today 89 (2004) 255.
- Guibal, E., Milot, C., Tobin, J.M., Metal-Anion Sorption by Chitosan Beads: Equilibrium and Kinetic Studies, Ind. Eng. Chem. Res. 37 (1998) 1454.
- Guibal, E., Interactions of metal ions with chitosan-based sorbents: a review, Sep. Purific. Technol. 38 (2004) 249.
- Guibal, E., Heterogeneous catalysis on chitosan-based materials: a review, Prog. Polym. Sci. 30 (2005) 71.
- Gupta, K.C., Sutar, A.K., Polymer supported catalysts for oxidation of phenol and cyclohexene using hydrogen peroxide as oxidant, J. Molec. Catal. A: Chemical 280 (2008) 173.
- Hancock F.E., Catalytic strategies for industrial water re-use, Catalysis today 53 (1999) 3.
- Hocevar, S., Batista, J., Levec, J., Wet Oxidation of Phenol on $Ce_{1x}Cu_xO_{2x}$ Catalyst, Journal of Catalysis 184 (1999) 39.
- Juang, R., Lee, T., Oxidative pyrolysis of organic ion exchange resins in the presence of metal oxide catalysts, J. Hazard. Mater. B92 (2002) 301.
- Kucherov. A., Finashina, E., Kramareva, N., Rogacheva, V., Zezin, A., Said-Galivev, E., Kustov, L., Comparative study of Cu(II) catalytic sites immobilized onto different polymeric materials, Macromol. Symp. 204 (2003a) 175.
- Kucherov, A.V., Kramareva, N.V., Finashina, E.D., Koklin, A.E., Kustov, L.M., Heterogenized redox catalysts on the basis of the chitosan matrix 1. Copper complexes, J. Molec. Catal. A198 (2003b) 377.
- Kurniawan, T.A., Chan, G.Y.S., Lo, W., Babel, S., Physico–chemical treatment techniques for wastewater laden with heavy metals, Chem. Eng. J. 118 (2006) 83.
- Lázaro, J.M., Leal, M.F., Piehl, L.L., Rubín, E., Buldain, G.Y., Campo, V., Studies on the activation of hydrogen peroxide for color removal in the presence of a new

- Ley sobre vertidos industriales al sistema integral de saneamiento, Servicio de coordinación legislativa y relaciones institucionales, Law 10/1993, October 26th, Spain.
- Levec, J., Pintar, A., Catalytic wet-air oxidation processes: A review, Catal. Today 124 (2007) 172.
- Li, N., Bai, R., Copper adsorption on chitosan–cellulose hydrogel beads: behaviors and mechanisms, Sep. Purif. Technol. 42 (2005) 237.
- Liou, R., Chen, S., Hung, M., Hsu, C., Lai, J., Fe (III) supported on resin as effective catalyst for the heterogeneous oxidation of phenol in aqueous solution, Chemosphere 59 (2005) 117.
- Luck, F., Wet air oxidation: past, present and future, Catalysis Today 53 (1999) 81.
- Luo, M., Bowden, D., Brimblecombe, P., Catalytic property of Fe-Al pillared clay for Fenton oxidation of phenol by H_2O_2, Applied Catalysis B: Environ. 85 (2009) 201.
- Malynich, S., Luzinov, I., Churmanov, G., Poly(Vinyl Pyridine) as a Universal Surface Modifier for Immobilization of Nanoparticles, J. Phys. Chem. 106 (2002) 1280.
- Massa, P., Ivorra, F., Haure, P., Medina, F., Fenoglio, R., Catalytic wet air oxidation of phenol aqueous solutions by 1% Ru/CeO_2–Al_2O_3 catalysts prepared by different methods, Catalysis communications 8 (2007) 424.
- Matatov-Meytal, Y.I., Sheintuch M., Catalytic abatement of water pollutants, Ind. Eng. Chem. Res. 37 (1998) 309.
- Mbeleck, R., Ambroziak, K., Saha B., Sherrington, D.C., Stability and recycling of polymer-supported Mo(VI) alkene epoxidation catalysts, React. Funct. Polym. 67 (2007) 1448.
- Mocioi, M., Albu, A.M., Mateescu, C., Voicu, G., Rusen, E., Marculescu, B., Mutihac, L., New Polymeric Structures Designed for the Removal of Cu(II) Ions from Aqueous Solutions, J. Appl. Pol. Sci. 103 (2007) 1397.

- Moura, M.C.C., Araujo, M.H., Dalmazio, I., Alves, T.M.A., Santos, L.S., Eberlin, M.N., Agusti, R., Lago, R.M., Investigation of reaction mechanisms by electrospray ionization mass spectrometry: characterization of intermediates in the degradation of phenol by a novel iron/magnetite/hydrogen peroxide heterogeneous oxidation system, Rapid commun. Mass Spectrom. 20 (2006) 1859.
- Ngah, W.S., Endud, C.S., Mayanar, R., Removal of copper(II) ions from aqueous solution onto chitosan and cross-linked chitosan beads, React. Funct. Pol. 50 (2002) 181.
- Okawa K., Suzuki, K., Takeshita, T., Nakano, K., Degradation of chemical substances using wet peroxide oxidation under mild conditions, J. Hazard. Mater. B127 (2005) 68.
- Olason G., Sherrington, D.C., Oxidation of cyclohexene by t-butylhydroperoxide and dioxygen catalysed by polybenzimidazole-supported Cu, Mn, Fe, Ru and Ti complexes, React. Funct. Polym., 42 (1999) 163.
- Paraskeva, P., Diamadopoulos, E., Technologies for olive mill wastewater (OMW) treatment: a review, J. Chem. Technol. Biotechnol. 81 (2006) 1475.
- Pera-Titus, M., García-Molina, V., Baños, M.A., Giménez, J., Esplugas, S., Degradation of chlorophenols by means of advanced oxidation processes: a general review, Applied Catal. B: Environ. 47 (2004) 219.
- Pestunova, O.P., Ogorodnikova, O.L., Parmon, V.N., Studies on the phenol wet peroxide oxidation in the presence of solid catalysts, Chem. Sustain. Develop. 11 (2003) 227.
- Pignatello, J.J., Oliveros, E., MacKay, A., Advanced Oxidation Processes for Organic Contaminant Destruction Based on the Fenton Reaction and Related Chemistry, Critical Reviews Environ. Sci. Technol. 36 (2006) 1.
- Pintar, A., Catalytic processes for the purification of drinking water and industrial effluents, Catal. Today 77 (2003) 451.
- Pirkanniemi, K., Sillampää, M., Heterogeneous water phase catalysis as an environmental application: a review, Chemosph. 48 (2002) 1047.
- Ramanathan, R., Sugunan, S., Styrene oxidation by H_2O_2 using Ni–Gd ferrites prepared by co-precipitation method, Catalysis communications 8 (2007) 1521.

- Ramirez, J.H., Costa, C.A., Madeira, L.M., Mata, G., Vicente, M.A., Rojas, M.L., Lopez, A.J., Martín, R.M., Fenton-like oxidation of Orange II solutions using heterogeneous catalysts based on saponite clay, Appl. Catal. E: Environ. 71 (2007) 44.
- Saha, B., Streat, M., Adsorption of Trace Heavy Metals: Application of Surface Complexation Theory to a Macroporous Polymer and a Weakly Acidic Ion-Exchange Resin, Ind. Eng. Chem. Res. 44 (2005) 8671.
- Santos, A., Yustos, P., Quintanilla, A., Ruiz, G., García-Ochoa, G., Study of the copper leaching in the wet oxidation of phenol with CuO-based catalysts: Causes and effects, Appl. Catal. B: Environ. 61 (2005) 323.
- Schmuhl, R., Krieg, H.M., Keizer, K., Adsorption of Cu(II) and Cr(VI) ions by chitosan: Kinetics and equilibrium studies, Water S.A. 27 (2001) 1.
- Sheldon, R.A., Downing, R.S., Heterogeneous catalytic transformations for environmentally friendly production, Appl. Catal. A189 (1999) 163.
- Sherrington, D.C., Preparation, structure and morphology of polymer supports, Chem. Comm. (1998) 2275.
- Sherrington, D.C., Polymer-Supported Reagents, Catalysts, and Sorbents: Evolution and Exploitation—A Personalized View, J. Polym. Sci. A:Polym. Chemist. 39 (2001) 2364.
- Simister, C., Caron, F., Geyde, R., Determination of the thermal degradation rate of polystyrene-divinyl benzene ion exchange resins in ultra-pure water at ambient and service temperature, J. Radionalytic. Nucl. Chem. 261 (2004) 523.
- Stewart, J.M., Bradykinin in Solid-phase Peptide Synthesis, Inter. J. Pepti. Res. Therapeut. 13 (2007) 3.
- Stohs, S.J., Bagchi, D., Oxidative mechanisms in the toxicity of metal ions, Free Radical Biology and Medicine 18 (1995) 321.
- Stüber, F., Font, J., Fortuny, A., Bengoa, C., Eftaxias, A., Fabregat, A., Carbon materials and catalytic wet air oxidation of organic pollutants in wastewater, Topics in catalysis 33 (2005) 1.

- Sulakova, R., Hrdina, R., Soares, G.M.B., Oxidation of azo textile soluble dyes with hydrogen peroxide in the presence of Cu(II)-chitosan heterogeneous catalysts, Dyes and Pigments 73 (2007) 19.
- Syukri, S., Sun, W., Kühn, F.E., Immobilization of ruthenium(II) salen complexes on poly(4-vinylpyridine) and their application in catalytic aldehyde olefination, Tetrahedrom letters 48 (2007) 1613.
- The International Programme on Chemical Safety (IPCS) Nº 200 (1998), ISBN 92 4 157200 0.
- Vicente J., PhD Thesis: “Wet oxidation of phenol and tiocianate”. Oviedo’s university (2003).
- Wan Ngah, W.S., Endud, C.S., Mayanar, R., Adsorption of Cu(II) ions in aqueous solution using chitosan beads, chitosan–GLA beads and chitosan–alginate beads, React. Funct. Polym. 50 (2002) 181.
- Weng, Ch., Tsai, Ch., Chu, S., Sharma, Y.C., Adsorption characteristics of copper(II) onto spent activated clay, Separation and Purific. Technol. 54 (2007) 187.
- Wu, Q., Hu, X., Yue, P., Kinetics study on catalytic wet air oxidation of phenol, Chem. Eng. Sci. 58 (2003) 923.
- Wu, Q., Hu, X., Yue, P., Kinetics Study on Heterogeneous Catalytic Wet Air Oxidation of Phenol using Copper/Activated Carbon Catalyst, Inter. J. Chem. React. Eng. 3 (2005) A29.
- Yamashita, K., Kanamori, T., Nango, M., Tsuda, K., The oxidation of hydroquinone catalysed by Poly(4-vinylpyridine-co-N-Vinylpyrrolidone)-Cu(II) complexes: effect of the copolymer composition distribution on the catalytic activity, Polym. 34 (1993) 2638.
- Yamashita, K., Okada, I., Suzuki, Y., Tsuda, K., Makromol. Poly(4-vinylpyridine-co-N-Vinylpyrrolidone)-Cu(II) complex, highly active polymeric complex catalyst for hydroquinone oxidation, Chem. Rapid communication 9 (1998) 705.
- Zazo, J. A., Casas, J. A., Mohedano, A.F., Rodríguez. J.J., Catalytic wet peroxide oxidation of phenol with a Fe/active carbon catalyst, Applied Catalysis B: Environ. 65 (2006) 261.

CHAPTER IV

HOMOGENEOUS CATALYTIC OXIDATION

In order to understand the behaviour of Cu(II) ions as homogeneous catalyst, the catalytic wet oxidation of phenol was carried out using air or hydrogen peroxide as oxidants.

4.1. EXPERIMENTAL

4.1.1. Materials

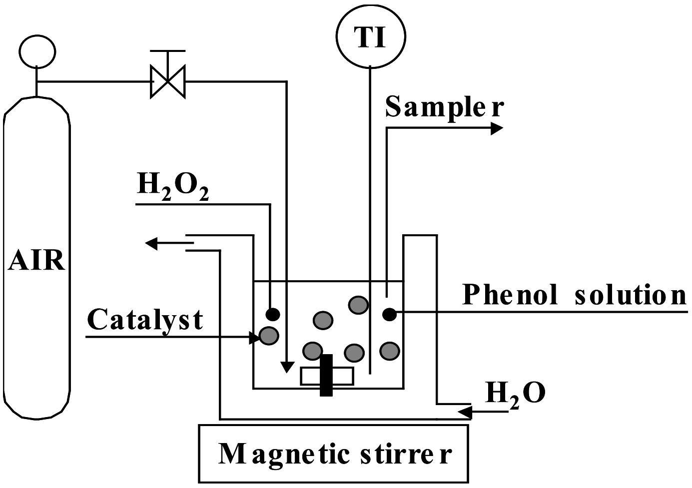
Copper sulphate pentahydrated ($CuSO_4·5H_2O$) was obtained from Sigma-Aldrich. Phenol crystallised was purchased from Panreac with purity higher than 99%. Catechol (99%), Hydroquinone (99%) and Formic acid (97%) were provided by Sigma-Aldrich. Fumaric acid (99,5%) was purchased from Fluka. Malonic (99%) and Succinic (99,5%) acids were obtained from Merck-Schuchardt. Hydrogen peroxide 30% w/v (100 vol.) was provided by Panreac. Millipore milli-Q deionised water was used to prepare all solutions.

4.1.2. Methods

The oxidation tests were conducted at low temperature in a stirred tank reactor of 200 mL operated batch wise. Scheme 4.1 presents the oxidation set-up. The initial phenol concentration was always 1 $g{\cdot}L^{-1}$ and oxidation was carried out at the temperature range 30-50ºC and atmospheric pressure. Either air or hydrogen peroxide were used as oxidants. When air was the oxidant, saturated air was bubbled through the reactor with a flow of 85 $mL{\cdot}min^{-1}$. When H_2O_2 was the oxidant, three different phenol/peroxide ($Ph:H_2O_2$) molar rates (1:1, 1:5 and the stoichiometric 1:14) were used following the reaction of phenol oxidation, represented as follows:

$$C_6H_5OH + 14\ H_2O_2 \rightarrow 6\ CO_2 + 17\ H_2O$$

The mass of the added catalyst for the homogeneous catalytic oxidation was calculated to provide Cu(II) concentrations of 5, 10, 50 and 200 $mg{\cdot}L^{-1}$. Samples were analysed immediately after taken apart from the reaction media because there was not an acquired scavenger for the present case of phenol oxidation.



Scheme 4.1. Catalytic Oxidation set-up of a batch stirred tank reactor.

The pH was monitored along the reaction time using an electronic pHmeter. Reaction progress was monitored withdrawing 1 mL samples at along the 120 min from starting. Then, they were analysed immediately by HPLC to determine the remaining concentration of phenol. Also, the total organic carbon (TOC) at 120 min was determined.

4.1.3. Analytical procedure

Phenol conversion was calculated by measuring the phenol concentration using HPLC (Agilent Technologies, model 1100) with a C18 reverse phase column (Agilent Technologies, Hypersil ODS). The analyses were performed using a mobile phase with a gradient mixture of methanol and ultra pure water (Milli-Q water, Millipore) from 0/100 V/V to 40/60 V/V. The flow rate increased from 0,6 at the fifth minute to 1,0 mL·min^{-1} at the seventh minute. The pH of the water was adjusted at 1.4 with sulphuric acid (H_2SO_4). The detection was performed by UV absorbance at a wavelength of 254 nm. Automatic injector took volumes of 20 µL per sample. A calibration curve of phenol was made using aqueous samples of known concentration. The identification of intermediates was made with HPLC analyser, where the information of aqueous samples of each intermediate was initially saved. Hence, an example of one chromatograph is presented on the appendix section.

Total organic carbon (TOC) values were obtained using a TOC Analyser (Analytic Jena, model NC 2100). Samples were acidified with 50 mL HCl 2N, then bubbled with synthetic air for 3 minutes to eliminate the inorganic carbon content and then injected.

4.2. RESULTS AND DISCUSSION

4.2.1. AIR AS OXIDANT

Preliminary experiments of phenol oxidation were carried out at homogeneous conditions using air as oxidant with a flow of 85 mL·min^{-1}. The first oxidation attempt tested two Cu(II) salts (chloride and sulphate) at Ph:Cu(II) molar ratio of 1:1. The oxidation was carried out for the period of 2 hours at 30ºC and under atmospheric pressure (Figure 4.1). A qualitative evaluation did not show important colour changes that represent the formation of quinones along the reaction time. Quinones were used as indicators of the oxidation occurrence because they are the first products formed from phenol oxidation and because they are physically characterised by a dark brown colour. The achieved phenol conversion at 30ºC was less than 4%, which was not satisfactory at all, also the difference between each Cu(II) salt was not significant. So, in order to enhance the reaction performance, the experiments were conducted with a Ph:Cu(II) molar ratio of 1:10 at 50ºC for a period of 24 hours. The intend of using more severe conditions just reported up to 20% of phenol conversion, although the reaction was not sufficiently improved even with 1:10 molar ratio of Ph:Cu(II).

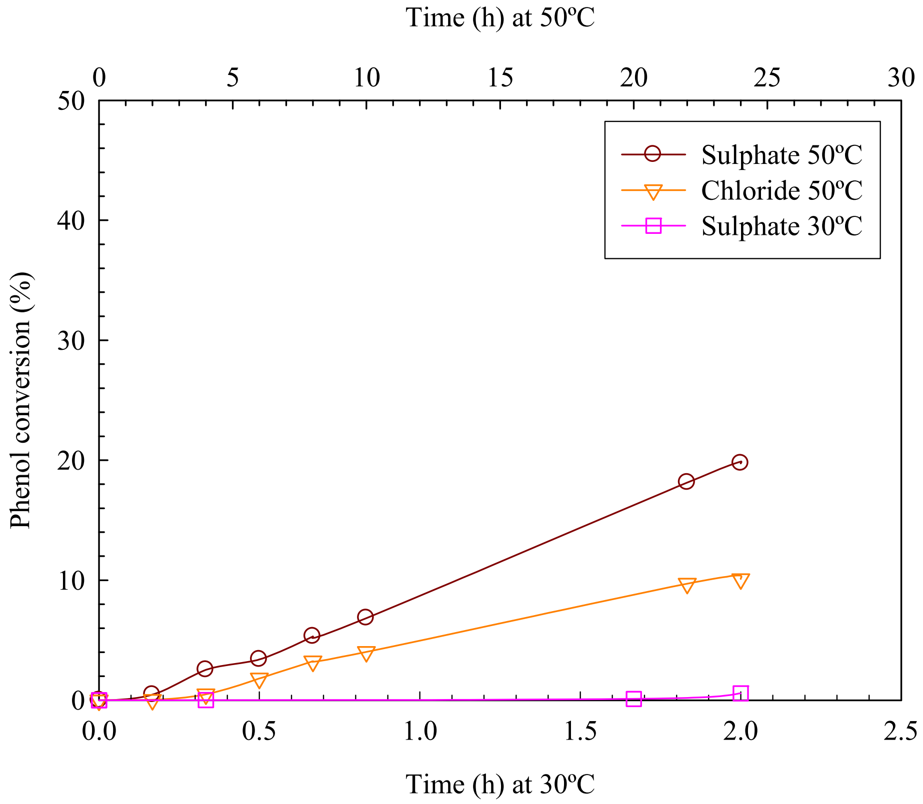


Figure 4.1. Phenol oxidation using different Cu(II) salts (sulphate and chloride) at different temperatures (30 and 50ºC). Phenol: 1 g·L^{-1}. Air flow: 85 mL·min^{-1}. At free pH and atmospheric pressure.

Finally, the conversion obtained on these first attempts cannot be accepted if the purpose of the work is to send the treated effluent to a municipal wastewater treatment plant (WWTP). Moreover Cu(II) concentration in the reaction solution was extremely high that would not be allowed as wastewater effluent in any WWTP. Thus, it was decided to use more powerful oxidants as hydrogen peroxide (H_2O_2) because oxidation results using air as oxidant were not suitable for the process.

4.2.2. HYDROGEN PEROXIDE AS OXIDANT

4.2.2.1. Temperature influence – blank experiment

Temperature is a determined variable on the oxidation of phenol, so in order to demonstrate its influence over phenol oxidation; reaction was carried out at three different temperatures (30, 40 and 50ºC), without the presence of catalysts and using the stoichiometric phenol/H_2O_2 molar ratio at free pH and atmospheric pressure. Results are presented on Figure 4.2 and demonstrate, as expected, that phenol conversion was not high enough to achieve deep mineralisation at these conditions. However, phenol conversion of 12% was achieved when temperature was 50ºC.

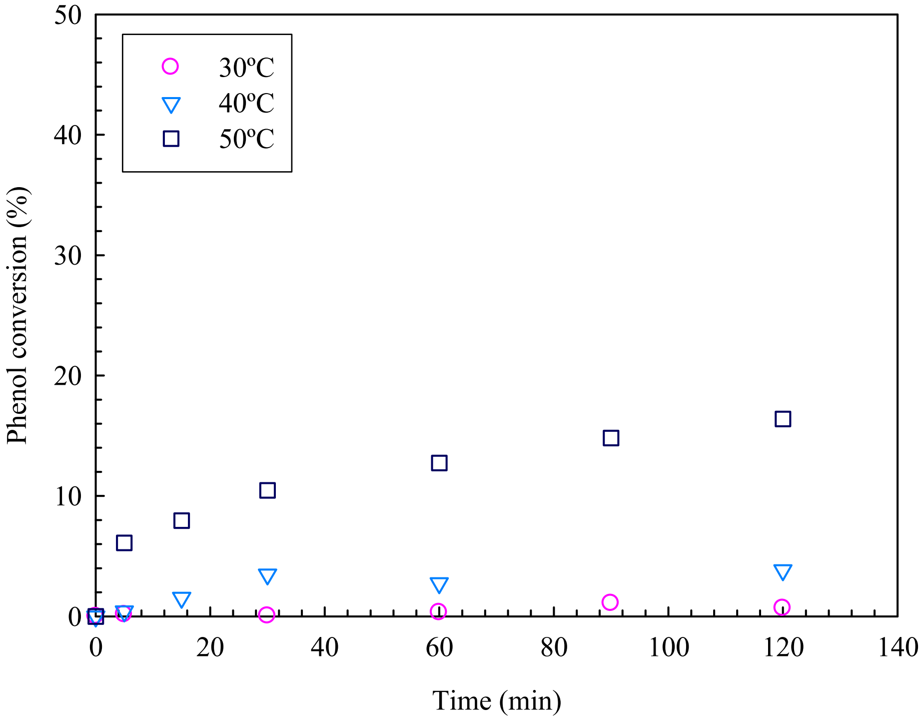


Figure 4.2. Phenol oxidation at different temperatures. Phenol: 1 g·L^{-1}. Ph/ H_2O_2 molar ratio: 1/14 (stoichiometric). At free pH and atmospheric pressure.

Therefore, if one objective of this research is to evaluate the influences of the amount of catalyst over the oxidation, it is important to establish the limits of the variables to be used. For instance, 12% of a possible oxidation without catalyst represents more than the expected experimental errors. Therefore, in order to avoid wrong control of phenol conversion, temperatures will fluctuate between 30 and 40ºC where the use of catalysts is necessary.

4.2.2.2. Cu(II) concentration influence

The next set of experiments was carried out to evaluate the effect of the Cu(II) catalyst on the oxidation. The initial phenol concentration was 1 $g \cdot L^{-1}$, the catalyst was the $CuSO_4 \cdot 5H_2O$ salt and the reaction time was 2 hours. Three different Ph:H_2O_2 molar ratios were tested (1:1, 1:5 and the stoichiometric 1:14) with four different initial Cu(II) concentrations (5, 10, 50, and 200 $mg \cdot L^{-1}$) at the temperature of 30ºC. In this case, the colour of the solution changed after the first 20 minutes, which demonstrated the formation of quinones, easily recognised because the liquid turned to brown colour, which reflected the production of these phenol intermediates.

Figure 4.3 presents the results of phenol conversion using H_2O_2 as oxidant agent after two hours at the conditions described above. As it can be seen, phenol conversion increased when Cu(II) concentration was increased and this behaviour occurs for the three molar ratios (1:1, 1:5 and 1:14). It is also observed that phenol conversions were not higher than 50% at the equimolar ratio, compared with the results at 1:5 Ph:H_2O_2 molar ratio, where conversions from 40 to 85% at different Cu(II) concentrations were obtained. As expected, phenol conversions at 1:5 Ph:H_2O_2 molar ratio showed better results than conversions at 1:1 Ph:H_2O_2 molar ratio, although this improvement in 100% of phenol conversion is remarkable. In addition, comparison between phenol conversions at 1:14 and 1:5 Ph:H_2O_2 molar ratios did not show high progress, suggesting that 1:5 molar ratio obtains acceptable conversion results up to 90%, but 1:14 molar ratio assures conversions of 95% due to the availability of 14 moles of hydrogen peroxide, which are activated by Cu(II) to attack phenol and phenol intermediates structures.

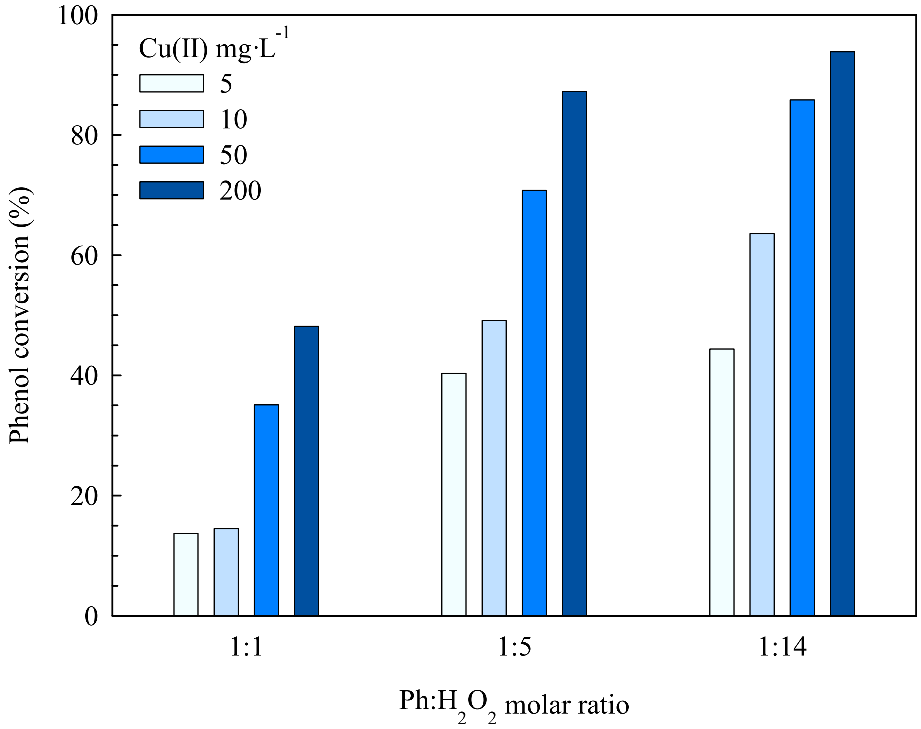


Figure 4.3. Homogeneous catalytic phenol oxidation: influence of [Cu(II)] (mg·L^{-1}) at different (Ph:H_2O_2) molar ratio. $[Ph]_0$ = 1 g L^{-1}. Reaction time = 2h. T = 30ºC.

In Figure 4.3, at 1:1 Ph:H_2O_2 molar ratio, phenol conversion had higher increment between 5-50 mg·L^{-1} than between 50-200 mg·L^{-1}. This behaviour is also observed at 1:5 molar ratio where phenol conversions increased from 40 to 71% in the range of 5-50 mg·L^{-1} and from 71 to 87% between 50 and 200 mg·L^{-1} of Cu(II) concentration. Furthermore, at 1:14 Ph:H_2O_2 molar ratio the phenol conversion follows the same tendency, that is, between 5-50 mg·L^{-1} phenol conversion raised from 44 to 86%, and had a small increase, from 86 to 94%, for the range of 50-200 mg·L^{-1} of Cu(II) concentration. Then, the variation of phenol conversions at different Cu(II) concentrations showed important changes at the first range of 5-50 mg·L^{-1} of Cu(II). Thus, better results were presented at 50-200 mg·L^{-1} range where phenol conversions were the highest, suggesting that the highest phenol conversion achieved, the best mineralisation degree is obtained. Additionally, it was demonstrated that the Cu(II) load had a positive effect on the conversion, confirming results presented by Aguiar and Ferraz (Aguiar et al., 2007). Even though, the high Cu(II) load should be lowered in order to follow the effluent directives, which do not permit higher Cu(II) concentrations than 5 mg·L^{-1} (EPER, 2004).

For instance, the catalytic activity at high Cu(II) concentrations was hindered due to hydrogen peroxide produced an excess of OH• radicals that were easily converted into O_2 with much lower oxidising power as reported by De Laat et al., (2006).

The conversions of total organic carbon (TOC) of the above tests are shown in Figure 4.4. It can be observed that TOC conversion increased with the increment either of $Ph:H_2O_2$ molar ratio, or Cu(II) concentration.

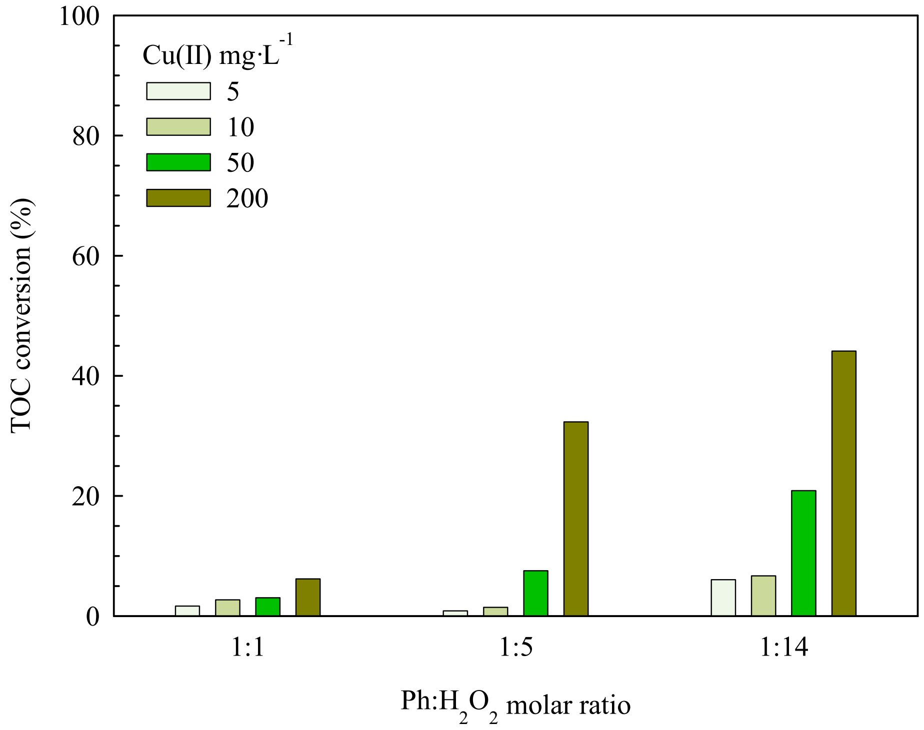


Figure 4.4. TOC conversion of homogeneous catalytic phenol oxidation: influence of Cu(II) concentration (mg·L^{-1}) at different $Ph:H_2O_2$ molar ratio. $[Ph]_0$ = 1 g·L^{-1}. Reaction time = 2h at 30°C.

At 1:1 $Ph:H_2O_2$ molar ratio, the mineralisation was low, between 1-6%, compared with the mineralisation achieved at 1:5 $Ph:H_2O_2$ molar ratio, where TOC conversions belong to the range of 1-32%. This improvement of the mineralisation, in more than four times the value of 1:1 molar ratio, suggests that OH• radicals reacted mostly with phenol molecules when 1:1 was the molar ratio. Although, for 1:14 molar ratio, it is assumed that OH• radicals were enough to react with both phenol and phenol intermediates along the reaction.

Additionally, knowing phenol conversions and their improvement when Cu(II) concentration varies, it was expected that TOC conversions at 1:14 $Ph:H_2O_2$ molar ratio were higher than the lower molar ratios, however there are some differences when mineralisation is evaluated. This time, the improvement of TOC conversion comparing 1:1 and 1:5 molar ratios was low (from 6 to 32%) compared with phenol conversions (from 50 to 90%). For instance, at 1:1 Ph:H_2O_2 molar ratio, the variation of Cu(II) concentration had low influence on the mineralisation of phenol due to the availability of OH• radicals were low. At 1:5 Ph:H_2O_2 molar ratio, there was a high improvement of TOC conversion when Cu(II) concentration varied from 50 to 200 mg·L^{-1}, that is from 8 to 32%. Similarly, at 1:14 Ph:H_2O_2 molar ratio, TOC conversion had the highest increment in the range of 50-200 mg·L^{-1} of Cu(II) concentration likely results obtained for phenol conversion.

Thus, on Figure 4.5 it is presented the conversion profiles of phenol and TOC results at 1:14 molar ratio. It can be seen at the Cu(II) concentration range between 50 and 200 mg·L^{-1}, phenol conversion seemed to be similar, while TOC conversion had an important improvement. This difference occurs because, at 50 mg·L^{-1} of Cu(II) in solution, phenol was almost totally oxidised while TOC indicated low phenol intermediates conversion, although at 200 mg·L^{-1} of Cu(II) content the oxidation of intermediates was more effective because the greater amounts of Cu(II), the higher production of OH• radicals capable to oxidise phenol and phenol intermediates.

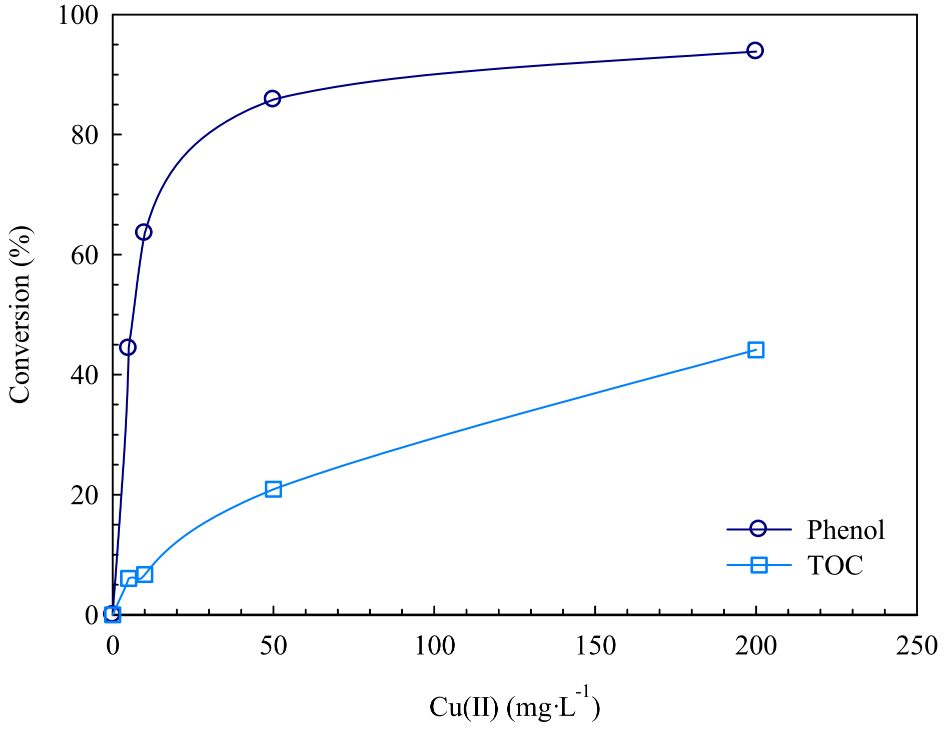
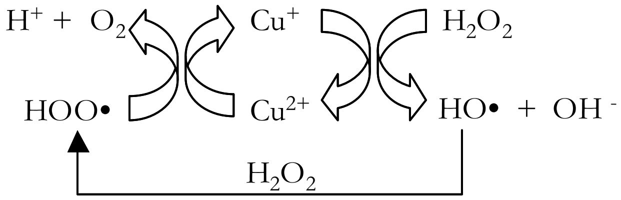


Figure 4.5. Homogeneous catalytic oxidation, phenol and TOC tendencies: influence of Cu(II) concentration at Ph:H_2O_2 1:14 molar ratio. $[Ph]_0$ = 1 g L^{-1}. Reaction time = 2h. T = 30ºC.

Therefore, the improvement of mineralisation was attributed to the Cu(II) charge on the reaction media, because the formation of OH• radicals was the result of the presence of Cu(II) ions, which participate on the H_2O_2 decomposition (Scheme 4.1). Hence, the formation of intermediates during the catalytic oxidation requires more OH• radicals, that means more Cu(II) ions to decompose the H_2O_2. In this way, the decomposition of H_2O_2 was directly associated to the amount of Cu(II) used, then the existence of high amounts of Cu(II) ions on the catalytic oxidation media increases the phenol mineralisation. Overall TOC conversion was obviously lower than phenol conversion because products, partially oxidised, also need to be mineralised. However, the difference between phenol conversion and TOC conversion gives the selectivity towards carbon dioxide. This selectivity increased as phenol conversion and TOC conversion become closer (Suarez-Ojeda et al., 2005). Further, TOC was low because the stoichiometric Ph:H_2O_2 molar ratio was not enough to achieve a total phenol mineralisation and because part of the peroxide was decomposed into O_2. For instance, according to experimental findings, scheme 4.1 shows a possible mechanism for the influence of Cu(II) on the hydrogen decomposition (Ghiselli et al., 2004). This mechanism shows the formation of OH• radicals, promoters of phenol oxidation.



Scheme 4.1. Reaction mechanisms of hydrogen peroxide with Cu(II) ions

4.2.2.3. Kinetics and mechanism of phenol oxidation

Kinetic analysis was applied to the experimental data for a better understanding of the catalytic process. The operational conditions employed the stoichiometric Ph:H_2O_2 molar ratio at 30ºC and 1 atm of pressure. Then, for this purpose, it was used the integrated rate law to evaluate phenol oxidation reaction with two kinetic models (first and second order) and respect to phenol concentration. For the first and second order models, the experimental data had a good fit with both models, however the first order model presented correlation coefficients between 0,99 and 0,97, which compared with the ones obtained for the second order (0,99 - 0,81), showed that the first order model can support the experimental data variation for more than 97%, as it is presented on Table 4.1.

Table 4.1. Rate law of first order model for the homogeneous catalytic oxidation of phenol

Rate law	Integrated rate law	[Cu(II)] mg·L^{-1}	k (min^{-1})	R^2
$-\frac{d[A]}{dt} = k[A]$	$[A] = [A]_0 \cdot e^{-kt}$	5	$1,6\cdot10^{-3}$	0,9991
		10	$4,1\cdot10^{-3}$	0,9991
		50	$7,3\cdot10^{-3}$	0,9991
		200	$13,8\cdot10^{-3}$	0,9752

It is noticeable that catalytic oxidation depends on the initial Cu(II) concentration because the reaction efficiency increased with higher Cu(II) concentration, although the use of high Cu(II) amounts needs to be controlled as an environmental issue.

4.2.2.4. Study of the oxidation of phenol intermediates

From the oxidation of phenol it is expected partially oxidised compounds, also called phenol intermediates. Their formation and classification was difficult to determine, however some experiments were carried out in order to determine how many intermediates were formed (Annexe 1) along the reaction time.

In order to identify the products from phenol oxidation when Cu(II) sulphate was the catalyst, hydroquinone and catechol were selected as the first two intermediates following Devlin et al. (1984) reaction pathway of phenol oxidation, then both compounds were oxidised following the same procedure employed for phenol oxidation (40ºC, pH 6 and atmospheric pressure). Taking into account that high temperatures increase the conversion of phenol oxidation, it is also expected the production of higher amounts of phenol intermediates, therefore it was convenient to use 40ºC since it is the maximum temperature to be employed as presented in section 4.2.2.1. Additionally it was used a constant pH 6 because it has already reported the influence of pH on the efficiency of the decomposition of hydrogen peroxide (Gemeay et al., 2004), where pH around 6 better promotes the decomposition of hydrogen peroxide and its application on oxidative degradation of dyes.

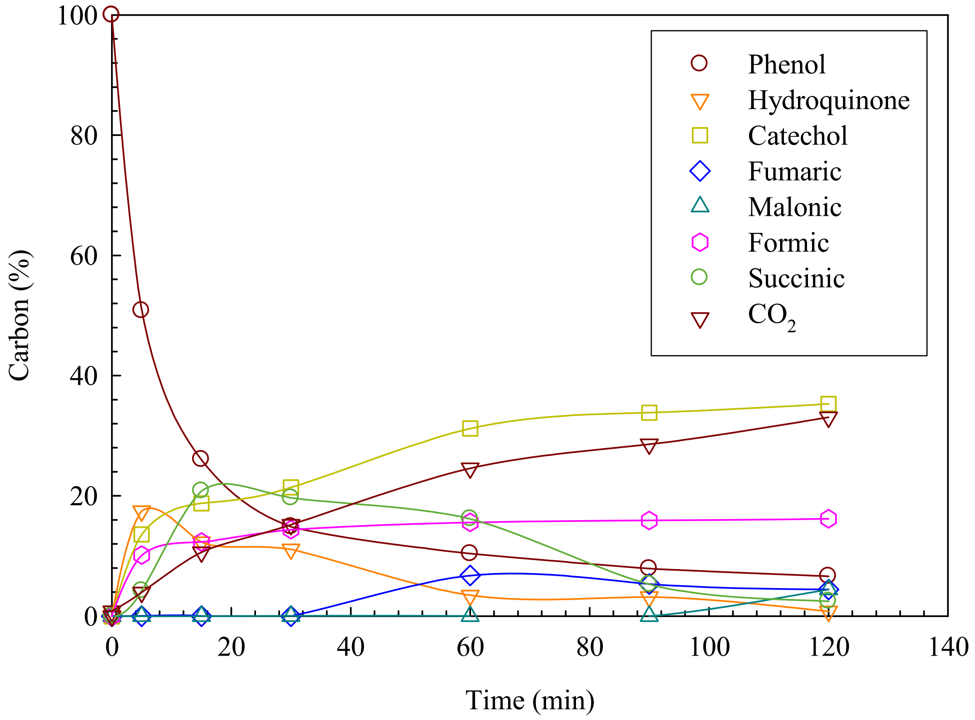


Figure. 4.6. Carbon percent formation of phenol oxidation. Phenol: 1 g·L^{-1}. Cu(II): 50 mg·L^{-1}. Ph/ H_2O_2 molar ratio: 1/14 (stoichiometric) at 40ºC, pH 6 and atmospheric pressure.

Figure 4.6 shows the formation of phenol intermediates along a period of 2 hours of reaction. It was obtained 88% of phenol conversion as well as the formation of intermediates like hydroquinone, cathecol, fumaric ac., malonic ac. and succinic ac. A mass balance was employed to obtain the carbon content of each intermediate by relating HPLC and TOC results, for instance CO_2 production was obtained from the variation of TOC results. Then again, in Figure 4.6, the formation of catechol was the highest after two hours of reaction with 35% of total organic carbon; hydroquinone and succinic acid showed higher formation at the first 20 minutes while fumaric acid seemed to appear after 30 minutes of reaction, thus mineralisation started from the very beginning and after two hours it achieved more than 30%. Overall, intermediates suggested continuing their formation with time, while mineralisation seems to increase after two hours because the formation of intermediates and their respective oxidation would be variable until the activity of OH• radicals stop.

In order to identify intermediates and their subsequent products, the catalytic oxidation of every intermediate was carried out independently and under the same conditions previously used on phenol oxidation. Figure 4.7 presents the formation of intermediates from the catalytic oxidation of hydroquinone. After making a mass balance using HPLC and TOC results it have been seen that malonic, formic and succinic acids were identified as products where formic acid represents the 40% of hydroquinone conversion. Also, despite of 40% of TOC, it was obtained a hydroquinone conversion of 100%, which suggests that it is possible to degrade effluents with hydroquinone content at 40ºC, pH 6 and atmospheric pressure.

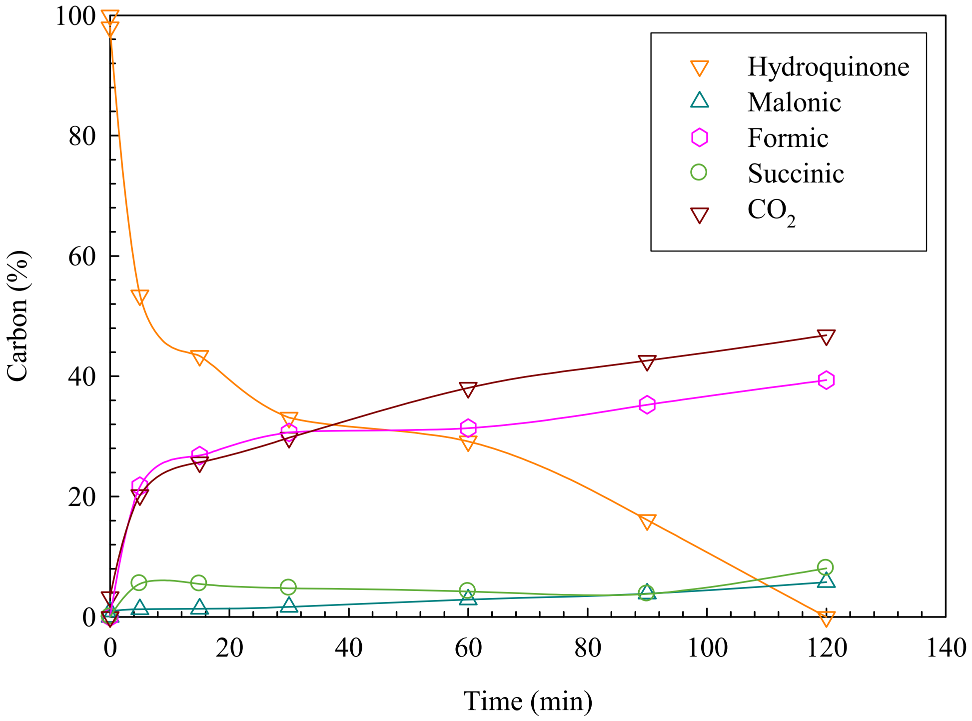


Figure 4.7. Carbon percent formation of hidroquinone oxidation. Hydroquinone: 1 g·L^{-1}. Cu(II): 50 mg·L^{-1} at 40ºC, pH 6 and atmospheric pressure.

Likewise, it was performed the catalytic oxidation of catechol and Figure 4.8 presents the carbon percent distribution for the formation of intermediates. In this case, catechol was degraded and produced fumaric, formic and succinic acids as intermediates. It can be appreciated in the figure that succinic acid formation presented high concentrations at the 15 and 30 minutes of reaction. This behaviour was also observed when phenol oxidation was performed (Figure 4.6), which suggests that production of succinic acid is due to catechol formation in first place.

Thereafter, comparing homologous hydroquinone and catechol intermediates, it was found that fumaric acid only was detected as product of catechol. Then, it is important to mention the formation of fumaric acid because according to the mechanisms reported by Devlin and Harris (1984) the formation of acids like formic, malonic or succinic occurs due to degradation of fumaric acid. On the other hand, the apparently non-existence formation of fumaric acid suggests a direct oxidation of hydroquinone into malonic, formic and succinic acids.

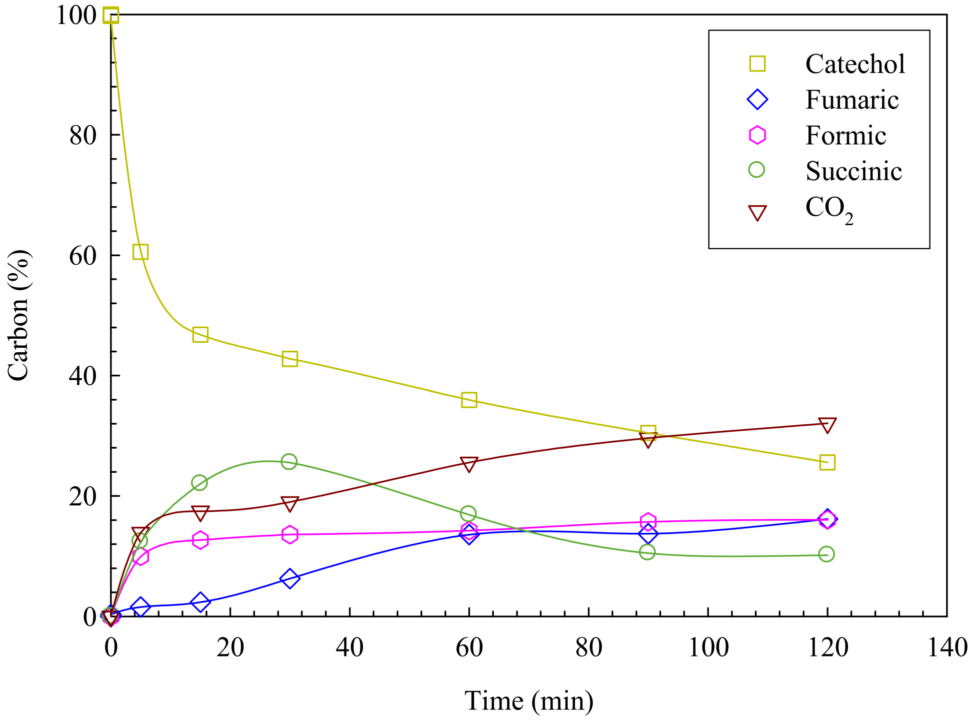


Figure 4.8. Carbon percent formation of catechol oxidation. Catechol: 1 g·L^{-1}. Cu(II): 50 mg·L^{-1} at 40ºC, pH 6 and atmospheric pressure.

Finally, in order to continue describing the formation of intermediates of phenol oxidation, fumaric acid was oxidised at the same conditions phenol and previous intermediates were oxidised. Figure 4.9 shows the carbon percent distribution of intermediates obtained from the fumaric acid oxidation. It was achieved a TOC conversion of 92%, which reflects the grade of mineralisation of fumaric acid at these conditions. As well, it was detected the formation of malonic and formic acids as products, but their presence was not higher than 8% along two hours of reaction, demonstrating the easy oxidation of fumaric acid at mild conditions (40ºC and pH6).

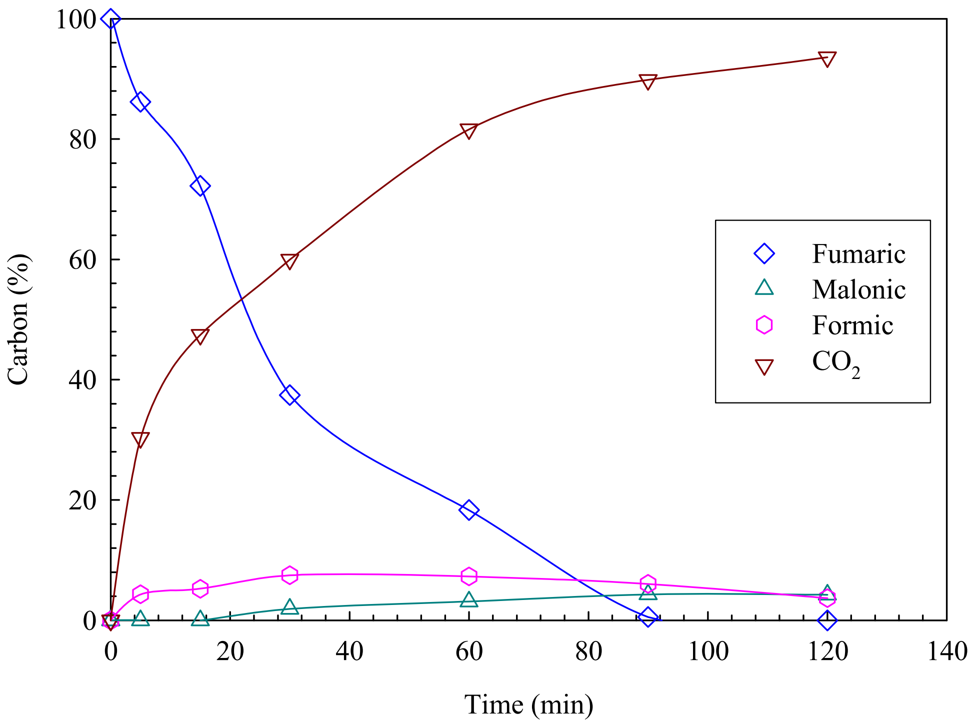
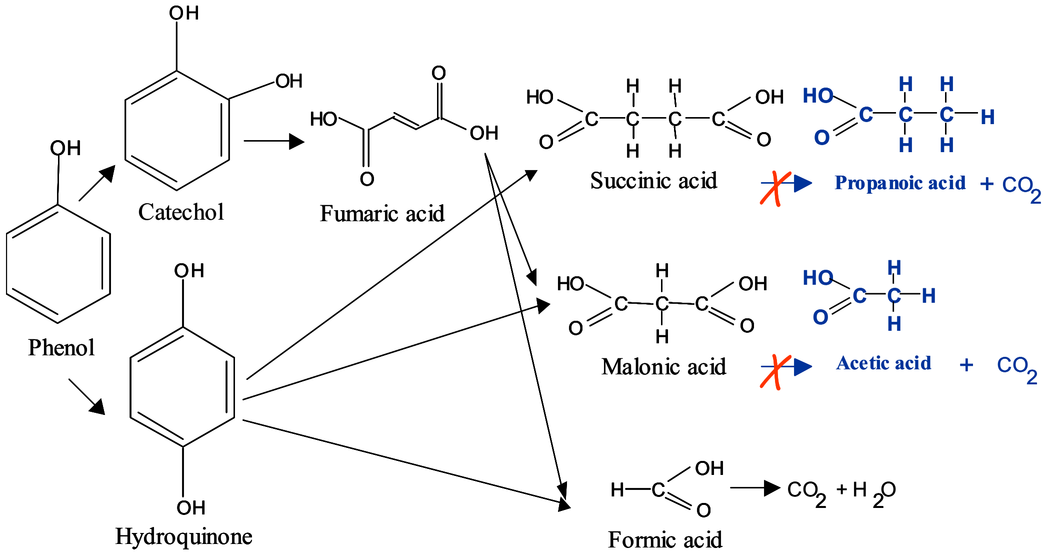


Figure 4.9. Carbon percent formation of fumaric acid oxidation. Fumaric: 1 g·L^{-1}, Cu(II): 50 mg·L^{-1} at 40ºC, pH 6 and atmospheric pressure.

After all, from the recognised compounds and following the reported mechanisms (Devlin et al., 1984), it is proposed a reaction pathway of the catalytic oxidation, Scheme 4.2.



Scheme 4.2. Proposed reaction pathway for the CWPO of phenol.

4.2.2.5. Kinetics for the CWPO of main phenol intermediates

After the determination of the reaction mechanism, reaction kinetics was calculated for the three main compounds (phenol, hydroquinone and catechol). Table 4.2 presents the values of the kinetic parameters according to the first order model of reaction rate. From the results and evaluating the influence of temperature and pH, the increment of the constant rate was evident for phenol and catechol compounds when temperature and pH were higher, while hydroquinone constants seemed to have the same behaviour even at different conditions. This behaviour suggests that phenol and catechol oxidations are more sensible to the change conditions than hydroquinone, therefore it is important to maintain the same initial conditions when evaluating intermediates formation.

Table 4.2. Kinetic parameters for the first order rate law for CWPO of phenol

	30ºC and free pH		40ºC and pH 6	
Compound	k_1 (min^{-1})	R^2	k_1 (min^{-1})	R^2
phenol	$3,9 \cdot 10^{-3}$	0,9434	$15,8 \cdot 10^{-3}$	0,8402
hydroquinone	$8,6 \cdot 10^{-3}$	0,9139	$7,8 \cdot 10^{-3}$	0,8609
catechol	$1,5 \cdot 10^{-3}$	0,8316	$6,7 \cdot 10^{-3}$	0,9830

CONCLUSIONS

The homogeneous catalytic oxidation of phenol using air as oxidant at 30ºC and atmospheric pressure showed negligible phenol conversions (2%) after 2 hours, even when the temperature (50ºC), Cu(II) concentration (1:10 Ph:Cu(II) molar ratio) and time (24 h) were elevated.

Phenol conversion was enhanced when H_2O_2 was the oxidant agent. Results were influenced by the employed Cu(II) concentration and the Ph:H_2O_2 molar ratio.

It was obtained a phenol conversion of 12% at 50ºC in absence of catalyst; therefore phenol oxidation was further carried out between 30 and 40ºC to avoid 12% of error before catalyst use.

TOC results at 1:14 molar ratio presented better results when Cu(II) concentration increased from 50 to 200 $mg \cdot L^{-1}$ because the greater amount of Cu(II), the higher production of OH• radicals to oxidise both phenol and its intermediates.

Kinetics respect to oxidation of phenol followed the first rate and increased under influence of Cu(II) concentration.

On the study of phenol oxidation, it was identified hydroquinone and catechol as main partially oxidised compounds and acids like fumaric, malonic, succinic and formic as final intermediates before the formation of CO_2 and water.

Finally it was found that reaction constant rates of phenol and main intermediates increased at neutral pH, promoting in this way the formation of acids derived from phenol oxidation.

REFERENCES

- Aguiar, A., Ferraz, A., Fe^{3+}- and Cu^{2+}-reduction by phenol derivatives associated with Azure B degradation in Fenton-like reactions, Chemosph. 66 (2007) 947.
- De Laat, L., Le, T.G., Effects of chloride ions on the iron(III)-catalyzed decomposition of hydrogen peroxide and on the efficiency of the Fenton-like oxidation process, Appl. Catal. B66 (2006) 137.
- Devlin, H.R., Harris, I.J., Mechanism of the Oxidation of Aqueous Phenol with Dissolved Oxygen, Ind. Eng. Chem. Fundam. 23 (1984) 387.
- Gemeay, A.H., Mansour, I.A., El-Sharkawy, R.G., Zaki, A.B., Kinetics of the oxidative degradation of thionine dye by hydrogen peroxide catalysed by supported transition metal ions complexes, J. Chem. Technol. Biotechnol. 79 (2004) 85.
- Ghiselli, G., Jardim, W.F., Litter, M.I., Mansilla, H.D., Destruction of EDTA using Fenton and photo-Fenton-like reactions under UV-A irradiation, J. Photoch. Photobio. A167 (2004) 59.
- Perkin-Elmer Corporation, Analytical Methods for atomic absorption spectrometry, USA (1994).
- Suarez-Ojeda, M.E., Stüber, F., Fortuny, A., Fabregat, A., Carrera, J., Font, J., Appl. Catal. B-Environ. 58 (2005) 105.
- The European Pollutant Emission Register (EPER), Review Report, (2004).

CHAPTER V

HETEROGENIZATION OF HOMOGENEOUS CATALYSTS

5.1. ADSORPTION

Adsorption process was performed through testing the adsorptive capacities of three different polymeric materials (poly(4 vinyl pyridine) 2% crosslinked (PVP_2), poly(4 vinyl pyridine) 25% crosslinked (PVP_{25}) and Chitosan) and one cationic resin of polystyrene matrix (CR).

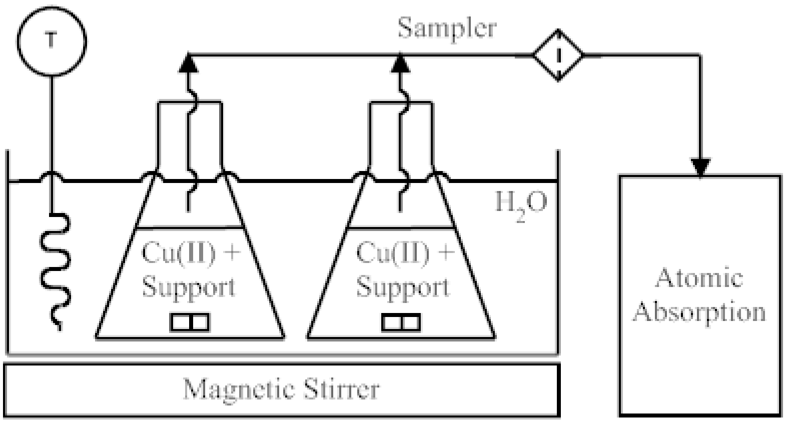
5.1.1. EXPERIMENTAL

5.1.1.1. Materials

Poly(4-vinylpyridine) 2% cross-linked powder (PVP_2) (Ref. 81391) and Poly(4-vinylpyridine) 25% cross-linked beads (PVP_{25}) (Ref. 81393) were purchased from Sigma-Aldrich. Chitosan beads were supplied by E. Guibal (Laboratoire de Génie de l'Environnement Industriel, Ecole des Mines d'Alès, France) and synthesised according to an original procedure (Guibal et al., 1998), Lewatit S-100-G1 cationic resin was provided from Bayer. Copper sulphate pent hydrated with 99% of purity ($CuSO_4 \cdot 5H_2O$) was obtained from Sigma-Aldrich, while hydrochloric acid (HCl) 2N standard solution and sulphuric acid (H_2SO_4) 99% were purchased from Fluka. Millipore milli-Q deionised water was used for all reagent solutions.

5.1.1.2. Methods

The adsorption isotherms of Cu(II) were performed by using a batch adsorption system, which consists on beakers of 250 mL submerged in a thermostatic water bath, Scheme 5.1. First of all, it was prepared a solution of copper sulphate containing 1,0 $g \cdot L^{-1}$ of Cu(II), then six solutions with different Cu(II) concentrations (0,1; 0,2; 0,4; 0,6; 0,8 and 1,0 $g \cdot L^{-1}$) of 0,2 L were prepared from the dilution of the mother solution. Every batch adsorption system was agitated with a magnetic stirrer (90 rpm) for 5 h at 20, 30 and 40ºC, and the pH was measured twice, before the adsorbent was put in contact with the Cu(II) solutions and at the end of the adsorption period. The adsorption began when 1g of the adsorbent was added into each Cu(II) solution. Samples of 0,1 mL were taken with a syringe and filtered (45 μm pore membrane) at different time intervals. Then, the residual Cu(II) concentration in the supernatant was determined by using the taken samples and analysing them in an Atomic Absorption Spectrometer (Perkin Elmer, model 3110). Once adsorption achieves equilibrium, the polymer-Cu(II) material is recovered by filtration (150 mm pore membrane), then cleaned with distilled water, dried at room temperature and stored in a dry container.



Scheme 5.1. Batch adsorption set-up for the heterogenization of homogeneous catalysts

Additionally, the adsorption capacities (q) of Cu(II) onto PVP_2, PVP_{25}, Chitosan and cationic resin are calculated by a mass balance where the initial (C_0) and final (C_e) concentration of Cu(II), the volume (V) of bulk solution and the mass (m) of the adsorbent are correlated by Eq. (5.1):

$$q = \frac{C_0 - C_e}{m} \cdot V \tag{5.1}$$

5.1.1.3. Analytical Procedure

The residual Cu(II) concentration in the supernatant was determined by an Atomic Absorption Spectrometer (Perkin Elmer, model 3110) with a specific lamp for the element of copper (Perkin Elmer, serial number 01074). The samples were diluted in order to avoid saturation of the detector signal for the case of copper concentrations more than 10 $mg \cdot L^{-1}$. The dilution was made with a solution of HCl 1%. The analyses were performed at 325 nm of wavelength, (Perkin-Elmer, 1994). Calibration curve of Cu(II) was made using aqueous samples of known Cu(II) concentration and some example are presented on annex section.

5.1.2. RESULTS AND DISCUSSION

5.1.2.1. Equilibrium studies

a. Effect of the adsorbent

The uptake of Cu(II) was periodically evaluated, the initial copper concentration in solution was 1,0 $g \cdot L^{-1}$ for PVP_2, PVP_{25} and CR cases, but for Chitosan the initial copper concentration was 0,1 $g \cdot L^{-1}$ because initial experimental attempts showed that Chitosan presented low adsorption capacities. Besides, the experiments were carried out at the initial pH 5 and the adsorption process was evaluated at three temperatures (20, 30 and 40ºC), however graphical representation was reported at 20ºC. The Cu(II) concentration in solution was monitored in a period of 5 hours, for instance all the adsorbents or polymeric materials presented quite rapid adsorption rates at the first 2 hours, after this, polymers reached the equilibrium, then equilibrium contact time of 5 hours was used for all further experiments. For instance, Verbych et al., (2005) worked with Chitosan and reported immediate adsorption uptake at the first hour, then after 70 hours it was found the equilibrium of the system but the last 20 hours it was not noticed variation of Cu(II) concentration.

It must also be noticed from Figure 5.1 that the differences between adsorption capacities of each support were considerable. That is, the adsorption capacity of CR was higher than PVP_2 and PVP_{25}, and those at the same time, higher than Chitosan.

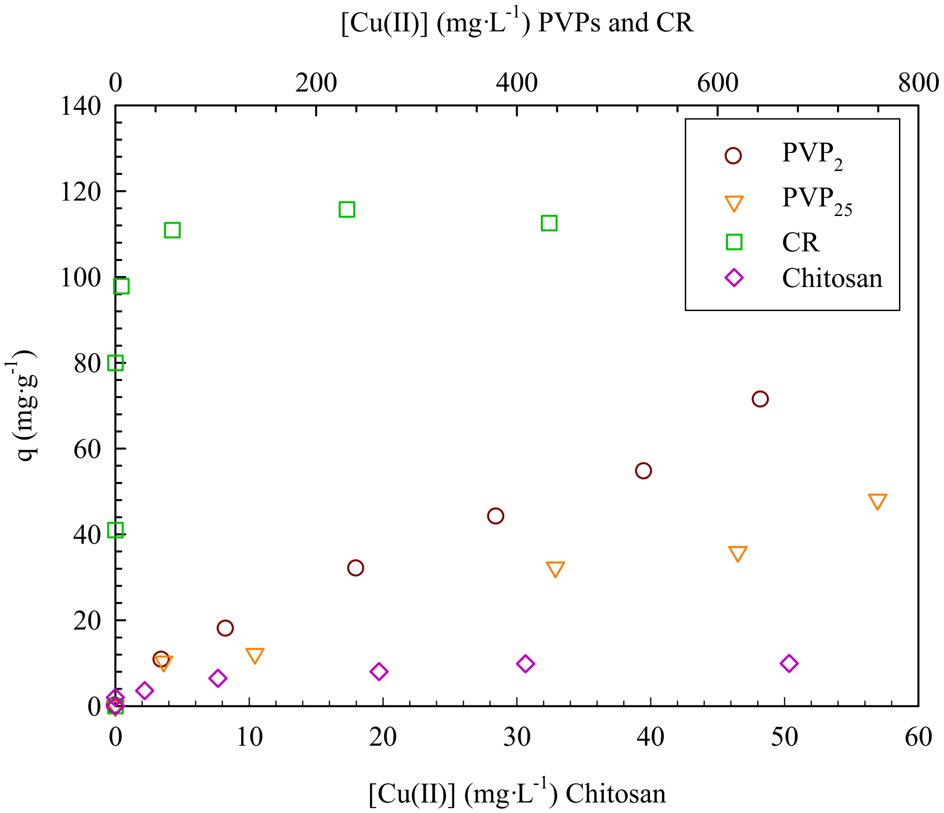


Figure 5.1. Adsorption capacities of PVP_2, PVP_{25}, CR and Chitosan at 30°C. $[Cu(II)]_0$= 1 g·L^{-1} for PVPs and CR, $[Cu(II)]_0$= 0,1 g·L^{-1} for Chitosan, m = 1g.

This difference was partially caused by the particle size of each material, because it was reported that adsorption capacity of materials with small particle size were higher compared with beads (Ahmad et al., 2005), for instance beads can experiment obstruction problems in their contact area due to cross-linkage. However, the surface interaction between copper and polymer was also an important variable, because while PVPs and Chitosan had -NH_2 radicals, CR presented sulfonic groups on its contact surface, which were highly favourable for the adsorption of copper ions.

b. Effect of initial Cu(II) concentration

The adsorption data were used to examine the rate of the adsorption process. Normally, the pseudo-first-order equation is expressed in the first contact time; on this period the adsorption is highly favourable because the surface of the supports has great availability of energetic sites.

The pseudo-first-order, generally applicable over the initial stage of adsorption processes, is based on the adsorption capacity and is expressed as (Eq. (5.2)):

$$\frac{dq}{dt} = k_1 \cdot (q_e - q) \tag{5.2}$$

where the adsorption capacity (q_e) of the support at the equilibrium ($mg \cdot g^{-1}$) and the pseudo first-order rate k_1 constant (min^{-1}) are related. So that, if the adsorption capacity of the material at the zero time is $q = 0$ and at the t time is $q = q_t$, then Eq. (5.2) becomes:

$$q_t = q_e (1 - e^{-k_1 t}) \tag{5.3}$$

Additionally, for adsorption isotherms that do not follow the pseudo-first-order model, it exists the possibility to follow the pseudo-second-order behaviour, which is represented by two-step linear relationships (Ahmad et al., 2005). The pseudo-second-order kinetic rate equation is based on the adsorption equilibrium capacity (Eq. (5.4)):

$$\frac{dq}{dt} = k_2 \cdot (q_e - q)^2 \tag{5.4}$$

The rate constant of pseudo-second-order sorption is represented by k_2 ($g \cdot mg^{-1} \cdot h^{-1}$), which is directly proportional to q_e and inversely proportional to the difference between adsorption capacities (q) at different periods of time (t). After integration of Eq. (5.4), it is obtained Eq. (5.5), which is in agreement with the chemisorption:

$$\frac{t}{q} = \frac{1}{k_2 \cdot q_e^{\,2}} + \frac{1}{q_e} \cdot t \tag{5.5}$$

Figure 5.2 presents the pseudo-first-order adsorption kinetics of PVP_2 polymer. It can be seen that results from the adsorption with PVP_2 follow the pseudo-first-order model. Moreover, it evident that the increment of Cu(II) concentration did not change the adsorption tendencies, then the adsorption with PVP_2 follows the pseudo-first-order model as Figure 5.2 shows.

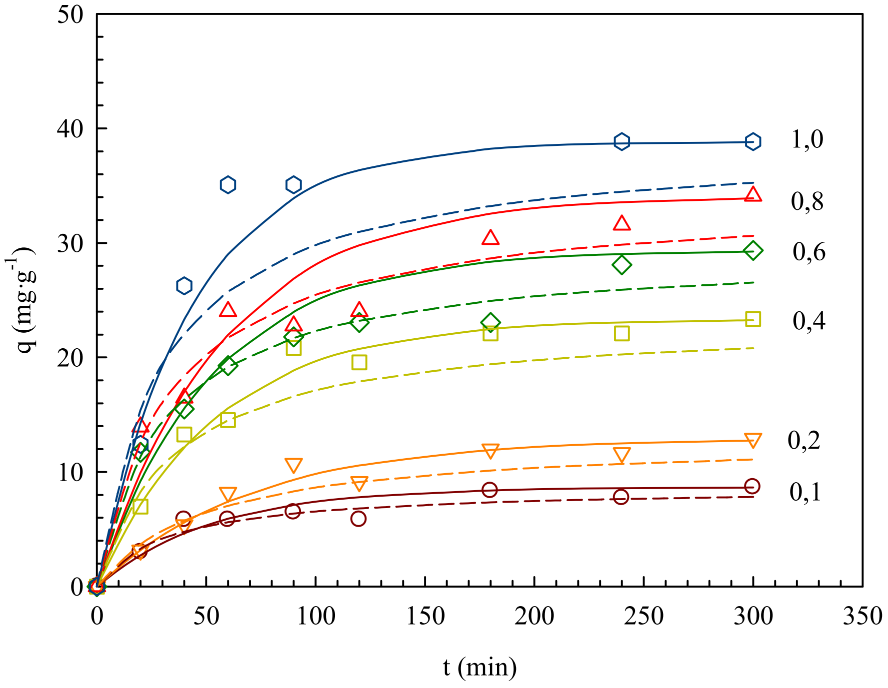


Figure 5.2. Time profiles and fitting of the pseudo-first —— and second order kinetic - - - models for Cu(II) adsorption onto PVP_2. $[Cu(II)]_0$ = 0,1-1,0 g·L^{-1}, m = 1g, T = 20ºC.

On Figure 5.3 the experimental PVP_{25} results are presented. The adsorption capacities also followed the pseudo-first-order model, but the slopes had a variation at concentrations more than 0,4 g·L^{-1}. This fact obviously described that there were higher adsorption capacities at higher availability of Cu(II) ions. Furthermore the equilibrium seems to occur faster than at lower Cu(II) concentrations, from where it could be eliminated the hypothesis of a possible saturation of PVP_{25} contact surface. Again, the pseudo-first-order model described the adsorption of Cu(II) even at different concentrations.

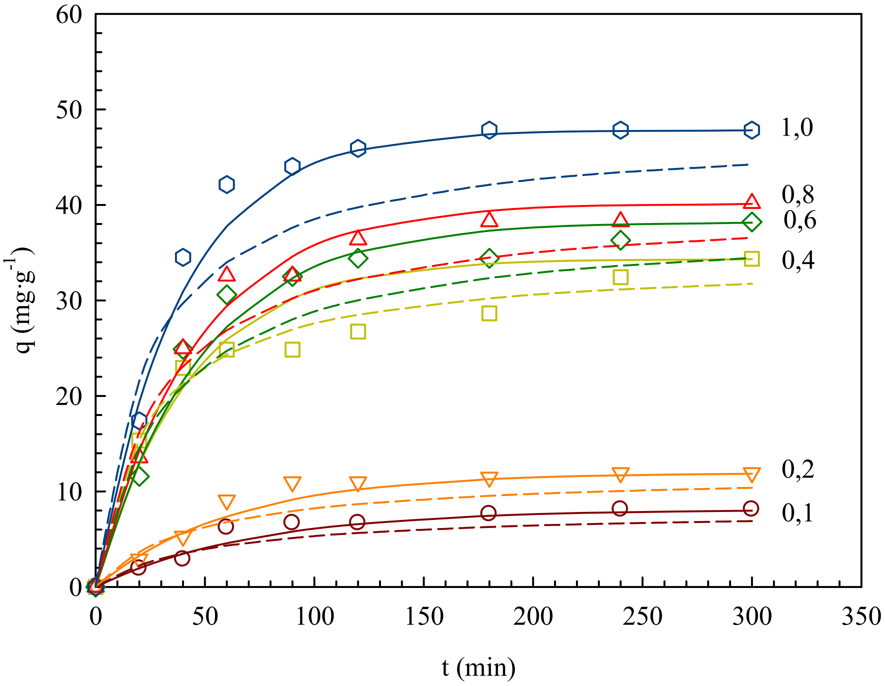


Figure 5.3. Time profiles and fitting of the pseudo-first —— and second order - - - kinetic models for Cu(II) adsorption onto PVP$_{25}$. $[Cu(II)]_0$ = 0,1-1,0 g·L^{-1}, m = 1g, T = 20ºC.

Then, on Figure 5.4 Chitosan results followed the pseudo-first-order adsorption kinetics as well, where Cu(II) concentration changes did not modify the kinetic tendencies of this group of adsorption experiments.

Additionally, all the catalysts were also evaluated by using the pseudo-second-order model then slope tendencies were plotted on each figure where the pseudo-first-order model was presented. The pseudo-second-order model did not have better adsorption description for PVPs and Chitosan, as presented with the pseudo-first-order model, however CR data had a perfect fit while using the pseudo-second-order model. From these results, CR adsorption behaviour is represented by a chemical adsorption, which occurs when the contact surface of CR, provided by sulfonic radicals, showed its strong attraction energy over Cu(II) ions, for instance, the equilibrium of CR was described at the first 20 minutes with surface saturation around 550 mg of Cu(II) onto 1 g of CR. Then it is concluded a strong bond formation between resin and Cu(II) cations.

Therefore, for the CR case (Figure 4.5), it was shown that the pseudo-first-order kinetic model could not describe the adsorption rate of CR; from where it was necessary to employ the pseudo-second-order model.

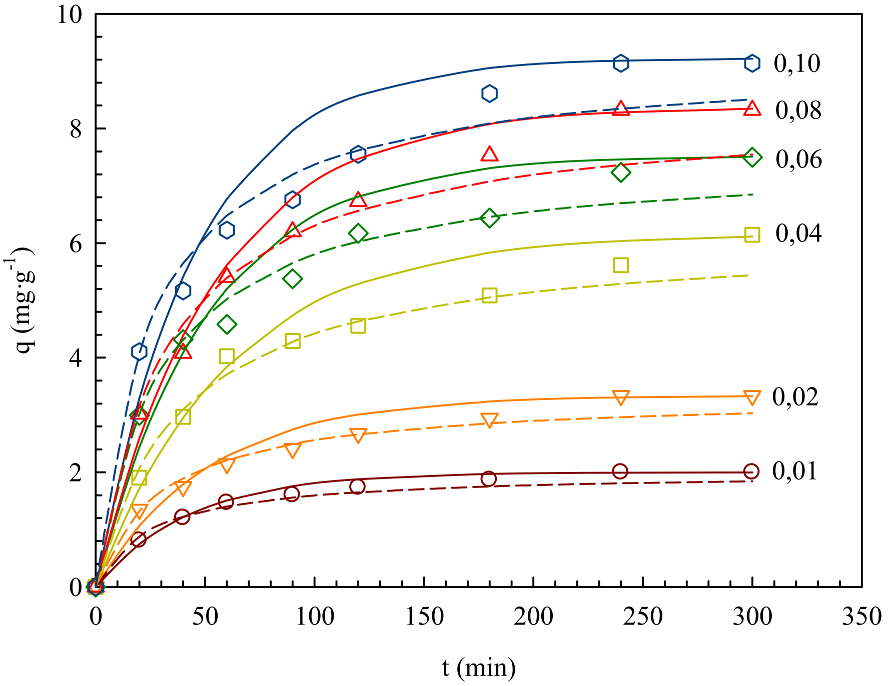


Figure 5.4. Time profiles and fitting of the pseudo-first —— and second order - - - kinetic models for Cu(II) adsorption onto Chitosan. $[Cu(II)]_0$ = 0,01-0,10 g·L^{-1}, m = 1g, T = 20ºC.

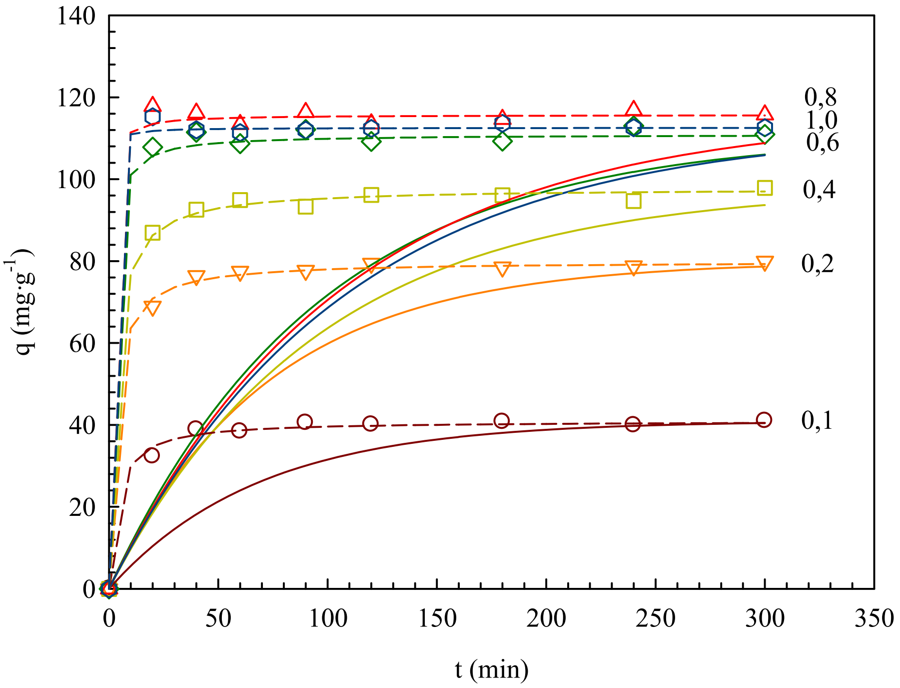


Figure 5.5. Time profiles and fitting of the pseudo-first —— and second order - - - kinetic models for Cu(II) adsorption onto cationic resin (CR). $[Cu(II)]_0$ = 0,1-1,0 g·L^{-1}, m = 1g, T = 20ºC.

Therefore, further kinetics evaluation will be using the pseudo-first-order model for PVPs and Chitosan, while pseudo-second-order model will be needed for CR.

Table 5.1 lists the rate constants of the adsorption isotherms of all supports under study. PVP_2 rate constants were similar to PVP_{25} and both were slightly different from Chitosan, while CR had its kinetic development at the second-order adsorption model. It must be also noticeable that temperature had influence on constant rates of PVP_2 and PVP_{25} showing lower constant rates at 30 and 40ºC than at 20ºC. On the other hand Chitosan had the opposite behaviour, where its constant rates had a slight increment when temperature increases.

Table 5.1. Kinetic adsorption rate constant (k_1 or k_2) and theoretical adsorption capacity (q_c*) of Cu(II) onto PVP_2, PVP_{25}, Chitosan and CR. $[Cu(II)]_0$ = 0,1-1,0 $g\cdot L^{-1}$ for PVP_2, PVP_{25} and CR, $[Cu(II)]_0$ = 0,01-0,10 $g\cdot L^{-1}$ for Chitosan, m = 1g, T = 20, 30 and 40ºC.

Support	Particle size	Temperature	k_1 (min^{-1})
PVP_2	~ 0,25 mm	20 ºC	$2,3\cdot10^{-2} \pm 2\cdot10^{-3}$
		30 ºC	$1,2\cdot10^{-2} \pm 2\cdot10^{-3}$
		40 ºC	$0,9\cdot10^{-2} \pm 2\cdot10^{-3}$
PVP_{25}	~ 0,85 mm	20 ºC	$2,6\cdot10^{-2} \pm 2\cdot10^{-3}$
		30 ºC	$1,1\cdot10^{-2} \pm 6\cdot10^{-3}$
		40 ºC	$0,8\cdot10^{-2} \pm 9\cdot10^{-3}$
Chitosan	~ 2,50 mm	20 ºC	$2,2\cdot10^{-2} \pm 2\cdot10^{-3}$
		30 ºC	$2,7\cdot10^{-2} \pm 4\cdot10^{-3}$
		40 ºC	$3,9\cdot10^{-2} \pm 5\cdot10^{-3}$
Cationic resin (CR)	~ 0,30 mm	30ºC	$1.1\cdot10^{-2*} \pm 1,1\cdot10^{-3}$

* The constant k value for CR represents the constant rate of the pseudo-second-order model ($g\cdot mg^{-1}\cdot h^{-1}$).

c. Effect of the temperature

In order to study the equilibrium of the adsorption of Cu(II) onto polymeric materials, it was schemed the adsorption capacity against the equilibrium concentrations of Cu(II) ions in solution at three different temperatures (20, 30 and 40ºC).

In Figure 5.6 it is showed the evolution of PVP_2 adsorption capacity when temperature varied. As reported by Ahmad et al. (2005) and Chu (2002) who worked with Chitosan in powder or flakes, it was expected to obtain the highest q with powder materials, in all the three tested temperatures because PVP_2 with 2% of cross-linking presents high percent of ordered active radicals and high exposed area, but results showed better q results for PVP_{25} at 20ºC. Moreover, PVP_2 seemed to expose more amino radicals at high temperatures because its adsorption tendency reached the saturation at 20ºC, except for 30 and 40ºC. Then, the q of PVP_2 at 40ºC (90 $mg \cdot g^{-1}$) and 30ºC (71 $mg \cdot g^{-1}$) represent the equilibrium of an unsaturated material compared with the values obtained at 20ºC (39 $mg \cdot g^{-1}$).

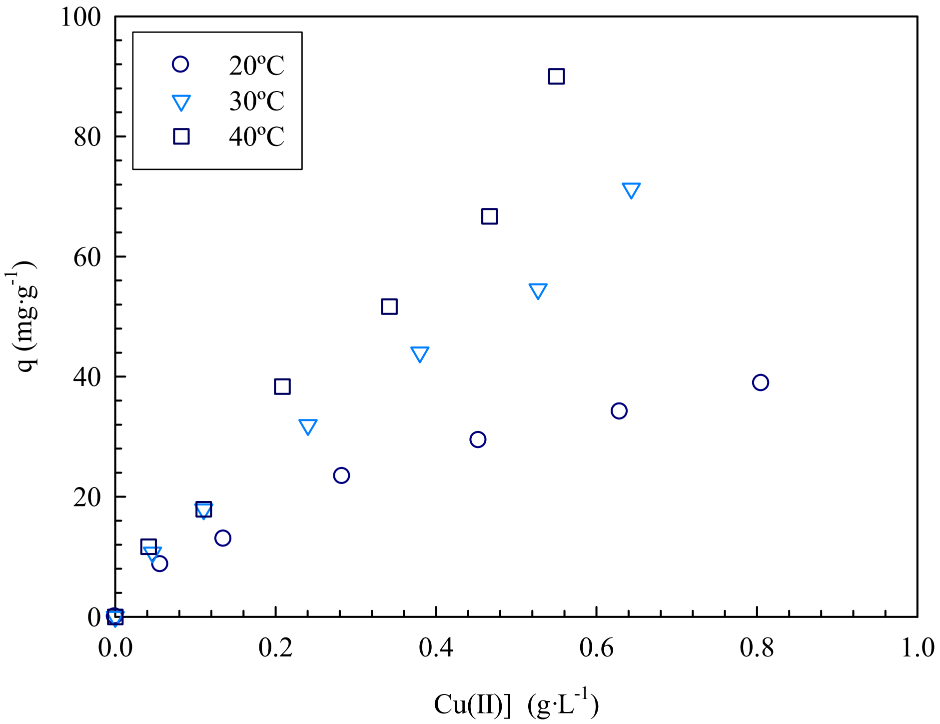


Figure 5.6. Adsorption isotherms of Cu(II) onto PVP_2 at different temperatures: 20, 30 and 40ºC. $[Cu(II)]_0 = 0{,}1\text{-}1{,}0\ g \cdot L^{-1}$, m = 1 g.

PVP_{25} results are presented in Figure 5.7, from this diagram it is deduce that this support performed a higher adsorption capacity than PVP_2 and Chitosan at 20ºC despite of its 25% of cross-linking. For instance in a previous work (Li et al., 2005), it was described a lower adsorption capacity while the cross-linking increased. However, the adsorption capacities of PVP_{25} decreased as a result of the temperature increment and there was no better adsorption activity at temperatures more than 40ºC.

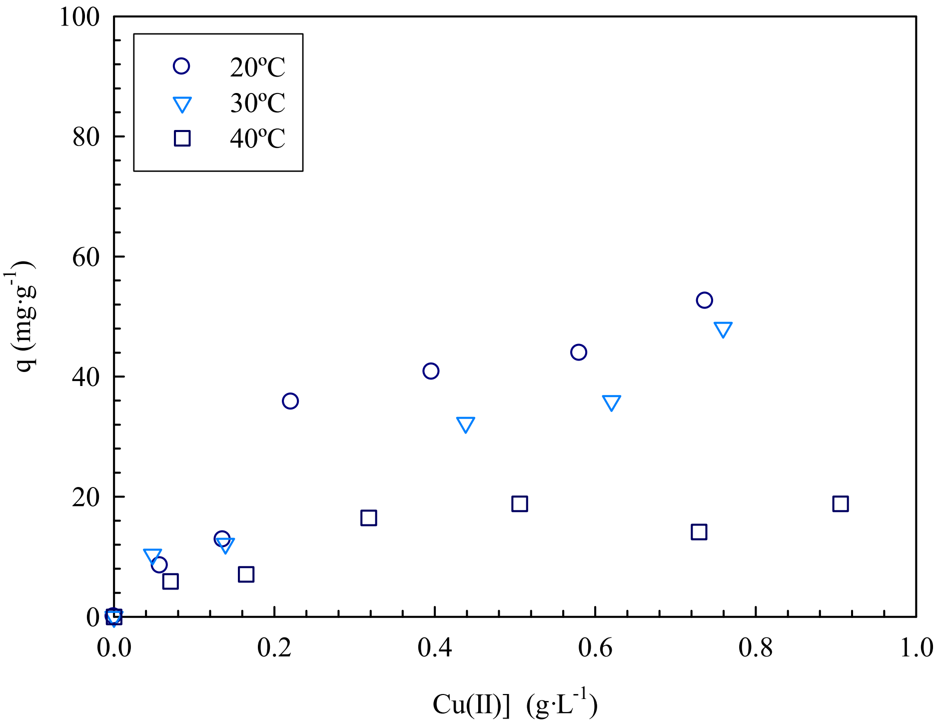


Figure 5.7. Adsorption isotherms of Cu(II) onto PVP_{25} at different temperatures: 20, 30 and 40ºC. $[Cu(II)]_0$ = 0,1-1,0 $g·L^{-1}$, m = 1 g.

Finally, in Figure 5.8, Chitosan results showed that adsorption capacity kept constant even when temperature changed. This behaviour qualifies Chitosan as a polymer capable to adsorb the same amount of Cu(II) ions between 20 and 40ºC. Then it is suggested that Chitosan did not just presented less adsorption capacities than the rest of polymers because of the external configuration (particle size) but also because it contains a higher cross-linking degree (Guibal, 2004).

Therefore, it was also observed that the temperature effect had high influence on PVP_2 and PVP_{25} adsorption capacities while had no effect on Chitosan. From here, it is confirmed that the exposed surface, which is formed by energy sites or available radicals changed when temperature increased, afterwards this change had a great influence on adsorption behaviour as previously reported (Chu, 2002).

UNIVERSITAT ROVIRA I VIRGILI
PHENOL OXIDATION CATALYSED BY POLYMER-SUPPORTED METAL COMPLEXES
Ursula Isabel Castro Cevallos
ISBN: 978-84-692-5927-6/DL:T-1666-2009

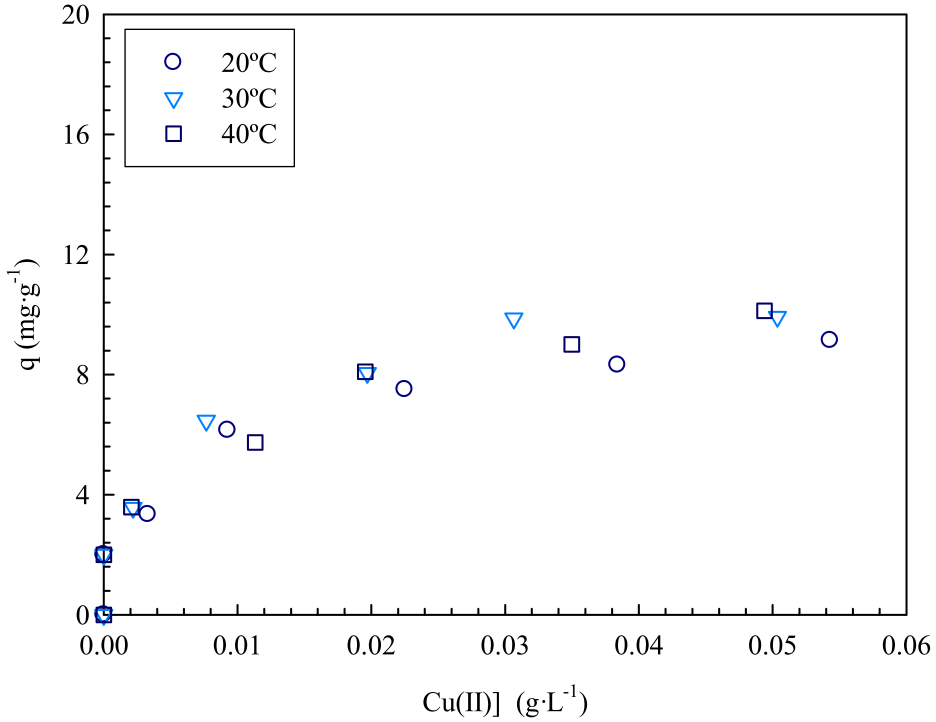


Figure 5.8. Adsorption isotherms of Cu(II) onto Chitosan at different temperatures: 20, 30 and 40°C. $[Cu(II)]_0$ = 0,01-0,10 $g \cdot L^{-1}$, m = 1 g.

d. Langmuir study

The equilibrium data was analysed by known adsorption isotherm models, which provided the basic theory in adsorption behaviour. The Langmuir theory (1916) follows the idea of a monolayer surface adsorption onto an ideal surface. This model is based on a kinetic principle, which states that the rate of adsorption is equal to the rate of desorption from the surface. Thus, the model assumes that the surface of the sorbate is homogeneous and has localised adsorption sites. Moreover, by rearrangements and simplifications, it is arrived at the familiar Langmuir isotherm where each site can accommodate only one ion, molecule or atom. Then, the model is expressed in Eq (5,6):

$$q = \frac{q_{max} \cdot K \cdot C_e}{1 + K \cdot C_e} \tag{5.6}$$

where the adsorption capacity q ($mg\cdot g^{-1}$) is a function of Cu(II) concentration at the equilibrium C_e ($mg\cdot L^{-1}$), the Langmuir equilibrium constant K ($L\cdot mg^{-1}$) and the maximum adsorption capacity q_{max} ($mg\cdot g^{-1}$). So that, linearisation of Eq. (5.6) gives Eq. (5.7):

$$\frac{C_e}{q} = \frac{C_e}{q_{max}} + \frac{1}{K \cdot q_{max}} \qquad (5.7)$$

Langmuir constant K and q_{max} were calculated from the plot of C_e/q vs C_e. Then, on Table 5.2 Langmuir parameters are listed (K and q_{max}) as indicators of the adsorption process, where K represents the equilibrium constant and q_{max} expresses the maximum adsorption capacity at monolayer levels (Wan et al., 2005).

Table 5.2. Langmuir parameters of Cu(II) adsorption onto PVP_2, PVP_{25} and Chitosan, m = 1 g at 20, 30 and 40ºC.

Support	Temperature	K ($L\cdot mg^{-1}$)	q_{max}($mg\cdot g^{-1}$)	R^2
PVP_2 (powder)	20º C	$2.6\cdot10^{-3}$	56	0,9724
	30º C	$1.5\cdot10^{-3}$	128	0,8356
	40º C	$0,9\cdot10^{-3}$	238	0,4853
PVP_{25} (beads)	20º C	$1.6\cdot10^{-3}$	98	0,7029
	30º C	$2,9\cdot10^{-3}$	63	0,7478
	40º C	$4,7\cdot10^{-3}$	22	0,8596
Chitosan (beads)	20º C	$2.4\cdot10^{-1}$	10	0,9867
	30º C	$3,1\cdot10^{-1}$	11	0,9880
	40º C	$2,2\cdot10^{-1}$	11	0,9715
Cationic resin (CR)	30ºC	$9,8\cdot10^{-1}$	113,64	0,9998

Then, for PVP_2 case, it can be seen that K constant decreased when temperature increased, so this variable made clear that equilibrium constant decreases at high temperatures because of the lack of saturation onto the sorbent surface, moreover these results described PVP_2 as a material with high adsorption capacities and easy Cu(II)-polymer formation at high temperatures. For instance q_{max} was higher at 40ºC, demonstrating better adsorption capacities when Cu(II) ions were well spread in the sorbet media, then high temperatures gave the facility to cover most of the energetic areas of PVP_2.

On the other hand, Langmuir constants of PVP_{25} were reported on Table 5.2 as well. K values increased when temperature increased, showing higher equilibrium coefficients at 30 and 40ºC, then it is suggested that the effect of temperature increase over PVP_{25} surface reduces the adsorption capacity of PVP_{25}, therefore its equilibrium constant increases because the Cu(II) cations have difficulties to form bonds with the polymeric surface. Finally, PVP_{25} showed low q_{max} values at high temperatures, which described as well PVP_{25} difficulties to form Cu(II)-polymer bonds at 40ºC. So, PVP_{25} showed better adsorption properties at 20ºC, temperature where heat does not change tits adsorption surface.

Likewise, Chitosan Langmuir constants are presented on Table 5.2. It was seen that K constants at different temperatures were similar. This behaviour described Chitosan as a polymer capable to obtain equivalent adsorption capacities at different temperatures; in consequence q_{max} did not change at any tested temperature.

Finally, the Langmuir constant of CR was also presented in Table 5.2 and it was just presented for the 30ºC, because knowing that CR had a chemical adsorption, its study was not continued since the catalyst has to provide Cu(II) cations to the reaction media with the energy enough to act as a catalyst and without breaking the metal-polymer bond formation. So, as a reference, K Langmuir constant and q_{max} of CR showed to have higher results at 30ºC than the rest of supports, describing that CR has the best adsorption capacity of the group but its bond formation are not favourable for further catalyst use.

Finally and after Langmuir evaluation, PVP_2 presented the best energetic properties at monolayer coverage and high temperatures compared with PVP_{25} and Chitosan at this temperature range. However, data was also evaluated by Freundlich model as follows.

e. Freundlich study

Then again, the data was analysed by the Freundlich model, which is one of the earliest empirical equation used to describe equilibrium of adsorption systems (Wan et al., 2004). The model assumes a heterogeneous surface with unequal adsorption sites and different associated adsorption energies. Freundlich described the adsorption as a multi-layer adsorption where the secondary layer is formed above an incomplete first layer. The model expresses the adsorption capacity of the material (Eq. (5.9)) as a function of two constants called Freundlich K_f and 1/n parameters respectively:

$$q = K_f \cdot (C_e)^{1/n} \tag{5.9}$$

Where K_f ($mg \cdot g^{-1}$) indicates the Freundlich adsorption coefficient of the polymer and 1/n ($L \cdot g^{-1}$) represents the adsorption intensity of formed bonds. Besides, for n values between 1-10 range it can be stated that the adsorption is favourable. The linearisation of Eq. (5.9) gives Eq. (5.10):

$$Ln\,(q) = Ln\,(K_f) + \frac{1}{n} \cdot Ln\,(C_e) \tag{5.10}$$

Freundlich constants K_f and 1/n were obtained from the linearisation of experimental results. Freundlich constants were obtained from the plot of Eq. (5.10) and the results are listed in Table 5.3.

Table 5.3. Freundlich parameters of Cu(II) adsorption onto PVP_2, PVP_{25} and Chitosan, m = 1 g at 20, 30 and 40ºC.

Support	Temperature	1/n ($L \cdot g^{-1}$)	K_f ($mg \cdot g^{-1}$)	R^2
PVP_2 (powder)	20º C	0.58	0,80	0,9914
	30º C	0.71	0,67	0,9943
	40º C	0.79	0,54	0,9727
PVP_{25} (beads)	20º C	0.74	0.43	0,9059
	30º C	0.55	1.18	0,8001
	40º C	0.48	0.78	0,8055
Chitosan (beads)	20º C	0.38	2.16	0,9688
	30º C	0.41	2,36	0,9540
	40º C	0.39	2,30	0,9702
Cationic resin (CR)	30ºC	0,04	93,22	0,8572

For PVP_2 case K_f constant decreased when temperature increased, this effect showed less affinity of absorbance when temperature increased. Additionally, 1/n described the strength of Cu(II)-polymer bonds, indicating that small 1/n value described the formation of strong bonds, then it was observed that 1/n values of PVP_2 increased when temperature increased, showing that bond strength was weaker at high temperatures.

Overall, PVP_2 presented better adsorption capacities at 40ºC but at the same time its Cu(II)-polymer bonds lost strength.

Freundlich K_f parameter for PVP_{25} presented different adsorption coefficients when temperature changed. At 20 and 40ºC K_f were nearly similar, while at 30ºC K_f was almost the double than the previous temperatures, this lack of tendency at different temperatures described PVP_{25} as an unsteady energetic surface. Moreover, the decrease of 1/n parameter indicated the formation of stronger bonds, so that it was assumed that PVP_{25} had better strength of Cu(II)-polymer bond formation with the increase of temperature.

In contrast, from the evaluation of Chitosan K_f and 1/n parameters, it was seen that these parameters were almost non-sensible respect to temperature. Moreover, data showed that Chitosan formed strong bonds and had the ability to obtain better adsorption coefficients than PVP polymers.

Additionally, Freundlich K_f parameter for CR described a high adsorption capacity, while 1/n parameter showed strength bond formation between Cu(II) ions and adsorbent surface, highlighting again, like in Lagmuir evaluation, the well performance of CR as absorbent of copper ions.

Figure 5.9 plots Langmuir and Freundlich models for PVP_2, the comparison between models showed that experimental data fitted either with Langmuir and Freundlich models. Then, it is suggested that PVP_2 had a homogeneity adsorption process with heterogeneous superficial energies (Guibal, 2004).

Figure 5.10 illustrates Langmuir and Freundlich isotherms for PVP_{25} case. Results showed to follow Langmuir and Freundlich models. Then, it is assumed that PVP_{25} had a homogeneous adsorption activity with a heterogeneous energy distribution of its contact surface; then the homogeneous adsorption represented by Langmuir model is partially ideal.

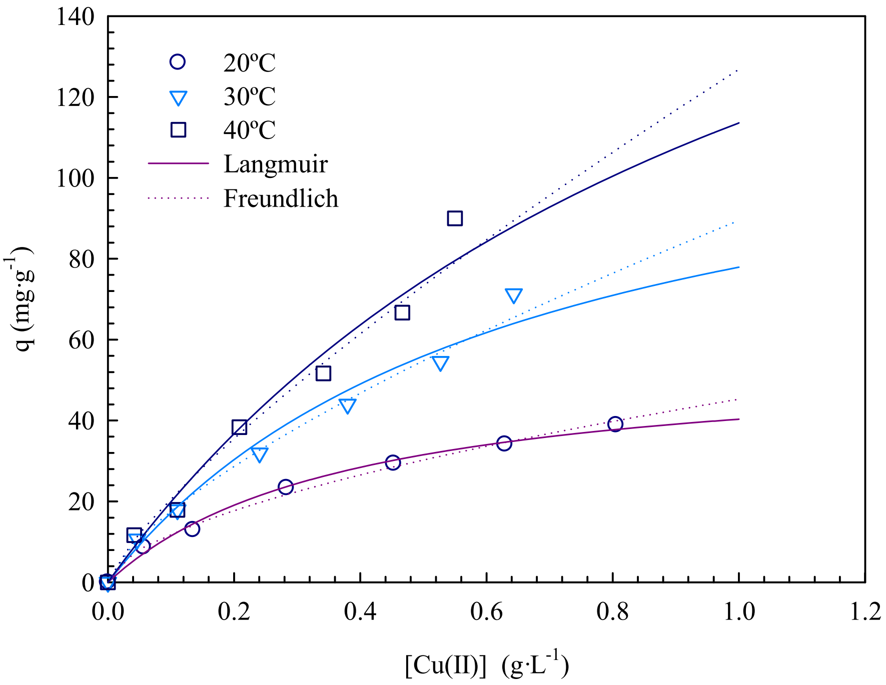


Figure 5.9. Langmuir and Freundlich isotherms of Cu(II) adsorption capacities onto PVP$_2$, [Cu(II)]$_0$ = 0,1-1,0 g·L^{-1}, m = 1g, T = 20, 30, and 40ºC.

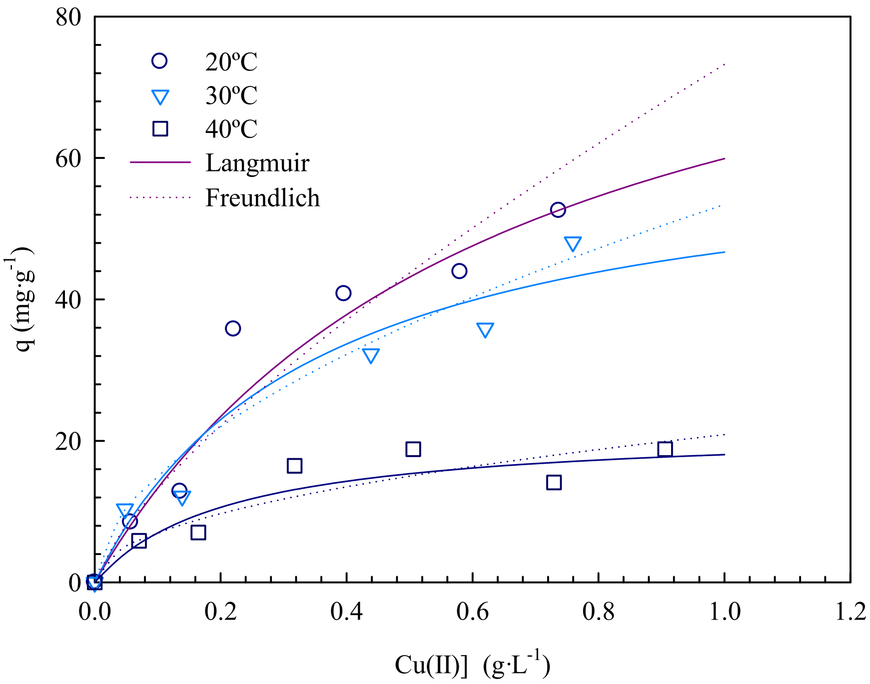


Figure 5.10. Langmuir and Freundlich isotherms of Cu(II) adsorption capacities onto PVP$_{25}$, [Cu(II)]$_0$ = 0,1-1,0 g·L^{-1}, m = 1g, T = 20, 30, and 40ºC.

For Chitosan case, Figure 5.11 showed that the Langmuir tendencies fitted well with the experimental data, describing Chitosan as a support with homogenous surface. This effect implies a well distribution of superficial energies when temperature increased. Moreover, comparison of both models showed that Langmuir was the best model to be used for Chitosan case. Hence, the distribution of superficial energies of Chitosan described a polymer with homogeneous energetic adsorption areas.

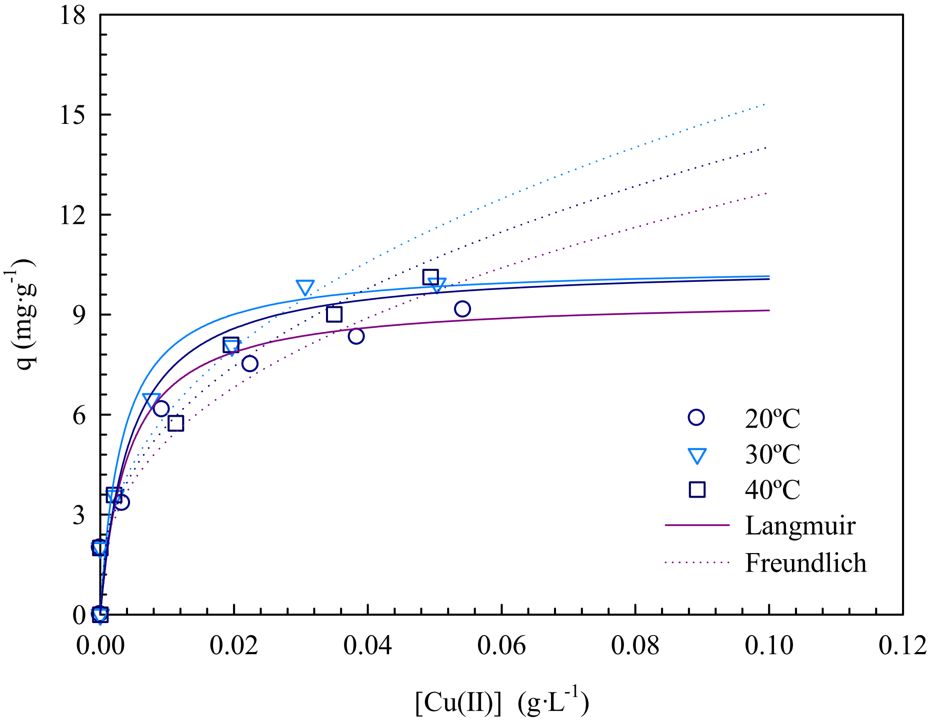


Figure 5.11. Langmuir and Freundlich isotherms of Cu(II) adsorption capacities onto Chitosan: $[Cu(II)]_0 = 0{,}01\text{-}0{,}01\ g\cdot L^{-1}$, m = 1g, T = 20, 30, and 40ºC.

CR isotherms are presented in Figure 5.12, where it can be seen that either Langmuir or Freundlich can describe the adsorption isotherm, although exists a better fit with Langmuir model, demonstrating that CR presented a homogeneous adsorption with a well radicals distribution on its contact surface, which is a favourable for the easy and organised formation of metal-polymer bonds.

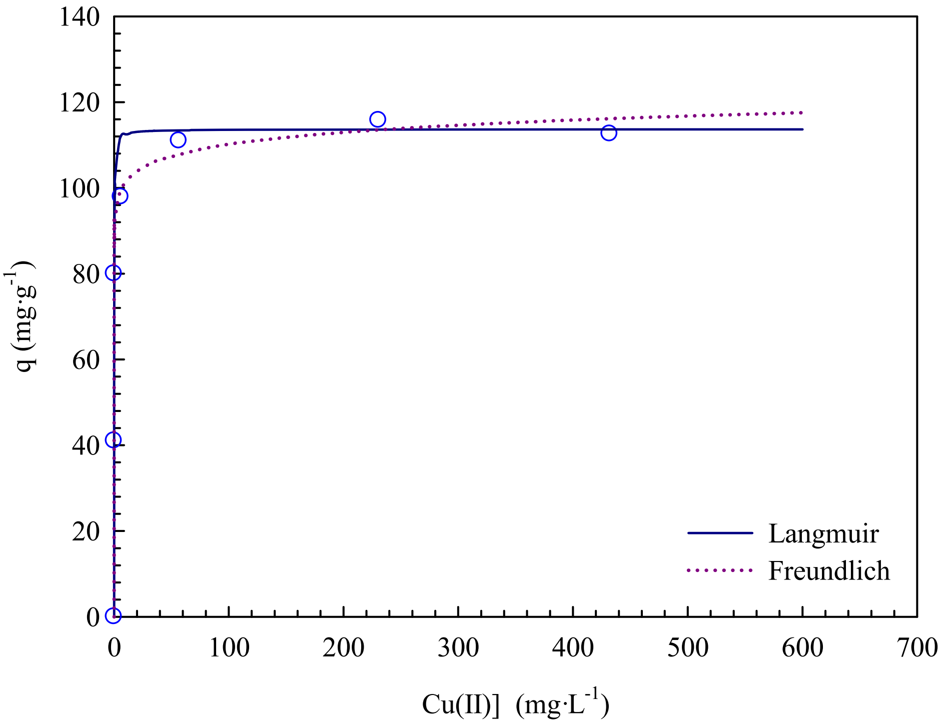


Figure 5.12. Langmuir and Freundlich isotherms of Cu(II) adsorption capacities onto CR: $[Cu(II)]_0$ = 0,1-1,0 $g{\cdot}L^{-1}$, m = 1g, T = 30°C.

5.1.2.2. Thermodynamic study

Thermodynamic parameters were stated to describe the effect of temperature on Cu(II) removal and to evaluate the nature of the adsorption process. The thermodynamic constants, Gibbs free energy variation, ΔG^o ($kJ{\cdot}mol^{-1}$), enthalpy variation, ΔH^o ($kJ{\cdot}mol^{-1}$) and entropy variation, ΔS^o ($kJ{\cdot}mol^{-1}{\cdot}K$), were calculated to evaluate the thermodynamic feasibility of the process. The Gibbs free energy change of adsorption is defined by Eq. (5.11):

$$\Delta G^0 = -RT \cdot Ln(K) \tag{5.11}$$

Where K ($L{\cdot}mol^{-1}$) is taken from the evaluation of the Langmuir model and R is the Universal gas constant (8,314 $J{\cdot}mol^{-1}{\cdot}K^{-1}$). The ΔG^o values were calculated (Eq. (5.11)) and listed in Table 5.4. The ΔG^o negative values describe qualitatively that adsorption process is spontaneous for the four of the polymeric supports. The materials were qualitatively described because the adsorption conditions were not standards. Although, literature determines the range of –8 to –6 kJ·mol^{-1} for ΔGº represents the bonding energy for an ion-exchange mechanism.

Table 5.4. Thermodynamic sorption parameters of Cu(II) removal onto PVP_2, PVP_{25} and Chitosan, m = 1g, at 20, 30 and 40ºC.

Support	T	K (L·mg^{-1})	ΔGº (kJ·mol^{-1})	ΔHº (kJ·mol^{-1})	ΔSº (kJ·mol^{-1}·K^{-1})
PVP_2 (powder)	20ºC	2,6·10^{-3}	- 12,4	- 40,5	- 0,10
	30ºC	1,5·10^{-3}	- 11,5		
	40ºC	0,9·10^{-3}	- 10,5		
PVP_{25} (beads)	20ºC	1,6·10^{-3}	- 11,3	41,1	0,18
	30ºC	2,9·10^{-3}	- 13,1		
	40ºC	4,7·10^{-3}	- 14,8		
Chitosan (beads)	20ºC	2,4·10^{-1}	- 23,5	- 3,1	- 0,10
	30ºC	3,1·10^{-1}	- 24,9		
	40ºC	2,2·10^{-1}	- 24,9		
Cationic resin	30ºC	9,8·10^{-1}	-27,8	-	-

Note, for PVP_2, the increment of ΔGº implies less adsorption at high temperatures, this agreed with K Langmuir constant that presented less bond affinity. Hence, PVP_2 adsorption capacity suggested a physical adsorption with high desorption possibility, its ΔGº range (-12,4 to -10,5 kJ·mol^{-1}) indicated that the ion exchange played a significant role in the adsorption process, then PVP_2–Cu(II) bond was formed by electrostatic interactions between adsorption sites and Cu(II) ions, also called physical adsorption (Dermibas et al., 2009).

The ΔGº for PVP_{25} showed an opposite behaviour compared with PVP_2, that is PVP_{25} ΔGº variation decreased while temperature increased. It is evident that ΔGº values for PVP_{25} were lower than PVP_2, but they suggested a feasible adsorption process promoted by low temperatures. Moreover, the ΔGº range (-14,8 to -11,3 kJ·mol^{-1}) showed an ion-exchange adsorption with values near to -16 kJ·mol^{-1}. Thus, adsorption is described as a charge transference from the adsorbent surface to Cu(II) ions to form a coordinate bond (Weng et al., 2007).

ΔGº parameter for Chitosan did not vary with temperature. Moreover, the ΔGº range (-24,9 to -23,5 kJ·mol^{-1}) indicated that the ion exchange did not play a significant role in the adsorption process. Moreover, the interaction Cu(II)-Chitosan involves a charge sharing from Chitosan active radicals to Cu(II) ions.

Finally, after thermodynamic evaluation CR presented a high negative value of ΔGº (-27,8 kJ·mol^{-1}), which indicated that between Cu(II) and CR active radicals exists a charge sharing, which is difficult to break at the same adsorption conditions.

Additionally, adsorption is also characterised by thermodynamic potentials like enthalpy ΔHº and entropy ΔSº variations, so the effect of temperature on the equilibrium constant is determined by Eq. (5.12).

$$\frac{d(\ln K)}{dT} = \frac{\Delta H^0}{R \cdot T^2} \tag{5.12}$$

From Eq. 5.12 ΔHº classifies the adsorption as endothermic or exothermic process, also expressed by Eq. (5.13)

$$\mathrm{Ln}(K) = -\frac{\Delta H^0}{R \cdot T} + \frac{\Delta S^0}{R} = -\frac{\Delta G^0}{R \cdot T} \tag{5.13}$$

and Eq. (5.14)

$$\Delta G^0 = \Delta H^0 - T \cdot \Delta S^0 \tag{5.14}$$

ΔHº and ΔSº parameters were taken from the Van't Hoff plots Eq. (5.13) showed on Figure 5.13, where ΔHº is the slope and ΔSº is the intercept (Eq. (5.14)). In Figure 5.13 the thermodynamic behaviour of PVP_2 tend to decrease when temperature increased. Then, the adsorption capacity of PVP_2 was classified as exothermic process (-40,45 kJ·mol^{-1}), also known as favourable adsorption. On the other hand, PVP_{25} presented an endothermic behaviour, which could be due to the increase in temperature increased the rate of diffusion of the adsorbate molecules across the external boundary layer and the space in between the polymeric matrix (Tan et al. 2009). Moreover, Chitosan thermodynamic behaviour presented no changes either exothermic or endothermic at temperature variation. Then, Chitosan adsorption had a constant adsorption activity at different temperatures.

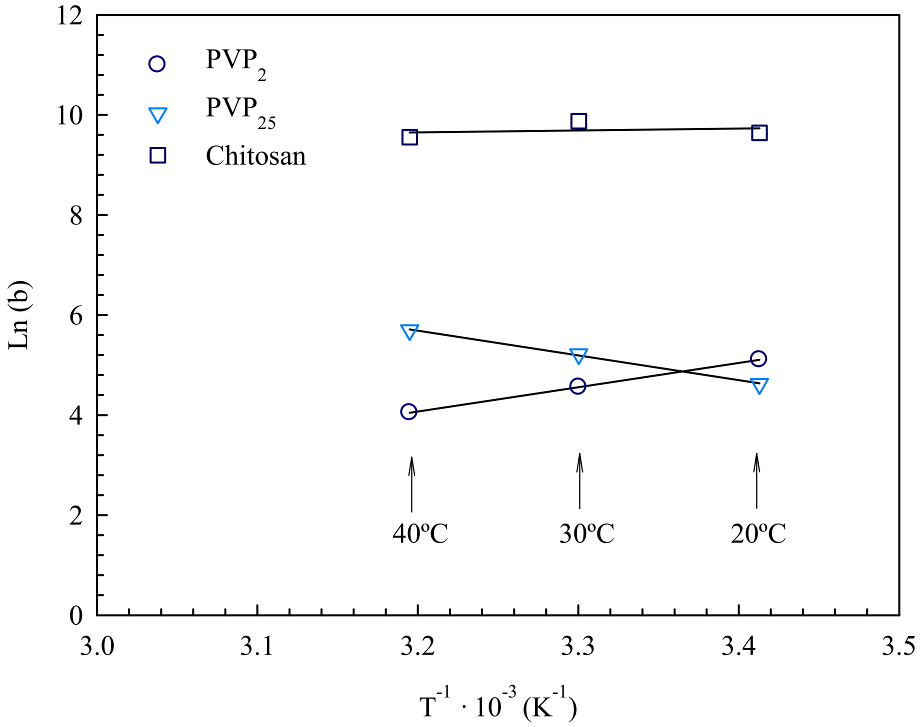


Figure 5.13. Van't Hoff diagram. Ln(b) versus T^{-1}. Difference of thermodynamic behaviour of PVP_2, PVP_{25} and Chitosan. $[Cu(II)]_0$ = 0,1-1,0 $g \cdot L^{-1}$ for PVP_2 and PVP_{25}, $[Cu(II)]_0$ = 0,01-0,10 $g \cdot L^{-1}$ for Chitosan, m = 1g, T = 20, 30 and 40ºC.

Thermodynamically, the best adsorption system is based on high negative ΔHº values and high positive ΔSº values. Also, the free energy must decrease for adsorption occurrence and the entropy change should be negative due to freedom degree decreases. Nevertheless, these standards are not always followed, for instance it was reported that adsorption capacity for Cu(II) onto sand increased when temperature decreased (Boujelben et al., 2009), and studies of organic compounds adsorbed onto activated carbon also reported endothermic adsorption (Tan et al., 2009).

At the end, the ΔSº analysis describes the randomness degree of the adsorption process. For instance, PVP_{25} adsorption presented a positive ΔSº value, which is a favourable degree of freedom expressed by randomness increment, also indicates that the adsorption leads to order through the formation of activated complex (Dogan et al., 2009), suggesting that Cu(II) adsorption onto PVP_{25} surface is an associated mechanism. On the other hand, PVP_2 and Chitosan showed negative values, which usually reflects that no significant change occurs in the internal structure of the adsorbent during the adsorption process.

5.1.2.3. Effect of pH

During the adsorption, the pH of solution at equilibrium changed from 5 to 5,5 at the end of the process. The change on the pH is explained by the competition of Cu(II) and H_3O^+ for binding available sites on the polymer surface (Chu, 2002). Figure 5.14 shows the adsorption capacities of PVP_2, PVP_{25} and Chitosan as a function of the pH. Sulphuric acid was used to adjust the pH of Cu(II) solutions. The removal of an initial $1 g \cdot L^{-1}$ (15,7 mM) of Cu(II) at 20ºC was evaluated at pH < 5, since the distribution of Cu(II) species (Figure 5.15) presented precipitations of copper hydroxide at values above pH 6. Finally the results showed that Cu(II) adsorption presented different behaviour depending on each adsorbent. For the case of PVP_2, the adsorption capacity declined when pH was increased, presenting better results on acid media, up to 140 $mg \cdot g^{-1}$. PVP_{25} presented values around 40 $mg \cdot g^{-1}$ between pH 2-5, but at pH < 2 the adsorption capacity was negligible because it is assumed that the acid media with high content of H_3O^+ ions compete with Cu(II) ions for the formation of bonds with available radicals of PVP_{25}. On the other hand, Chitosan presented better results at pH 5 (20 $mg \cdot g^{-1}$) where Cu(II) removal was more effective than at pH 2.

Overall, the pH-dependent adsorption showed that PVP_2, PVP_{25} and Chitosan polymers had structural differences (cross-linking), moreover they represented clear examples of Cu(II) adsorption at different conditions, e.g. PVP_2 was the best material for the adsorption of Cu(II) in acid media, PVP_{25} was favourable at different pH presenting the same adsorption capacity, however Chitosan was very efficient near pH 5 because it is expected that cationic adsorption increases with pH increase (Dogan et al., 2009).

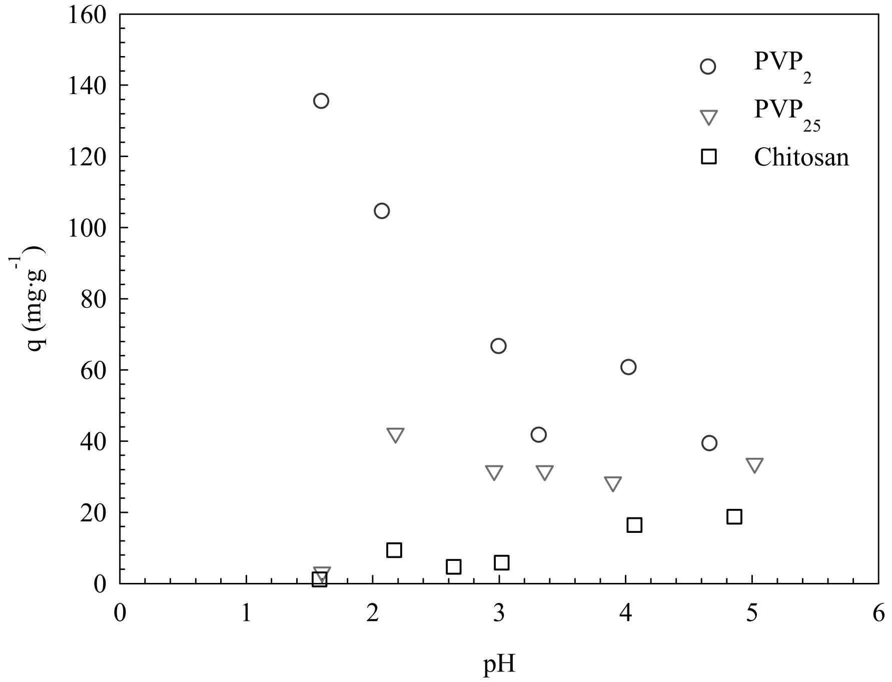


Figure 5.14. Adsorption capacity of Cu(II) onto PVP_2, PVP_{25} and Chitosan. $[Cu(II)]_0$ = 0,1-1,0 $g·L^{-1}$ for PVPs and $[Cu(II)]_0$ = 0,01-0,10 $g·L^{-1}$ for Chitosan, m = 1g, T = 30ºC, as a function of pH.

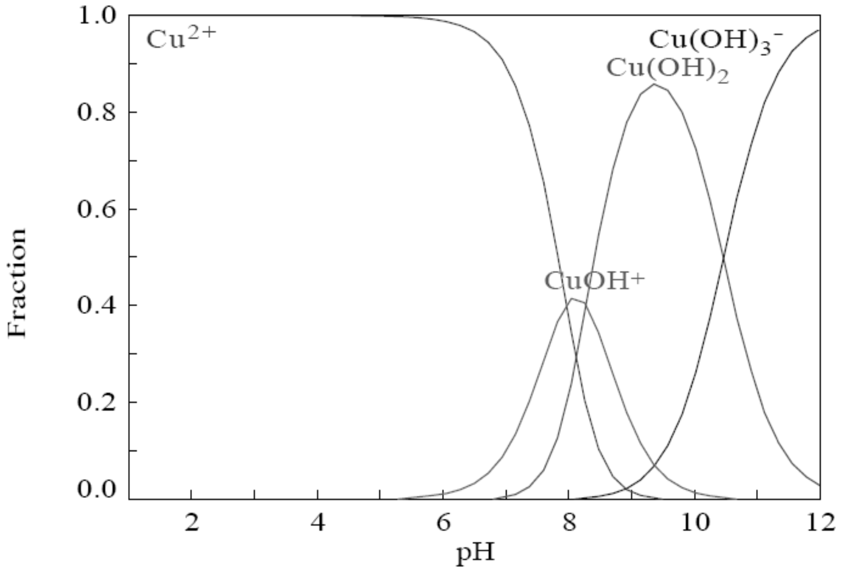


Figure 5.15. Distribution of Cu(II) species as a function of pH.

5.2. CO-PRECIPITATION

Co-precipitation was the second technique employed for the heterogenization of Cu(II) catalyst. Moreover it is important to mention that after the heterogenization of Cu(II) by adsorption and before the total evaluation of each material, the catalysts were preliminary tested in the catalytic wet oxidation of phenol (results will be presented in the following chapters). In general, the catalytic study was continued if the catalysts promoted the oxidation. The catalytic activity was detected when there was a phenol conversion at mild conditions. For instance, in these preliminary experiments of CWPO of phenol, where hydrogen peroxide was used as the oxidant, it was noticed that after 15 minutes of reaction using Cu(II)-chitosan as catalyst, the catalyst was destroyed and Cu(II) was released from the polymeric matrix. This fact made impossible the use of the provided Chitosan as support in the catalytic oxidation while hydrogen peroxide was the oxidant source. So, taking this background, it was necessary to stabilise the Cu(II)-chitosan catalyst by using an inert support (γ-alumina) that should be stable in hydrogen peroxide presence. Further more, the hypothesis would be that using an inert support, it would avoid the Cu(II)-Chitosan destruction and further Cu(II) lost into the reaction medium.

In addition, the preparation and characterisation of the co-precipitated catalyst were performed in the Department of Chemical Engineer, INTEMA-CONICET of the Universidad Nacional de Mar del Plata, Mar del Plata, Argentina.

5.2.1. EXPERIMENTAL

5.2.1.1. Materials

Hydrochloric acid fuming 37% was obtained from Merck (Ref. 100317), Chitosan at medium molecular weight was purchased from Sigma-Aldrich (Ref. 448877). Dihydrated copper chloride 97% was obtained from Cicarelli laboratories (Argentine) and γ-alumina was provided by Sasol (Argentine) in form of cylinders with an average of 3 mm of diameter and 3 mm of height.

5.2.1.2. Methods

The catalysts were synthesized by co-precipitation of the Cu-Chitosan complex onto γ-alumina. It is important to mention that γ-alumina was previously washed with distilled water in order to wet the alumina surface to promote the easy contact of the complex Cu(II)-Chitosan and the solid support (Massa et al. 2007), therefore wet alumina was exposed to the co-precipitation. Different impregnation layers were performed and in every impregnation step, the Cu-Chitosan complex was prepared by dissolving 2g of Chitosan and 4g of Cu(II) ions (dihydrated copper chloride provided Cu(II) ions), into 300 mL of HCl (0,1M). Then in a beaker of 500 mL, 40 g of γ-alumina were put in contact with the Cu-Chitosan complex at constant agitation (150 rpm). After 15 min, the liquid was drained and the excess of complex solution was removed by washing with distilled water. The catalyst was then dried at room temperature in air. The drying process was completed in a stove at 100ºC during 30 min. The co-precipitation steps were repeated, following the same experimental protocol, and therefore three catalysts were prepared: P1, P2 and P3, in which γ-alumina pellets were exposed to one, two or three co-precipitation cycles.

Content of Cu(II) after co-precipitation was measured by digestion. For this purpose 0,5 g of catalyst was ground to a fine powder and mixed with 5 mL of nitric acid for 24 hours. After that, solid was removed by filtration (150 mm pore membrane) and the liquid phase, which contains the Cu(II) amount adsorbed onto γ-alumina is analysed by an Atomic Absorption Spectrometer (Perkin Elmer, model 3110), following the procedure applied on the heterogenization of Cu(II) by adsorption.

5.2.2. RESULTS AND DISCUSSION

5.2.2.1. Catalytic characterisation - evaluation of copper content

Results for fresh samples are reported in Table 5.5 where P1, P2 and P3 represented the catalyst with 1 to 3 co-precipitation cycles. It was observed, when the number of impregnation steps was increased, the amount of copper in the samples also increased, but the difference between two and three impregnation steps was not significant, that is only and increment of 1.5 mg·g^{-1} (4,7%). This low increment suggests that γ-alumina got saturation of Cu(II)-Chitosan complex.

Table 5.5. Cu content of fresh catalysts made by co-precipitation

Sample	Cu(II) (mg·g^{-1})
P1	20.4
P2	31.8
P3	33.3

5.2.2.2. Thermo-gravimetric analysis (TGA)

TGA results of the catalyst are presented in Table 5.6. It can be seen that at the lowest temperature range, weight loss was attributed to the liquid evaporation (water), which was presented in the catalysts. In the second range of studied temperatures (110º-300ºC), the weight loss was attributed to the decomposition of Chitosan. For instance, the use of this technique would have been better applied if co-precipitation of Cu(II)-Chitosan complex onto γ-alumina surface were higher than the obtained.

Table 5.6. TGA results of the catalyst after synthesis

	TGA – weight loss (%)	
Sample	27º-110ºC	110º - 300º
P1 fresh	24,3	5,4
P2 fresh	8,4	6,2
P3 fresh	9,7	6,6

5.2.2.3. Thermal programmed reduction (TPR) analysis

TPR analysis were performed in fresh samples of catalyst P1 and in a catalyst based on $CuCl_2$ adsorbed onto γ-alumina. Results are presented in Figure 5.16. For Chitosan based samples, the presence of two reducible species was detected and assigned to the species of $CuCl_2$ and Cu-Chitosan complex, chromatograph (a). The existence of Cu-

Chitosan is confirmed by chromatograph (b) where the sample did not was synthesised by the co-precipitation of Cu(II)-Chitosan complex.

Evaluation of TPR outcome obtained with fresh catalyst P1 and the catalyst based on $CuCl_2$ adsorbed onto γ-alumina showed that the amount of $CuCl_2$ was higher for catalyst P1. This is in agreement with the ability of Chitosan to adsorb metal ions (Anipsitakis et al., 2004).

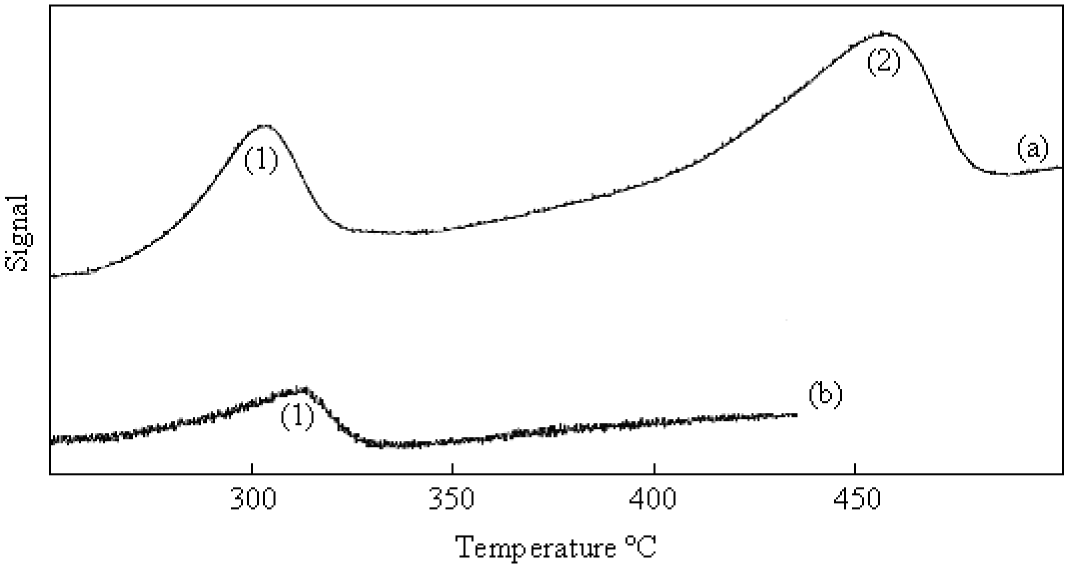


Figure 5.16. TPR profiles of two species (1) $CuCl_2$ and (2) Cu-Chitosan contained on (a) Fresh P1 catalyst, (b) $CuCl_2$ supported onto γ-alumina.

5.3. POLYMERISATION AND METAL LOADING

The interest for the better performance of catalytic oxidation processes (Pestunova et al., 2003; Caudo et al., 2007 and Pignatello et al., 2006) and the use of metals as catalysts of these processes (Gupta et al., 2008) is increasing with the application of polymeric matrices as carriers of metals (Vicente et al., 2005 and Olason et al., 1999). Previous work (Kulkarni et al., 1991) reported the importance and competence of polymer supported metal complexes, specifically for the phenol oxidation, where it was highlighted the use of copper as catalyst for phenol mineralisation.

In order to use polymerisation and metal loading techniques to the heterogenization of homogeneous catalysts, the experimental work of synthesis and characterisation of polymer-supported-Cu(II) catalysts were developed in the Department of Pure and Applied Chemistry of the University of Strathclyde, Glasgow, United Kingdom.

5.3.1. EXPERIMENTAL

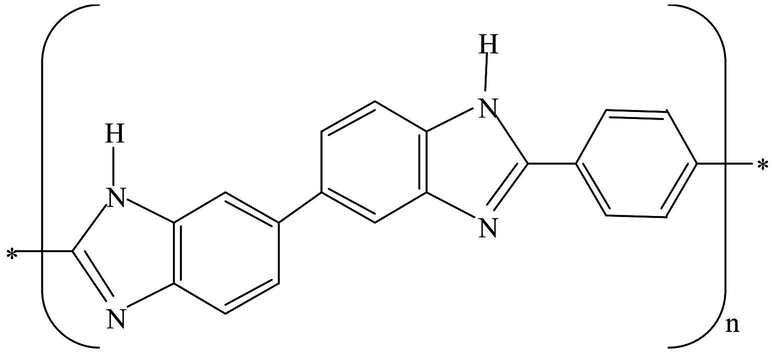
5.3.1.1. Materials

Poly benzyl imidazol PBI was supplied by the Celanese Co. while NaOH by Sigma-Aldrich. Polyvinylalcohol (Mowiol 40-88), sodium chloride, 2-ethyl-1-hexanol, and toluene were used as supplied by Aldrich Chemical Co. Azobisisobutyronitrile (AIBN) from BDH Company was recrystallised from methanol. Divinyl benzene (DVB) (80% grade) from BDH Laboratory and Vinyl benzyl chloride (mixed of m- and p- isomers) (VBC) from Sigma-Aldrich were each freed of inhibitors by passing down columns of silica. 2-menminomethyl pyridine (AMP), iminodiacetic acid (IMDA) and ethanol were used as supplied by Sigma-Aldrich. Molybdenyl acetylacetonate ($MoO_2(acac)_2$), Copper acetylacetonate ($Cu(acac)_2$) and Copper sulphate ($CuSO_4$) were used as provided by Aldrich Chemical Co. Nitric acid 65% and Hydrochloric acid 37% were used as supplied by Sigma-Aldrich.

5.3.1.2. Methods

a- Poly benzyl imidazol resin (PBI) – Cleaning process

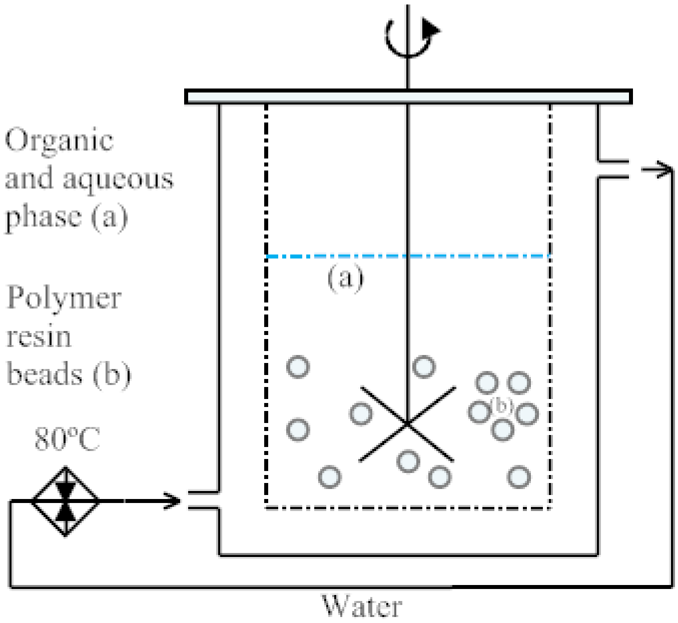
First the supplied PBI beads (Scheme 5.2) were cleaned, and for this purpose PBI was gently added to a solution of 1M NaOH and poured into a plastic bottle. This was hermetically closed and the cleaning process was carried out by continuously agitating the mixture overnight on a roller bed. Afterwards the beads were washed until the residual water had a neutral pH and they were extracted overnight with acetone in a Soxhlet system before finally being dried overnight in a vacuum oven at 40ºC.



Scheme 5.2. Poly benzyl imidazol resin structure

b. Synthesis of Poly(DVB-co-VBC) macroporous (P)

This polymer was prepared by the suspension polymerisation method (D.C. Sherrington, 1998) with a VBC loading of 88 wt%, the set-up is showed on Scheme 5.3.

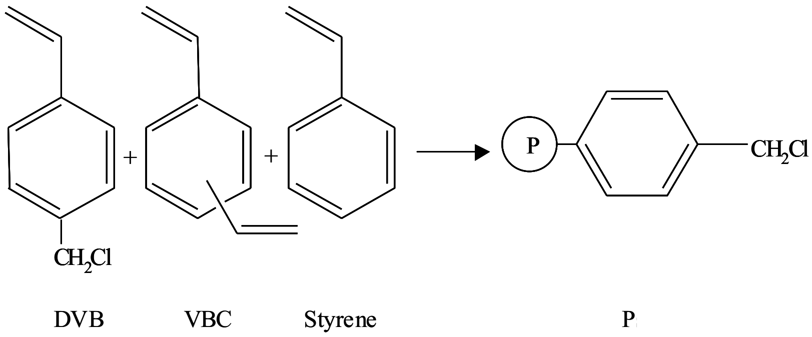


Scheme 5.3. Suspension polymerisation set up

The polymerisation system involved an organic phase, and aqueous phase, and a free radical initiator. The organic phase was a mixture of VBC and DVB monomers and the porogen (2-ethyl-1-hexanol) with a porogen/monomers volume ratio of 1/1. The aqueous

UNIVERSITAT ROVIRA I VIRGILI
PHENOL OXIDATION CATALYSED BY POLYMER-SUPPORTED METAL COMPLEXES
Ursula Isabel Castro Cevallos
ISBN: 978-84-692-5927-6/DL:T-1666-2009

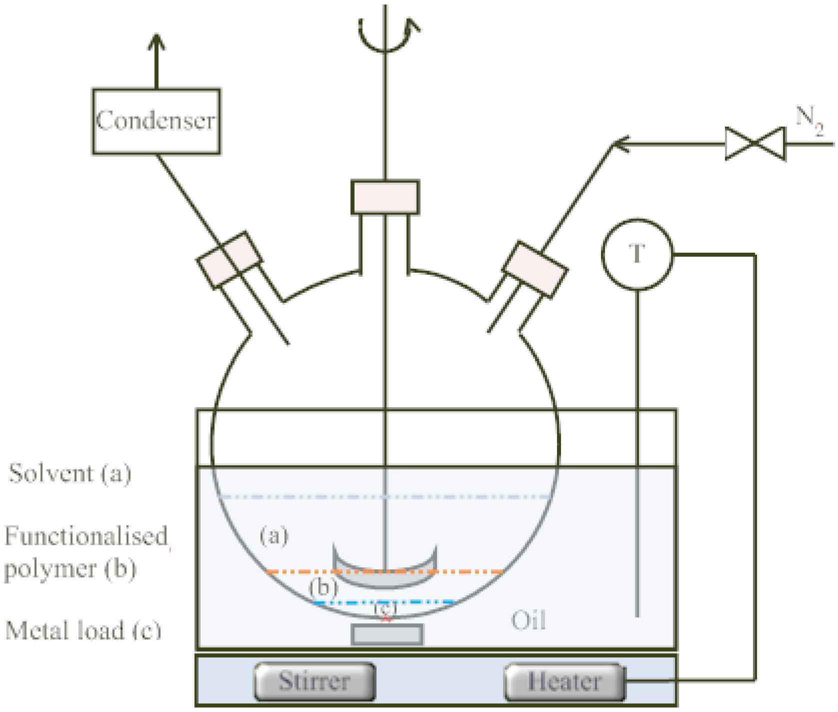
phase contained 0,75 wt% polyvinyl alcohol (PvOH) and 3,3 wt% NaCl, in 20/1 volume ratio relative to the organic phase. Finally, the amount of initiator AIBN was proportional to the mixture of monomers, i.e. 1 wt% of VBC and DVB mixture (Olason et al., 1999). Then the reaction is expressed on Scheme 5.4.



Scheme 5.4. Synthesis of poly(DVB-co-VBC macroporous) (P)

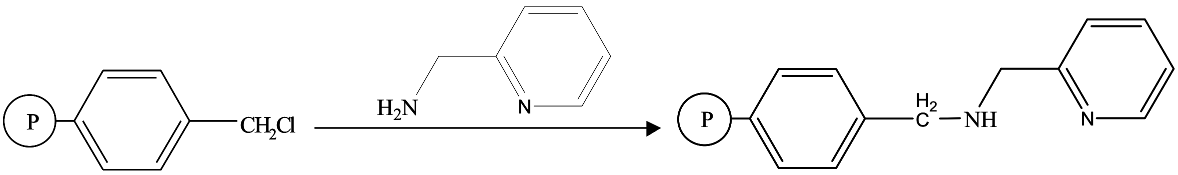
c. Functionalisation of Poly(DVB-co-VBC) or P

The functionalisation of P was performed under reflux conditions (Scheme 5.5).



Scheme 5.5. Functionalisation and metal loading set up.

The DVB-co-VBC resin was reacted either an excess of 2-aminomethyl pyridine (AMP) or iminodiacetic acid (IMDA) with a resin/ligand molar rate of 1/4 in ethanol. The reaction (Scheme 5.6) was run for a period of 48 hours, and then the functional polymer was washed with acetone/water and methanol/water before an overnight extraction with acetone.



Scheme 5.6. Functionalisation of Poly(DVB-co-VBC) with 2-aminomethyl pyridine

d. Metal loading

The PBI or P resin was loaded with molybdenum or copper, which were to be evaluated as catalyst in the phenol oxidation. Copper because it presents important catalytic properties for the CWO of phenol, as described on Chapter III. On the other hand molybdenum was selected because in previous works (Olason et al., 1999; Mbeleck et al., 2007) it was reported the efficient catalytic activity of polymer-supported-molybdenum catalysts.

So that, each reaction was carried out in a three necked 100 mL round-bottomed flask, which was fitted with a reflux condenser and overhead mechanical stirrer (Olason et al., 1999), and reaction was performed with 1/2 ligand/metal molar ratio, which was calculated from the known ligand loading of each polymer deduced from the microanalytical data for the polymers (Table 5.7). The metal loading was carried out using an excess of metal salt or complex in an appropriate solvent under an inert atmosphere (see Table 5.8) and under reflux using an oil bath with continuous heating for 4 days (Scheme 5.5). Afterwards each polymer-supported metal complex obtained was exhaustively extracted overnight with the same reaction solvent in a Soxhlet system. Finally, the polymer complexes were dried overnight at 40ºC under vacuum. Additionally, some details of the preparation of the polymer-supported metal complexes are presented in Table 5.8.

Table 5.8 shows as well eight catalyst configurations combining polymer-supports and metal sources, besides the different sources of Cu(II) are organised by groups called Cua and Cus, which represent the use of acetylacetonate and sulphate salts respectively for the metal loading.

5.3.1.3.Analytical methods

The Microanalytical laboratory staff of the Department of Pure and Applied Chemistry, University of Strathclyde, with a Perkin-Elmer 2400 Series II Analyser, carried out elemental Microanalysis.

Metal analyses were carried out on a Perkin-Elmer Analyst 200 spectrophotometer. Each sample of metal complex, was ground to a fine powder, digested with 15 mL of aqua regia (solution formed by the mixture of concentrated nitric and hydrochloric acids at 1/3 mole ratio) for three-days and after digestion filtered (150 mm pore membrane) and diluted to 100 mL with distilled water. Finally the samples were assayed by standard methods provided by the atomic absorption spectrophotometer.

5.3.2. RESULTS AND DISCUSSION

5.3.2.1. Functionalisation of Poly(styrene-divinylbenzene) P

The functionalisation of the P was achieved using AMP and IMDA as functional ligands. In Table 5.7, it is presented the amount of C, H, N and Cl contained in every prepared polymer. The amination percent of CH_2Cl is determined using the elemental microanalytical data, which showed the fall in Cl % and rise in N %, giving the exchange of $-CH_2Cl$ by $-NH_2$ radicals after functionalisation. Results demonstrated that functionalisation with either AMP or IMDA were successful because conversions more than 80% describe materials capable to build amine-metal bonds 8 times more than a polymer without functionalisation.

Table 5.7. Elemental analysis of resins under study

Polymer	C	H	N	Cl	Conversion %
Polybenzimidazole or PBI	73,72	4,51	15,73	0,63	
Poly(styrene-divinylbenzene) or P	74,95	6,45	0,02	17,18	
P-2-aminomethyl-pyridine or P-AMP	82,49	6,93	6,13	3,34	81
P-imino diacetic acid or P-IMDA	74,25	6,76	2,60	2,20	88

5.3.2.2. Polymer-supported molybdenum and copper complexes

According to Table 5.8, molybdenum was successfully loaded onto both PBI and P-AMP as supports, both complexes were formed following the same procedure but the PBI obtained higher metal loading than P-AMP, demonstrating that PBI had more nitrogen content, which represents the existence of available radicals to build more metal-polymer bonds. In this case PBI has 15,73% of N content while P-AMP has 6,13%.

In the case PBI, Ps-AMP and P-IMDA resins were used as supports with $CuSO_4$ and $Cu(acac)_2$ as metal sources. In Table 5.8 data are shown for a group of six Cu(II) complexes that are classified by the Cu(II) source in each case. The group loaded using $Cu(acac)_2$ show the higher Cu(II) content when using P-AMP as support (49 $mg \cdot g^{-1}$). On the other hand, in $CuSO_4$ group, the higher metal content was achieved with PBI as the support (121 $mg \cdot g^{-1}$).

However, it is also important to know the moles of metal per ligand inside the catalysts because the catalytic activity will be evaluated by the metal content of the catalyst, so comparing supports on table 5.8 it was observed in the group of copper catalysts that while using P-AMP as support, it was obtained the highest metal/ligand ratio compared with the rest of catalysts.

Table 5.8. Abbreviation, metal loading conditions and metal ligand content of the polymer-supported metal complexes.

Complex	Metal complex	Abbreviation	Reaction solvent	Extraction solvent	Resin colour	Metal/ligand ratio
PBI-Mo(ac)	$MoO_2(acac)_2$	PBI-Mo	toluene anhydrous	acetone	light green	0,3/1
P-AMP-Mo(ac)	$MoO_2(acac)_2$	P-A-Mo	toluene anhydrous	acetone	green	0,7/1
PBI-Cu(ac)	$Cu(acac)_2$	PBI-Cua	ethanol	CH_2Cl_2	light brown	0,1/1
P-AMP-Cu(ac)	$Cu(acac)_2$	P-A-Cua	toluene anhydrous	acetone	light green	0,5/1
P-IMDA-Cu(ac)	$Cu(acac)_2$	P-I-Cua	toluene anhydrous	acetone	grey	0,3/1
PBI-Cu(sul)	$CuSO_4$	PBI-Cus	water	CH_2Cl_2	beige	0,5/1
P-AMP-Cu(sul)	$CuSO_4$	P-A-Cus	water	water	light green	0,8/1
P-IMDA-Cu(sul)	$CuSO_4$	P-I-Cus	water	water	grey	0,2/1

CONCLUSIONS

The adsorption capacities of Cu(II) onto PVP_2, PVP_{25}, Chitosan and CR demonstrated that the exposed polymeric surface was the main influence for adsorption behaviour. Powder (PVP_2) showed greater Cu(II) removal capacities than beads (PVP_{25} and Chitosan) at temperatures more than 30ºC. However, when comparing with CR, it is also remarkable the importance of the surface charge due to it determines the easy attraction of ions onto the support.

The kinetic evaluation presented better fitting of experimental data when the pseudo-first-order kinetic model was used for the first three cases (PVP_2, PVP_{25} and Chitosan), although CR adsorption profile followed the pseudo-second-order kinetic model, which also described a chemisorption process.

Besides, it was demonstrated that the adsorption rate of polymers had a slight variation when temperature changed, but this effect is not applicable to Chitosan as it presented the same behaviour at the three tested temperatures. On the other hand, while PVP_2, PVP_{25} and CR isotherms were well fitted by both Langmuir and Freundlich models, Chitosan was better described by Langmuir model, assuring in this way that Chitosan presented a homogeneous layer formation on its surface.

Thermodynamic evaluation showed that PVP_2 polymer performed an exothermic behaviour, because there is a possible destruction of the polymer matrix at high temperatures, where the bond brake provides energy to the system. Meanwhile, PVP_{25} developed an endothermic adsorption, describing a matter of sharing charges from the adsorbent surface to Cu(II) ion. On the other hand, Chitosan did not present either exothermic or endothermic behaviour, which suggested a lack of charge sharing between surface and adsorption medium.

It was evident the influence of the pH onto the adsorption, especially for PVP_2 because the adsorption of Cu(II) was considerably increased at acid levels, while PVP_{25} and Chitosan were less affected by the pH change.

The co-precipitation technique was employed to synthesis Cu(II) catalysts. The technique was employed up to three times in order to increase the amount of Cu(II) content into the catalyst, however there was no more than 5% of increment comparing the first and third co-precipitation cycles, so it was assumed the saturation of the inert support.

TGA results showed a weight loss no more than 7%, so the low values demonstrated that the co-precipitation of Cu(II)-Chitosan complex was not effective as expected because of the low Cu(II) content.

Finally, TPR chromatograph showed the presence of two species on the catalyst, which were classified as $CuCl_2$ and Cu-Chitosan complex.

The synthesis of Ps and its functionalisation was performed using two ligands. The functionalisation of Ps achieved high amination percents, it was obtained 81% when AMP was used, while 88% was achieved with IMDA.

Likewise, molybdenum and copper were used to be loaded onto each polymeric matrix, then from the use of two different copper salts it was obtained higher metal loadings when copper sulphate was used, this suggests that supported-metal complexes based on copper sulphate and synthesised with water have more possible catalytic active sites.

REFERENCES

- Ahmad, A.L., Sumathi, S., Hameed, B.H., Adsorption of residue oil from palm oil mill effluent using powder and flake chitosan: Equilibrium and kinetics studies, Water Research 39 (2005) 2483.
- Anipsitakis, G.P., Dionysiou, D.D., Radical generation by the interaction of transition metals with common oxidants, Environ. Sci. Technol. 38 (2004) 3705.
- Boujelben, N., Bouzid, J., Elouear, Z., Adsorption of nickel and copper onto natural iron oxide-coated sand from aqueous solutions: Study in single and binary systems, Jorunal of Hazardous materials 163 (2009) 376.
- Caudo, S. Centi, G., Genovese, C., Perathoner, S., Copper- and iron-pillared clay catalysts for the WHPCO of model and real wastewater streams from olive oil milling production, Appl. Catal. B: Environ. 70 (2007) 437.
- Chu, K.H., Removal of copper from aqueous solution by chitosan in prawn shell: adsorption equilibrium and kinetics, J. Hazard. Mater. B90 (2002) 77.
- Dermibas, E., Dizge, N., Sulak, M.T., Kobya, M., Adsorption kinetics and equilibrium of copper from aqueous solutions using hazelnut shell activated carbon, Chem. Eng. J. 148 (2009) 480.
- Dogan, M., Abak, H., Alkan, M., Adsorption of methylene blue onto hazelnut shell: Kinetics, mechanism and activation parameters, J. Hazard. Mater. 164 (2009) 172.
- Guibal, E., Milot, C., Tobin, J.M., Metal-Anion Sorption by Chitosan Beads: Equilibrium and Kinetic studies, Ind. Eng. Chem. Res. 37 (1998) 1454.
- Guibal, E., Interactions of metal ions with chitosan-based sorbents: a review, Separation Purificat. Technol. 38 (2004) 43.
- Gupta K.C., Sutar, A.K., Polymer supported catalysts for oxidation of phenol and cyclohexene using hydrogen peroxide as oxidant, J. Molec. Cata. A280 (2008) 173.
- Kulkarni, U.S., Dixit, S.G., Destruction of Phenol from Wastewater by Oxidation with $S0_3^{2-}$-0_2, Ind. Eng. Chem. Res. 30 (1991) 1916.
- Li, N. Bai, R., Copper adsorption on chitosan–cellulose hydrogel beads: behaviors and mechanisms, Separation purific. Technol. 42 (2005) 237.

- Massa, P., Ivorra, F., Haure, P., Medina, F., Fenoglio, R., Catalytic wet air oxidation of phenol aqueous solutions by 1% Ru/CeO_2–Al_2O_3 catalysts prepared by different methods, Catal. Commun. 8 (2007) 424.
- Mbeleck, R., Ambroziak, K., Saha, B., Sherrington, D.C., Stability and recycling of polymer-supported Mo(VI) alkene epoxidation catalysts, React. & Funtion. Polym. 67 (2007) 1448.
- Olason, G., Sherrington, D.C., Oxidation of cyclohexene by t-butylhydroperoxide and dioxygen catalysed by polybenzimidazole-supported Cu, Mn, Fe, Ru and Ti complexes, React. Funct. Polym. 42 (1999) 163.
- Perkin-Elmer Corporation, Analytical Methods for atomic absorption spectrometry, USA (1994).
- Pestunova, O.P., Ogorodnikova, O.L., Parmon, V.N., Studies on the phenol wet peroxide oxidation in the presence of solid catalysts, Chem. Sustain. Develop. 11 (2003) 227.
- Pignatello, J.J., Oliveros, E., MacKay, K., Advanced Oxidation Processes for Organic Contaminant Destruction Based on the Fenton Reaction and Related Chemistry, Critical reviews in Environ. Sci. Technol., 36 (2006) 1.
- Sherrington, D.C. Preparation, structure and morphology of polymer supports, Chem. Commun. (1998) 2275.
- Tan, I.A.W., Ahmad, A.L., Hameed, B.H., Adsorption isotherms, kinetics, thermodynamics and desorption studies of 2,4,6-trichlorophenol on oil palm empty fruit bunch-based activated carbon, J. Hazard. Mater. 164 (2009) 473.
- Verbych, S., Bryk, M., Chornokur, G., Fuhr, B., Removal of Copper(II) from Aqueous Solutions by Chitosan Adsorption Separation Sci. Technol 40 (2005) 1749.
- Vicente, J., Rosal, R., Diaz, M., Catalytic wet oxidation of phenol with homogeneous iron salts, J. Chem. Technol. Biotechnol. 80 (2005) 1031.
- Wan, M.W., Petrisor, I.G., Lai, H.T., Kim, D., Yen, T.F., Copper adsorption through chitosan immobilized on sand to demonstrate the feasibility for in situ soil decontamination, Carbohydrate Polym. 55 (2004) 249.

- Wan, W.S., Ab, S., Kamari, A., Adsorption behaviour of Fe(II) and Fe(III) ions in aqueous solution on chitosan and cross-linked chitosan beads Bioresource technol. 96 (2005) 443.

CHAPTER VI

HETEROGENEOUS CATALYTIC OXIDATION

Catalytic oxidation of phenol at homogeneous phase was analysed in Chapter IV and homogeneous catalysts were heterogenised and characterised in Chapter V. Hence, homogeneous catalytic oxidation showed dependency of Cu(II) concentration when using hydrogen peroxide as oxidant. Meanwhile, Chapter V demonstrated that Cu(II) was effectively supported onto polymeric materials by adsorption, co-precipitation and polymerisation-metal loading techniques. All heterogeneous catalysts synthesised in previous chapter were tested and results are reported in the present chapter. Their catalytic evaluation and effectiveness mainly depended on three variables, such as phenol conversion, total organic carbon conversion and leaching. Additionally in order to valuate the catalytic activity of these heterogeneous catalysts, a commercial copper catalyst is compared with a group of catalysts at the same operational conditions. Therefore, in the present chapter, homogeneous and heterogeneous catalytic oxidations are compared by the effectiveness of the catalyst and the leaching levels after oxidation.

6.1. EXPERIMENTAL

6.1.1. Materials

Commercial copper catalyst, 20% of CuO supported on γ-Al_2O_3, was provided by Harshaw (reference Cu0803 T1/8). Phenol crystallised was purchased from Panreac with purity higher than 99%. Catechol (99%), Hydroquinone (99%) and Formic acid (97%) were provided by Sigma-Aldrich. Fumaric acid (99,5%) was purchased from Fluka. Malonic (99%) and Succinic (99,5%) acids were obtained from Merck-Schuchardt. Hydrogen peroxide 30% w/v (100vol.) was provided by Panreac. Potassium phosphate dibasic anhydrous puriss. p.a. (K_2HPO_4) 99%, Sodium hydroxide (NaOH) pellets 99% and phosphoric acid 85% in H_2O (H_3PO_4) were provided by Sigma-Aldrich. Millipore milli-Q deionised water was used to prepare all solutions.

6.1.2. Methods

The oxidation tests were conducted at low temperature in a stirred tank reactor of 200 mL, the same set-up was presented on chapter IV on Figure 4.1, pg 44. Once again initial phenol concentration was always 1 $g \cdot L^{-1}$, the temperature 30ºC and atmospheric pressure. The sources of oxidants were air and hydrogen peroxide. When air was the oxidant, saturated air was bubbled through the reactor with a flow of 85 $mL \cdot min^{-1}$. When H_2O_2 was the oxidant, it was used the stoichiometric phenol/peroxide ($Ph:H_2O_2$) molar ratio (1:14). The mass of the added catalyst for the heterogeneous catalytic oxidation was calculated to provide Cu(II) concentrations of 10, 50,100 and 200 $mg \cdot L^{-1}$ and Mo(VI) concentration of 100 $mg \cdot L^{-1}$. That is, the amount of added catalyst (W_{CAT}), for the heterogeneous catalytic oxidation, was calculated from a mass balance in the catalyst. The Equation 6.1 relates the required amount of Cu(II) at the homogeneous oxidation (W_{Cu}) with the amount of supported Cu(II) onto a specific polymeric material by means of the adsorption capacity (q), which is expressed by weight of Cu(II) per gram of support (g $Cu(II) \cdot g_{support}^{-1}$).

$$W_{CAT} = W_{Cu} \cdot \left(1 + \frac{1}{q}\right) \qquad (6.1)$$

For the case in which co-precipitated catalysts were used, the amount of catalysts P1, P2 and P3 was 3 g, and for the rest of experiments the amount of every catalyst varied according to the Cu(II) content, which was homologous to 50 mg·L^{-1} of homogenous Cu(II) catalysts and these amounts are reported in Tables 6.1 and 6.5.

Knowing that Cu(II) has higher oxidative properties than Mo(VI) (Mbeleck et al., 2007), it was used an arbitrary 30% excess of Mo(VI) to make the comparison between both metals. Hydrogen peroxide decomposition was monitored along reaction time by the standard iodometric method 4500-CI B (Clesceri et al., 1989). K_2HPO_4, NaOH and H_3PO_4 were used to buffer phenol initial solutions and the pH was monitored along the reaction time with and electronic pHmeter. Finally, withdrawing samples of 5 mL along 120 min, it was monitored the reaction progress to determine the remained phenol and total organic carbon concentrations. HPLC and TOC protocols were the same than the ones reported for homogeneous catalytic oxidation, which can be seen in Chapter IV, pg 45.

6.1.3. Analytical procedure

Leaching of the catalyst at the end of the oxidation process was determined with an Atomic Absorption Spectrometer (Perkin Elmer, model 3110). The analyses were performed at 325 nm with a specific lamp for the elements of Cu or Mo following standard methods (Perkin-Elmer, 1994).

6.2. RESULTS AND DISCUSSION

6.2.1. AIR AS OXIDANT

It was demonstrated in Chapter IV that the homogeneous catalytic oxidation of phenol using air as oxidant was not significant for mineralisation purposes. However, as a reference and blank experiment, the heterogeneous catalytic oxidation using air as O_2 oxidant source was carried out. The catalytic activity of the Cu(II)-polymer and a commercial Cu(II) catalysts CuO/γ-Al_2O_3 were tested. The initial phenol concentration was 1 g·L^{-1} and the airflow rate was 85 mL·min^{-1}. The reaction occurred along 2 hours at 30ºC and the weight of every employed catalyst (W_{CAT}) is presented on Table 6.1.

It can be seen (Table 6.1) that catalyst weights had a lot of difference between them, this fact occurs because each material has an specific adsorption capacity, so that, their Cu(II) content is also different. Hence, employing Equation 6.1, it can be calculated the weight of catalyst with equal amount of Cu(II).

Table 6.1. Catalyst weights used for the heterogeneous catalytic oxidation of phenol

	Air	Hydrogen peroxide			
Cu(II) ($mg \cdot L^{-1}$) (i)	200	10	50	100	200
Cu-PVP$_2$ (mg) (ii)	133	6,7	33,3	66,6	133,3
Cu-PVP$_{25}$ (mg) (ii)	160	8,0	40,0	80,1	160,1
CuO/γ-Al_2O_3 (mg) (ii)	180	9,0	45,0	90,0	180,0
Cu-Chitosan (mg) (ii)	336	16,8	84,0	168,0	336,0

(i) Mass of Cu(II) presented in the reaction system
(ii) Mass of catalyst used in the experiment

Figure 6.1 displays the results of phenol conversion for these supported Cu(II) catalysts. In the figure, there are two catalysts that showed catalytic activity, Cu-PVP$_{25}$ obtained 10% of phenol concentration and Cu-PVP$_2$ even lower (2,5%). Considering that the homogeneous catalytic oxidation (Chapter IV) demonstrated that air could not be catalytically activated to degrade phenol at these conditions, it was assumed that results represented a phenol adsorption onto the catalysts. For instance CuO/γ-Al_2O_3 and Cu-Chitosan did not present phenol adsorption.

The use of air under the present reaction conditions did not offer its oxidising power; consequently oxygen is not probable to promote significant phenol conversions at these conditions because air, as oxygen source is poorly soluble in water, further un-reactive at low temperatures (Matatov et al., 1998). As a result of these adsorption results, it was not difficult to predict a nonexistent mineralisation because phenol intermediates were not detected by the HPLC.

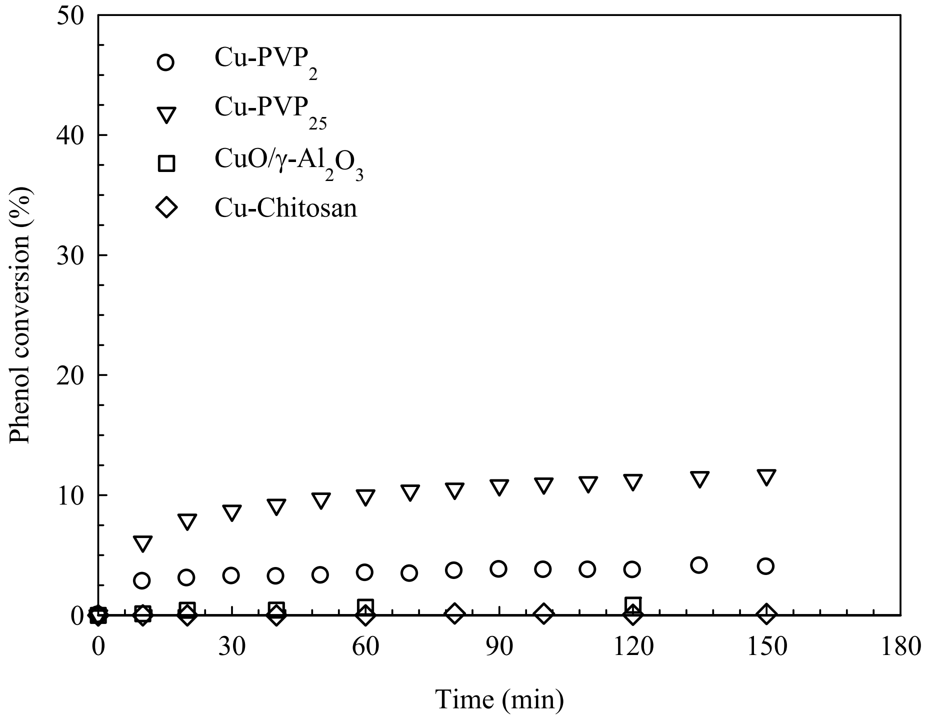


Figure 6.1. Heterogeneous catalytic phenol oxidation: comparison between Cu-polymers and a commercial catalyst. Airflow rate = 85 $mL\cdot min^{-1}$, $[Ph]_0 = 1\ g\cdot L^{-1}$, T = 30ºC.

The possibility of phenol adsorption onto the catalysts exists and it was demonstrated in Figure 6.1, although the adsorption capacity of phenol has been reported to be low. Dursun et al. (2005) studied the adsorption of phenol onto chitin and he reported that phenol adsorption depend on temperature and pH. The study concluded that near neutral pH and at low temperatures (10-40ºC) phenol adsorption was low (22 $mg\cdot g^{-1}$). To demonstrate this theory, some experiments were carried out to study the phenol adsorption capacity at the same operational conditions than oxidation. Figure 6.2 presents the phenol adsorption results of the polymeric material under study.

Results in Figure 6.2 showed low adsorption capacities when 0,5 g of polymeric material was used for each case. PVP$_2$ achieved the highest phenol adsorption capacity (15,8%), while PVP$_{25}$ and Chitosan showed 7 and 0,1% respectively. In any case, heterogeneous catalysts can be used as the carriers of active metals and as possible adsorbents of the substrate. For instance, the adsorption of the substrate onto the catalysts is beneficial for the catalytic activity of Cu(II) because the interaction between phenol and oxidant occurs in the catalyst surface where Cu(II) can effectively promote the reaction.

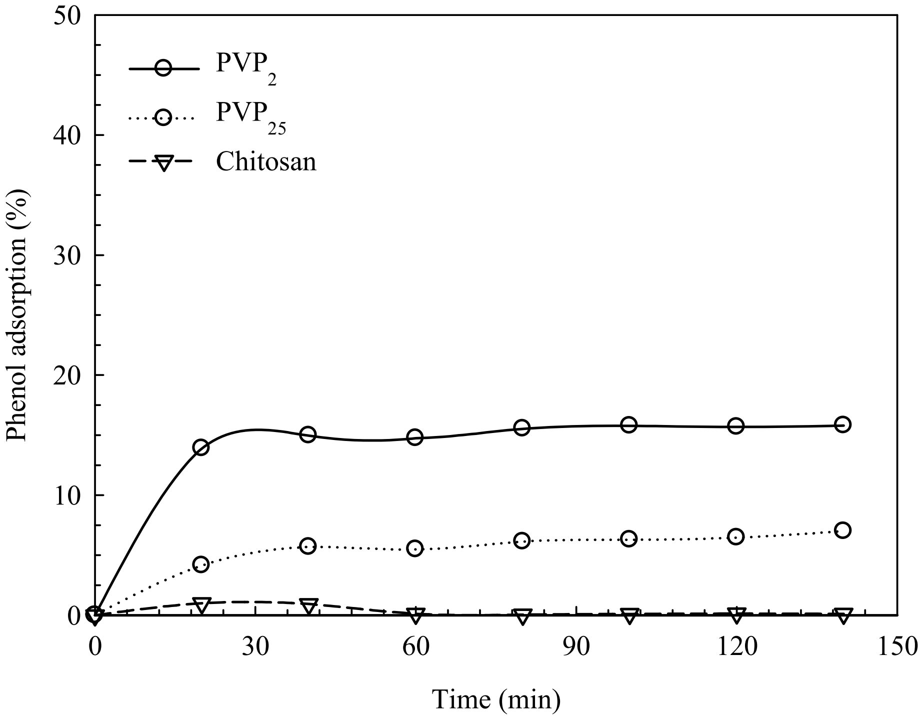


Figure 6.2. Adsorption of Phenol onto PVP and Chitosan. $[Ph]_0$ = 1 g·L^{-1}. Adsorption time = 5 h, Support weight = 0,5 g, T = 30ºC.

Hence, from these results it can be expected higher phenol conversions when using PVP_2 as catalysts support because its ability to adsorb phenol over its surface would be beneficial for the catalysis. Therefore, experiments employing hydrogen peroxide as oxidant were carried out after 30 minutes of substrate adsorption.

6.2.2. HYDROGEN PEROXIDE AS OXIDANT

Mechanisms of Fenton-like processes are extremely complex, even more when heterogeneous catalysts are used because leaching of these catalysts becomes an important variable for the oxidation system (Goldstein et al. 1999). In Chapter IV it was demonstrated that pH, temperature and initial concentrations of H_2O_2 or Cu(II) are important variables for the catalytic reaction, hence in this section it is evaluated the influence of variables such as H_2O_2 decomposition, pH, temperature and Cu(II) catalytic content over the heterogeneous catalytic oxidation and leaching.

6.2.2.1. Hydrogen peroxide decomposition

In Chapter IV, it was showed the importance of the interaction between Cu(II) and H_2O_2 in the catalytic oxidation of phenol, as a consequence the decomposition of hydrogen and the influence of pH and temperature was studied in the present section. For this purpose Cu(II)-PVP$_2$ was used as catalyst because on Chapter V it was demonstrated its high adsorption capacity of Cu(II) ions and because from previous section PVP$_2$ had the highest phenol adsorption capacity, further meet the requirements of a potential catalyst.

6.2.2.1.1. Catalytic decomposition of hydrogen peroxide: pH influence

In order to evaluate the behaviour of H_2O_2/Cu(II)-PVP$_2$ system, the decomposition of H_2O_2 was initially performed without the presence of phenol. Figure 6.3 shows the influence of pH between the range of 3 to 7 over the decomposition of H_2O_2 at 30ºC and atmospheric pressure with an initial Cu(II) concentration of 0,15 M (0,5g of Cu(II)-PVP$_2$ catalyst with 45 mg of Cu(II) per gram of support).

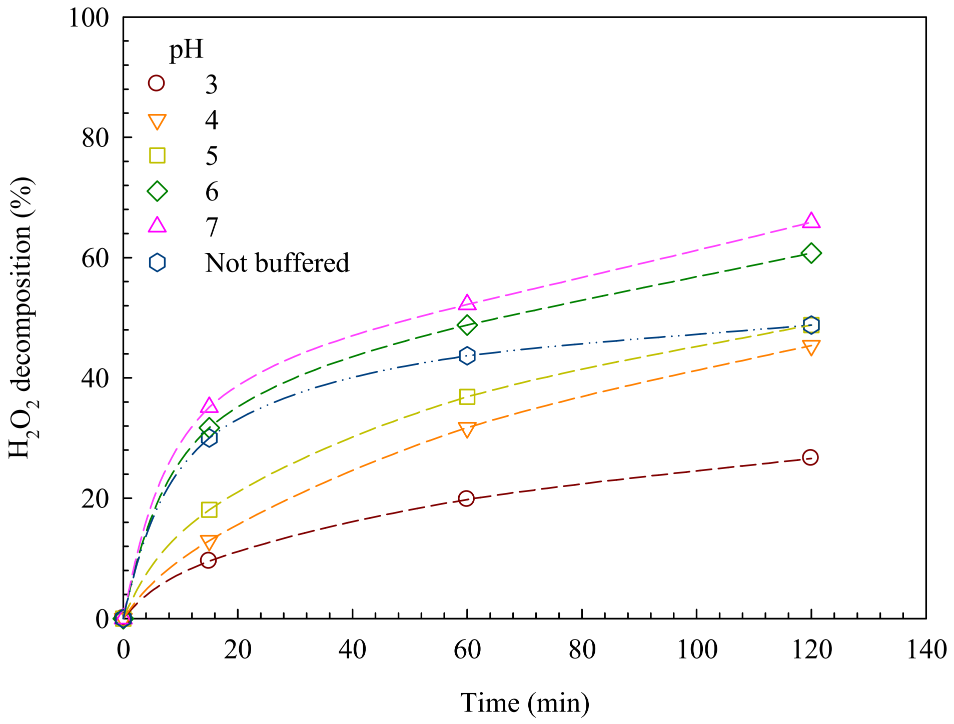


Figure 6.3. Hydrogen peroxide decomposition at different pH values. Catalyst: 0,15 M of Cu(II) supported on PVP$_2$, H_2O_2: 5 M at 30ºC and atmospheric pressure.

From literature, Bali et al. (2007) reported better H_2O_2 decomposition at pH 7 for the decolourisation of dyes when H_2O_2/pyridine/Cu(II) complex was used. Then for H_2O_2/Cu(II)-PVP_2 system, it was observed that H_2O_2 decomposition was higher with the pH increment, which suggests a better decomposition near basic pH, hence a higher formation of OH• radicals as expected.

In Figure 6.3, it is obtained the highest H_2O_2 decomposition (64%) at pH 7, but when pH was not buffered, the tendency of H_2O_2 decomposition at the first 20 minutes showed similar conversions than pH 6 or 7, then after one hour, the decomposition stopped at 48%, which was similar to the percent obtained at pH 5. Therefore this behaviour describes the high influence of pH over the system; hence fixed conditions can increase the decomposition of hydrogen peroxide and consequently the production of OH• radicals, which are the responsible of the oxidation.

In addition, the influence of pH was also evaluated trough the rate law of hydrogen peroxide decomposition. Experimental data was evaluated using two rate laws: the first and second-order rate laws, but results fitted better with the first-order rate law. Table 6.2 reports the constant rates obtained at different pH values. After calculations, it was found that activation of hydrogen peroxide followed the first order law rate, from which rate constant increased when the decomposition was carried out near neutral pH. For instance, the rate constant at free pH ($2{,}9\cdot10^{-3}$ min^{-1}) was similar to the values obtained between pH 3 and 4, confirming that rate constant depends of pH because experimental data state that H_2O_2 decomposition without buffering had a pH variation from 4,0 to 3,4.

Table 6.2. Rate of H_2O_2 decomposition using Cu(II)-PVP_2 as catalyst at 30°C and atmospheric pressure.

Rate law	Integrated rate law	pH	k (min^{-1})	R^2
$-\frac{d[A]}{dt} = k[A]$	$[A] = [A]_0 \cdot e^{-kt}$	3	$2{,}0\cdot10^{-3}$	0,9720
		4	$4{,}4\cdot10^{-3}$	0,9886
		5	$4{,}4\cdot10^{-3}$	0,9793
		6	$5{,}2\cdot10^{-3}$	0,9889
		7	$6{,}1\cdot10^{-3}$	0,9971
		Free	$2{,}9\cdot10^{-3}$	0,9106

Industrial wastewater treatments such advanced oxidation processes need high values of H_2O_2 decomposition because they represent as well the formation of OH• radicals that are the responsible of the oxidation. Hence depending on the pH, the excessive activation of H_2O_2 could actually promote the formation of O_2 and eliminate at the same time the OH• radicals before the oxidation of phenol, as presented on Chapter IV, Scheme 4.1, pg. 52. Therefore, these values will be useful to understand the decomposition of H_2O_2 when it belongs to the mechanism of the heterogeneous catalytic oxidation of phenol.

The use of catalysts supported onto solid materials has an important variable to take into account such as the catalytic deactivation or release of the catalyst from the support to the oxidation media. This effect is usually caused by the decrease of pH, which is the consequence of the production of acids or phenol intermediates along phenol oxidation. The evaluation of Cu(II) leaching without the presence of substrate is important as well because it is evident that Cu(II) release can influence the oxidation of phenol at homogeneous phase, moreover homogeneous catalytic oxidation can predominate over heterogeneous catalytic oxidation if Cu(II) concentration in solution is high.

Figure 6.4 shows the leaching of Cu(II)-PVP_2 catalyst at different pH values. The Cu(II) release was determined using the Cu(II) concentration that was found in the reaction media. In the figure it is observed that Cu(II) release is extremely high at pH 3 (12 $mg\cdot L^{-1}$), while at pH 6 the leaching was avoided. Moreover, when the reaction media was not buffered, the release of Cu(II) was no more than 4 $mg\cdot L^{-1}$, which is a permissible metal content for an industrial effluent. Overall, the decomposition of H_2O_2 at free pH is still being attractive with 48% of decomposition and leaching levels of 4 $mg\cdot L^{-1}$.

Finally results demonstrated, without the presence of phenol, that decomposition of hydrogen peroxide obtained better results at neutral pH, which at the same time avoided the Cu(II) leaching. Moreover this behaviour is expected to be homologous in presence of phenol, unless phenol intermediates provoke analytical interferences. Therefore, it is important to evaluate the decomposition of hydrogen peroxide when the substrate is present.

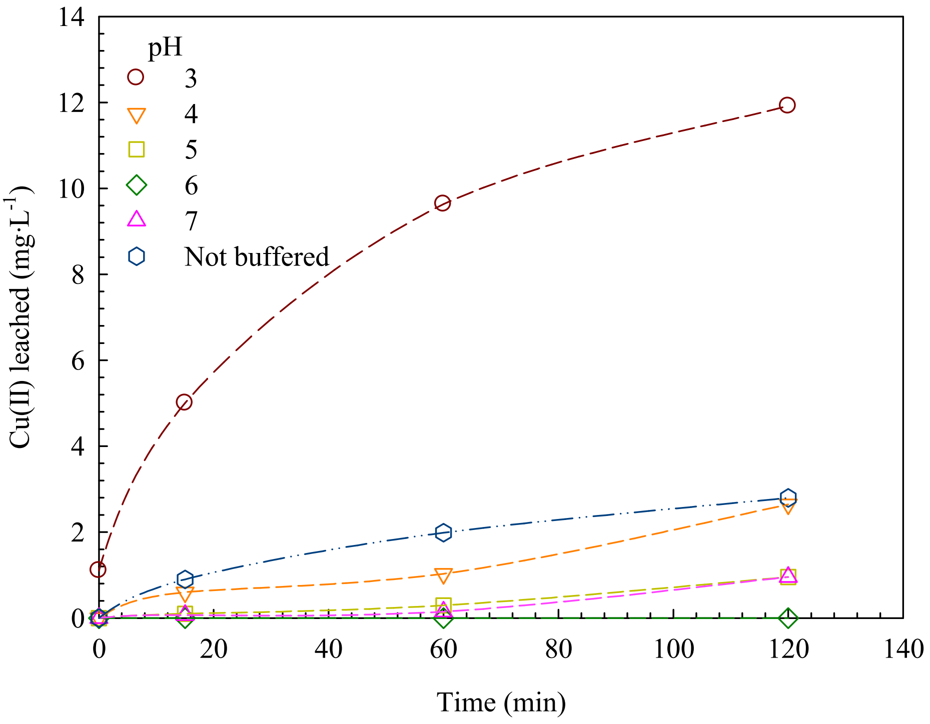


Figure 6.4. Cu(II) leaching at different pH values. Catalyst: 0,15 M of Cu(II) supported on PVP$_2$, H_2O_2: 5 M at 30ºC and atmospheric pressure.

6.2.2.1.2. Catalytic hydrogen peroxide decomposition employed for the phenol oxidation: pH influence

The production of OH• radicals is the key factor for the oxidation of phenol; therefore the influence of either variable like pH or temperature over H_2O_2 decomposition should be studied. In section 6.2.2.1.1 the influence of pH was evaluated for 3 to 7 pH-range, and results showed that neutral pH promoted the decomposition of H_2O_2. Now, pH influence over H_2O_2 decomposition is studied in presence of phenol between 4 to 6 pH. Even knowing that pH 7 was favourable for the process, it was decided to make the evaluation up to pH 6 because at pH 7 Cu(II) species precipitates, increasing in this way another variable to the system. Hence, the activation of H_2O_2 was evaluated in presence of phenol at pH 4, 5 and 6. On Figure 6.5, the decomposition of H_2O_2 as oxidant source is measured when a solution of phenol 1g·L^{-1} is oxidised using Cu(II)-PVP$_2$ as catalyst. The influence of pH variation (4-6) was tested at 30ºC and atmospheric pressure.

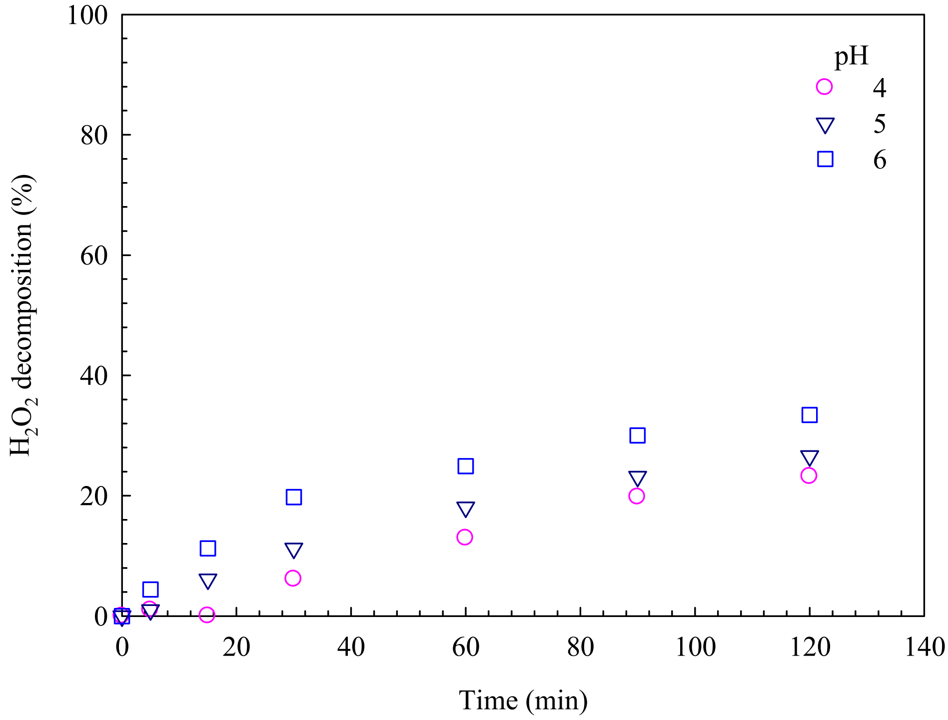
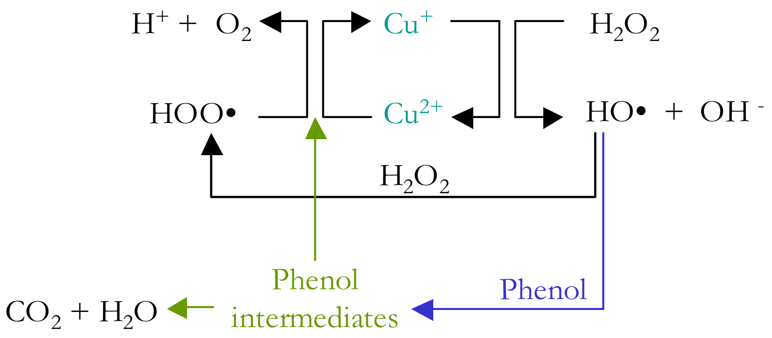


Figure 6.5. Hydrogen peroxide decomposition employed for phenol oxidation at different pH values. Catalyst: 0,15 M of Cu(II) supported on PVP_2, Ph/H_2O_2: 1/14 molar ratio at 30ºC and atmospheric pressure.

In Figure 6.5 it is observed that the H_2O_2 decomposition increases with pH, having the same tendency of the results presented in Figure 6.3 where phenol was missing. This time, when phenol is the substrate to be oxidised, the decomposition of H_2O_2 decreases. For instance, comparing results of H_2O_2 decomposition with and without phenol presence showed that without phenol presence at pH 6 it was achieved 60% of decomposition, whereas just 30% when phenol was present.

It was reported by Du et al., (2006) that intermediates like hydroquinone promoted the generation of the catalytic metal, for instance Du et al. (2006) presented a pathway for Fenton-like reactions where hydroquinone-like intermediates reduces de metallic catalyst e.g. Fe^{3+}/Fe^{2+}. Therefore it is suggested for the present case that hydroquinone-like intermediates can decrease the H_2O_2 consumption because some intermediates, instead of H_2O_2, are used on the generation of the catalyst ($Cu^{2+/}Cu^{+}$) and this effect is reflected in the decrease of hydrogen peroxide decomposition. Finally, in Scheme 6.1, taking as a reference Du et al. report, it is represented the pathway for hydrogen peroxide decomposition when phenol is oxidised.



Scheme 6.1. Reaction pathway of catalytic wet peroxide oxidation of phenol

In Chapter V it was demonstrated the importance of Cu(II), moreover after pH evaluation it was demonstrated that its generation from Cu^{+2} to Cu^{+} is important as well. In the present Chapter, leaching of Cu(II) is and additional variable to take into account, thus from the evaluation of H_2O_2 decomposition when pH varies, it was showed that leaching was similar for the three pH values, not exceeding the level of 3 $mg \cdot L^{-1}$, which is beneficial for the process. Then, the catalytic oxidation of phenol at pH 6 with Cu(II)-PVP_2 as catalyst obtained 36% of H_2O_2 decomposition, suggesting a favourable activation of H_2O_2 and avoiding metal contamination after reaction, consequently the possibilities of a longer catalytic operational life increase.

6.2.2.1.3. Catalytic hydrogen peroxide decomposition employed for the phenol oxidation: Temperature influence

The temperature is one of the most important variables to take into account, thus its influence over the decomposition of hydrogen peroxide in the CWPO of phenol is studied. For this purpose, the decomposition of H_2O_2 using Cu(II)-PVP_2 as catalyst is carried out at 30, 40 and 50ºC under atmospheric pressure.

Figure 6.6 shows the decomposition of H_2O_2 for the CWPO of phenol when the reaction media was buffered to pH 6.

Hydrogen peroxide conversions improved with temperature, but this increment was not significant between 30º and 40ºC (36% and 40% respectively) while increased up to 56% at 50ºC. Although, in agreement with reported results (Chapter IV, page 47), oxidation should be run between 30 and 40ºC because phenol conversion would be increased by the temperature influence, instead of the catalytic activity.

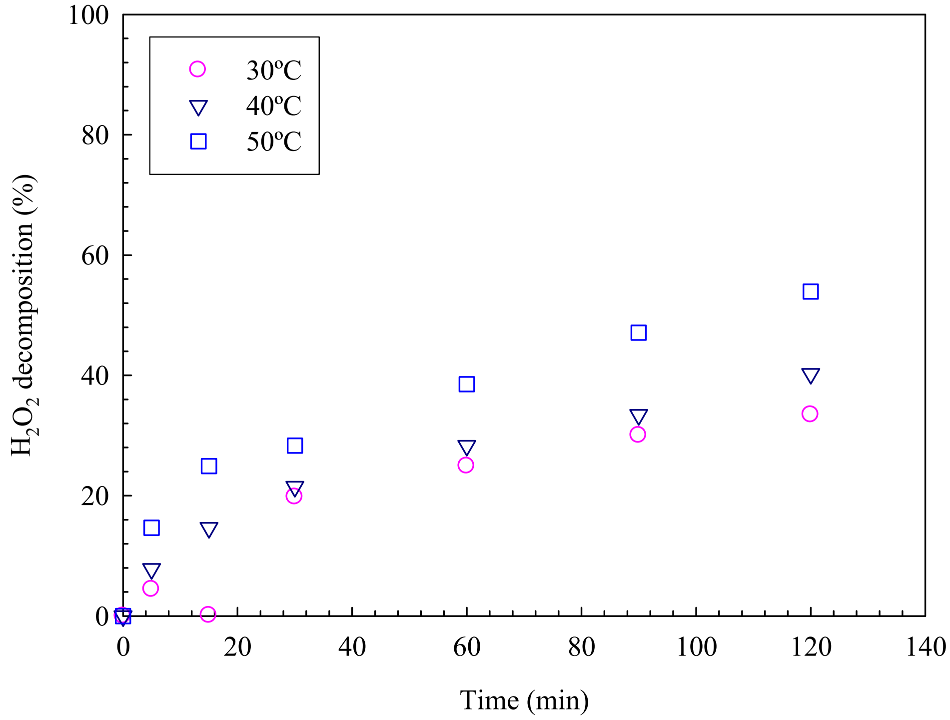


Figure 6.6. Hydrogen peroxide decomposition at different temperatures. Catalyst: 0,15 M of Cu(II) supported on PVP_2, $[Phenol]_0$= 1 g·L^{-1}, Ph/H_2O_2: 1/14 molar ratio at atmospheric pressure,

Once temperature was evaluated for H_2O_2 decomposition, then it is desirable to evaluate its influence over phenol oxidation. Hence, phenol conversion results at different temperatures are presented in Figure 6.7. It can be seen that phenol conversion increased around 20% for the increment from 30º to 40ºC and 30% from 40º to 50ºC, which means that at 50% the conversion of phenol is efficient, however this increment was not promoted just by the catalyst, but also for the temperature itself as presented in Chapter IV, page 47. Hence, results demonstrated an increment of phenol conversion with temperature, such as the tendency reported by Zazo et al. (2006), although phenol conversion of 33% for the maximum (40ºC) permissible temperature at this point are still low for the aim of the work.

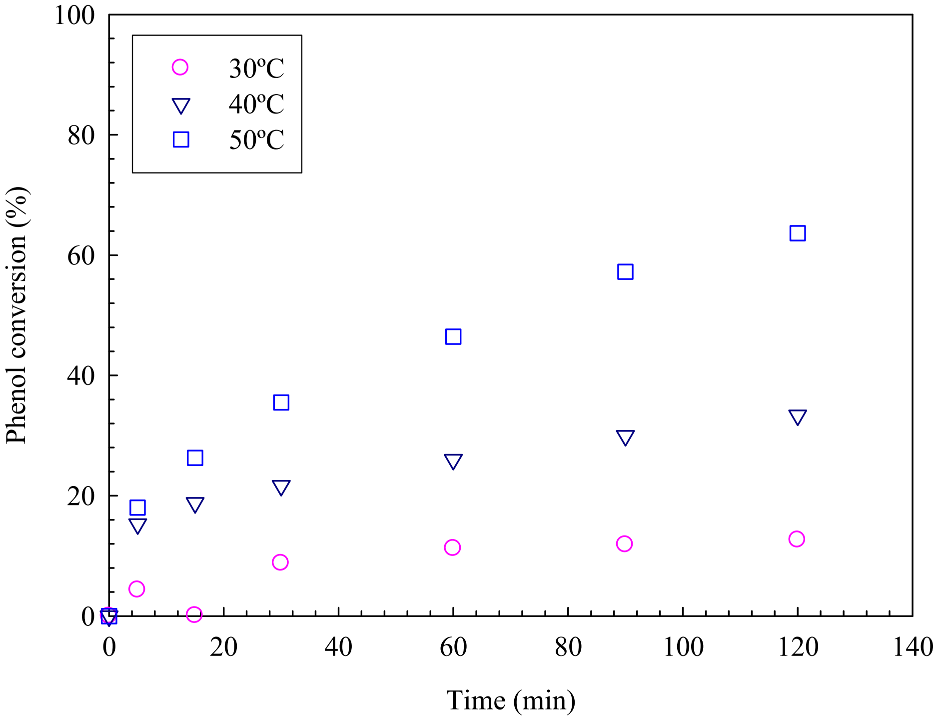


Figure 6.7. Phenol conversion at different temperatures. Catalyst: 0,15 M of Cu(II) supported on PVP_2, $[Phenol]_0$= 1 g·L^{-1}, Ph/H_2O_2: 1/14 molar ratio at atmospheric pressure.

Additionally, it is necessary to evaluate the catalyst along the reaction time by monitoring the Cu(II) release of Cu(II)-PVP_2. Figure 6.8 presents the Cu(II) leaching of the experimental results obtained from the CWPO of phenol when temperature changes. It can be noticed that temperature highly affected the stability of the catalyst and this affirmation is highlighted at 50ºC where Cu(II) was released up to 7,4 mg·L^{-1}. On the other hand at 30º or 40ºC, leaching was low (3 mg·L^{-1}), which indicates that CWPO of phenol can be performed either at 30º or 40ºC because results showed that both temperatures had similar H_2O_2 conversions with low leaching levels.

From the experimental section it is concluded that the efficiency of the activation of hydrogen peroxide is affected by pH and temperature changes. So, in order to choose the better conditions to perform the CWPO of phenol it is important to establish parameter like levels of permissible metal contamination. In this case, according to the European law of depuration system inlets (Decree, 57/2005), copper cannot exceed more than 5mg·L^{-1}, for this reason the system should be performed at pH 6, 40ºC and atmospheric pressure. For instance, it is important to consider that treatment of industrial effluents rarely have a previous buffering treatment, although these results provide information about the behaviour of the catalytic oxidation when pH or temperature change.

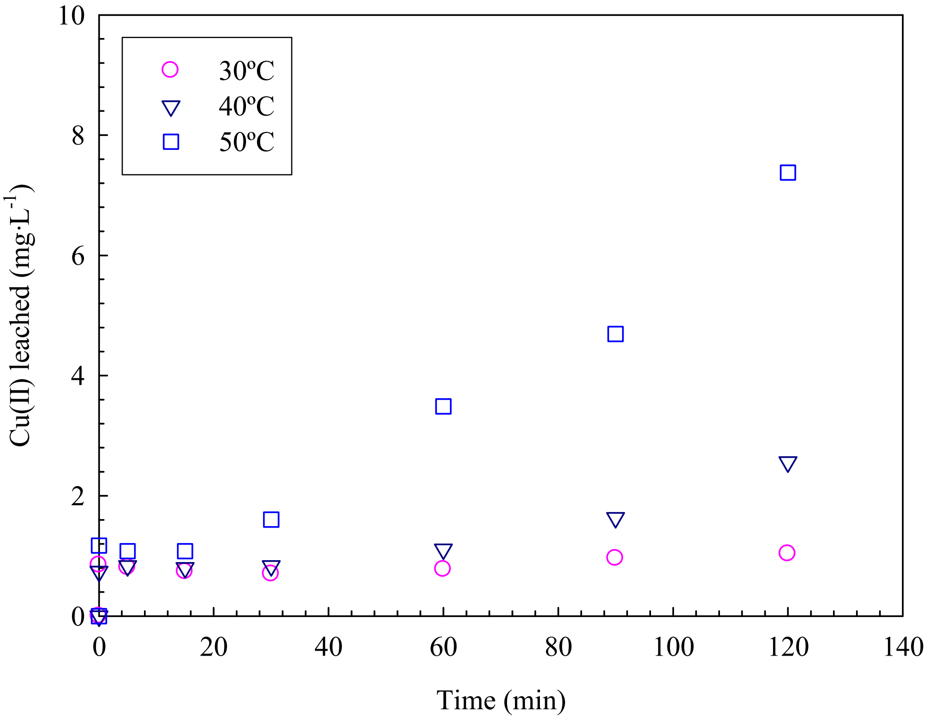


Figure 6.8. Cu(II) leaching at different temperatures. Catalyst: 0,15 M of Cu(II) supported on PVP_2. Phenol: 1 $g \cdot L^{-1}$. At pH 6 and atmospheric pressure.

6.2.2.2. Heterogeneous catalytic wet peroxide oxidation of phenol with Cu(II)-supported catalysts

Initially catalytic wet peroxide oxidation of phenol was carried out employing the Cu-supported catalysts, which were synthesised by adsorption method; moreover the performances of these catalysts were compared with a commercial catalyst. So, three catalysts ($Cu\text{-}PVP_{25}$, $Cu\text{-}PVP_2$ and $CuO/\gamma\text{-}Al_2O_3$) were tested. The amount of each used catalyst was presented in Table 6.1. Cu-Chitosan was excluded from the catalytic evaluation because its physical structure was easily destroyed in contact with hydrogen peroxide to finally promote the leaching of Cu(II).

In general industrial effluents (phenol) are not buffered before oxidation, then operational conditions have to simulate this situation carrying out the CWPO without previous pH adjust, that would be at 30ºC and atmospheric pressure. The initial phenol concentration was 1 g·L^{-1} with the stoichiometric Ph:H_2O_2 molar ratio of 1:14 and the reaction was run for a period of 2 hours.

Figure 6.9 depicts the results of phenol conversion at these conditions where they are compared with the conversions obtained at homogeneous oxidation at the same conditions. From the figure, Cu-PVP$_{25}$ obtained the lowest phenol conversion compared with the rest of catalyst, although its highest conversion (65%) represents an important percent for mineralisation purposes. It is also observed that Cu-PVP$_2$ catalyst had similar conversion to homogeneous oxidation when Cu(II) content of the catalysts was 10 mg·L^{-1}, even more its conversion (60%) was higher than the commercial catalyst (52%). Moreover, at 50 mg·L^{-1} of Cu(II) content, Cu-PVP$_2$ and CuO/γ-Al_2O_3 (commercial) catalysts provided the same phenol conversion of 64%, which differed in almost 20% from the homogeneous oxidation. On the other hand, at 100 mg·L^{-1} of Cu(II) content, CuO/γ-Al_2O_3 catalyst improved its catalytic activity and overtake Cu-PVP$_2$ activity.

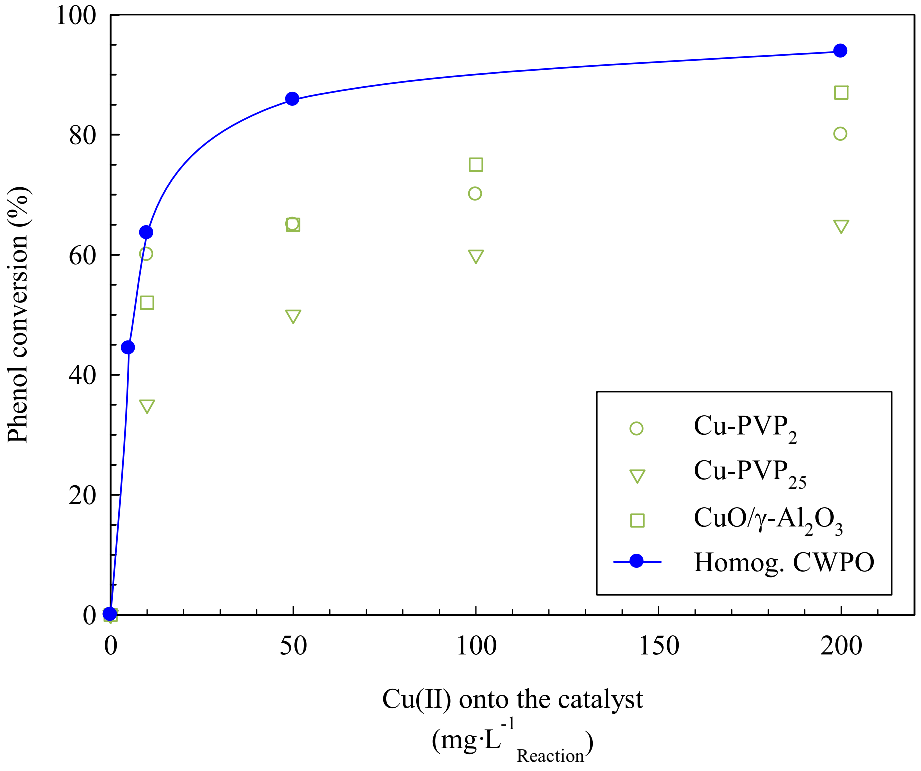


Figure 6.9. Heterogeneous catalytic phenol peroxide oxidation: influence of initial Cu(II) content. Ph:H_2O_2 1:14 molar ratio. $[Ph]_0$ = 1 g L^{-1}. Reaction time = 2 h. T = 30ºC.

Finally, catalysts with 200 mg·L^{-1} of Cu(II) content gave phenol conversions between 65 and 87%; in this group, Cu-PVP$_2$ achieved 80% of phenol conversion while the commercial CuO/γ-Al_2O_3 catalyst obtained 87%, suggesting that Cu-PVP$_2$ could be as good as a commercial catalyst.

In addition TOC conversions of the above experiments are presented in Figure 6.10 where CuO/γ-Al_2O_3 provided the best performance of all the tested catalysts, giving a TOC conversion up to 20% with 200 mg·L^{-1} of Cu(II) content. Once again Cu-PVP$_{25}$ presented the lowest conversions (5%) compared with the rest of catalyst under study. At last Cu-PVP$_2$ and CuO/γ-Al_2O_3 showed, like in phenol conversion, that both catalysts achieved similar results between 5-100 mg·L^{-1} of Cu(II) content, which means that Cu-PVP$_2$ is commercial competitive.

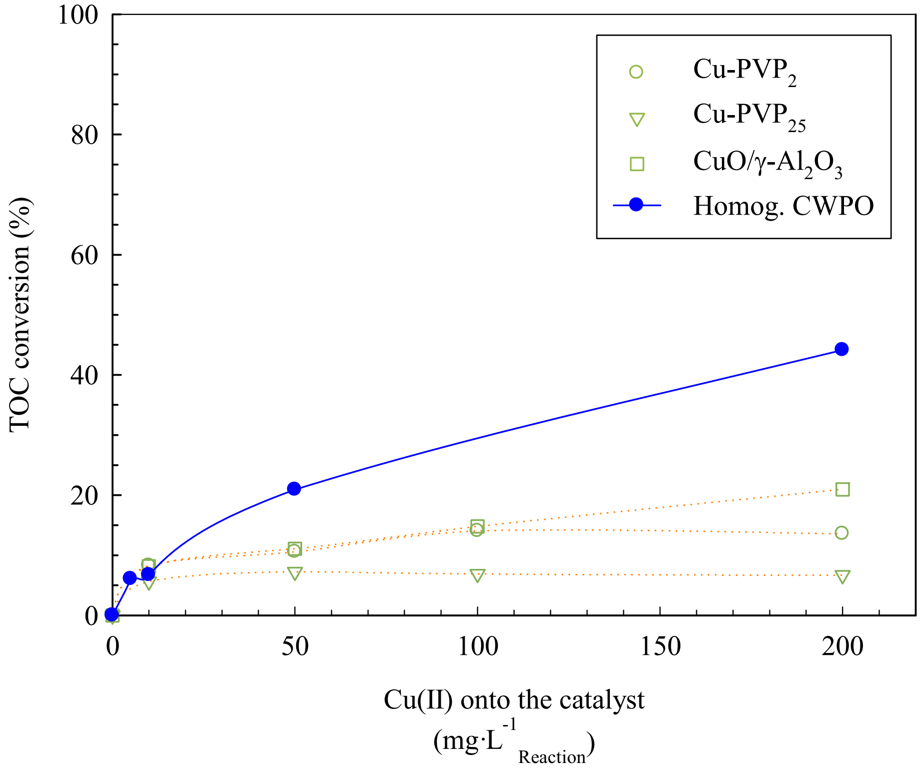


Figure 6.10. TOC conversion of heterogeneous catalytic phenol oxidation: influence of the initial Cu(II) content. Ph:H_2O_2 1:14 molar ratio. $[Ph]_0$ = 1 g L^{-1}. Reaction time = 2 h. T = 30°C.

In general terms, the TOC results of all catalysts were similar (6%) to the ones obtained for the homogeneous catalytic oxidation at 10 mg·L^{-1}, however at higher Cu(II) content, the differences were higher. Then, as mentioned on the homogeneous catalytic oxidation, the selectivity towards carbon dioxide was low because of the elevated presence of partially oxidised products, although this effect could not be an inconvenience if these intermediates are biodegradable enough as reported by Suarez-Ojeda et al., (2005).

The deactivation of the catalyst also represented by the leaching or metal release is an important issue that can become a problem either if Cu(II) content onto the catalyst the amount of catalyst is increased (Fortuny et al., 1999). Therefore, after evaluation of phenol and TOC conversion, it was measured the leaching of every catalyst.

Figure 6.11 shows the leaching of the Cu-supported catalysts after the heterogeneous catalytic peroxide oxidation of phenol. As expected, leaching was increased when Cu(II) content of the catalyst was high, for instance, leaching was no more than 2 mg·L^{-1} at 10 mg·L^{-1} of Cu(II) content and no more than 5 mg·L^{-1} at 50 mg·L^{-1} of Cu(II) content, but when Cu(II) content was 100 mg·L^{-1}, the highest Cu(II) leach was 10 mg·L^{-1}, which duplicated the permissible level of waste water treatment plants.

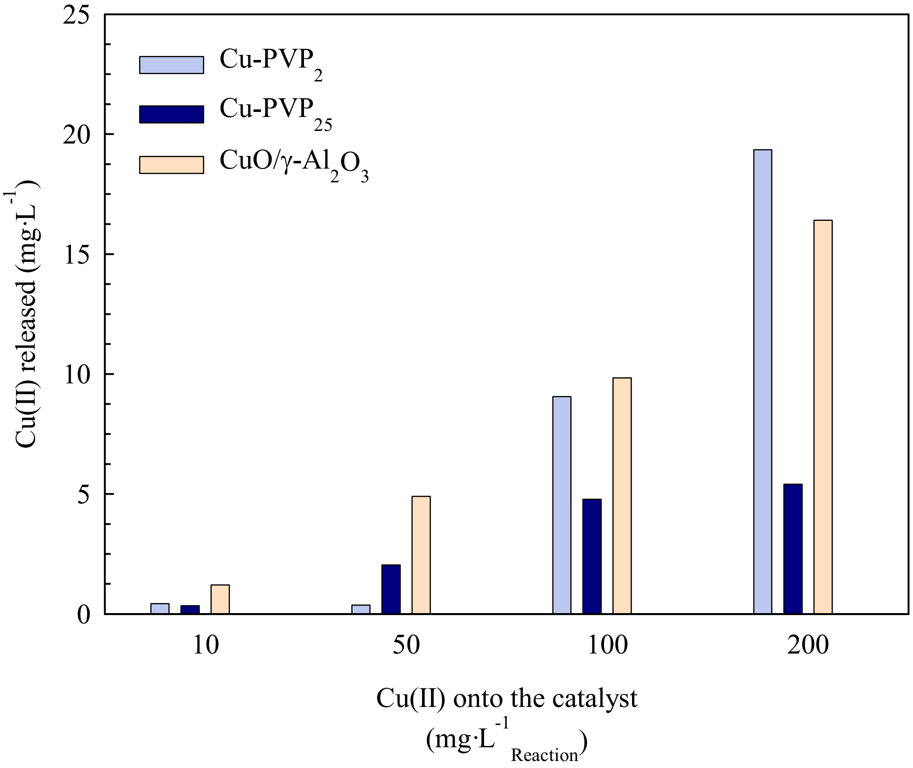


Figure 6.11. Leaching of Cu(II) catalyst from heterogeneous catalytic phenol oxidation: influence of the initial Cu(II) content. Ph:H_2O_2 1:14 molar ratio, $[Ph]_0$ = 1 g L^{-1} at T = 30ºC and atmospheric pressure.

Finally, when initial Cu(II) content was 200 mg·L^{-1}, Cu-PVP$_2$ and CuO/γ-Al$_2$O$_3$ released high copper concentrations, up to 20 mg·L^{-1}, but Cu-PVP$_{25}$ showed no more than 5 mg·L^{-1} in any of the experiments. This behaviour remarks the importance of the Cu(II) content on the catalyst because the most acquired catalyst should have enough Cu(II) content to promote the phenol oxidation but also avoid Cu(II) leaches as much a possible (Santos et al., 1999).

Overall, high leaching levels are not permissible for subsequent biological plant treatments because 5 mg·L^{-1} is the maximum permissible Cu(II) concentration for their inlets. So that, Cu-PVP$_2$ with 50 mg·L^{-1} of Cu(II) load seems to be the better option between the evaluated catalysts, because it achieved more than 60% of phenol conversion and its leaching levels were less than permissible levels, which qualify it as favourable catalyst for the process purpose.

It has been reported that the catalytic homogeneous-heterogeneous path involves the occurrence of both parallel and consecutive reaction phases (Arena et al. 2003). Then, the catalytic activity can be separated into homogeneous and heterogeneous phases by knowing the Cu(II) concentration in solution after oxidation. So, in order to obtain the phenol conversion (X$_H$) without the influence of leaching, it is used the Eq. 6.1:

$$X_H = X_T - X_L \tag{6.1}$$

where X$_T$ is the phenol conversion obtained from the experimental catalytic oxidation and X$_L$ is the phenol conversion expected from homogeneous phase, which is supposed to be due to the leaching of Cu(II). From Figure 6.11 it was obtained the amount of Cu(II) responsible for the catalysis at homogeneous phase. Then, the X$_L$ conversion values were estimated from Figure 4.5 in chapter IV, which shows the evolution of phenol conversion at different Cu(II) concentrations in homogeneous phase; and then X$_H$ is calculated. The same principle was applied to the homogeneous and heterogeneous contribution in TOC conversion. Thus, Figure 6.12 gives the variation of phenol and TOC conversions under the influence of released Cu(II).

Figure 6.12a shows phenol and TOC conversions with Cu-PVP$_2$ catalyst and the influence of Cu(II) either supported or leached. It can be observed either at 10 or 50 mg·L^{-1} that Cu-PVP$_2$ promotes 60 and 64% respectively of phenol conversion without leaching influence, but TOC results did not increase more than 8%. At 100 and 200 mg·L^{-1} of Cu(II) content, phenol and TOC conversion were higher as well as the leaching influence, then when conversion of homogeneous oxidation, promoted by Cu(II) in solution, was separated from total conversion, it was obtained 56 and 48% respectively of phenol conversion. From these results, it was obtained a better catalytic activity at 50 mg·L^{-1} because phenol conversion was totally attributed to the activity of supported Cu(II).

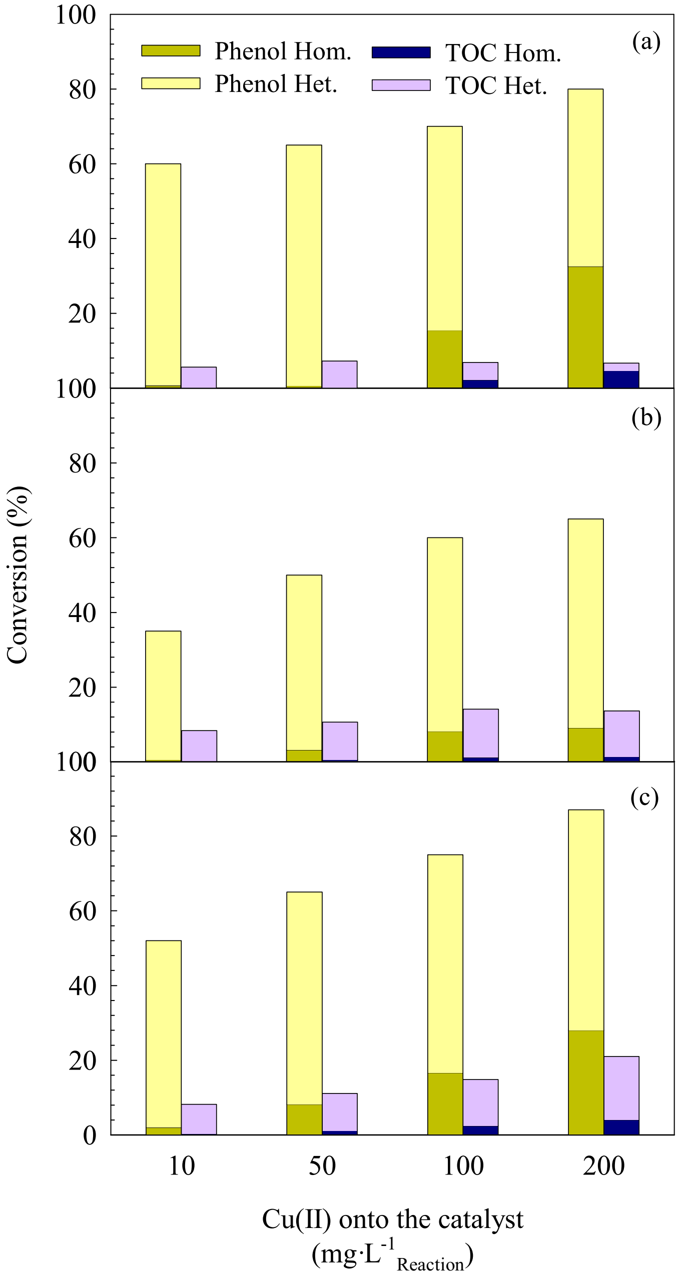


Figure 6.12. Phenol and TOC conversions from the CWPO of phenol: influence of the leaching at different initial Cu(II) content. Ph:H_2O_2 1:14 molar ratio with $[Ph]_0$ = 1 g L^{-1} at 30ºC and atmospheric pressure. (a) Cu-PVP_2, (b) Cu-PVP_{25}, (c) CuO/γ-Al_2O_3.

Figure 6.12b also presents the influence of leaching on phenol and TOC conversions, but this time when Cu-PVP$_{25}$ was the catalyst. Once again, Cu(II) leaching due to oxidation was low for catalysts with 10 and 50 mg·L^{-1} of Cu(II) content such as Cu-PVP$_2$ results, but Cu-PVP$_{25}$ just achieved 35 and 47% respectively of phenol conversion at the heterogeneous phase. Also, when catalytic Cu(II) content was 100 and 200 mg·L^{-1}, phenol and TOC conversions and Cu(II) leach increased as well, although their leaching levels were no more than 5 mg·L^{-1}. Hence, Cu-PVP$_{25}$ catalyst promoted the CWPO of phenol with low leaching interference and a satisfactory phenol conversion of 65% when Cu(II) content was 200 mg·L^{-1}. Even more Cu-PVP$_{25}$ was competitive to the best result presented for Cu-PVP$_{2,}$ which showed 8% of TOC conversion while Cu-PVP$_{25}$ achieved 12%. However, the problem with Cu-PVP$_{25}$ catalyst is still its leaching degree.

Figure 6.12c presents phenol and TOC conversions when CuO/γ-Al$_2$O$_3$ was the catalyst. Cu(II) released was presented at different Cu(II) content and its increment was proportional to higher Cu(II) load. At 100 and 200 mg·L^{-1} of Cu(II) content, total phenol conversions were 76 and 88% respectively, but their leaching were 10 and 16 mg·L^{-1} of Cu(II) in solution, which became an important contamination for waste water treatment plants. On the other hand, phenol conversions with CuO/γ-Al$_2$O$_3$ catalysts of 10 and 50 mg·L^{-1} of Cu(II) content were 52 and 65% respectively, from which the second catalyst experimented an acceptable leaching of 5 mg·L^{-1}. Hence, phenol and TOC conversions obtained with CuO/γ-Al$_2$O$_3$ (50 mg·L^{-1}) catalyst were alike to results obtained with Cu-PVP$_{25}$ (200 mg·L^{-1} of Cu(II) content) catalyst, which at the same time was similar to Cu-PVP$_2$ (50 mg·L^{-1} of Cu(II) content).

Overall, the three of the catalysts obtained important phenol and TOC conversions, even more the best choice of each catalyst group (Cu-PVP$_2$-50, Cu-PVP$_{25}$-200, CuO/γ-Al$_2$O$_3$-50) gave alike phenol and TOC conversions except of the of leaching, which favoured the election to Cu-PVP$_2$-50 because it did not present Cu(II) ions in the reaction media after oxidation.

6.2.2.3. Heterogeneous catalytic wet peroxide oxidation of phenol with Cu(II)-supported-resin catalysts

In the last section was established the importance of the metal loading and the catalytic leaching over the CWPO of phenol. Therefore, the second attempt to find a better

Cu(II)-supported catalyst was the use of the cationic resin (CR) supported with Cu(II) as catalyst. The synthesis of this resin-supported-Cu reported the highest adsorption capacity (116 mg·g^{-1}) compared with the rest of catalysts synthesised by adsorption methods, then its high Cu(II) content was expected to provide higher catalytic activity.

In section 6.2.1 (page 106) it was demonstrated that adsorption of the substrate occurs at the first 30 minutes of phenol catalyst contact. Then, it is necessary to make adsorption tests of the supports before they are used in the catalytic oxidation. Figure 6.13 shows the results obtained from phenol adsorption test onto the cationic resin before Cu(II) adsorption, so it is observed that phenol adsorption arrives up to 4%, which suggest that phenol molecules were not attracted by the acid surface of CR. On the other hand, in Figure 6.13 are also exposed the results of the catalytic oxidation of phenol when resin-supported-Cu was tested as catalyst on the CWPO of phenol along six hours. It can be appreciated that the catalyst did not develop any activity, obtaining up to 4% of apparent phenol conversion, which perfectly fitted with the adsorbed percent, so it can be concluded that oxidation did not take place because HPLC analyses did not present formation of phenol intermediates.

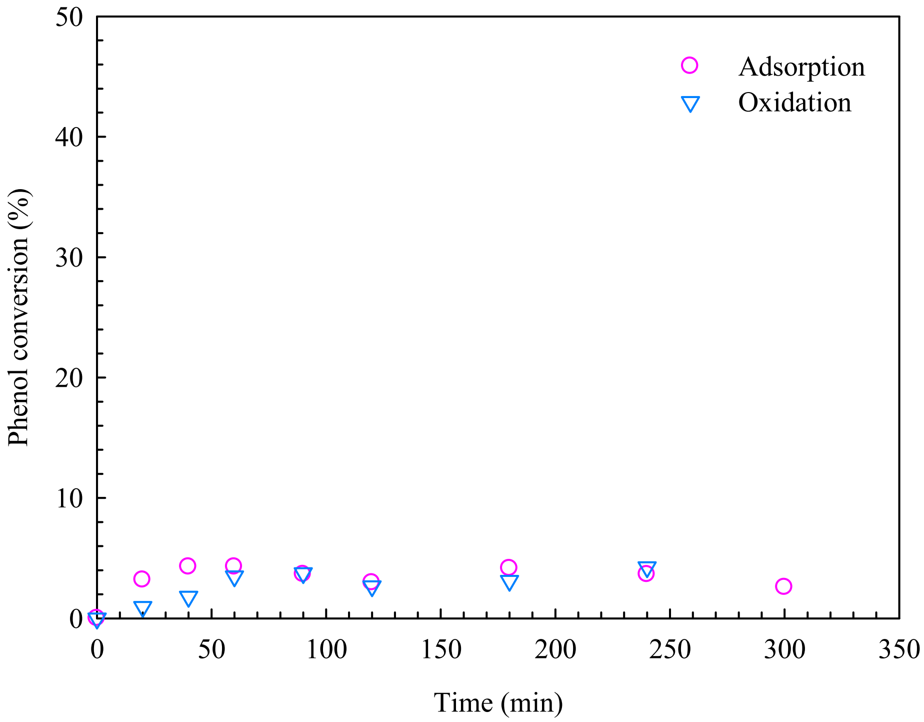


Figure 6.13. Overall adsorption and phenol oxidation with resin-supported-Cu catalyst. Ph:H_2O_2 1:14 molar ratio, $[Ph]_0$ = 1 g L^{-1} at 30°C and atmospheric pressure.

In consequence, the explanation for this lack of catalytic activity is based on the bond formation between cationic resin and Cu(II), which was strong enough to prevail over the catalytic properties of Cu(II). Hence, the lost of Cu(II) catalytic activity is because of the formation of bonds between the cationic resin and Cu(II) also called chemical adsorption (Chapter V, page 74). Therefore, it was decided to stop the evaluation of CR as potential catalytic support for the CWPO of phenol.

6.2.2.4. Heterogeneous catalytic wet peroxide oxidation of phenol with Cu(II)-chitosan-alumina catalysts

In section 6.2.2.2, it was tested the catalytic properties of Cu-supported materials, however it was not possible to test the catalytic activity of Cu-Chitosan because preliminary experiments showed the destruction of this catalyst after 15 minutes of reaction when hydrogen peroxide was the oxidant. Then, the aim of this section would be the evaluation of new Cu-Chitosan composite catalysts obtained by the co-precipitation technique, then to employ them on the CWPO of phenol.

First of all, like Cu-support catalysts, there is always a simultaneous adsorption and oxidation process, for this reason it is important to evaluate the adsorption capacity of the material before use. Table 6.3 collects the Cu(II) content the three Cu-chitosan-alumina co-precipitated catalysts, their phenol adsorption capacity and their phenol oxidations results like phenol and TOC conversion and leaching degree. It is noticed that there is no more than 3% of phenol adsorption, which assures no adsorption significant interferences for the oxidation evaluation.

Table 6.3. Catalyst behaviour for CWPO of phenol

Sample	Phenol adsorption capacity (%)	Initial Cu content ($mg\cdot g^{-1}$)	Phenol conversion at 180 min (%)	TOC conversion at 180 min (%)	Cu leached (%)
P1	2,3	20,4	100	74	50,5
P2	1,2	31,8	100	84	60,1
P3	1,7	33,3	100	83	58,3

Figure 6.14 presents phenol conversions against time for the three previously synthesised catalysts Cu-chitosan-alumina with one (P1), two (P2) or three (P3) co-precipitation cycles. It was observed that all the samples were able to oxidise phenol at 30ºC and atmospheric pressure. Slopes described phenol and TOC conversion along three hours, highlighting that phenol conversions for the three catalysts were 100% after 80 minutes of reaction, whereas mineralisation degree was near 80%. Evidently, Phenol and TOC conversions were highly effective because analyses after oxidation gave elevated amounts of Cu(II) in solution (Table 6.3), which suggests an easy destruction of Cu-chitosan complex from the alumina support, probably caused by the use of hydrogen peroxide.

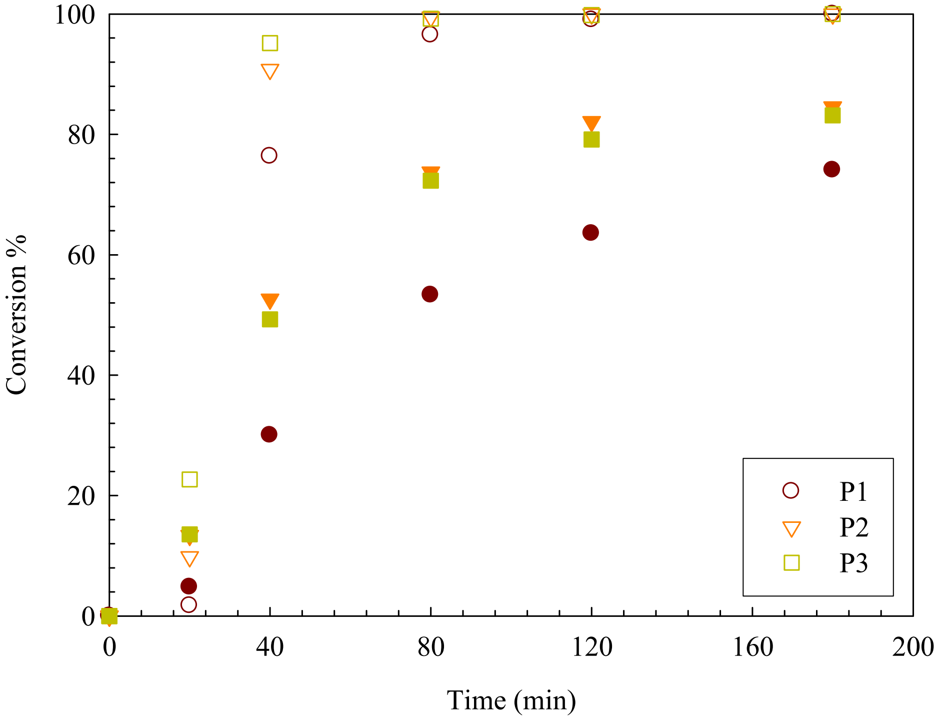


Figure 6.14. Phenol (empty symbols) and TOC (filled symbols) conversion vs time. $[Ph]_0$ = g·L^{-1}, Phenol:H_2O_2 molar ratio = 1:14, T=30°C. Reaction time = 3h.

Figure 6.14 depicts TOC profiles obtained for the three samples during reaction. It was evident the increment of TOC values when catalyst with higher Cu(II) content were used because in Chapter IV it was demonstrated the influence of Cu(II) over phenol and TOC conversions. It was also seen that TOC conversions for P2 and P3 were similar since both had almost the same amount of Cu(II) content, therefore reaction media was analysed by atomic adsorption to quantify the Cu(II) release. Leaching results are presented in Table

6.3 and the leaching was significant for all the samples (155, 287 and 290 mg·L^{-1} respectively to P1, P2 and P3); thus the occurrence of homogeneous reactions cannot be ignored.

In addition, pH evolution and hydrogen peroxide conversion were plotted in Figure 6.15. It is observed for the three catalysts that pH values decrease with time, indicating the presence of acidic intermediates, which are also responsible for the differences between phenol and TOC conversions (Figure 6.14). Furthermore, results of hydrogen peroxide conversion are also presented in Figure 6.15. Once again H_2O_2 conversions were higher for the catalysts with two or three impregnations steps (P2 and P3) than for the catalyst with just one impregnation cycle P1. This is because the production of OH• radicals strongly depends (among other factors) on the amount of copper presence in the system.

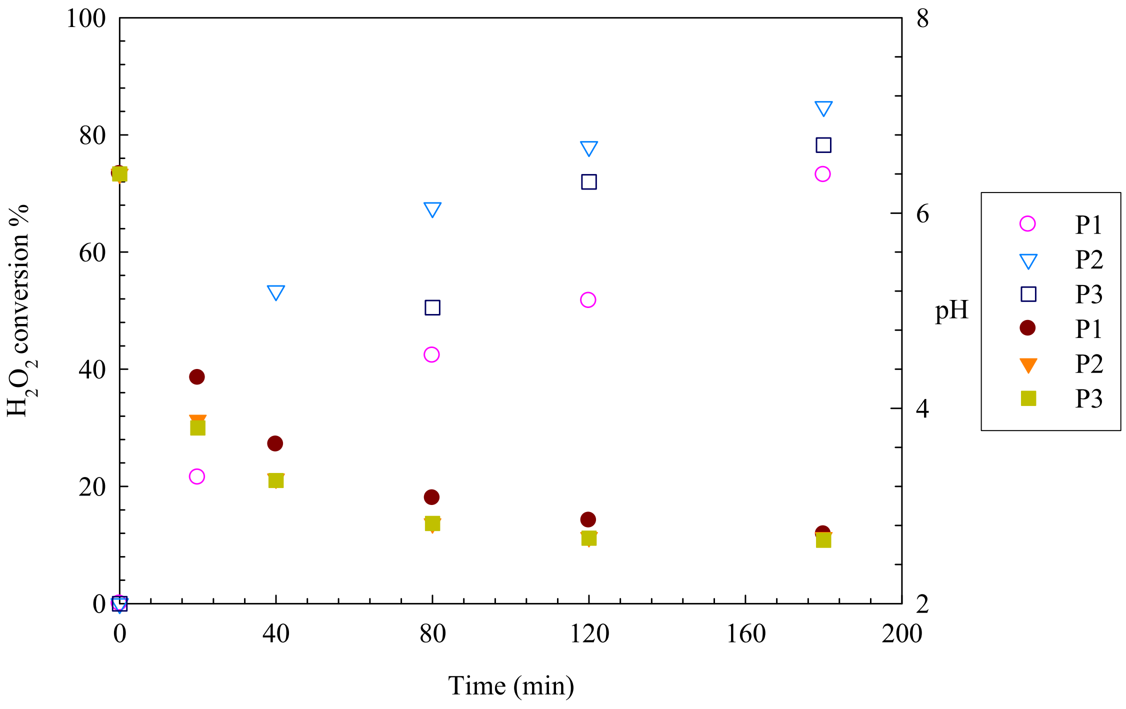


Figure 6.15. H_2O_2 conversion and pH evolution along reaction time. $[Ph]_0$ = 1g·L^{-1}, Ph:H_2O_2 molar ratio = 1:14, T=30°C, Reaction time = 3 h.

Finally, the used catalysts (P1, P2 and P3) were evaluated by TGA and TPR techniques to find possible changes on their structure after oxidation.

6.2.2.4.1. Thermo-gravimetric analysis (TGA)

Thermogravimetric analysis is an analytical technique used to determine the thermal stability of a material and its fraction of volatile components by monitoring the weight change that occurs as a specimen is heated. TGA results with fresh and used catalysts are presented in Table 6.4. At the lower temperature range, weight loss can be attributed to the evaporation of liquids in the catalysts (water in fresh samples and water, phenol and phenol intermediates in used samples). In the second range of temperatures studied (110º-300ºC), the weight loss is attributed to the decomposition of Chitosan.

Table 6.4. Weight loss of TGA consumed mass between ranges of temperature.

	TGA – weight loss (%)	
Sample	27º-110ºC	110º - 300º
P1 fresh	24,3	5,4
P1 used	41,9	3,8
P2 fresh	8,4	6,2
P2 used	42,9	5,5
P3 fresh	9,7	6,6
P3 used	35,6	12,2

Differences between fresh and used samples could indicate that used samples have lost Chitosan during reaction, probably because depolimerization was induced by the presence of hydrogen peroxide at acid conditions. For instance, Tian et al., (2004) studied the depolymerisation behaviour of chitosan by hydrogen peroxide, which depended on the temperature and concentrations of hydrogen peroxide employed on the reaction.

6.2.2.4.2. Temperature Programmed Reduction analysis (TPR)

Generally, temperature programmed reduction is used to provide information on the influence of support materials, preparation and metal additives on catalyst reducibility (Kanervo et al., 2001). TPR analyses were performed in fresh and used samples of P1 catalyst. Back in chapter V, it was described the existence of species like $CuCl_2$ and Cu-Chitosan complex, this time, Figure 6.16 shows a reduction on the amount of $CuCl_2$ (pick 1) and Cu-Chitosan complex (pick 2) presented in the used sample, this effect was also analogous to reported results of atomic adsorption data, which reported from 50 to 60% of catalytic deactivation of Cu(II) release. Then, it can be concluded that Cu-chitosan complex co-precipitated onto alumina needs of an additional compound or cross-linkage to avoid destruction when hydrogen peroxide is the oxidant of a catalytic reaction.

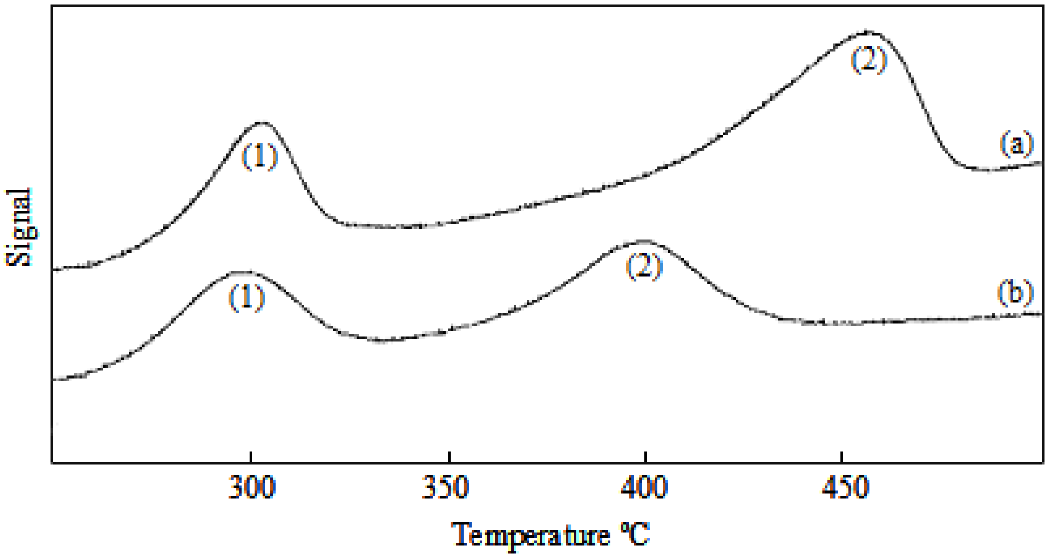


Figure 6.16. TPR profiles of two species (1) $CuCl_2$ and (2) Cu-Chitosan contained on (a) Fresh P1 catalyst and (b) Used P1 catalyst.

6.2.2.5. Heterogeneous catalytic wet peroxide oxidation of phenol with polymer-supported-metal catalysts

Following the same procedure for oxidation of phenol at soft conditions and knowing the importance of operational conditions, it was performed the CWPO of phenol using polymer-supported metal complexes (Cu(II) or Mo(VI)). The use of polymers in section 6.2.2.2 presented favourable oxidation results with low leaching degrees but their mineralisation potential was low, then the use of Cu-polymer complex co-precipitated onto an inert support presented favourable phenol and TOC conversions but the contamination by Cu(II) release was extremely high in section 2.2.2.4. Therefore, it is suggested the use of polymers-supported-metal catalysts, which were synthesised by polymerisation and metal loading methods (Chapter V).

6.2.2.5.1. Blank phenol oxidation

Most of the heterogeneous catalytic processes develop an adsorption step where a part of the substrate is adsorbed onto the catalytic surface. For this reason, it was made a series of blank experiments (Table 6.5) where oxidation process was performed using either poly benzyl imidazole (PBI) resin or functionalised poly(styrene-divinylbenzene) resins (P-AMP and P-IMDA) as catalyst. At 30ºC and atmospheric pressure the oxidation of phenol cannot occur without catalytic presence, so it is evident that these polymers free of metal loading perform a classical phenol adsorption process.

Table 6.5. Adsorption capacity of polymeric supports and employed weight of polymer-supported metal complexes.

Polymer	q ($mg \cdot g^{-1}$)	Cua[1] complex (g)	Cus[2] complex (g)	Mo complex (g)
PBI	65,64	0,387	0,092	0,195
P-AMP	73,08	0,211	0,142	0,216
P-IMDA	84,76	0,373	0,120	-

[1]Cua: copper acetate as Cu(II) source for the metal loading (Table 5.8 – Chapter V)

[2]Cua: copper sulphate as Cu(II) source for the metal loading (Table 5.8 – Chapter V)

Table 6.5 lists the adsorption capacities of PBI, P-AMP and P-IMDA, but also reports the catalyst weight of each experimental run, considering that the amount of Cu(II) catalytic content was equivalent to 50 $mg \cdot L^{-1}$ even despite of the diversity of polymer-supports. The same principle was employed with Mo(VI) group where the amount of catalytic content was 100 $mg \cdot L^{-1}$.

Using the data from Table 6.5, the adsorption capacity was calculated considering the catalyst weight of each run to obtain the amount of adsorbed phenol for each experiment, and surprisingly in any of the cases the adsorption of phenol was more than 4%. Therefore, the adsorption interference was controlled pre-treating the catalyst with a half an hour of initial adsorption process, which was the initial contact of catalyst and substrate (phenol) without the presence of the oxidant source, thus the catalyst was ready to be used on the oxidation experiments.

6.2.2.5.2. Heterogeneous catalytic wet peroxide oxidation of phenol with polymer-supported-Mo(VI) complexes

Polymer-supported-Mo(VI) complexes were tested on the catalytic oxidation of phenol under the conditions described on the experimental section. The first perception of the reaction was qualitative, the experiments showed low phenol conversions because the formation of intermediates (quinones), identified by their dark colour, did not change the reaction media into brown colour.

Figure 6.17 shows the conversion of phenol when poly benzyl imidazol loaded with Mo(VI) *(PBI-Mo)* and poly (styrene-divinylbenzene) functionalised with 2-aminomethyl-pyridine and loaded with Mo(VI) *(P-A-Mo)*, even more when catalysts were re-used.

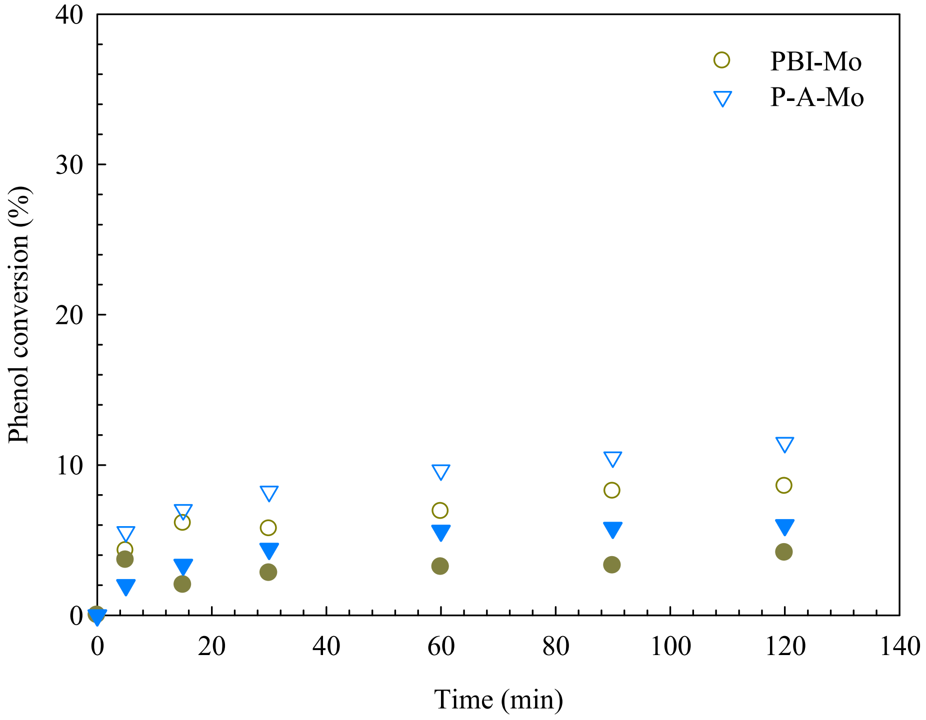


Figure 6.17. Phenol conversion using polymer-supported Mo(VI) complexes as catalysts. First reaction (empty symbols), Second reaction (filled symbols). [Phenol] = 1 g·L^{-1}, Phenol/H_2O_2 ratio = 1:14, T = 30°C, Pressure = 1 atm.

Overall, the catalytic activity was low for both cases at the two reaction sequences, for instance the conversions of PBI-Mo (12%) and P-A-Mo (8%) did not represent a significant conversion for the mineralisation of phenol. From these results it was demonstrated that either PBI-Mo or P-A-Mo were not as effective for phenol oxidation as for the epoxidation of alkenes (Mbeleck et al., 2007).

Table 6.5 lists TOC conversion, leaching and deactivation of PBI-Mo and P-A-Mo as catalysts. TOC conversions of PBI-Mo or P-A-Mo suggest that there is no high mineralisation possibilities with Mo(VI) complexes since their maximum TOC conversions were 6 and 5% respectively, although these values were expected since phenol conversions were low as well.

In addition, previous reports state that every heterogeneous catalytic system can become a problem when leaching is high (Arena et al., 2003 and Luo et al., 2009). Hence, Table 6.6 shows the leaching results after the reaction time of the Mo(VI) group. P-A-Mo released 11,6 mg·L^{-1} of Mo(VI) in the first reaction sequence, which became a problem since the products of the reaction should be less contaminant than the reactants, this means without high concentrations of metals in solution. In the second run P-A-Mo had less leaching problems with almost 3% of catalytic deactivation, which would assure at least a process without metal contamination in case it would have had catalytic activity for phenol oxidation. The case of PBI-Mo catalyst was similar to P-A-Mo, but PBI-Mo released around 8 mg·L^{-1} at the first run and less than 4 mg·L^{-1} in the second run, although the problem continues being its low catalytic activity.

Table 6.6. TOC conversion and leaching of the catalytic oxidation of phenol using polymer-supported Mo(VI) complexes as catalysts.

	TOC conversion (%)		Leaching (mg·L^{-1})		Deactivation (%)	
Catalyst	1st run	2nd run	1st run	2nd run	1st run	2nd run
PBI-Mo	6	4	7,9	3,4	8	4
P-A-Mo	5	3	11,6	2,6	12	3

The deactivation of this group of catalysts was calculated from the amount of molybdenum in solution after oxidation. PBI-Mo had 8% of deactivation in the first run, while 4% in the second one. For the case of P-A-Mo, the first run provoked an important deactivation of 12%, however Mo(VI) release decreased to 3% at the second run. All these results are relatively low but significant for metal contamination levels because the maximum permissible value for soluble compounds is 4 mg·L^{-1} (IMOA, 1970). Overall, because of the low catalytic activity to obtain higher phenol and TOC conversion, and their consequent catalytic deactivation, neither PBI-Mo nor P-A-Mo were suitable catalysts for the oxidation of phenol at the established conditions.

6.2.2.5.3. Heterogeneous catalytic wet peroxide oxidation of phenol with polymer-supported-Cu(II) catalysts

In order to continue testing the catalytic activity of catalysts previously prepared or synthesised, in this section polymer-supported Cu(II) complexes are used as catalysts of the heterogeneous catalytic oxidation of phenol. The substrate was buffered to pH 6 and oxidation was carried out at 40ºC and atmospheric pressure. This time, Cu(II) catalysts were divided in two groups, which were classified by the use of Cu(II) acetylacetonate or Cu(II) sulphate, then called Cua and Cus catalysts respectively.

The experimental section provided a qualitative description of the catalytic activity of each catalyst by the colour change of the reaction media, which evidenced the formation of colourful compounds like quinones, also described in Chapter IV for the homogeneous catalytic oxidation of phenol. Hence, all polymer-supported Cu(II) complexes probed to catalyse the oxidation of phenol because all of them promoted the formation of quinones.

Figure 6.18 shows the progress of phenol conversion when polymer-supported-Cu(II) catalysts were used. Note that P-I-Cua promoted a final phenol conversion of 93% after three hours, and the rest of catalysts obtained lower phenol conversions as follows: PBI-Cus (72%) > P-A-Cus (67%) > P-I-Cus (43%) > PBI-Cua (29%) > P-A-Cua (13%).

Catalysts presented different tendencies along reaction time, such as PBI-Cua and P-A-Cua, which showed their highest catalytic capacity for the phenol oxidation after 30 minutes. This fact suggests that PBI-Cua and P-A-Cua suffered a surface contamination, which was caused by the adsorption of phenol intermediates onto the catalytic surface, thus difficulties for the interaction of Cu(II) with hydrogen peroxide radicals appeared and these difficulties decreased the activity of the catalysts. Then, phenol conversions arose at 29 and 13% respectively.

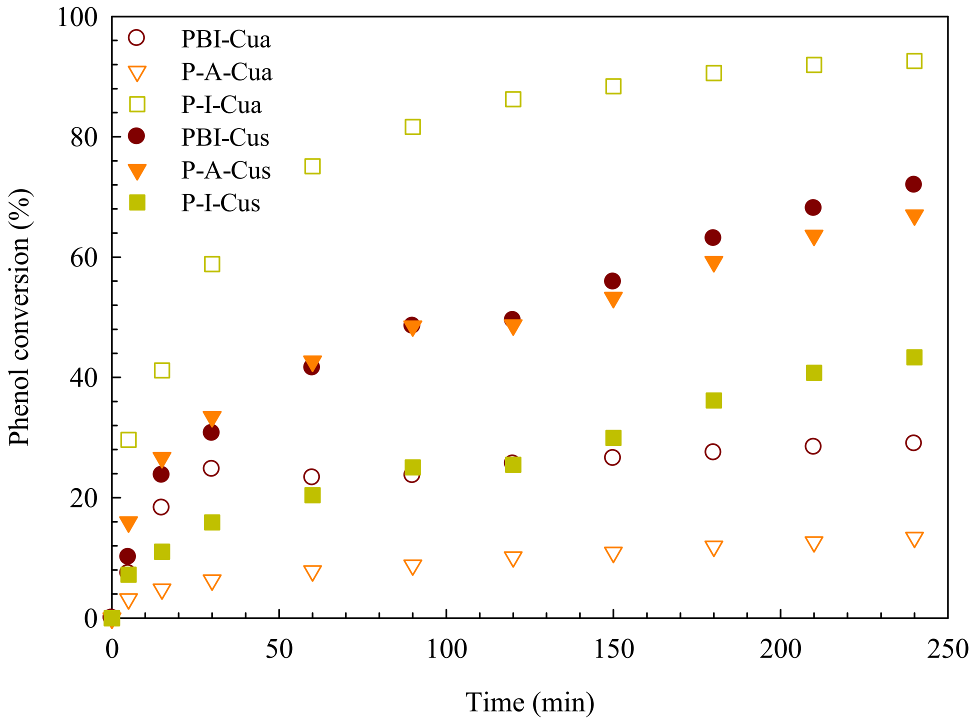


Figure 6.18. Phenol conversion of polymer-supported Cu(II) complexes. $[Phenol]_0 = 1\ g{\cdot}L^{-1}$, Phenol:$H_2O_2$ ratio = 1:14, pH = 6, T = 40ºC, Pressure = 1 atm.

From Figure 6.18, it was also observed that P-I-Cua, PBI-Cus, P-A-Cus and P-I-Cus achieved a continuous increment of phenol conversion with the time. Then, the possibility of catalytic contamination by the adsorption of phenol intermediates was low because phenol conversion demonstrated that Cu(II) was continuously promoting the reaction of H_2O_2 with phenol and phenol intermediates. After 3 hours of reaction, PBI-Cus and P-A-Cus had similar phenol conversions, 72 and 67% respectively, however it cannot be selected any of these catalysts as a suitable one for the process before the evaluation of TOC conversion or mineralisation efficiency are made.

Table 6.7 shows phenol and TOC conversions obtained when polymer-supported-copper complexes were used as catalysts. Apart from the catalytic leaching and deactivation, there is a column designed for the mineralisation efficiency, which was calculate by the relation of TOC/phenol conversions.

The best TOC conversion results were obtained when PBI-Cus with 54% of conversion and P-I-Cua with 43% were the catalysts. Plus, considering that it was already presented that P-I-Cua obtained higher phenol conversion than PBI-Cus, then analysing the mineralisation efficiency, it was found an effective TOC/phenol relation of 0,75 for PBI-

Cus case. Although, the mineralisation relation of 0,47, for P-I-Cua catalyst, represented that 50% of phenol conversion was reacted to CO_2 while the other 50% was still being phenol intermediates, which are probably easy to decompose or oxidise. In addition, P-I-Cus, PBI-Cua and P-A-Cua obtained high mineralisation efficiency, but their low phenol conversion values were not appropriate for the purpose of the work. In contrast, P-A-Cus had the lowest mineralisation efficiency of 0,22, although 67% of phenol conversion indicates that P-A-Cus provided catalytic activity to the first stage of the reaction where phenol intermediates were produced, and after that its activity was decreased.

On the whole, P-I-Cua provided better results than the rest of the Cu(II) catalysts, although PBI-Cus effectiveness seems to obtain better results when mineralisation is the main goal. Anyway these promising results have to be contrasted with the results of metal leaching along the reaction period.

Table 6.7 lists Cu(II) leaching and catalytic deactivation after oxidation. From the group of Cu(II) catalyst, the highest amount of Cu(II) release was 6,2 mg·L^{-1}, which was obtained by P-I-Cua and was higher in 1.2 mg·L^{-1} than the permissible contamination levels, however it could be easily solved by a final dilution of the reaction media.

Table 6.7. Phenol and TOC conversion of the catalytic oxidation of phenol using polymer-supported Cu(II) complexes as catalysts and their leaching and deactivation after oxidation.

Catalyst	Phenol conversion (%)	TOC conversion (%)	Relation TOC/Phenol	Leaching (mg·L^{-1})	Deactivation (%)
PBI-Cua	29	20	0,69	0,1	0,1
P-A-Cua	13	9	0,69	1,4	3
P-I-Cua	92	43	0,47	6,2	13
PBI-Cus	72	54	0,75	2,7	6
P-A-Cus	67	15	0,22	5,1	10
P-I-Cus	43	32	0,74	0,4	1

From the group of Cu(II) catalysts P-I-Cua and PBI-Cus obtained important phenol and TOC conversions. However, it is important to know the activity of Cu(II) when the metal was supported or in solution; for this purpose, values and tendency of the homogeneous catalytic oxidation of phenol reported in Chapter IV (Figure 4.5, page 51) were employed. Thus, Cu(II) leaching of P-I-Cua (6,2 mg·L^{-1}) promoted near 32% of phenol conversion and represented 13% of the catalyst deactivation, while Cu(II) leaching of PBI-Cus (2,7 mg·L^{-1}) obtained 21% of phenol conversion with 6% of catalytic deactivation. Contrary to previous examples, the rest of catalysts did not have more than 2 mg·L^{-1} of Cu(II) release, which means that the oxidation was almost completely done in the heterogeneous phase.

The catalytic activity at homogeneous phase was important for both cases, however if phenol conversion is related with leaching in Figure (6.18), P-I-Cus leaching seems to occur at the first 90 minutes of reaction, because after this time, phenol oxidation remains constant. On the other hand, PBI-Cus presented a progressive phenol conversion, which suggested a constant leaching with time, this means that catalytic deactivation could probably increase for processes more than three hours.

After the evaluation, P-I-Cua and PBI-Cus were selected as suitable catalysts for the CWPO of phenol because they obtained promising results of phenol and TOC conversions and their Cu(II) desorption or polymer destruction did not represented contamination problems. Hence, it was demonstrated with these catalyst that Cu(II) supported on PBI and P-I conserve the catalytic activity of Cu(II).

6.2.2.5.4. Kinetics of the catalytic wet peroxide oxidation of phenol with polymer-supported-metal complexes

The kinetic evaluation was applied to the experimental data obtained from the CWPO of phenol. Moreover it is important to remind that the catalytic oxidation of phenol at homogeneous phase follows the rate law of first order model (Santos et al., 1999 and Esplugas et al., 2002), thus kinetics was firstly evaluated following the first rate order model.

Calculations to obtain the kinetic constants have been made for the group of polymer-supported-molybdenum complexes and constant rates of fresh and re-used catalysts are listed in Table 6.8. First-rate model fitted well with experimental data of both catalysts and it was noticed that the constant rates had a small decrease when catalysts were re-used, demonstrating that deactivation of the catalyst directly influences to the kinetics of phenol oxidation.

Table 6.8. Kinetic constant rate of polymer-supported Mo(VI) complexes: first rate order model.

	Fresh		Re-used	
	k (min^{-1})	R^2	k (min^{-1})	R^2
PBI-Mo	$3{,}6\cdot10^{-4}$	0,8997	$2{,}0\cdot10^{-4}$	0,9003
P-A-Mo	$5{,}2\cdot10^{-4}$	0,9359	$4{,}4\cdot10^{-4}$	0,8509

Later, for the group of polymer-supported-Cu(II) catalysts, the first rate model was also applied and results are presented in Table 6.9. For instance, the constant rate of P-A-Cua was the lowest of the Cu(II) group of catalysts also reflected on the lowest phenol conversion. Although, with this value it could be predicted a low reaction rate caused by a lack of interaction between the supported Cu(II) and OH• radicals.

In previous section, it was selected two suitable catalysts for the process P-I-Cua and PBI-Cus, but kinetic constant of P-I-Cua demonstrated to be the highest of the group of catalysts, which means that P-I-Cua had a better disposition of Cu(II) to promote the catalytic oxidation of phenol.

Table 6.9. Kinetic rate of polymer-supported Cu(II) complexes.

Catalyst	k (min^{-1})	R^2
PBI-Cua	$9{,}3\cdot10^{-3}$	0,9492
P-A-Cua	$4{,}4\cdot10^{-4}$	0,9546
P-I-Cua	$9{,}5\cdot10^{-3}$	0,9347
PBI-Cus	$4{,}5\cdot10^{-3}$	0,9780
P-A-Cus	$3{,}6\cdot10^{-3}$	0,9662
P-I-Cus	$2{,}0\cdot10^{-3}$	0,9824

6.2.2.5.5. Mechanisms of the heterogeneous CWPO of phenol using polymer-supported-Cu(II) complexes

The production of intermediates along phenol oxidation represents the first step to achieve the mineralisation of phenol. Therefore, following the proposed reaction pathway for CWPO of phenol at homogenous phase (Chapter IV, Scheme 4.2, page 57), it was made the evaluation of phenol intermediates when using polymer-supported Cu(II) complexes. The catalytic oxidation was buffered to pH 6 and 40ºC was the employed temperature, like in the homogeneous catalytic evaluation for the evaluation of intermediates (Chapter IV). Once again these conditions were selected as appropriates for the evaluation of phenol intermediates.

Figure 6.19 shows the phenol conversion and the formation of phenol intermediates along the time. When PBI-Cua was the catalysts, it was identified five intermediates such as catechol, fumaric ac., malonic ac., formic ac. and succinic ac. From the figure, it is observed the initial formation of catechol, thereafter catechol concentration decreased and the four mentioned acids appear in the same proportion. Hence, it is important to notice that PBI-Cua catalyst was not just catalysing phenol oxidation but also the oxidation of catechol, promoting the formation of phenol intermediates.

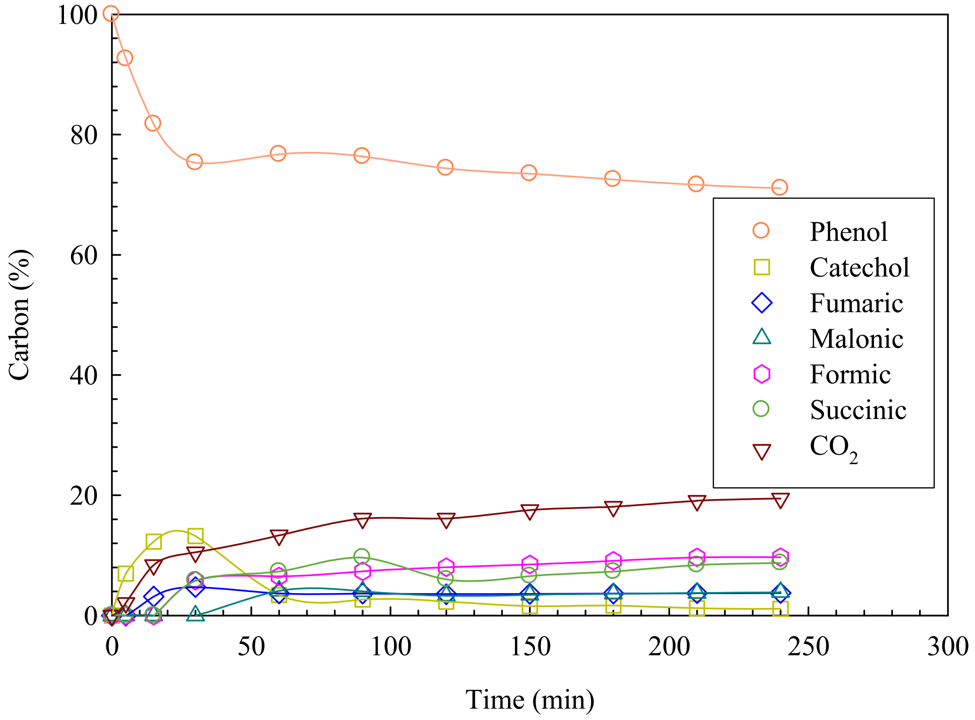


Figure 6.19. Carbon percent formation of phenol oxidation. Phenol: 1 g·L^{-1}, PBI-Cua catalysts: 0,387g equivalent to 50 mg·L^{-1}, Ph/ H_2O_2 molar ratio: 1/14 (stoichiometric) at 40ºC, pH 6 and atmospheric pressure.

Figure 6.20 presents the distribution of carbon for phenol oxidation when P-I-Cua was the catalyst. The obtained phenol conversions did not permit to obtain clear phenol intermediate tendencies, although after analysis, it was detected the presence of cathecol, fumaric, malonic, formic, and succinic acids. For instance, intermediate concentrations along the time did not present big changes of phenol concentration, which indicates that phenol oxidation occurred at the first hour, then the possible changes in phenol or phenol intermediates concentrations were not significant.

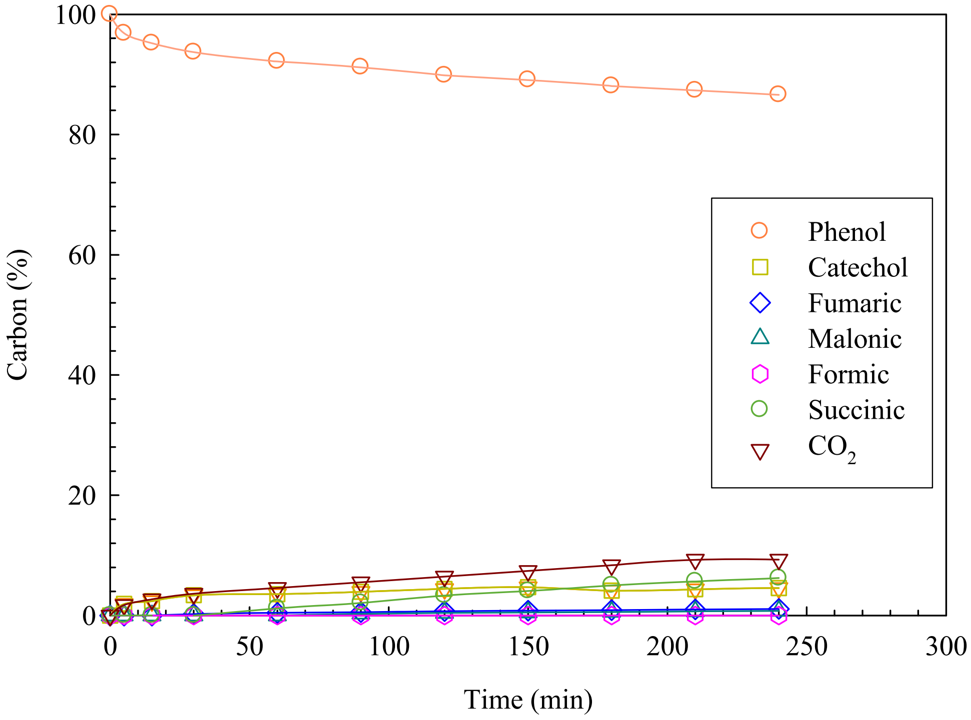


Figure 6.20. Carbon percent formation of phenol oxidation. Phenol: 1 g·L^{-1}, P-A-Cua catalysts: 0,211g equivalent to 50 mg·L^{-1}, Ph/H_2O_2 molar ratio: 1/14 (stoichiometric) at 40ºC, pH 6 and atmospheric pressure.

Likewise, the catalytic oxidation and the formation of intermediates were represented on Figure 6.21, when P-I-Cua was the catalyst. It was detected the formation of the same intermediates as the two previous catalysts, but this time the distribution of carbon along the process was clearer because of a higher phenol conversions. It was observed at the first 30 minutes that it was produced up to 36% of Catechol, while acids production was low until this period. Therefore, it is demonstrated the proposed mechanism in Chapter IV (Scheme 4.2, page 57) where malonic, formic and succinic acids were produced from the oxidation of catechol, to finally produce CO_2. For instance after 90 minutes of reaction, catechol (28%) decreases to produce fumaric acid (14%), which at the same time reacts and produces malonic (6%), formic (8%) and succinic (9%).

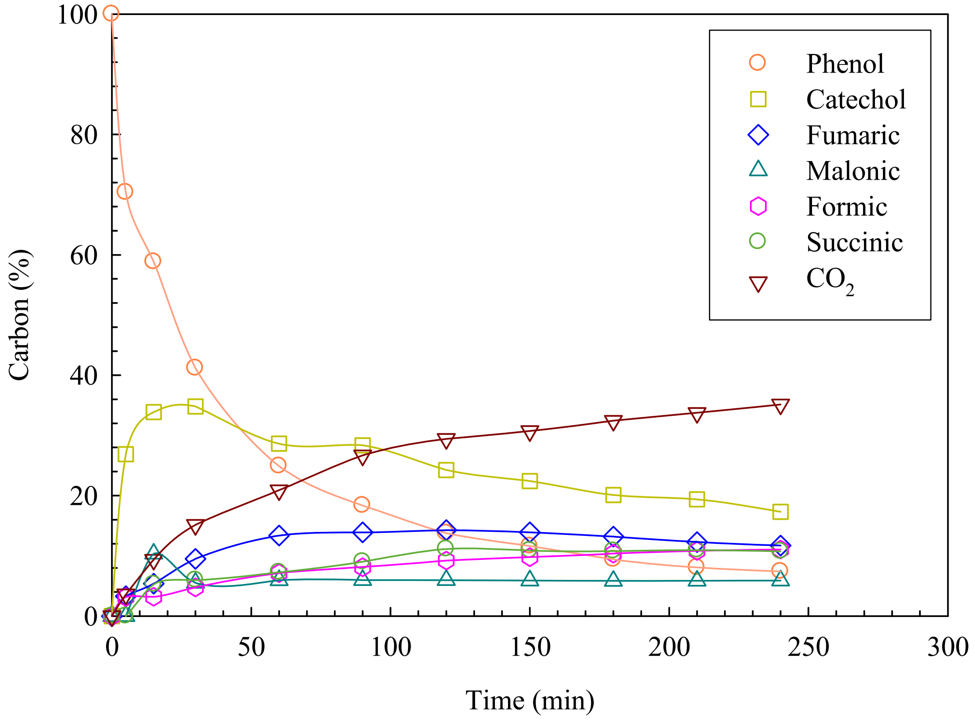


Figure 6.21. Carbon percent formation of phenol oxidation. Phenol: 1 g·L^{-1}, P-I-Cua catalyst: 0,373 g equivalent to 50 mg·L^{-1}, Ph/H_2O_2 molar ratio: 1/14 (stoichiometric) at 40ºC, pH 6 and atmospheric pressure.

Figure 6.22 shows as well the carbon distribution of CWPO of phenol when PBI-Cus was used as catalyst. Phenol intermediates were the same as previous catalysts although with some differences of intermediates formation. Cathecol production was the half than for P-I-Cua catalyst; and malonic (5%), formic (5%) and succinic (7%) acids presented similar percent amounts of carbon formation along the reaction time.

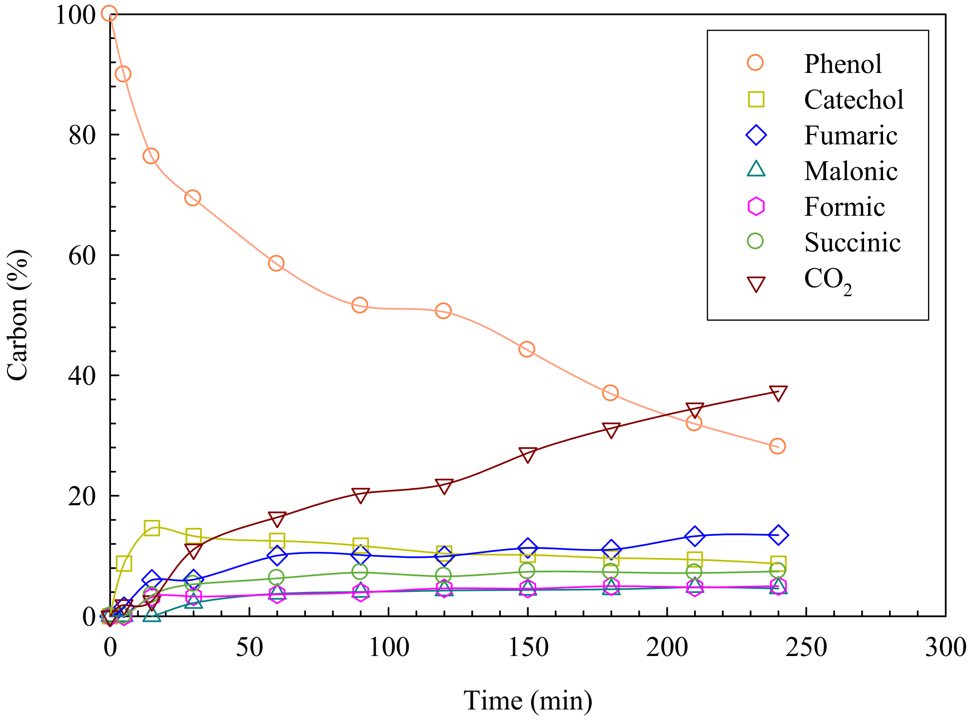


Figure 6.22. Carbon percent formation of phenol oxidation. Phenol: 1 g·L^{-1}, PBI-Cus catalyst: 0,092 g equivalent to 50 mg·L^{-1}, Ph/H_2O_2 molar ratio: 1/14 (stoichiometric) at 40ºC, pH 6 and atmospheric pressure.

What is more, Figure 6.23 shows the carbon distribution when P-A-Cus was employed as catalyst. It can be observed the presence of the five phenol intermediates, already detected on previous catalysts (catechol, fumaric, malonic, formic and succinic acids). It can be suggested that the problem is the low production of CO_2, which refers to the low mineralisation levels. Thus, it is assumed that P-A-Cus had a better affinity to oxidise phenol, but not for the formed intermediates.

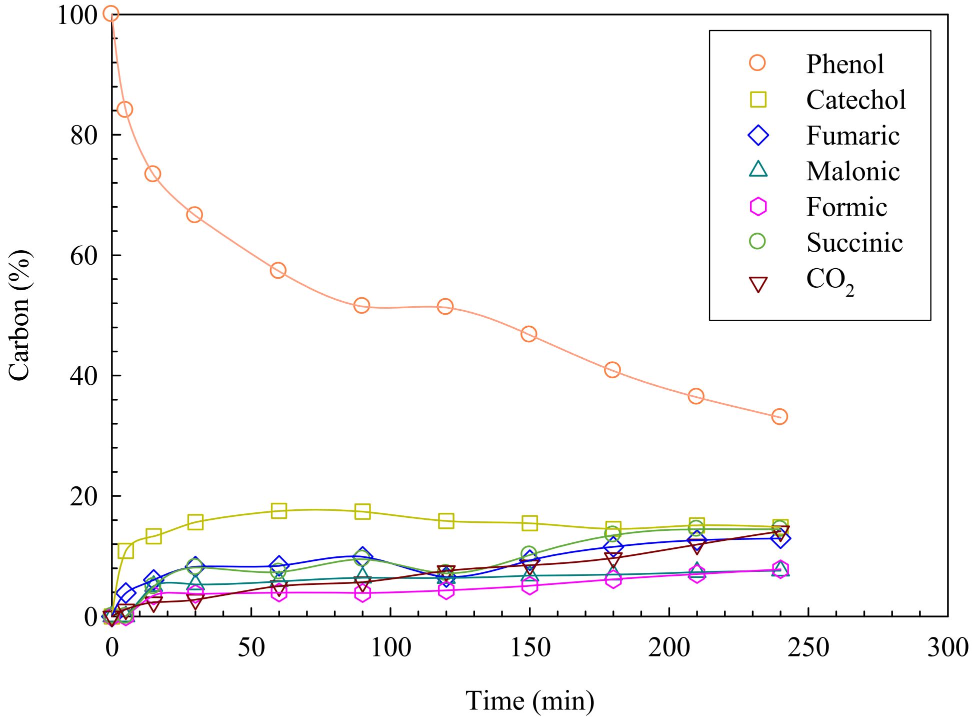


Figure 6.23. Carbon percent formation of phenol oxidation. Phenol: 1 g·L^{-1}, P-A-Cus catalyst: 0,142 g equivalent to 50 mg·L^{-1}, Ph/H_2O_2 molar ratio: 1/14 (stoichiometric) at 40°C, pH 6 and atmospheric pressure.

Finally P-I-Cus catalytic influence on phenol oxidation is plotted in Figure 6.24. Five intermediates were identified as previous catalysts. This time, phenol conversion was not high; therefore cathecol production did not exceed 16% of the total carbon presented in the reaction. After all, the production of intermediates was not sufficiently high to achieve a mineralisation as reported on previous section.

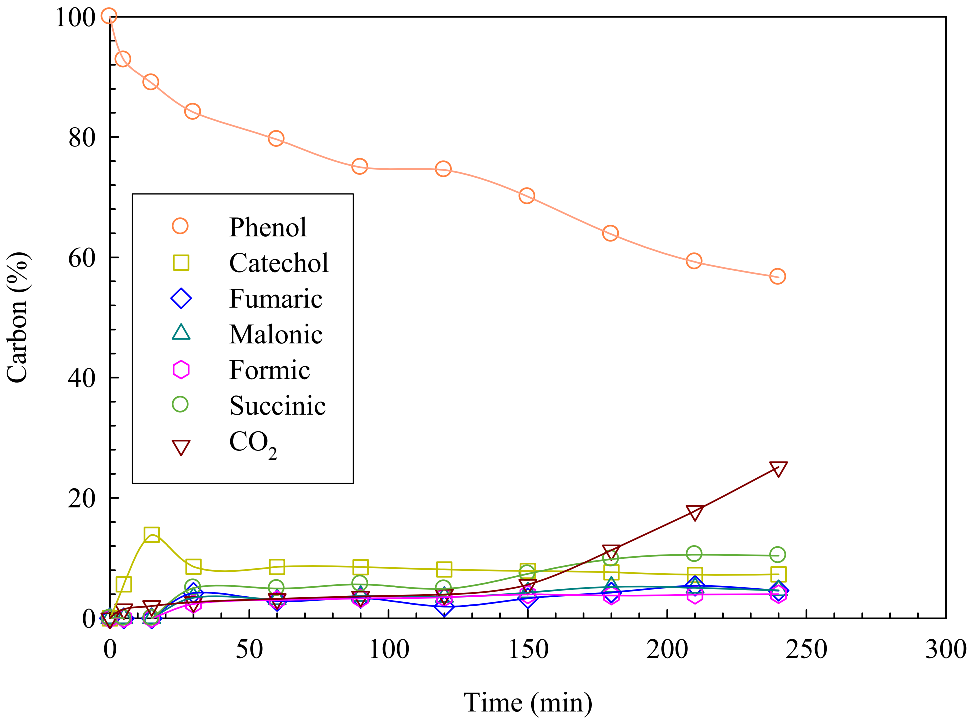


Figure 6.24. Carbon percent formation of phenol oxidation. Phenol: 1 g·L^{-1}. P-I-Cus catalyst: 0,120 g equivalent to 50 mg·L^{-1}, Ph/H_2O_2 molar ratio: 1/14 (stoichiometric) at 40ºC, pH 6 and atmospheric pressure.

At the end and following the proposed reaction pathway reported in Chapter IV, phenol intermediates described the general route of phenol oxidation when using different Cu(II) catalysts. The first step of phenol oxidation produced catechol, which at the same time develops a brown colour derived of its oxidation. Then, it was observed the presence of carboxylic acids such as fumaric, malonic, formic and succinic acids, which do not represent toxicity or inhibitory effects according to Santos et al, (2004), even more it was reported that these acids are biodegradable, so their environmental impact is lower (Mijangos et al., (2006). On the other hand, the possibility of hydroquinone formation would represent high levels of toxicity, even higher than phenol itself as reported by Zazo et al. (2005).

At last, it can be conclude that phenol oxidation when using polymer-supported-Cu catalysts generate different intermediates, which can perfectly follow the mechanisms already presented for the homogeneous catalytic oxidation of phenol.

CONCLUSIONS

The heterogeneous catalytic oxidation of phenol using air as oxidant at 30ºC and atmospheric pressure presented an apparent phenol conversions of 12%, after 3 hours. However, at the absence of phenol intermediates, it was concluded that there was an adsorption stage in spite of oxidation activity.

The decomposition of hydrogen peroxide was evaluated at different conditions such as pH and temperature without the presence of phenol. The results without substrate characterised the H_2O_2 decomposition, which was found to follow the first order rate. It was also found that rate constants increased at neutral pH, where the leaching of Cu(II) ions was avoided.

After pH influence on hydrogen peroxide decomposition, it was carried out the phenol oxidation at pH 6 to evaluate the temperature influence. At high temperatures, H_2O_2 decomposition (53%) and phenol conversions (60%) were elevated and favourable for a better phenol degradation, although the leaching of Cu(II) was also high (7 $mg \cdot L^{-1}$). Finally, in order to obtain higher phenol conversions at mild conditions, it is suggested to carry out the reaction at pH 6 and 40ºC. Although, these conditions were used when phenol mechanism was identified.

Heterogeneous catalytic oxidation of phenol using Cu-supported catalysts presented the best catalytic activity when Cu-PVP_2 (80%) and the commercial $CuO/\gamma\text{-}Al_2O_3$ (87%) catalysts were tested. Although after leaching evaluation it was avoided the use of catalysts with more than 100 $mg \cdot L^{-1}$ of Cu(II) content, hence Cu-PVP_2 catalyst with 50 $mg \cdot L^{-1}$ of Cu(II) content was selected as the best catalyst of this group because it promoted 65% of phenol conversion without leaching problems.

Despite of the important adsorption capacity that cationic resin presented for Cu(II) ions, it was not possible the oxidation of phenol at soft conditions. This lack of catalytic activity had its origin on the chemisorption performed by the cationic resin. Then, it is concluded that since adsorption is represented by chemisorption, the formed bonds are strong enough to prevent Cu(II) ions from interacting with hydrogen peroxide and eliminating the possibility to produce hydroxyl radical.

When Cu-chitosan-alumina was used, all samples showed phenol conversion up to 100% and TOC conversions up to 80% at room conditions, assuring a high phenol mineralisation, although the presence of refractory carboxylic acids cannot be neglected when this process is thought to be the pre-treatment of a biological treatment. P2 and P3 had approximately the same copper content (32 mg of Cu(II) per gram of catalyst) but after oxidation reaction Cu(II) leaching was extremely high. Therefore, the use of Cu-chitosan-alumina was stopped because the heterogenization of Cu(II)-chitosan complex in alumina was not achieving its purpose, of being active in heterogeneous catalysis as in homogeneous catalytic oxidation, avoiding the leaching.

After testing the group of polymer-supported-metal catalysts it can be concluded that between Mo(VI) and Cu(II) catalysts, Cu(II) had better catalytic activity for the CWPO of phenol at soft conditions. From the kinetic evaluation, it was found the importance of the leaching over the rate constants because Cu(II) ions in solution accelerated the catalytic oxidation of phenol.

Finally, poly(styrene-divinylbenzene) functionalised with imino diacetic acid and loaded with Cu(II) acetyl acetate (P-I-Cua) showed the highest catalytic activity with 93% of phenol conversion, 43% of TOC conversion and a permissible catalytic leaching of 6,2 $mg\cdot L^{-1}$. Then, it is advised the use of this catalyst for continuous processes because this catalyst achieved 80% of phenol conversion in 90 minutes and its Cu(II) release was not a sign of contamination.

In general, the aim of pre-treatments for phenol mineralisation is to destroy the aromatic ring in order to produce easier degradable intermediates for a wastewater treatment plant. For this reason, the results obtained in the present work, with more than 50% of phenol degradation, reflected a good way to continue working with polymer-supported metal complexes as catalysts for pre-treatments of industrial wastewaters.

REFERENCES

- Arena, F., Giovenco, R., Torre, T., Venuto, A., Parmaliana, Activity and resistance to leaching of Cu-based catalysts in the wet oxidation of phenol, A., Appl. Catal. B: Environ. 45 (2003) 51.
- Bali, U., Karagozoglu, B., Performance comparison of Fenton process, ferric coagulation and H_2O_2/pyridine/Cu(II) system for decolorization of Remazol Turquoise Blue G-133, Dyes and pigments 74 (2007) 73.
- Du, Y., Zhou, M., Lei, L., Role of the intermediates in the degradation of phenolic compounds by Fenton-like process, J. Hazard. Mater. B136 (2006) 859.
- Dursun, A.Y., Kalayci, Ç.S., Equilibrium, kinetic and thermodynamic studies on the adsorption of phenol onto chitin, J. Hazard. Mater. B123 (2005) 151.
- Clesceri, L.S., Greenberg, A.E., Trusel, R.R., Franson, M.A., Standard Methods for the Examination of Water and Wastewater, 17th edition, American Public Health Association and American Water Works Association, Washington (1989) USA.
- Esplugas, S., Giménez, J., Contreras, S., Pascual E., Rodríguez, M., Comparison of different advanced oxidation processes for phenol degradation, Water Research 36 (2002) 1034.
- Fortuny, A., Bengoa, C., Font, J., Fabregat, A., Bimetallic catalysts for continuous catalytic wet air oxidation of phenol, J. Hazard. Mater. B64 (1999) 181.
- Goldstein, S., Meyerstein, D., Comments on the mechanisms of “Fenton-like” reaction, Accounts of chemical research 32 (1999) 547.
- International Molybdenum Association (IMOA), Molybdenum in human health, web site: http://www.imoa.info/index.html
- Kanervo, J.M., Krause, A.O.I., Kinetic Analysis of Temperature-Programmed Reduction: Behavior of a CrO_x/Al_2O_3 Catalyst, J. Physic. Chem. B 105 (2001) 9778.
- Luo, M., Bowden, D., Brimblecombe, P., Catalytic property of Fe-Al pillared clay for Fenton oxidation of phenol by H_2O_2, Appl. Catal. A: Environ. 85 (2009) 201.

- Matatov-Meytal, Y.I., Sheintuch M., Catalytic abatement of water pollutants, Ind. Eng. Chem. Res. 37 (1998) 309.
- Mbeleck, R., Ambrosiak, K., Saha, B., Sherrington, D.C., Stability and recycling of polymer-supported Mo(VI) alkene epoxidation catalysts, React. Funct. Polym. 67 (2007) 1448.
- Mijangos, F., Varona, F., Villota, N., Changes in solution colour during Phenol Oxidation by Fenton Reagent, Environ. Sci. Technol. 40 (2006) 5538.
- Perkin-Elmer Corporation, Analytical Methods for atomic absorption spectrometry, USA (1994).
- Santos, A., Barroso E., García-Ochoa, F., Overall rate of aqueous-phase catalytic oxidation of phenol: pH and catalyst loading influences, Catal. Today 48 (1999) 109.
- Santos, A., Yustos, P., Quintanilla, A., García-Ochoa, F., Casas, J.A., Rodríguez, J.J., Evolution of Toxicity upon Wet Catalytic Oxidation of Phenol, Environ. Sci. Technol. 38 (2004) 133.
- Suarez-Ojeda, M.E., Stüber, F., Fortuny, A., Fabregat, A., Carrera, J., Font, J., Appl. Catal. B-Environ. 58 (2005) 105.
- Tian, F., Liu, Y., Hu, K., Zhao, B., Study of the depolymerization behavior of chitosan by hydrogen peroxide, Carbohy. Pol. 57 (2004) 31.
- Zazo, J.A., Casas, J.A., Mohedano, A.F., Gilarranz, M.A., Rodríguez, J.J., Chemical pathway and kinetics of phenol oxidation by Fenton's reagent, Environ. Sci. Technol. 39 (2005) 9295.
- Zazo, J.A., Casas, J.A., Mohedano, A.F., Rodríguez, J.J., Catalytic wet peroxide oxidation of phenol with a Fe/active carbon catalyst, Appl. Catal. B: Environ. 65 (2006) 261.

OVERALL CONCLUSIONS

The expertise background of the catalytic wet oxidation of phenol was obtained from the bibliographic review. The information of general concepts and technologic processes were joined to the necessity of solving environmental problems, hence it was proposed to employ the heterogeneous catalytic oxidation to treat a simulated effluent (phenol).

Firstly, it was evaluated the catalytic oxidation of phenol when the catalyst was a salt of Cu(II).

- It was used two oxidant sources such as air and hydrogen peroxide. However, when air was the oxidant at 30ºC and atmospheric pressure of operational conditions, phenol oxidation did not occur. Although, when conditions were increased (50ºC, 1:10 Phenol:Cu molar ratio at 24 hours of reaction), phenol conversions were no more than 20%.
- When hydrogen peroxide was the oxidant source of phenol oxidation at soft conditions, the process became efficient with phenol conversions up to 95 % and TOC conversions up to 45 %.
- It was demonstrated that either Cu(II) or H_2O_2 initial concentrations had direct influence over the phenol oxidation because the production of OH• radicals was originated on the decomposition of H_2O_2, which depended on the amount of Cu(II).
- From the identification of phenol intermediates, it was found two main partially oxidised compounds such as hydroquinone and catechol, likewise it was found some acids such as fumaric, malonic, succinic and formic before the formation of CO_2 and water. Thus, it was proposed a pathway mechanism for the present oxidation process.

Once phenol oxidation was studied at the homogeneous phase, it was synthesised and characterised a group of heterogeneous Cu(II) catalysts. For this purpose it was employed three different techniques such as the adsorption, co-precipitation and polymerisation-metal loading.

- The adsorption capacities of Cu(II) was carried out using three different supports: poly(4-vinylpyridine) or PVP, poly(D-glucosamine) or Chitosan and a commercial cationic resin or CR. Results demonstrated that the exposed polymeric surface was the main influence for adsorption behaviour. However it is also remarkable the importance of the surface charge due to it determines the easy attraction of ions onto the support.
- Adsorption results showed that the cationic resin had the highest adsorption capacity between all four supports, followed by poly(4-vinylpyridine) 2% of cross-link, poly(4-vinylpyridine) 25% of cross-linking and finally chitosan. Then, this group of catalysts presented an important catalytic potential, because the highest Cu(II) amount the catalyst has, the highest phenol conversion can be achieved.

The co-precipitation technique was satisfactory employed, from which it was produced three catalysts that differed on the number of co-precipitations.

- Successive co-precipitations increase the amount of Cu(II) content into the catalyst, however this increment was no more than 5% when comparing the first and third co-precipitation cycles, so it was assumed the saturation of the inert support.
- TGA results demonstrated that the co-precipitation of Cu(II)-Chitosan complex was not effective as expected because of the low Cu(II) content, however TPR chromatographs showed the presence of two species on the catalyst, which were classified as $CuCl_2$ and Cu-Chitosan complex.

The polymerisation-metal loading technique was suitable to perform the heterogenization of Cu(II).

- Salts of copper and molybdenum were used to be loaded onto the synthesised polymeric matrix, then from the use of two different copper salts it was obtained higher metal loadings when copper sulphate was used, suggesting that supported-metal complexes based on copper sulphate and synthesised with water have more possible catalytic active sites.

After the heterogenization of homogeneous catalysts, it was evaluated the catalytic activity of every catalyst.

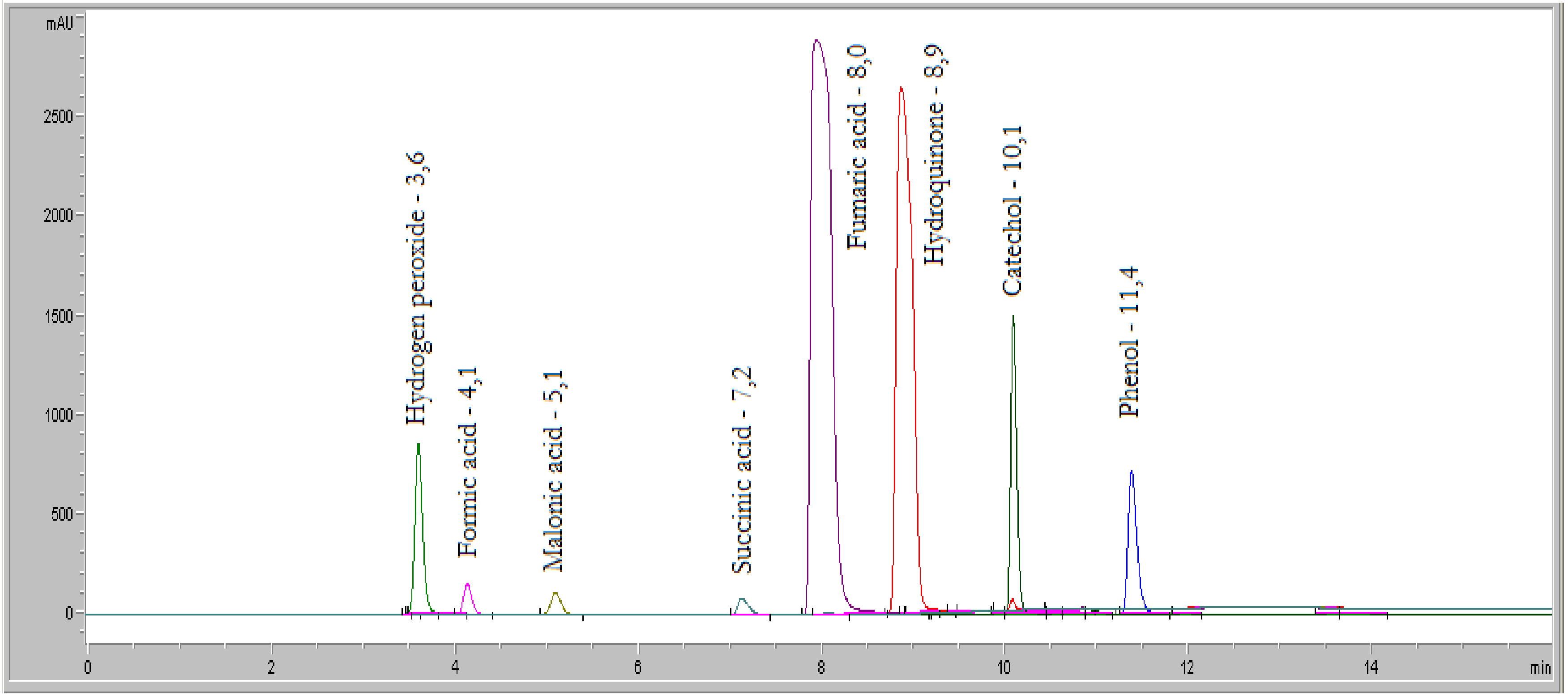
- The heterogeneous catalytic oxidation of phenol using air as oxidant at 30ºC and atmospheric pressure presented an apparent phenol conversions of 12%, after 3 hours. However, at the absence of phenol intermediates, it was concluded that there was an adsorption stage instead of oxidation activity.
- Heterogeneous catalytic oxidation of phenol using Cu-supported catalysts presented the best catalytic activity when Cu-PVP$_2$ (80%) and the commercial CuO/γ-Al$_2$O$_3$ (87%) catalysts were tested. Although after leaching evaluation it was avoided the use of catalysts with more than 100 mg·L^{-1} of Cu(II) content, hence Cu-PVP$_2$ catalyst with 50 mg·L^{-1} of Cu(II) content was selected as the best catalyst of this group because it promoted 65% of phenol conversion without leaching problems.
- Despite of the important adsorption capacity that cationic resin presented for Cu(II) ions, it was not possible the oxidation of phenol at soft conditions. This lack of catalytic activity had its origin on the chemisorption performed by the cationic resin. Then, it is concluded that since adsorption is represented by chemisorption, the formed bonds are strong enough to prevent Cu(II) ions from interacting with hydrogen peroxide and eliminating the possibility to produce hydroxyl radical.
- When Cu-chitosan-alumina was used, all samples showed phenol conversion up to 100% and TOC conversions up to 80% at room conditions, assuring a high phenol mineralisation. P2 and P3 had approximately the same copper content (32 mg of Cu(II) per gram of catalyst) but after oxidation reaction Cu(II) leaching was extremely high. Therefore, the use of Cu-chitosan-alumina was stopped because the heterogenization of Cu(II)-chitosan complex in alumina was not achieving its purpose, of being active in heterogeneous catalysis as in homogeneous catalytic oxidation, avoiding the leaching.
- Finally, from the catalytic evaluation of the group of catalysts synthesised by polynerisation-metal loading technique, it was found that poly(styrene-divinylbenzene) functionalised with imino diacetic acid and loaded with Cu(II)

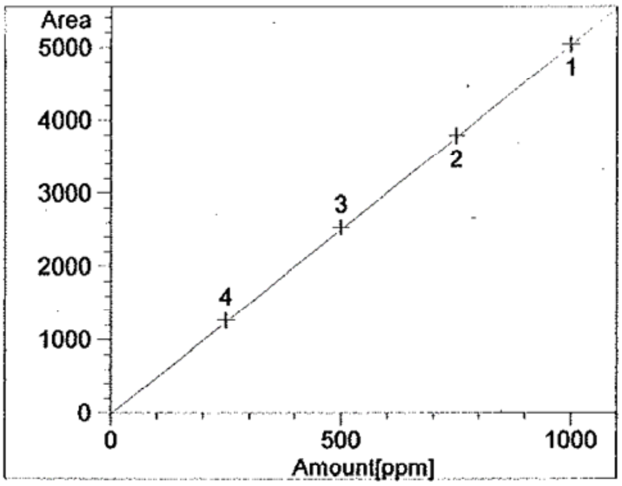
acetyl acetate (P-I-Cua) showed the highest catalytic activity with 93% of phenol conversion, 43% of TOC conversion and a permissible catalytic leaching of 6,2 mg·L^{-1}. Then, it is advised the use of this catalyst for continuous processes because this catalyst achieved 80% of phenol conversion in 90 minutes and its Cu(II) release was not a sign of contamination.

- In general, the aim of pre-treatments for phenol mineralisation is to destroy the aromatic ring in order to produce easier degradable intermediates for a wastewater treatment plant. For this reason, the results obtained in the present work, with more than 50% of phenol degradation, reflected a good way to continue working with polymer-supported metal complexes as catalysts for pre-treatments of industrial wastewaters.

ANNEXES

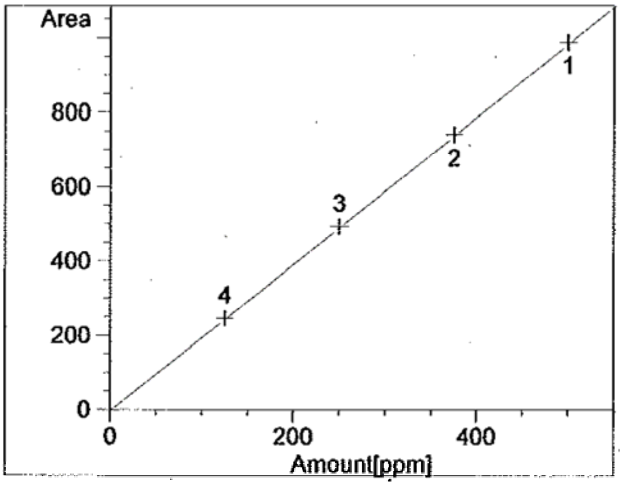
Annexe 1. Chromatogram of phenol and phenol intermediates





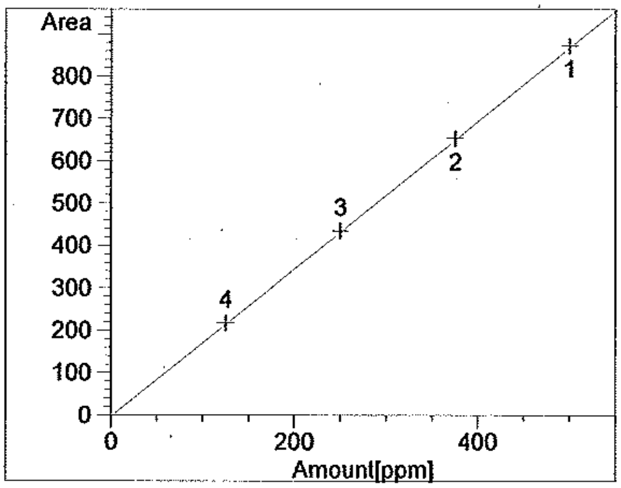
```
H2O2 at exp. RT: 3.605
DAD1 A, Sig=254,5 Ref=360,100
Correlation:                 1.00000
Residual Std. Dev.:          5.46271
Formula: y = mx
        m:        5.04926
        x: Amount[ppm]
        y: Area
```

Annexe 2. HPLC calibration of hydrogen peroxide



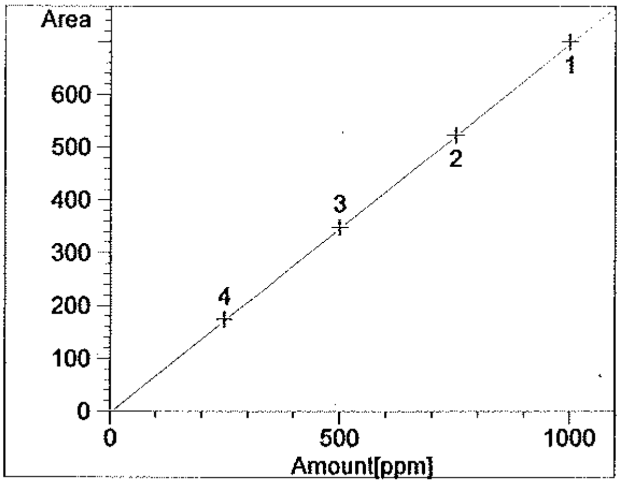
```
Formic at exp. RT: 4.118
DAD1 B, Sig=210,5 Ref=360,100
Correlation:                 1.00000
Residual Std. Dev.:          0.70320
Formula: y = mx
        m:        1.97509
        x: Amount[ppm]
        y: Area
```

Annexe 3. HPLC calibration of Formic acid



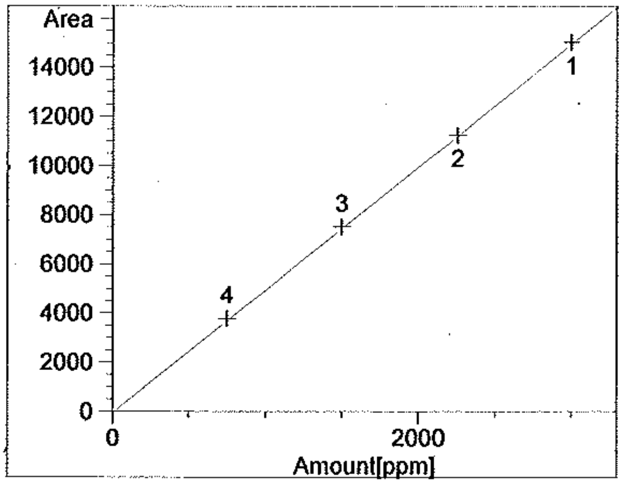
```
Malonic at exp. RT: 5.081
DAD1 B, Sig=210,5 Ref=360,100
Correlation:                 1.00000
Residual Std. Dev.:          0.84603
Formula: y = mx
        m:        1.74447
        x: Amount[ppm]
        y: Area
```

Annexe 4. HPLC calibration of Malonic acid



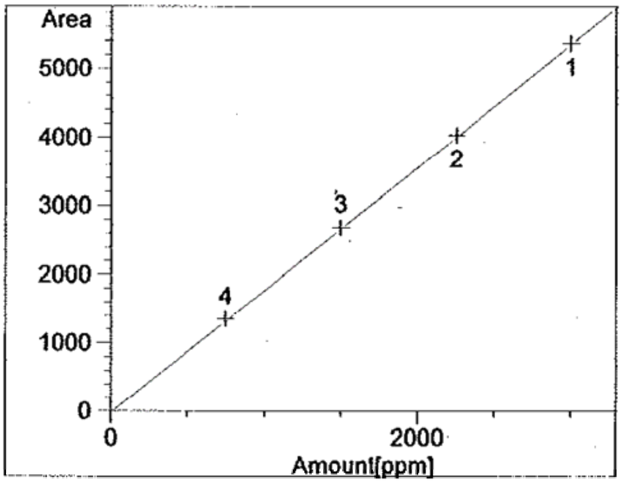
```
Succinic at exp. RT: 7.162
DAD1 B, Sig=210,5 Ref=360,100
Correlation:              1.00000
Residual Std. Dev.:       1.09328
Formula: y = mx
      m:       6.97973e-1
      x: Amount[ppm]
      y: Area
```

Annexe 5. HPLC calibration of Succinic acid



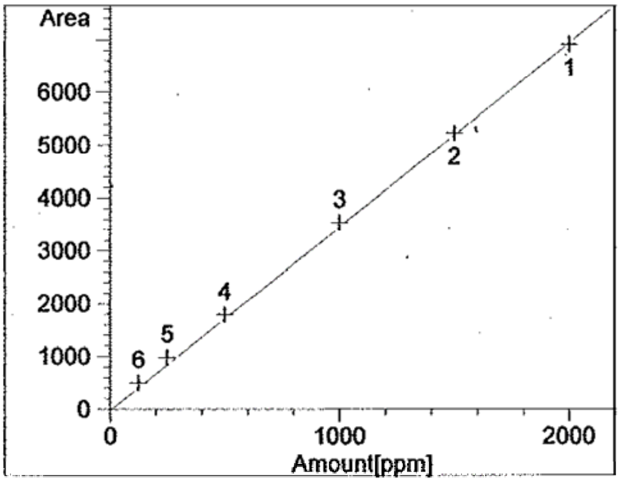
```
Fumaric at exp. RT: 7.935
DAD1 A, Sig=254,5 Ref=360,100
Correlation:              1.00000
Residual Std. Dev.:      18.11914
Formula: y = mx
      m:       4.99951
      x: Amount[ppm]
      y: Area
```

Annexe 6. HPLC calibration of Fumaric acid



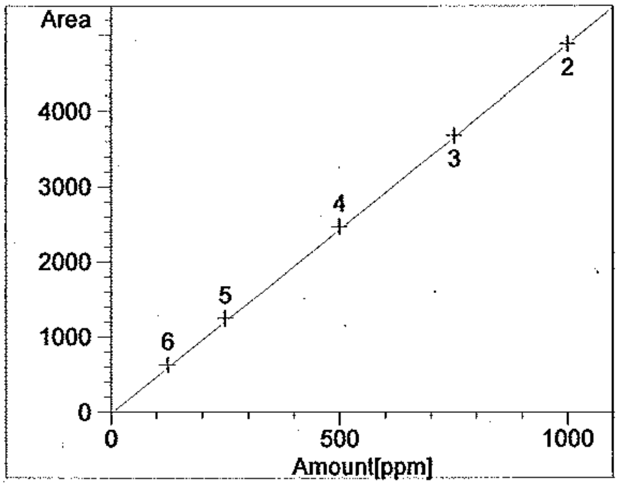
```
Hidroq2 at exp. RT: 9.003
DAD1 A, Sig=254,5 Ref=360,100
Correlation:              1.00000
Residual Std. Dev.:       8.01566
Formula: y = mx
      m:       1.78716
      x: Amount[ppm]
      y: Area
```

Annexe 7. HPLC calibration of Hydroquinone



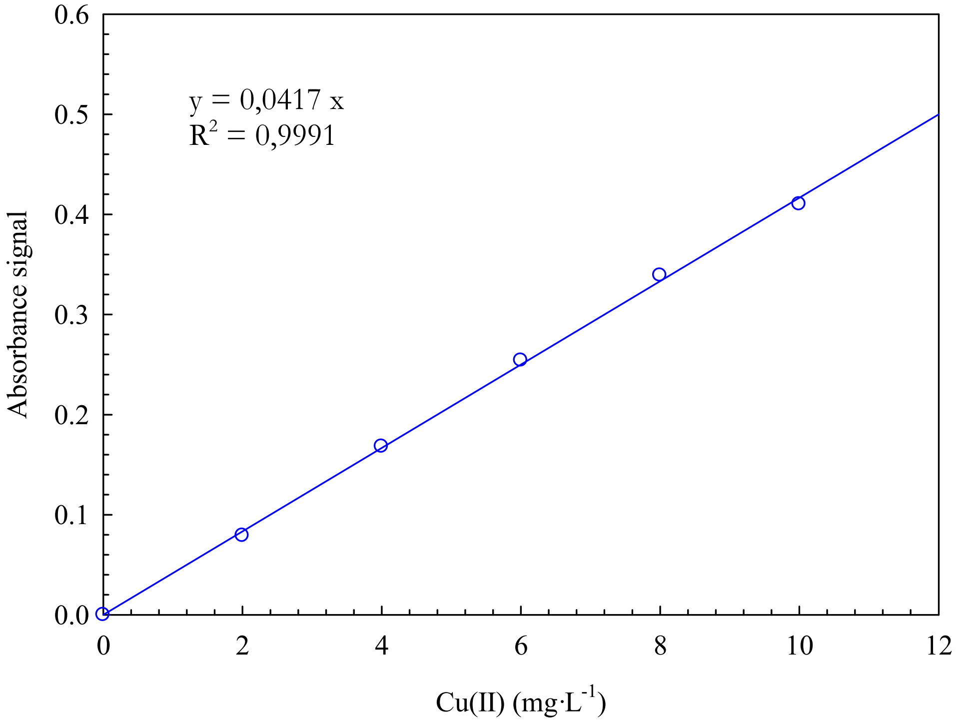
```
catechol at exp. RT: 10.101
DAD1 A, Sig=254,5 Ref=360,100
Correlation:                0.99987
Residual Std. Dev.:      69.82605
Formula: y = mx
        m:        3.48488
        x: Amount[ppm]
        y: Area
```

Annexe 8. HPLC calibration of Catechol



```
phenol at exp. RT: 11.400
DAD1 A, Sig=254,5 Ref=360,100
Correlation:                0.99999
Residual Std. Dev.:      17.95439
Formula: y = mx
        m:        4.90664
        x: Amount[ppm]
        y: Area
```

Annexe 9. HPLC calibration of Phenol



Annexe 10. Example of the calibration curve to calculate Cu(II) concentrations by the Atomic Adsorption analyser.

Curriculum vitae

Personal information:

Last Name: CASTRO CEVALLOS
Name: Ursula Isabel
Nationality: Peruvian
Residence: Spain

Professional situation

Organism: Universitat Rovira i Virgili
Faculty, School or Institute: Escuela Técnica Superior de Ingeniería Química
Dept./Secc./Unity.: Departament d'Enginyeria Quimica
Postal address: Av. Països Catalans Nº 26 (Tarragona - 43007)
Contact phone: 0034 977558561
Fax: +34 977559667
e-mail: ursulaisabel.castro@urv.net

Academic Formation

Title	Center	Date
Doctor	Universitat Rovira i Virgili - Spain	24/07/2009
Diploma de Estudios Avanzados – DEA or MSc	Universitat Rovira i Virgili - Spain	10/10/2006
Bach/ Ingeniería Química	Universidad Nacional del Centro del Perú	23/12/2003

Research Stage abroad

Center: University of Strathclyde science, Department of Pure and Applied Chemistry
Place: Glasgow
Country: Scotland
Year: 2008
Duration: 03 Months
Issue: Preparation of polyestyrene-based resin support using the suspension-polymerisation method, Functionalisation of these resins with metal chelating ligand, Metal loading of the final resin-bound ligand. Catalytic testing of polymer-metal complexes.
Supervisor: Prof. D.C. Sherrington - FRS FRSE

Center: Ecole des Mines d'Alès, Laboratoire Génie de l'Environnement Industriel
Place: Alès
Country: France
Year: 2007
Duration: 04 days

Issue: To learn the techniques to produce Chitosan beads.
Supervisor: Dr. Eric Guibal

Center: Universidad Nacional de Mar del Plata
Place: Mar del Plata
Country: ARGENTINA
Year: 2006
Duration: 02 months
Issue: Research work at the division of Catalysts and surfaces at INTENA department-Universidad Nacional de Mar del Plata
Supervisor: Dr. Patricia Haure

Publications in International journals

Authors: Isabel U. Castro, Frank Stüber, Azael Fabregat , Josep Font, Agustí Fortuny, Christophe Bengoa
Title: Supported Cu(II) polymer catalysts for aqueous phenol oxidation
Journal: Journal of Hazardous materials
DOI: 10.1016/j.jhazmat.2008.07.054
Publication: Journal of Hazardous Materials 163 (2009) 809–815

Publications or scientific-technical documents

Authors: Castro, I.U.; Stübert, F.; Font, J.; Fabregat, A.; Fortuny, A.; Bengoa, C.
Title: New Strategies for Phenol Oxidation by Copper at room temperature.
Book: International Water Conference
Editorial: Centro de Estudos de Água
Volume: 1 **Númber:** 1 **Initial page:** 332 **final:** 338 **Year:** 2006
Publication place: Porto-(Portugal) **ISBN:** 972-8688-40-7

Authors: Castro, I.U.; Sanchez, I.; Stübert, F.; Font, J.; Fabregat, A.; Fortuny, A.; Bengoa, C.
Títle: Copper catalyst by immobilising Cu(II) ions on Chitosan and PVP
Book: CHISA - Summaries 1 - Reaction Engineering
Editorial: Process Engineering Publisher
Volume: 6 **Número:** 1 **Initial page:** 252 **final:** 253 **Year:** 2006
Publication place: Praha (Check Republic) **ISBN:** 80-86059-45-6

Authors: Castro, I.U.; Stübert, F.; Font, J.; Fabregat, A.; Fortuny, A.; Bengoa, C.
Títle: Polymer supported copper catalysts for aqueous phenol oxidation.
Book: Récents Progrès en Génie des Procédés (1st International Congress on Green Process Engineering)
Editorial: Société Française de Génie des Procédés
Volume: --- **Number:** 94 **Initial page:** 1 **final:** 8 **Year:** 2007
Publication place: Toulouse (France) **ISBN:** 2-910239-68-3

Contributions to Congresses

Authors Castro, I.U.; Sanchez, I.; Font, J.; Fortuny, A.; Stüber, F.; Fabregat, A.; Bengoa, C.
Title: Copper catalyst by immobilising Cu(II) ions on chitosan and PVP
Participation: Poster
Congress: 17th International congress of chemical and Process Engineering CHISA-2006
Place: Praha (Check Republic) **Year:** 2006

Authors: Castro, I.U.; Stüber, F.; Font, J.; Fabregat, A.; Fortuny, A.; Bengoa, CH.
Title New strategies for phenol oxidation by copper at room temperature
Participation: Poster
Congress: International Water Conference IWC-2006
Place: Porto (Portugal) **Year:** 2006

Authors: Castro, I.U.; Bengoa, C.; Font, J.
Títle: Polymer supported Cu2+ catalyst for phenol oxidation at soft conditions
Participation: Poster
Congress: Jornada Doctoral - Concurso de posters 2006 PhD program- Etseq.
Place: Tarragona (Spain) **Year:** 2006

Authors: Castro, I.U.; Stüber, F.; Font, J.;Fabregat, A.; Fortuny, A.; Bengoa, C.
Títle: Polymer supported copper catalyst for aqueous phenol oxidation
Participation: Oral presentation
Congress: 1th International congress of Green Process Engineering
Place: Toulouse (France) **Year:** 2007

Authors: Castro, I.U.; Fortuny, A.; Stüber, F.; Fabregat, A.;Font, J.; Haure, P.; Bengoa, C.
Títle: Synthesis of copper catalysts by coprecipitation of Cu(II) and chitosan onto alumina
Participation: Poster
Congress: European Congress of Chemical Engineering - 6
Place: Copenhagen (Denmarck) **Year:** 2007

Authors: Castro, I.U.; Sherrington, D.C.; Mbeleck, R.; Macdonald, I.; Cormack, P.A.G.; Fortuny, A.; Fabregat, A.; Stüber, F.; Font, J.; Bengoa, C.
Títle: Synthesis and characterisation of polymer-supported metal complexes for the oxidation of phenol under mild conditions**.**
Participation: Poster
Congress: 2nd International Congress on Green Process Engineering, 2nd European Process Intensification Conference
Place: Venice (Italy) **Year:** 2009

Authors: Castro, I.U.; Sherrington, D.C.; Fortuny, A.; Fabregat, A.; Stüber, F.; Font, J.; Bengoa, C.
Títle: Polymer-supported metal complexes: catalysts for the CWHPO of phenol
Participation: Oral presentation
Congress: 6th World Congress on Oxidation Catalysis
Place: Lille (France) **Year:** 2009

Journal of Hazardous Materials 163 (2009) 809–815

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Supported Cu(II) polymer catalysts for aqueous phenol oxidation

Isabel U. Castro [a], Frank Stüber [a], Azael Fabregat [a], Josep Font [a], Agustí Fortuny [b], Christophe Bengoa [a,*]

[a] *Departament d'Enginyeria Química, Escola Tècnica Superior d'Enginyeria Química, Universitat Rovira i Virgili, Av. Països Catalans 26, 43007 Tarragona, Catalonia, Spain*
[b] *Departament d'Enginyeria Química, EPSEVG, Universitat Politècnica de Catalunya, Av. Víctor Balaguer s/n, 08800 Vilanova i la Geltrú, Barcelona, Catalonia, Spain*

ARTICLE INFO

Article history:
Received 24 August 2007
Received in revised form 7 July 2008
Accepted 8 July 2008
Available online 19 July 2008

Keywords:
Poly(4-vinylpyridine)
Chitosan
Phenol oxidation
Mild operation conditions
Hydrogen peroxide

ABSTRACT

Supported Cu(II) polymer catalysts were used for the catalytic oxidation of phenol at 30 °C and atmospheric pressure using air and H_2O_2 as oxidants. Heterogenisation of homogeneous Cu(II) catalysts was achieved by adsorption of Cu(II) salts onto polymeric matrices (poly(4-vinylpyridine), Chitosan). The catalytic active sites were represented by Cu(II) ions and showed to conserve their oxidative activity in heterogeneous catalysis as well as in homogeneous systems. The catalytic deactivation was evaluated by quantifying released Cu(II) ions in solution during oxidation, from where Cu–PVP_{25} showed the best leaching levels no more than 5 mg L^{-1}. Results also indicated that Cu–PVP_{25} had a catalytic activity (56% of phenol conversion when initial Cu(II) catalytic content was 200 mg L^{-1}_{Reaction}) comparable to that of commercial catalysts (59% of phenol conversion). Finally, the balance between activity and copper leaching was better represented by Cu–PVP_{25} due to the heterogeneous catalytic activity had 86% performance in the heterogeneous phase, and the rest on the homogeneous phase, while Cu–PVP_2 had 59% and CuO/γ-Al_2O_3 68%.

1. Introduction

About 97% of water belongs to the oceans and only 3% is fresh water. Moreover, 0.3% of fresh water is distributed in lakes (87%), swamps (11%) and rivers (2%). Thus, available fresh water sources must be preserved from pollution as there is already a deficit on water [1].

Among the wide variety of water pollutants, phenol and its derivatives have became an important environmental water pollution concern [2]. However most of wastewater from industrial effluents contains compounds or inhibitors poorly degradable, or even toxic. Phenolic compounds are strong bactericide even at mild concentrations, in addition, most of phenol derivatives are contemplated as harmful for human health [3].

Between the large variety of soft cleaning technologies, catalytic wet air oxidation (CWAO) with active carbon allows the use of mild operation conditions [4], enhances the oxidation and requires a lower energy than WAO [5]. On the other hand Fenton-based treatments work at lower pressure and temperature conditions [6], providing a rapid and total destruction of phenolic compounds [7]. Nevertheless, these processes have drawbacks when are operated in continuous and it is necessary to remove the homogeneous catalyst [8].

On the other hand, some studies demonstrated that active metal salts are capable to effectively promote the oxidation of recalcitrant compounds [9]. Moreover, the catalytic activity of Cu(II) is greatly enhanced when H_2O_2 is the oxidant [10]. In particular, the oxidation using Fenton's like reagent is an attractive treatment method for a large number of hazardous and organic materials [11]. For the heterogeneous systems this is still less clear, being a matter of controversy between an initial adsorption step of the H_2O_2 [12] or the organics [13].

The heterogenisation of homogeneous catalysts by immobilisation improves the easy separation of the catalyst and the simple application on continuous processes [14,15]. Moreover the sorption onto materials of biological origins as synthetic and natural polymers is also recognised as emerging technique [16–19]. For instance, the Chitosan or poly(D-glucosamine), is a new class of potentially inexpensive and environmentally friendly substance that exhibits a high specificity towards metal ions [20].

Polymeric metal complexes are synthesised by adsorption processes using a polymer with a content of donating groups such as amine [21–23]. Chitosan-supported metal complexes are employed as catalysts of industrial processes [24]. Some parameters influence the capacity for adsorbing the metal such as its source, the nature of the metal ion or the solution conditions [25]. However, the cross-linking can also cause a decrease in the reactivity of the polymer, due to a reduction in the diffusion properties [26]. The porosity of the material has a great relevance and limits the adsorption capacity [27].

The poly(4-vinylpyridine) (PVP) is also an attractive polymer for immobilisation of metal ions, because of the strong affinity of pyridyl group to metals and its ability to undergo hydrogen bounding. Analysis of the behaviour of PVP–copper complex show that

---

[*] Corresponding author. Tel.: +34 977 558619; fax: +34 977 559667.
E-mail address: christophe.bengoa@urv.cat (C. Bengoa).

0304-3894/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2008.07.054

carbonyl bond group is a function of the metal concentration [22]. The enhancement of the thermal properties by the formation of more than one nitrogen–copper bond with the same atom of copper allows high temperature processes that improve mass transport inside the reaction system [23].

This research is devoted to the catalytic oxidation of phenol, at mild conditions, through a heterogeneous Cu(II) onto Chitosan and PVP catalysts in a batch stirred tank reactor. The treatment is not seen as an ultimate treatment but has to provide the demanded biodegradability to be sent to a municipal wastewater treatment process.

2. Methodology

2.1. Materials

Copper sulphate pent hydrated ($CuSO_4{\cdot}5H_2O$) (reference 61245), as well as poly(4-vinylpyridine) 2% cross-linked powder, PVP_2 (reference 81391) and poly(4-vinylpyridine) 25% cross-linked beads, PVP_{25} (reference 81393) were purchased from Sigma–Aldrich. The Chitosan beads were supplied by Dr. E. Guibal (Laboratoire de Génie de l'Environnement Industriel, Ecole des Mines d'Alès, France). The beads were synthesized according to an original procedure [20] and stored in a solution of NaOH 10% (v/v). The commercial copper catalyst, 20% of CuO supported on γ-Al_2O_3, was provided by Harshaw (reference Cu0803 T1/8). Phenol crystallised (reference 144852) was purchased from Panreac with purity higher than 99%. Catechol 99% (reference 13,5011) and hydroquinone 99% (reference H17902) were provided by Sigma–Aldrich. 1,4-Benzoquinone 98% (reference 12309) and Resorcinol 99% (reference 83600) were purchased from Fluka. Hydrogen peroxide 30% (w/v) (100 vol.) PA (reference 121076.1211) was provided by Panreac. Millipore Milli-Q deionised water was used to prepare all solutions.

2.2. Catalyst preparation

The Cu(II) catalysts were prepared by adsorption of Cu(II) ions onto polymeric materials where $CuSO_4{\cdot}5H_2O$ salt was used as source of Cu(II). The catalyst preparation is based on the immersion of 1 g of the polymeric material (either PVP_2, PVP_{25}, or Chitosan) into 200 mL of Cu(II) solutions. The variation of copper concentrations was monitored after 24 h and analysed by UV–vis spectrophotometer at 800 nm of wavelength in the visible range. The adsorption capacity of Cu(II) onto every support was obtained from the adsorption capacity evaluation, where the variation of Cu(II) before and after adsorption, the volume of the substrate and the weight of the used support were related. Then, the obtained catalysts presented adsorption capacities of PVP_2: 370 mg g^{-1}, PVP_{25}: 290 mg g^{-1} and Chitosan: 120 mg g^{-1} representing great amount of active catalytic sites. The full characterisation of these catalysts can be found elsewhere [28].

2.3. Oxidation process

The oxidation tests were conducted at low temperature in a batch stirred tank reactor of 180 mL. Fig. 1 presents the oxidation setup. The initial phenol concentration was always 1 g L^{-1}, the temperature 30 °C and at atmospheric pressure air and hydrogen peroxide were used as oxidants. When air was the oxidant, saturated air was bubbled through the reactor with a flow of 85 mL min^{-1}. When H_2O_2 was the oxidant, three different phenol/peroxide (Ph:H_2O_2) molar rates (1:1, 1:5 and the stoichiometric 1:14) were used. The mass of the added catalyst for the homogeneous catalytic oxidation was calculated to provide Cu(II) concentrations of 5, 10, 50 and 200 mg L^{-1}. On the other hand, the amount of added catalyst (W_{CAT}), for the heterogeneous catalytic oxidation, was calculated from a mass balance in the catalyst. It was obtained a equation that related the required amount of Cu(II) at the homogeneous oxidation (W_{Cu}) with the amount of supported Cu(II) onto a specific polymeric material by means of the adsorption capacity (q):

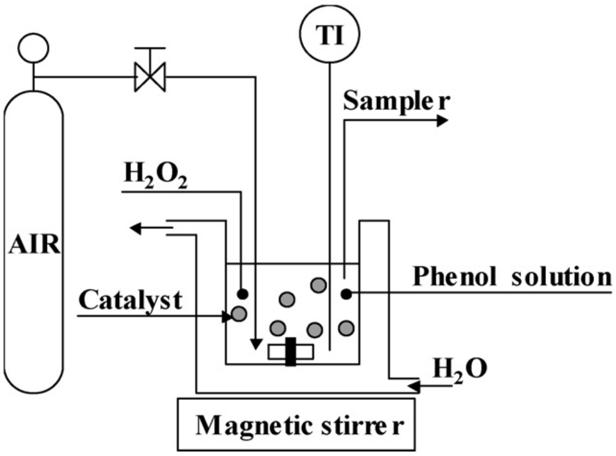


Fig. 1. Catalytic oxidation setup of a batch stirred tank reactor. Heterogeneous catalysis.

$$W_{CAT} = W_{Cu} \cdot \left(1 + \frac{1}{q}\right)$$

The pH was monitored along the reaction time. Reaction progress was monitored by withdrawing 1 mL samples at 5, 20, 40, 60 and 120 min from starting. Then, they were analysed by HPLC to determine the remaining concentration of phenol. Also, the total organic carbon (TOC) at 120 min was determined.

2.4. Analytical procedure

Phenol conversion was calculated by measuring the phenol concentration by HPLC (Agilent Technologies, model 1100) with a C18 reverse phase column (Agilent Technologies, Hypersil ODS). The analyses were performed using a mobile phase with a gradient mixture of methanol and ultra pure water (Milli-Q water, Millipore) from 0/100 (v/v) to 40/60 (v/v). The flow rate increases from 0.6 at the fifth minute to 1.0 mL min^{-1} at the seventh minute. The pH of the water was adjusted at 1.4 with sulphuric acid (H_2SO_4). The detection was performed by UV absorbance at a wavelength of 254 nm. Automatic injector took volumes of 20 μL per sample. A calibration curve of phenol was made using aqueous samples of known composition. Intermediates identification was performed by HPLC analyser using aqueous samples of known patterns of each intermediate.

Total organic carbon (TOC) values were obtained by a TOC Analyser (Analytic Jena, model NC 2100). Samples were acidified with 50 mL HCl 2N then were bubbled with synthetic air for 3 min to eliminate the inorganic carbon content and then injected.

Leaching of the catalyst at the end of the oxidation process was determined with an Atomic Absorption Spectrometer (PerkinElmer, model 3110). The analyses were preformed at 325 nm with a specific lamp for the element of Cu (PerkinElmer, serial number 01074).

3. Results and discussion

3.1. Homogeneous catalysis

3.1.1. Air as oxidant

Preliminary experiments of phenol oxidation were performed at homogeneous conditions using air as oxidant with a flow of 85 mL min^{-1}. The first attempt was done with a Ph:Cu(II) molar ratio of 1:1, testing two Cu(II) salts (chloride and sulphate) and for the period of 2 h at 30 °C. A qualitative evaluation did not show important colour changes promoted by the formation of quinones after the reaction time The achieved phenol conversion at 30 °C was less than 5%, which was not satisfactory at all and the difference between each Cu(II) salt was not significant. So, in order to enhance the reaction performance, the experiments were conducted with a Ph:Cu(II) molar ratio of 1:10 at 50 °C for a period of 24 h. The idea of using more severe conditions just reported up to 20% of phenol conversion, although the reaction was not sufficiently improved even with 1:10 molar ratio of Ph:Cu(II). Finally, the conversion obtained after 24 h, 20%, was not acceptable if the purpose is to subsequently send the effluent to a municipal wastewater treatment plant (WWTP). On the other hand the Cu(II) concentration in the reaction solution was too high and it would not be allowed as wastewater influent in any WWTP. Due to the results using air as oxidant were not suitable, it was decided to use a more powerful oxidants as the hydrogen peroxide (H_2O_2).

3.1.2. Hydrogen peroxide as oxidant

The second set of experiments was carried out to evaluate the effect of H_2O_2. The initial phenol concentration was 1 g L^{-1}, the salt used was $CuSO_4{\cdot}5H_2O$ and the reaction time was 2 h. Three different Ph:H_2O_2 molar ratios were tested (1:1, 1:5 and the stoichiometric 1:14) with four different initial Cu(II) concentrations (5, 10, 50 and 200 mg L^{-1}) at the temperature of 30 °C. In this case, the colour of the solution changed, especially at the 20th min where the formation of quinones was evident due to the substrate turned to a dark brown colour, which reflected the formation of phenol intermediates.

Fig. 2 presents the results of phenol conversion using H_2O_2 as oxidant agent after 2 h at the conditions described above. As it can be seen in the figure, phenol conversion increased when Cu(II) concentration was increased and this behaviour occurs for the three molar ratios (1:1, 1:5 and 1:14). It also can be seen that at the equimolar ratio, the phenol conversions were not higher than 50%. Also, at 1:5 Ph:H_2O_2 molar ratio, the phenol conversions were better than the equimolar ration results, presenting conversions from 40 to 85% at different Cu(II) concentrations.

Comparisons between conversions at different molar ratios showed that, phenol conversions achieved at 1:5 Ph:H_2O_2 molar ratio showed a high improvement, almost doubled, compared to conversion at 1:1 Ph:H_2O_2 molar ratio. However, phenol conversions at 1:14 Ph:H_2O_2 molar ratio did not present high increment compared to conversions achieved at 1:5 Ph:H_2O_2, presenting 1:14 as an approximation of the upper limit of the use of H_2O_2.

Afterwards, it was expected a proportional increment of phenol conversion when Cu(II) concentration was increased, but the experimental experience showed a different behaviour. From Fig. 2 at 1:1 Ph:H_2O_2 molar ratio it can be seen that phenol conversion had higher increment between 5 and 50 mg L^{-1} than between 50 and 200 mg L^{-1}. This behaviour was also observed at 1:5 molar ratio where phenol conversions increased from 40 to 71% in the range of 5–50 mg L^{-1} and from 71 to 87% between 50 and 200 mg L^{-1} of Cu(II) concentration. Furthermore, at 1:14 Ph:H_2O_2 molar ratio the phenol conversion follows the same tendency, that is, between 5–50 mg L^{-1} phenol conversion raised from 44 to 86%, and had a small increase, from 86 to 94%, for the range of 50–200 mg L^{-1} of Cu(II) concentration. Then, the variation of phenol conversions at different Cu(II) concentrations showed important changes at the first range of 5–50 mg L^{-1} of Cu(II). Thus, better results were presented at the 50–200 mg L^{-1} range where phenol conversion was the highest. Afterwards, the Cu(II) load had a positive effect on the conversion, confirming results presented by Aguiar and Ferraz [29]. Even though the high-Cu(II) load could be lowered in order to follow the effluent directives, where there are not permissible higher Cu(II) concentrations than 5 mg L^{-1} [2]. However, the catalytic activity at high-Cu(II) concentrations was hindered due to hydrogen peroxide produced an excess of OH$^{\bullet}$ radicals that were easily converted into O_2 with a much lower oxidising power [30]. As expected, phenol seemed to react according to reported reaction pathways [31], from which cathecol, hydroquinone, resorcinol and 1,4-benzoquinone were identified as main earlier reaction intermediates.

The conversions of total organic carbon (TOC) of the above tests are shown in Fig. 3. It can be observed in the figure, that TOC conversion increased with the increment either of Ph:H_2O_2 molar ratio, or Cu(II) concentration. At 1:1 Ph:H_2O_2 molar ratio, the mineralisation was low, between 1–6%, compared with the mineralisation achieved at 1:5 Ph:H_2O_2 molar ratio, where the values were between the ranges of 1–32%. This improvement of the mineralisation, in more than four times the value achieved at 1:1

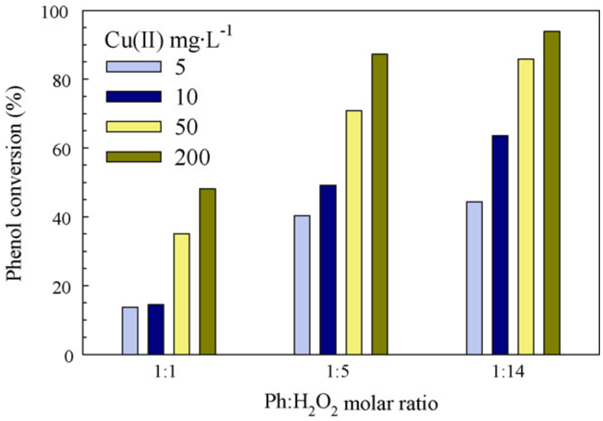


Fig. 2. Homogeneous catalytic phenol oxidation: influence of Cu(II) concentration (mg L^{-1}) at different (Ph:H_2O_2) molar ratio. $[Ph]_0$ = 1 g L^{-1}; reaction time = 2 h; T = 30 °C.

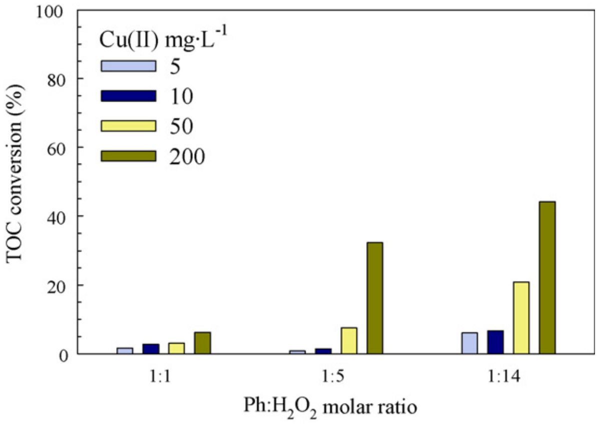


Fig. 3. TOC conversion of homogeneous catalytic phenol oxidation: influence of Cu(II) concentration (mg L^{-1}) at different Ph:H_2O_2 molar ratio. $[Ph]_0$ = 1 g L^{-1}; reaction time = 2 h; T = 30 °C.

Ph:H_2O_2 molar ratio, was attributed to the increment of H_2O_2. Moreover, the TOC conversion at 1:14 Ph:H_2O_2 molar ratio was also higher than 1:5 Ph:H_2O_2 molar ratio. This time, the increment was lower than comparison between 1:1 and 1:5 because presenting values were between 6 and 44% of TOC conversion. Additionally, it can be observed that at 1:1 Ph:H_2O_2 molar ratio, the variation of Cu(II) concentration had low influence on the mineralisation of phenol due to the proportion of $OH^\bullet$ radicals were low, at this Ph:H_2O_2 molar ratio. At 1:5 Ph:H_2O_2 molar ratio, there was a high improvement of TOC conversion, it was presented between the range of 50–200 mg L^{-1} of Cu(II) concentration, where TOC values increased from 8 to 32%. Besides, at 1:14 Ph:H_2O_2 molar ratio, TOC conversion also had the highest increment in the range of 50–200 mg L^{-1} of Cu(II) concentration, which can explain the pseudo stationary behaviour, at this range, presented on the phenol conversion profiles. Thus, comparing phenol and TOC conversion results, it could be understood that at the range of 50–200 mg L^{-1} of Cu(II) concentration, phenol conversion seemed to have no high differences, while TOC conversion had the highest difference. This effect can be attributed to the amount of Cu(II), because the formation of $OH^\bullet$ radicals is the result of the presence of Cu(II) ions, which participate on the H_2O_2 decomposition. Thus, the formation of intermediates during the catalytic oxidation requires more $OH^\bullet$ radicals, so that more Cu(II) ions to decompose the H_2O_2. In this way, the decomposition of H_2O_2 is directly associated to the amount of Cu(II) used, then the existence of high amounts of Cu(II) ions on the catalytic oxidation media increases the phenol mineralisation. Overall, the presence of partially oxidised products, TOC conversion was obviously lower than phenol conversion. However, the difference between phenol conversion and TOC conversion gives the selectivity towards carbon dioxide. This selectivity increased as phenol conversion and TOC conversion become closer [32]. Besides, TOC was low because the stoichiometric Ph:H_2O_2 molar ratio was not enough to achieve a total phenol mineralisation and because part of the peroxide was decomposed into O_2.

3.1.3. Kinetics and mechanism

Kinetic analysis was applied to the experimental data for a better understanding of the catalytic process. The operational conditions employed the stoichiometric Ph:H_2O_2 molar ratio at 30 °C and 1 atm of pressure. Then, for this purpose, it was used the integrated rate law to evaluate the oxidation process with three kinetic models: zero, first and second order. Zero order model did not fit well with the experimental data due to the correlation coefficients R^2 were lower than 0.81, suggesting that zero order model is not adequate for this process. For the first and second order models, the experimental data have better fitting to the models, the first order model presented correlation coefficients between 0.99 and 0.97, which compared with the ones obtained for the second order (0.99–0.81), showed that the first order model can account for more than 97% of the experimental data variation, as it is shown in Table 1. It is also noticeable that catalytic oxidation depends of the initial Cu(II) concentration because the efficiency increased with increasing Cu(II) concentration, although the use of high-Cu(II) concentrations needs to be controlled. Therefore, according to experimental findings and previous discussion, the following scheme shows a possible mechanism [33].

Table 1
Rate law of first order model for the homogeneous catalytic oxidation of phenol

Rate law	Integrated rate law	[Cu(II)] (mg L^{-1})	k (min^{-1})	R^2
$-\frac{d[A]}{dt} = k[A]$	$[A] = [A]_0 \cdot e^{-kt}$	5	1.6×10^{-3}	0.9991
		10	4.1×10^{-3}	0.9991
		50	7.3×10^{-3}	0.9991
		200	13.8×10^{-3}	0.9752

Table 2
Catalyst weights used for the heterogeneous catalytic oxidation of phenol

	Air	Hydrogen peroxide			
	200[a]	10[a]	50[a]	100[a]	200[a]
Cu–PVP_2 (mg)	133	6.7	33.3	66.6	133.3
Cu–PVP_{25} (mg)	160	8.0	40.0	80.1	160.1
CuO/γ-Al_2O_3 (mg)	180	9.0	45.0	90.0	180.0
Cu–Chitosan (mg)	336	16.8	84.0	168.0	336.0

[a] Cu(II) (mg L^{-1}).

This mechanism shows the formation of $OH^\bullet$ radicals, which promote the oxidation of phenol. Besides, the catalytic oxidation is carried since products like hydroquinone and 1,4-benzoquinone are generated as part of the intermediate compounds.

3.2. Heterogeneous catalysis

3.2.1. Air as oxidant

The catalytic activity of the polymer-supported-Cu(II) and the commercial Cu(II) catalysts CuO/γ-Al_2O_3 were tested on the oxidation of phenol. The initial phenol concentration was 1 g L^{-1}, the air flow rate was 85 mL min^{-1}, the reaction time was 2 h, the used temperature was 30 °C and the amount of employed catalyst W_{CAT} is presented in Table 2, where the used Cu(II) concentrations of the homogeneous catalytic systems were taken as a reference.

Fig. 4 displays the results of phenol conversion for the heterogeneous catalysis using air as oxidant. Cu–PVP_{25} shows a phenol conversion of 20% mostly promoted by the adsorption of phenol onto the catalyst surface. Oxidation with Cu–PVP_2 catalyst presented a conversion even lower (2.5%), while CuO/γ-Al_2O_3 and Cu–Chitosan do not allow neither phenol oxidation nor phenol adsorption at these conditions. So that, the low-oxidising power of the molecular oxygen at 30 °C and 1 atm of pressure could probably explain these poor results. At these conditions, the oxidation rates were too low to see any significant phenol conversion. Then, adsorption effect must be taken into account although the possibility of phenol adsorption onto the catalysts is low [34]. For this reason, in Fig. 5 it is presented the phenol adsorption test of the used polymeric materials without Cu(II) content. Results showed low-adsorption degrees when using 0.5 g of polymeric material, that is the case of PVP_2 (15.8%), which presented the highest phenol adsorption capacity, while PVP_{25} and Chitosan presented 7 and 0.1%, respectively. In any case, the heterogeneous catalysts should

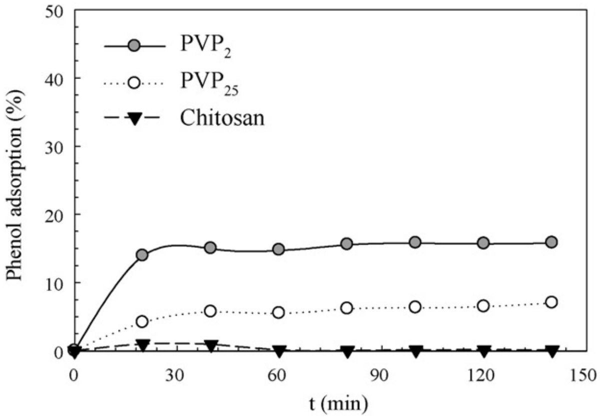


Fig. 4. Adsorption of phenol onto PVP and Chitosan. $[Ph]_0 = 1\ g\ L^{-1}$; adsorption time = 5 h; $T = 30\ °C$; $V = 180\ mL$.

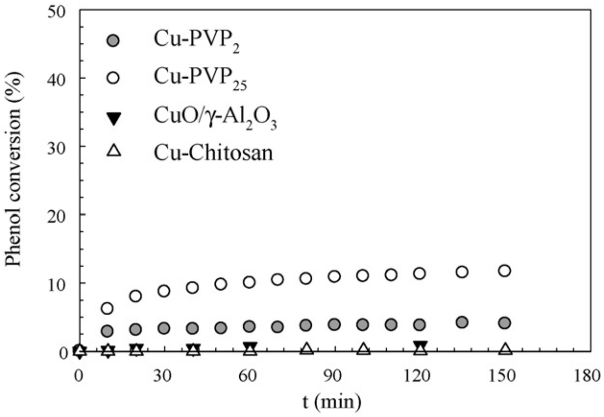


Fig. 5. Heterogeneous catalytic phenol oxidation: comparison between Cu–polymers and a commercial catalyst. Airflow rate = 85 mL min^{-1}; Cu(II) content = 0.05 g; $[\mathrm{Ph}]_0 = 1\,\mathrm{g\,L^{-1}}$; $T = 30\,^\circ\mathrm{C}$.

be understood in a double way: as the carrier of the Cu(II) ions and as adsorbent due to its ability to adsorb phenol. This last characteristic should enhance the catalytic activity of Cu(II), but when the air is under the present reaction conditions, there is a low possibility of promoting a significant conversion. Consequently it was not difficult to predict a nonexistent TOC conversion because phenol intermediates were not detected by the HPLC.

3.2.2. Hydrogen peroxide as oxidant

In order to improve the phenol conversion, hydrogen peroxide was again used as oxidant. Three catalysts (Cu–PVP$_{25}$, Cu–PVP$_2$ and CuO/γ-Al$_2$O$_3$) were tested. The amount of each used catalyst is presented in Table 2. At this point Cu–Chitosan was not used due to the structure of the catalyst was easily destroyed in contact with hydrogen peroxide. The other operation conditions were as follows: initial phenol concentration of 1 g L^{-1}, stoichiometric Ph:H$_2$O$_2$ molar ratio (1:14), temperature of 30 °C and 2 h of reaction time. Fig. 6 depicts the results of phenol conversion at these conditions. As it can be seen in the figure, the catalysts with the highest Cu(II) content gave phenol conversions between 65 and 80%. From this range, the performance of Cu–PVP$_2$ with a Cu(II) content of 200 mg L^{-1} in solution achieved 80% of phenol conversion. Then, the commercial CuO/γ-Al$_2$O$_3$ catalyst with an achieved phenol conversion of 87% demonstrated that Cu–PVP$_2$ can be as good catalyst as a commercial catalyst. On the other hand, Cu–PVP$_{25}$ achieved 65% of phenol conversion on its highest Cu(II) content, presenting much lower conversions at lower amounts of catalyst. Comparing these results with those of homogeneous catalytic oxidation, the conversions were similar at the highest Cu(II) content, but poorer at lower amounts of catalyst. This effect can be explained due to the organisation of these polymeric chains were capable to admit Cu(II) ions between their structures but they were not able to admit the entrance of phenol molecules; as a result, a percent of Cu(II) ions could not participate on the reaction media. Anyway, the catalytic activity of the polymer-supported-Cu(II) catalysts was probed to be competitive with commercial catalysts like CuO/γ-Al$_2$O$_3$.

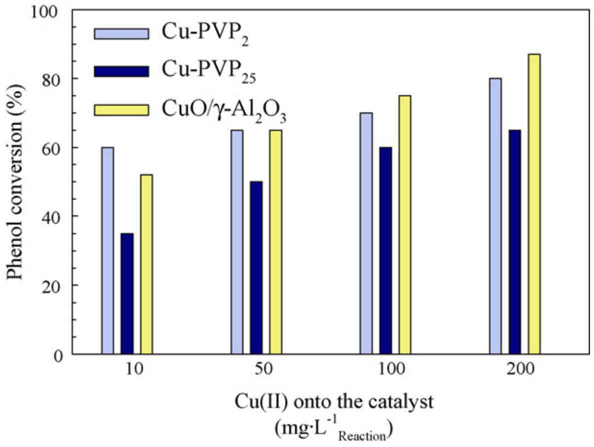


Fig. 6. Heterogeneous catalytic phenol oxidation: influence of initial Cu(II) content. Ph:H$_2$O$_2$ 1:14 molar ratio. $[\mathrm{Ph}]_0 = 1\,\mathrm{g\,L^{-1}}$; reaction time = 2 h; $T = 30\,^\circ\mathrm{C}$.

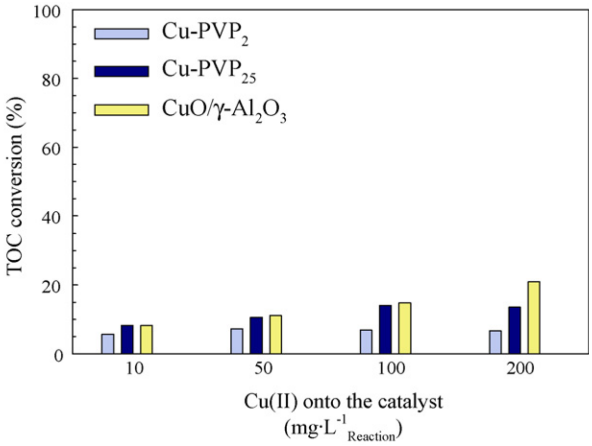


Fig. 7. TOC conversion of heterogeneous catalytic phenol oxidation: influence of the initial Cu(II) content. Ph:H$_2$O$_2$ 1:14 molar ratio. $[\mathrm{Ph}]_0 = 1\,\mathrm{g\,L^{-1}}$; reaction time = 2 h; $T = 30\,^\circ\mathrm{C}$.

The TOC conversions of the above experiments are presented in Fig. 7. In this figure, CuO/γ-Al$_2$O$_3$ provided the best performance of all the tested catalysts, giving a TOC conversion larger than 20% at the highest Cu(II) content. In general terms, the TOC results were equal or somewhat lower than those obtained at homogeneous catalysis. Then, as mentioned on the homogeneous catalytic oxidation, the selectivity towards carbon dioxide was low because of the presence of partially oxidised products, although this effect could not be an inconvenience if these intermediates are biodegradable enough [32].

One thing to take into account is to avoid high levels of catalytic leaching because one of the heterogeneous catalytic aim is to recycle the Cu(II) catalyst. Therefore, it was measured the leaching of the catalyst, which is an important issue promoted by the catalytic deactivation and the increment of Cu(II) content onto the catalyst [4]. In order to know the total copper content in solution, samples of the phenol oxidation reaction were analysed by atomic absorption. Then, the obtained leaching values were graphically presented in Fig. 8, where Cu–PVP$_2$ and CuO/γ-Al$_2$O$_3$ showed a high-copper concentrations in solution after phenol oxidation, up to 20 mg L^{-1}. These leaching levels are not permissible for a subsequent biological plant treatments that allows no more than 5 mg L^{-1}of copper concentrations. So that, Cu–PVP$_{25}$ seems to be the better option, between the evaluated catalyst, due to its low-leaching levels are favourable for the process purpose. Then, once it is known the quantities of Cu(II) in solution after oxidation, the catalytic activity can be delimited in homogeneous and heterogeneous phases. So, phenol conversion (X) at the real heterogeneous phase (X_H) can be calculated by the following relation:

$$X_\mathrm{H} = X_\mathrm{T} - X_\mathrm{L}$$

where X_T is the phenol conversion obtained from the experimental catalytic oxidation and X_L is the phenol conversion obtained from

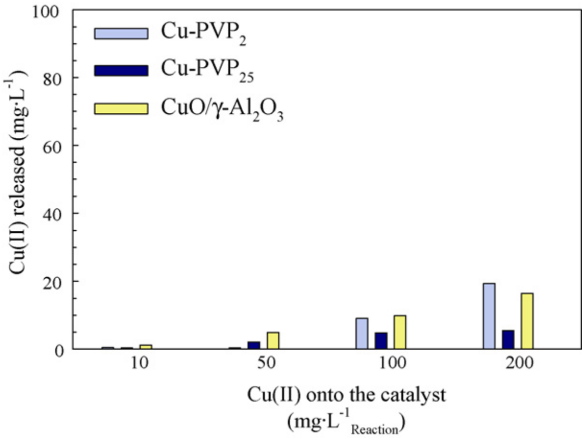


Fig. 8. Leaching of Cu(II) catalyst from heterogeneous catalytic phenol oxidation: influence of the initial Cu(II) content. Ph:H_2O_2 1:14 molar ratio. $[Ph]_0 = 1\,g\,L^{-1}$; $T = 30\,^\circ C$.

homogeneous phase and promoted by the leaching of Cu(II). The X_L conversion values were obtained by using Fig. 8, which shows the evolution of phenol conversion at different Cu(II) concentrations in homogeneous phase. Then, X_H conversion values were obtained by using the equation described before, after that, they were presented in Fig. 9. Afterwards, the principle used to separate the phenol conversion of homogeneous and the heterogeneous phase was also applied to the TOC conversion. Thus, in Fig. 10, it can be seen the variation of phenol and TOC conversions under the influence of released Cu(II).

In Fig. 10(a), it is also noticeable that at the increment of Cu(II) content, the percent of homogeneous catalytic activity increased. So that, when using Cu–PVP$_2$ catalyst with elevated Cu(II) content, phenol and TOC conversions would be highly promoted by the amount of released Cu(II), which would also increase the homogeneous catalytic phenol oxidation. So that, for Cu–PVP$_2$ case, the maximum phenol conversion, without leaching interference, was 48%.

Fig. 10(b) presents the leaching influence on phenol and TOC conversions when Cu–PVP$_{25}$ was the catalyst. Phenol conversions augmented in the same way as Cu(II) content on the catalyst was increased. In contrast, TOC conversion increased up to 14% in the range of 10–100 mg L^{-1} of Cu(II) in solution, but in the last range of 100–200 mg L^{-1} of Cu(II) in solution, the TOC conversion did not increase as phenol conversion increased at this range. However, for Cu–PVP$_{25}$ case, the leaching degree was not high and the phenol conversion at the heterogeneous phase, without leaching interference, got a satisfactory value of 56%. Thus, the increment of the amount of Cu(II) was beneficial to due it promoted the phenol oxidation avoiding leaching increments.

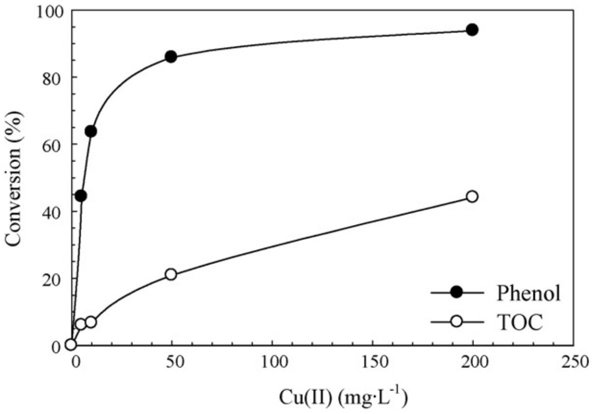


Fig. 9. Homogeneous catalytic oxidation, phenol and TOC tendencies: influence of Cu(II) concentration at Ph:H_2O_2 1:14 molar ratio. $[Ph]_0 = 1\,g\,L^{-1}$; reaction time = 2 h; $T = 30\,^\circ C$.

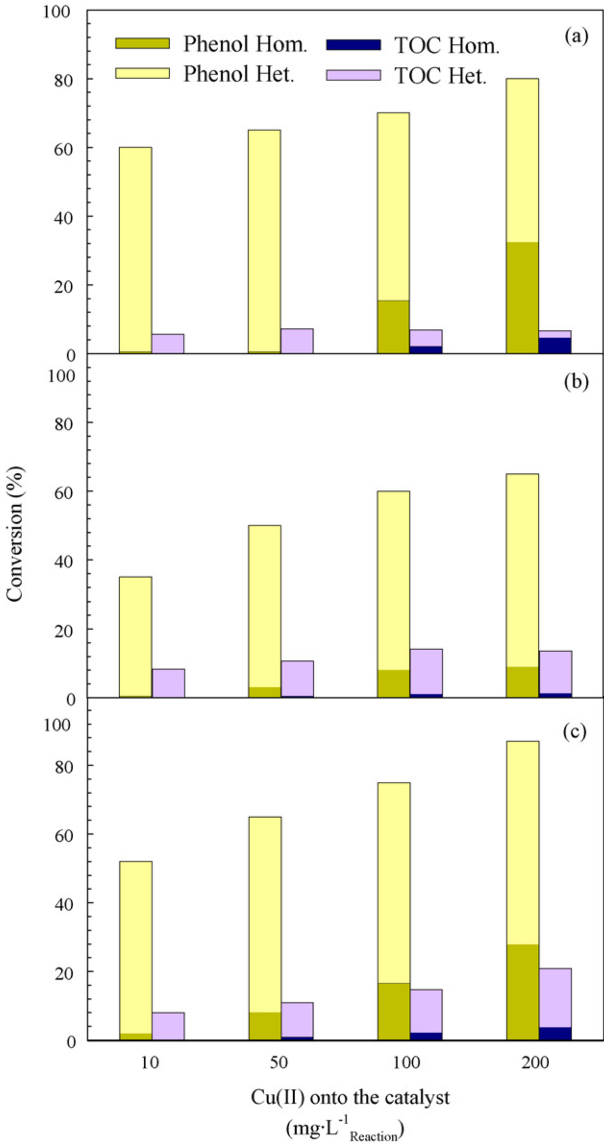


Fig. 10. Phenol and TOC conversions from the heterogeneous catalytic phenol oxidation: influence of the leaching at different initial Cu(II) content. Ph:H_2O_2 1:14 molar ratio. $[Ph]_0 = 1\,g\,L^{-1}$; $T = 30\,^\circ C$: (a) Cu–PVP$_2$, (b) Cu–PVP$_{25}$; (c) CuO/γ-Al$_2$O$_3$.

In Fig. 10(c), it is presented the CuO/γ-Al$_2$O$_3$ case, this figure shows the difference between conversions with and without leaching influence and it is noticeable the difference on phenol conversion. Even though phenol conversions were up to 59% without leaching contribution, the leaching of Cu(II) was significant even at low-initial Cu(II) catalyst content. After all, the necessity to increase the amount of catalyst could promote more the homogeneous catalytic activity than the heterogeneous.

Finally, it can be stated from the presented experimental results that the best catalytic oxidation was performed by Cu–PVP$_{25}$ catalyst due to the 65% of phenol conversion was promoted in more than the 86% by the heterogeneous phase and the 14% was promoted by the leaching.

4. Conclusions

The homogeneous catalytic oxidation of phenol using air as oxidant at 30 °C and atmospheric pressure showed negligible phenol conversions (20%) after 2 h, even when the temperature (50 °C), Cu(II) concentration (1:10 Ph:Cu(II) molar ratio) and time (24 h) were elevated.

Phenol conversion was enhanced when H_2O_2 was the oxidant agent. The results were influenced by the Cu(II) concentration (5, 10, 50 and 200 mg L^{-1}) and the Ph:H_2O_2 molar ratio (1:1, 1:5 and the stoichiometric 1:14).

The heterogeneous catalytic oxidation of phenol using air as oxidant at 30 °C and atmospheric pressure presented low-phenol conversions, up to 12%, after 3 h. There was a possible adsorption stage in spite of an oxidation activity or a combination of both.

Heterogeneous catalytic oxidation of phenol using Cu–polymer catalysts presented the best catalytic activity when Cu–PVP_2 and the commercial CuO/γ-Al_2O_3 catalysts were tested. Cu–PVP_2 showed a phenol conversions of 80% while CuO/γ-Al_2O_3 gave 87%, at the described conditions of 30 °C, atmospheric pressure, 1:14 Ph:H_2O_2 molar ratio and catalysts with the content of 200 mg L^{-1} of Cu(II) in solution. Although after the leaching evaluation, Cu–PVP_{25} catalyst, with 65% of phenol conversion, represented the best option because it presented a Cu(II) released up to 5 mg L^{-1}.

Comparison of conversions with and without leaching influence showed that Cu–PVP_{25} is the best catalytic option due to its leaching levels did not have great influences on the final heterogeneous catalytic oxidation.

Thus, phenol oxidation can be performed at soft conditions using polymer-supported-Cu(II) catalysts and hydrogen peroxide as oxidant agent, although further studies must be conducted to control the catalyst activity, copper leaching and mineralisation degree.

Acknowledgments

Financial support for this research was provided in part by the Spanish Ministerio de Educación y Ciencia, project “CTM2005-01873”. U. Isabel Castro is indebted to the Universitat Rovira i Virgili for providing a pre-doctoral scholarship. Also, Christophe Bengoa thanks Ramón y Cajal program of Spanish Ministerio de Educación y Ciencia for its economic support.

References

[1] Food and Agriculture Organisation of the United Nations (FAO), Water Resources Development and Management Service, The World Bank, 2005.
[2] The European Pollutant Emission Register (EPER), Review Report, 2004.
[3] A. Santos, P. Yustos, A. Quintanilla, F. Garcia-Ochoa, J.A. Casas, J.J. Rodriguez, Evolution of toxicity upon wet catalytic oxidation of phenol, Environ. Sci. Technol. 38 (2004) 133–138.
[4] A. Fortuny, C. Bengoa, J. Font, A. Fabregat, Bimetallic catalysts for continuous catalytic wet air oxidation, J. Hazard. Mater. B64 (1999) 181–193.
[5] A. Pintar, Catalytic processes for the purification of drinking water and industrial effluents, Catal. Today 77 (2003) 451–465.
[6] R.J. Bigda, Consider Fenton’s chemistry for wastewater treatment, Chem. Eng. Prog. 91 (1995) 62.
[7] S.S. Gupta, M. Stadler, C.A. Noser, A. Ghosh, B. Steinhoff, D. Lenoir, C.P. Horwitz, K.W. Schramm, T.J. Collins, Rapid total destruction of chlorophenols by activated hydrogen peroxide, Chem. Eng. Sci. 296 (2002) 326.
[8] S. Caudo, G. Centi, Ch. Genovese, S. Perathoner, Homogeneous versus heterogeneous catalytic reaction to eliminate organics from waste water using H_2O_2, Top. Catal. 40 (2006) 207–219.
[9] K. Yamashita, I. Okada, Y. Suzuki, K. Tsuda, Poly(4-vinylpyridine-co-*N*-vinylpyrrolidone)–Cu(II) complex, a highly active polymeric complex catalyst for hydroquinone oxidation, Makromol. Chem. 9 (1988) 705–708.
[10] M.R. Maurya, S. Sikarwar, Oxidation of phenol and hydroquinone catalysed by copper(II) and oxovanadium(IV) complexes of *N*,*N*′-bis(salicyledene) diethylenetriamine (H_2 saldien) covalently bonded to chloromethylated polystyrene, J. Mol. Catal. A: Chem. 263 (2007) 175–185.
[11] J.H. Ramirez, C.A. Costa, L.M. Madeira, G. Mata, M.A. Vicente, M.L. Rojas-Cervantes, A.J. López-Peinado, R.M. Martín-Aranda, Fenton-like oxidation of orange II solutions using heterogeneous catalysts based on saponite clay, Appl. Catal. B: Environ. 71 (2007) 44–56.
[12] T.L.P. Dantas, V.P. Mendoça, H.J. José, A.E. Rodríguez, R.F.P.M. Moreira, Treatment of textile wastewater by heterogeneous Fenton process using a new composite Fe_2O_3/carbon, Chem. Eng. J. 118 (2006) 77–82.
[13] J. Araña, E. Pulido, V.M. Rodríguez, A. Peña, J.M. Doña, O. Gonzáles, J. Pérez, Photocatalytic degradation of phenol and phenolic compounds. Part I. Adsorption and FTIR study, J. Hazard. Mater. 146 (2007) 520–528.
[14] M. Louloudi, K. Mitopoulou, E. Evaggelou, Y. Deligiannakis, N. Hadjiliadis, Homogeneous and heterogenized copper(II) complexes as catechol oxidation catalysts, J. Mol. Catal. A: Chem. 198 (2003) 231.
[15] R.A. Sheldon, R.S. Downing, Heterogeneous catalytic transformations for environmentally friendly production, Appl. Catal. A: Gen. 189 (1999) 163–183.
[16] W.S. Wan Ngah, C.S. Endud, R. Mayanar, Removal of copper(II) ions from aqueous solution onto Chitosan and cross-linked Chitosan beads, React. Funct. Polym. 50 (2002) 181–190.
[17] K.H. Chu, Removal of copper from aqueous solution by Chitosan shell: adsorption equilibrium and kinetics, J. Hazard. Mater. B90 (2002) 77–95.
[18] N. Li, R. Bai, Copper adsorption on Chitosan-cellulose hydrogel beads: behaviour and mechanisms, Sep. Purif. Technol. 42 (2005) 237–247.
[19] A. Kucherov, E. Finashina, N. Kramareva, V. Rogacheva, A. Zezin, E. Said-Galiyev, L. Kustov, Comparative study of Cu(II) catalytic sites immobilised onto different polymeric supports, Macromol. Symp. 204 (2003) 175.
[20] E. Guibal, Heterogeneous catalysis on Chitosan-based materials: a review, Prog. Polym. Sci. 30 (2005) 71–109.
[21] E. Guibal, Interactions of metal ions with Chitosan-based sorbents: a review, Sep. Purif. Technol. 38 (2004) 43–74.
[22] S. Malynych, I. Luzinov, G. Churmanov, Poly(vinylpyridine) as universal surface modifier for immobilisation of nanoparticles, J. Phys. Chem. B106 (2002) 1280–1285.
[23] J.R.S. Rodrigues, D. Gonçalves, A.S. Mangrich, V. Soldi, J.R. Bertolino, A.T.N. Pires, Thermal behaviour and electrical conductivity of poly(vinylpyridine)/copper complexes, Adv. Polym. Technol. 19 (2000) 113–119.
[24] N.V. Majeti, R. Kumar, A review of chitin and Chitosan applications, React. Funct. Polym. 46 (2000) 1–27.
[25] E. Guibal, C. Milot, J.M. Tobin, Metal-anion sorption by Chitosan beads: equilibrium and kinetic studies, Ind. Eng. Chem. Res. 37 (1998) 1454–1463.
[26] L. Dumbies, T. Vincent, A. Domand, E. Guibal, Preparation of Chitosan gel beads by ionotropic molibdate gelation, Biomacromelules 2 (2001) 1198–1205.
[27] A. Findon, G. McKay, H.S. Blair, Transport studies for the sorption of copper ions by Chitosan, J. Environ. Sci. Health A28 (1993) 173–185.
[28] U.I. Castro, I. Sanchez, J. Font, A. Fortuny, F. Stüber, A. Fabregat, C. Bengoa, Copper catalyst by immobilizing Cu(II) ions on Chitosan and PVP, 17th International Congress of Chemical and Process Engineering (CHISA 06), CD-ROM of Full Texts, 2006, pp. 1–15, ISBN: 8086059456.
[29] A. Aguiar, A. Ferraz, Fe^{3+}- and Cu^{2+}-reduction by phenol derivatives associated with Azure B degradation in Fenton-like reaction, Chemosphere 66 (2007) 947–954.
[30] L. De Laat, T.G. Le, Effects of chloride ions on the iron(III)-catalysed decomposition of hydrogen peroxide and on the efficiency of the Fenton-like oxidation process, Appl. Catal. B: Environ. 66 (2006) 137–146.
[31] H.R. Devlin, I.J. Harris, Mechanism of the oxidation of phenol with dissolved oxygen, Ind. Eng. Chem. Fundam. 23 (1984) 387–392.
[32] M.E. Suarez-Ojeda, F. Stüber, A. Fortuny, A. Fabregat, J. Carrera, J. Font, Catalytic wet air oxidation of substituted phenols using activated carbon as catalyst, Appl. Catal. B: Environ. 58 (2005) 105–114.
[33] G. Ghiselli, W.F. Jardim, M.I. Litter, H.D. Mansilla, Destruction of EDTA using Fenton and photo-Fenton-like reactions under UV-A irradiation, J. Photochem. Photobiol. A167 (2004) 59–67.
[34] A.Y. Dursun, Ç.S. Kalayci, Equilibrium kinetics and thermodynamic studies on the adsorption of phenol onto chitin, J. Hazard. Mater. B123 (2005) 151–157.