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Phenol degradation by heterogeneous Fenton-like reaction using Fe supported over activated carbon

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Abstract

The main objective of the work is to prepare catalysts based on iron supported over activated carbon (AC) and to test its activity for catalytic wet peroxide oxidation (CWPO) of phenol in a batch system. The catalysts were characterized by XRD, SEM, ICP and 77K N₂ adsorption-desorption. Their performances were evaluated in terms of phenol and TOC conversions. The effect of the catalysts preparation condition (Fe load) and catalyst stability in the oxidation process has been investigated. The possible leaching of iron from the catalyst into the aqueous solution has been also examined. The experimental results indicate that the use of such catalyst makes possible the total degradation of phenol and considerably high reduction of TOC for the initial phenol concentration of 150-250 mg/l.

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1. Introduction

The treatment of wastewater has increasingly become a challenge for industries. In many cases, biological treatment is sufficient and the most economic solution for this problem. Nevertheless, many industrial and some of the municipal effluents contain refractory and/or biotoxic compounds, which need a specific chemical treatment in order to eliminate or partly reduce the pollutant concentration to the required level which allows direct discharge to conventional sewage plants [1].

Phenol is usually taken as model compound for wastewater treatment studies, because it is considered

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as starting or an intermediate compound in chemical, petrochemical and pharmaceutical industries and also formed in the oxidation pathway of high-molecular-weight aromatic hydrocarbons [2,3].

Most of the treatment technologies applied for refractory compounds are based on expensive chemical oxidation employing drastic operating conditions (CWAO), expensive equipments ($\text{H}_2\text{O}_2/\text{UV}$) or dedicated oxidants (O_3) [4]. In this regard, the well known Fenton reagent ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) has shown some significant advantages like: (i) iron is a widely available and non-toxic element (ii) H_2O_2 is easy to handle and its decomposition leads to harmless products [5] and (iii) the process can be applied at room conditions and with simple equipment [6-8]. However, its application to the treatment of real waste water has been limited due to the disposal of iron containing waste sludge (needing subsequent separation steps) and most importantly, the usual poor usage of peroxide results in a high operational cost. In turn, it is well known that activated carbon is widely used as a good adsorbent and supporting material due to its excellent properties in mechanical strength and porous structures [9,10]. Also, several studies have suggested that Fe/AC effectively degrade organic contaminants [11,12].

Therefore, taking into consideration the aforementioned inconveniences of Fenton system, a strategy is proposed to confine the catalyst in the reaction media, so that only water containing mostly biodegradable species will leave the system. Thus, heterogenisation of this originally homogeneous catalytic system should mostly overcome these inconveniences.

2. Materials and Methods

2.1. Chemicals

All chemicals used in this work were reagent grade and used without further purification. Phenol was an analytical standard purchased from Panreac (purity 99%). Hydrogen peroxide (H_2O_2 30%wt), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, sulphuric acid (98%) were purchased from Sigma-Aldrich. The activated carbon used in this study was obtained from Merck with the particle size $d_p=1.5$ mm and specific surface area of $952 \text{ m}^2/\text{g}$. Deionised water was used to prepare all the aqueous solutions.

2.2. Catalyst preparation and characterization

The Fe/AC catalysts were prepared by incipient wetness impregnation with an aqueous solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ using a procedure adapted from Zazo et al. [11]. Prior to use, the commercial activated carbon was ground and sieved with US standard sieve to obtain 25-50 mesh uniform particles and washed with deionised water in order to remove residuals or mineral matters adsorbed on the surface. Finally it was dried in the oven at 105°C for 15 h. This sample was hereafter labelled as AC. Calculated amount of ferrous nitrate to obtain 3-9% wt of iron load on the catalyst was dissolved in a small quantity of deionized water and then mixed with the AC for 10 min. After impregnation, the slurry was left for 2 h at room temperature, dried overnight at 60°C , calcinated at 200°C for 4 h, and allowed to cool down naturally. Unincorporated free Fe was removed using a sieve.

Different techniques were used for the characterisation of the catalysts. Specific surface areas and pore volumes of the catalysts were studied by N_2 adsorption/desorption at 77 K. The Fe content of the catalyst was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-OES) after microwave assisted digestion of samples. X-ray diffraction (XRD) analysis was employed to determine the crystal structure and crystallinity of the catalyst (AC composite). The surface morphology was investigated by scanning electron microscopy (SEM).

2.3. Adsorption and catalytic activity tests

All degradation assays were carried out in a magnetically stirred jacketed batch reactor. The reactor was filled with 100 ml of phenol solution of initial concentration range of 150-1000 mg/l. Reaction temperature was set to 30°C and maintained constant by circulating water from a thermostatic bath through the jacket. The pH of the solution was adjusted to pH 3.0 with sulphuric acid. The theoretical stoichiometric amount of H₂O₂ (750-5000 mg/l) and catalyst weight range of 50-200 mg were added simultaneously to start the reaction. Most of the experiments were carried out at 30°C and other temperatures (50 and 70°C) were checked. All the experiments were carried out at a stirring rate of 250 rpm and for 120 min. Phenol adsorption assays were carried out in the same conditions, without H₂O₂ addition.

During the reaction, liquid samples of 1 ml were withdrawn at regular time interval. Each sample was immediately quenched by using NaOH 6 N to quickly decompose H₂O₂ and precipitate iron, which stops the reaction. Then it was filtered with a syringe filter of 0.45 µm nylon (Teknokroma, ref.TR-200101) and placed in a glass vial for further analysis.

3. Results and discussion

3.1. Catalyst characterization

The values of the BET area, pore volume and Fe content are reported in Table 1. It can be seen that impregnation leads to a decrease of surface area in good agreement with that of micropore volume. A higher Fe load gives more reduction of surface area and pore volume. This indicates that the pores in AC were partially blocked by the active iron species. The iron content of the catalysts was determined by ICP-OES and slight variations (<10%) are noticed between the expected and the determined iron content of the Fe/AC catalyst.

Table 1. Properties of the catalyst

| Samples | Surface area (m ² /g) | Pore volume (cm ³ /g) | Fe load (wt %) |
|----------|----------------------------------|----------------------------------|----------------|
| AC | 969 | 0.55 | 0.13 |
| Fe/AC-3% | 847 | 0.47 | 2.80 |
| Fe/AC-6% | 710 | 0.41 | 5.80 |
| Fe/AC-9% | 577 | 0.32 | 8.80 |

3.2. Catalytic activity

The results (Figure 1a) show that removal of phenol using virgin AC was quite similar, around 70%, both adding hydrogen peroxide or not, which indicates that the parent AC does not possess significant catalytic activity and phenol disappearance is due to adsorption. On the contrary, the AC containing supported Fe enhances the initial rate in the addition of H₂O₂, so after 120 min of reaction, the phenol conversion is 98% for Fe/AC-9%, 90% for Fe/AC-6% and 80% for Fe/AC-3%.

Similarly, Figure 1b shows that the parent AC catalyst in the absence and presence of H₂O₂ provided the highest performance of all the tested catalysts, having a TOC conversion above 60%. However, the TOC conversion is much better for Fe/AC catalysts in the presence of H₂O₂ compared to without H₂O₂. In general, the TOC removal was lower for catalysts, even phenol elimination from the solution being higher, than for the virgin AC. This apparent contradiction is due to the fact that virgin AC removes phenol and its associated TOC essentially by adsorption, whereas catalysts effectively oxidize phenol

giving partially oxidized intermediate products [13], which are returned back to the solution because of their poor adsorption over the AC and the lower available surface area of the Fe/AC catalysts.

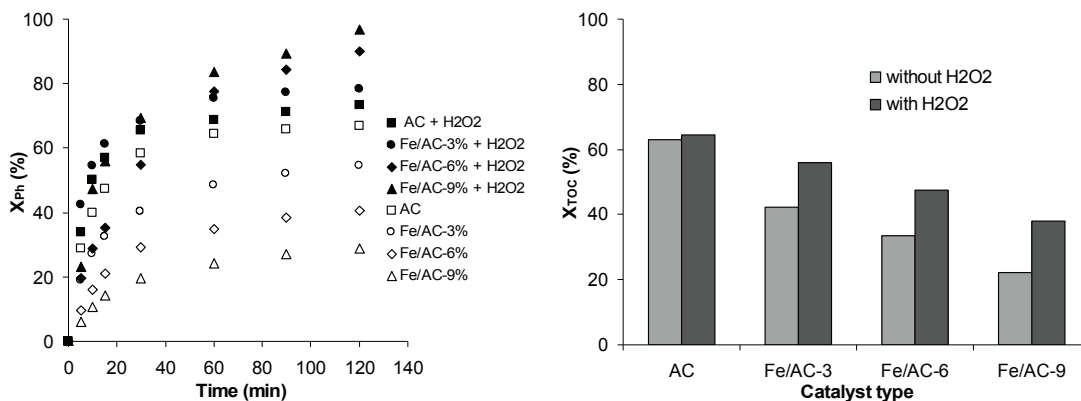


Fig. 1. (a) Phenol and (b) TOC removal through adsorption and oxidation with different Fe loads of Fe/AC catalysts. ($T = 30^{\circ}\text{C}$, pH 3.0, 150 mg/l of phenol, 100 mg of catalyst, 750 mg/l of H_2O_2 , 120 min)

3.3 Catalyst stability

It is important to evaluate the stability of the catalyst for heterogeneous catalytic system. For this purpose, consecutive runs were performed with the same sample. The used catalyst sample was filtered and washed with distilled deionised water after each run. The sample was then dried at 105°C for 15 h, and then the CWPO of phenol was repeated with initial phenol concentration of 150 mg/l in the presence of the dried catalyst and 750 mg/l of phenol at pH 3.0 and 30°C .

The results illustrate that (not shown), the phenol conversion has a declining trend with the increasing of run times; this might be due to either the leaching of the active component (Fe) of the catalyst during the reaction and/or accumulation of carbonaceous materials deposited on the catalyst.

Even though significant activity decay is observed, phenol conversion decreases only from 97% to 91% in four runs, after 120 min of reaction for each. Similar trend was also observed by Melero et al. [14]. After testing a $\text{Fe}_2\text{O}_3/\text{SBA-15}$ catalyst for the CWPO of phenolic aqueous solutions and they came up with the conclusion that the presence of residual organic compounds adsorbed on to the catalyst had a negative effect on its reusability. In spite of this good enough stability, the active species leached from the catalyst are almost similar for each run (2–3 mg/l). Anyway, phenol conversion over 90% was assured in all cases.

4. Conclusions

The catalytic activity towards phenol degradation was found to be enhanced by iron supported on activated carbon catalysts. Phenol conversion above 95% can be reached using this catalyst for 120 min of reaction and the stoichiometric hydrogen peroxide for phenol concentration of 150 mg/l. It is shown that the phenol conversion and TOC removal strongly depend on the Fe load. Moreover, the recycling and consecutive reutilization of catalyst drove to final phenol conversion nearly the same as that obtained with fresh catalyst. Further studies are needed to expand the scope of this synthesized catalyst.

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