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New sludge-based carbonaceous materials impregnated with different metals for anaerobic azo-dye reduction

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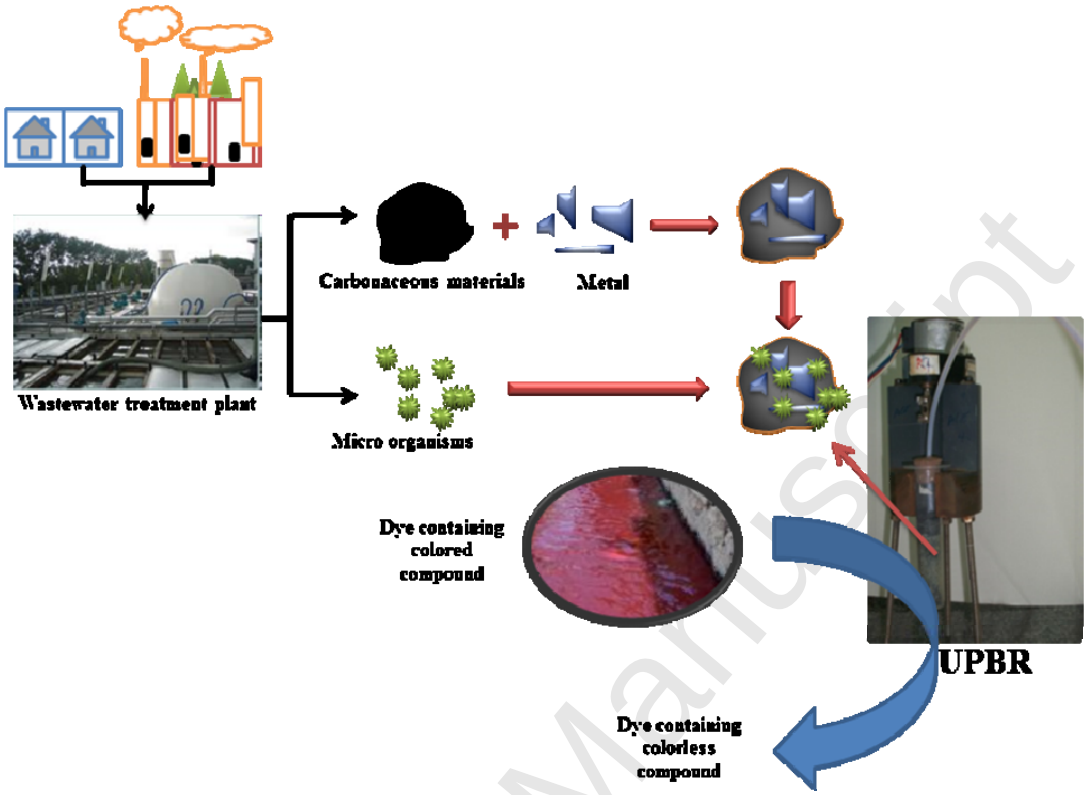
Graphical abstract



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21 Highlights

22 Sludge based catalysts were prepared from harmful sludge materials.

23 Impregnation process of different metals followed by carbonization at 600 ^{o}C was carried out.

24 The performance of sludge based catalysts for anaerobic reduction of AOII dye was notable.

25 Isotherm batch adsorption with AOII dye showing good fitting to the Langmuir isotherm model.

26

27

28 Abstract

29 The addition of Ni^{2+}, Zn^{2+}, Fe^{2+} and Co^{2+} to the carbonaceous materials obtained from waste

30 exhausted solid sludges and their use in the heterogeneous anaerobic reduction of aqueous

solutions of the azo dye Acid Orange II (AOII) in a continuous up flow packed bed biological reactor (UPBR) were investigated. The surface chemistry of new sludge based catalysts (SBCs) was characterized by various tools in order to reveal the physico-chemical properties of the materials. The catalysts were also tested for isotherm batch adsorption with AOII dye showing good fitting to the Langmuir isotherm. The impregnation process of the dried sludge was carried out through 1 mol/L solution of salts of the different metals, followed by carbonization at 600 ^{o}C. In the UPBR, high values of AOII dye reduction were achieved at very short space times (τ). AOII conversion was 78 % for SBCZn600, 57 % for SBCFe600, and 55 % for SBCNi600 at a space time of 1.0 min, comparable with that obtained with commercial activated carbons (CAC). 97 % of AOII conversion was achieved for SBCFe600 catalyst at 4.0 min of space time, during 100-days continuous operation without loss of catalytic activity. The results show that the catalytic abilities of impregnated catalyst in the heterogeneous anaerobic reduction of dye molecules is depended on the distribution of metal particle on the surface and, can substitute commercial activated carbons for their use in the elimination of contaminated dye solutions from textile industries.

Keywords: Anaerobic reactor; Biodecolorization; Biofilm; Carbonaceous materials; Impregnation process.

1. Introduction

In recent years, the use of activated carbons for removal of pollutants in wastewater, through both physico-chemical and biological processes, has been reported. Such types of pollutants come from textile, paper and cosmetic industries; most of them are dye pollutants that are

coloured, highly toxic in nature, and they are discharged in an open-water reservoir to potentially hazardously affect health and limit photosynthesis in the aquatic living organism. Textile industry is one of the most economic growth engines, particularly in the developing countries and azo dyes are the major constituents of textile wastewater. These substances have a complex structure that contains one or more azo bonds (-N=N-), are synthetic in origin, are hard to degrade in biological aerobic conditions and are also resistant into natural environments [1-2].

In general, the following techniques are used for treatment in the wastewater treatment plants (WWTPs): (i) Adsorption, (ii) Advanced Oxidation Processes (AOPs) (iii) Ozonation (iv) Photo catalysis and (v) Membrane filtration [3], etc. However, these conventional techniques are inefficient in many cases and very limited to destroy the complex compounds, also from an economic point of view. In the current scenario, the use of biomass (fungi, algal and bacteria) in the biologic anaerobic treatment of textile effluents has proven to be a better alternative option to the conventional methods. Recently, authors have been demonstrated the goodness of this approach in continuous mode, using a UPBR bio reactor system with carbonaceous materials (CMs) acting as both adsorbent and catalyst, for the destruction of azo-dye molecules under anaerobic conditions [4]. The effective degradation of azo dyes in wastewater effluents has also been successfully carried out by Coughlin et al. [5] and Khehra et al. [6], and they also reported that selected microorganisms such as bacteria, fungal and algal species have been able to absorb or degrade azo-dyes. Most of the biological reactions are non-specific extra-cellular processes, and the reaction is the interaction between the cellular enzymes and the dye molecules [7].

The biological treatment is one of the best options for the destruction of azo-dyes, considered as environmentally safe and cost effective methods [8]. To date, many studies have been conducted on the use of biological methods for the treatment of water and wastewaters

contaminated by dye effluents [9]. The study has been reported on the kinetic parameters of some important catabolic reactions in digesting sludge [10].

Most of the purification methods are carried out through the adsorption onto activated carbons, and those carbons have complex structures and are relatively expensive for their use in catalytic oxidation reactions or other emerging wastewater treatment applications. The sludge based catalysts have been recently presented as good candidate materials in the wastewater treatment because on their surface chemistry and catalytic abilities [11]. Lately, the production of sewage sludge has been estimated around 9 million tonnes during the year of 2005 [12]. The sludge materials have increased tremendously due to the rapid urbanization and industrialization, and these huge amounts of waste materials are available free of cost. If these solid waste materials are converted into adsorbents or carbonaceous materials, they can solve the waste material disposal problems [13]. In general, sludge based adsorbents are a good candidate for removing the organic compounds or inorganic compounds in the aqueous solutions [14-22].

Interestingly, the sludge carbons are capable to attract various active chemical species, which leads to increase the catalytic activity [23-24], there are different protocols to modify their surface textures and access to a variety of pollutants, especially dye molecules. For example, NaOH, KOH, H_2SO_4, $ZnCl_2$, and H_3PO_4 are chemical reagents commonly used to produce the sludge based adsorbents or supporting catalysts [25-30].

Some studies have reported that the heavy metals, such as Zn, Fe, Ni, Co, Mg and Cu, enhance some enzymatic reactions, methane biogenesis and the chemical metabolism [31-34]. The researchers are still focused on the advanced techniques, cost effective, and environmentally friendly practices in the wastewater treatment applications.

The goal of the present work is to investigate the effect of the addition of either Ni^{2+}, Fe^{2+} and Co^{2+} to the carbonaceous materials and to compare them with a carbon prepared using $ZnCl_2$ as a chemical activator and agglomerator, and to test them in the bio reactor system for the biodecolorization of aqueous solutions of AOII. The obtained catalysts were characterized by various parameters such as, carbonaceous yields, ash content, BET surface area, total pore volume, TGA, SEM, XRD, FTIR and EDS micro elemental analysis in order to reveal the physico-chemical properties of the catalysts. The catalysts were also tested in an isotherm batch adsorption experiment with AOII dye. To the best of our knowledge, there is no research work reported on the metals impregnation on the carbonaceous materials and their use in biodecolorization of azo dyes.

2. Materials and methods

Dye and chemicals

The Acid Orange II (dye content, 87 %) and sulfanilic acid (min. 99%), sodium acetate (99 %), and acetic acid (99.8%), hydrochloric acid (min. 37%), were obtained from Sigma Aldrich. The carborundum granules (Carlo Erba Reagents) were used as inert diluents for the catalyst.

The zinc chloride ($ZnCl_2$), nickel chloride ($NiCl_2 \cdot 6H_2O$), ferrous sulphate ($FeSO_4 \cdot 7H_2O$) and cobalt sulfate ($CoSO_4 \cdot 7H_2O$) were used for impregnation process, and all chemicals were obtained from Sigma Aldrich.

Basal media composition

The basal media contained the following chemical compounds: $MnSO_4 \cdot H_2O$ (0.155 mg/L), $CuSO_4 \cdot 5H_2O$ (0.285 mg/L), $ZnSO_4 \cdot 7H_2O$ (0.46 mg/L), $CoCl_2 \cdot 6H_2O$ (0.26 mg/L), $(NH_4)_6 \cdot MO_7O_{24}$ (0.285 mg/L), $MgSO_4 \cdot 7H_2O$ (15.2 mg/L), $CaCl_2$ (13.48 mg/L), $FeCl_3 \cdot 6H_2O$ (29.06

mg/L), NH_4Cl (190.9 mg/L), KH_2PO_4 (8.5 mg/L), $Na_2HPO_4 \cdot 2H_2O$ (33.4 mg/L), and K_2HPO_4 (21.75 mg/L) were obtained from Fluka and Sigma Aldrich. The stock solution of basal media was prepared in 1000 mL of distilled water. One mL of basal media solution was added per litter of feed AOII dye solution and mixed well. The feed solution was placed in the refrigerator at below 5 ^oC in an inert condition for further study.

Preparation of SBCs

The new materials, Zn/sludge, Fe/sludge, Ni/sludge and Co/sludge, were prepared through an impregnation process, where 10 g of dried solid sludge (0.5 to 0.7 mm in diameter size) were soaked into 25 mL of 1 mol/L of metal salts solution for 2 h under stirring at 300 rpm at room temperature. The metal impregnated solid was separated from the solution, and the solid sample was dehydrated in an oven at 105 °C for 15 h. The solid sample was then carbonized at 600 ^oC for 2 h in a quartz reactor (AFORA, Ref no: V59922). The carbonized material was washed three times with 5 mol/L hydrochloric acid solution and then thoroughly washed with deionized water until the pH of 6.0 to 7.0 and, finally, the product was dried in an oven at 105 ^oC for 15h. The carbonaceous product yield was calculated as weight of produced carbonaceous materials divided by the weight of dried sludges material. The produced materials was stored in plastic bottles for further studies, and designated as SBCZn600, SBCNi600, SBCFe600 and SBCCo600.

Characterization of SBCs

The microstructure of catalysts was observed by electronic scanning microscopy (FEI Quanta 600, USA). Main elemental compositions of the catalysts were analyzed by EDS (Inca system, Oxford instruments) instrument. The specific surface area and total pore volume were obtained from N_2 adsorption-desorption isotherms at 77 K (Quadrasorb^{TM} SI Quanta chrome Instruments). The surface area was determined by the BET (Brunauer-Emmett-Teller)

method. The inorganic content of the catalysts was determined by XRD (Bruker-AXS D8-Discover diffractometer). The functional groups of catalysts were analyzed by Fourier transform infrared spectrometer (FTIR) in the range of 400 - 4000 cm^{-1}. Thermo gravimetric analysis by the TGA thermal analyzer (Perkin-Elmer TGA7) was carried out to investigate the weight loss of catalysts. The amount of ashes was determined according to standard procedure [35].

Batch adsorption equilibrium tests

Different AOII solutions with concentrations ranging from 12.5 to 400 mg/L were set in a set of six 250 mL in Erlenmeyer flasks each containing 0.100 g of catalyst and 50 mL of AOII solutions and kept for 15 days at ambient temperature (20 ^{o}C). The pH of the solutions was maintained without any control and the flaks were shaken each day for 30 s to maintain a uniform contact between the catalysts and AOII dye solution.

The equilibrium (mg/L) adsorption capacity was calculated using the equation (1):

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where, C_0 and C_e (mg/L) are the initial and the equilibrium concentrations of AOII, respectively; q_e is the amount of azo dye adsorbed per unit mass of adsorbent (mg/g); V (L) is the volume of AOII solution; and W (g) the weight of catalyst used.

UPBR bio reactor operation

The catalysts are used for the heterogeneous anaerobic reduction of AOII dye in the continuous UPBR system [4]. Operating conditions of continuous UPBR reactor during the experiments are presented in Table.1.

Table 1

Before starting the operation, the mixed culture, filtered anaerobic sludge was continuously pumped through the reactor for one week in order to immobilize the microorganisms on the catalyst surface, thus forming a biofilm.

Feedstock contains AOII dye, sodium acetate and basal media and their solution was kept in inert conditions through bubbling helium gas at the bottom of the feed reservoir kept at 5 ºC. The inlet and outlet of AOII dye concentration was measured by High Pressure Liquid Chromatography (HPLC) using an Agilent 1100 series system equipped with a gradient pump, which impulsed a methanol–water (M:W) ratio of 70:30 for detecting AOII, M:W of 0:100 for sulfanilic acid and M:W of 70:30 for acetate with flow rate of 1 mL min^{-1} through a C18 Hypersil ODS column. A Diode array detector was used to identify the compounds. The outlet concentration of the UPBR reactor system was analyzed by specific wavelengths of each compound, at 487 nm for Acid Orange II, 252 nm for sulfanilic acid and 210 nm for acetate.

3. Results and discussion

Characterization of SBCs

Table 2 presents the carbonaceous yields, carbon, oxygen, silicon and ashes content of the dried sludge (DS) and impregnated catalysts. The carbonaceous product yield of the impregnated catalysts was 63.5 to 70.6 wt % and the ashes content level was 36.33 to 62.44 wt %, more than that of 35.0 wt % in the dried sludge (DS). Due to the heat treatment most of the volatile substances removed from the sludge materials. The sludge materials is decomposed into carbon dioxide and water in the carbonization finally it became a rough shape and metal particles are uniformly distributes on the surface, some metal particles also entrap into the pore cavity.

Table 2

The carbon, oxygen and silicon amounts are significantly changed after the carbonization at 600 ^{o}C. The carbon content was increased up to 44.68 % and the amount of oxygen was slightly decreased. The product of catalysts has become hard and brittle because the amount of silicon content increased, that also may forms binary compounds with Zn, Fe, Ni and Co metal particle. The least amounts of metal elements such as, Na, Ca, K, P, Cl, Mg, and Al besides present on the catalyst; they are detected by EDS spectra.

Surface area and porosity

The measured values of BET surface area and total pore volume are presented in Table 3. The porosity measurement is an important factor while considering the adsorption of organic compounds on to carbonaceous catalysts. The addition of Ni, Zn, Fe and Co metal particle to carbonaceous materials became a better development of porosity. After the washing of hydrochloric acid solution the produced carbonaceous catalysts surface, area was greatly improved and may remove impurities like, organic, inorganic and ashes in the SBCs.

Table 3

For heterogeneous catalysts, surface area is a critical factor while considering in the catalytic reaction. The surface area and total pore volume of produced catalysts were measured 107 to 194 m^2/g and 0.15 to 0.24 cm^3/g, respectively. The SBCNi600 catalyst gave a highest BET surface area of 194 m^2/g and the total pore volume of 0.24 cm^3/g. Table 3 also presents the structural parameters determined by N_2 adsorptions/desorption. The lower curve of each isotherm measurement was obtained by adsorption, and the upper curve was obtained by desorption. The isotherms results of catalysts are close to each other indicating similar

surface textures, and they are followed Type - IV adsorption isotherms model. The isotherm curves are shown in figure 1.

Figure 1

The surface porosity of the catalysts has a significant role in the term of adsorption of AOII dye on to catalysts. The pore volume of the catalyst was obtained in the following sequence Co > Fe > Zn > Ni. They are shown in figure 2.

Figure 2

Thermo gravimetrical analysis

Figure 3 shows (a) DTG and (b) TGA curves of dried sludge and SBCs. The highest weight loss of materials was observed between 200 to 600 ◦C, which may be due to the decomposition of inorganic matters and oxy (hydroxide) compounds. The first peak was shown at nearly 100 ºC, that represented the physical desorption of water. Overall weight loss of SBCs was 20 to 37 %, less than that of dried sludge 54 % once temperature reached at 900 ^{o}C.

Figure 3

Crystalline contents

The XRD technique is used to get information of inorganic compositions in the catalysts. XRD spectra of dried sludge (DS) material obtained four major sharp peaks at 2 theta 26.5, 28, 29.5 and 31, these peaks are related to quartz (SiO_2), polyhalite ($K_2Ca_2Mg\ (SO_4)_4 \cdot 2H_2O$), calcite ($CaCO_3$) and dolomite ($CaMg\ (CO_3)_2$, respectively. After the heat treatment at 600 ^{o}C, the calcite levels gradually decrease. The inorganic content may help to increases catalytic activity. Figure 4 shows the XRD spectra of dried sludge and SBCs.

Figure 4

Functional groups

FTIR spectra give the functional groups present on the surface of the catalyst. The strong peaks of dried sludge measured at 3286 cm^{-1}, 2924, 2853, 1635, 1539, 1419, 1020 and 873 cm^{-1}, after the heat treatment these peaks are eliminated or reduced (2923, 1539 and 1419 cm^{-1}). The deep bands between 800 and 1020 cm^{-1} are represented to Si-O-Si bond. The band measured in the wave numbers of 3200-3300 cm^{-1} is related to the vibration of -OH groups. The spectral results of various catalysts are very close to each other indicating they have identical structure and functional groups on the surface. After the heat treatment at 600 ^{o}C, the obtained peaks show slightly displacement. FTIR spectra are shown in Figure 5.

Figure 5

Micro structure images

The microstructure analysis is used to obtain clear images on the internal surface of the catalyst. Figure 6 shows the micro structure images and EDS spectra of the SBCs. The images of the catalysts are seen as rigid and hard surface that are irregular shape. The metal particles were uniformly distributed in the internal wall of the catalyst. The AOII dye molecule diffuses through the metal-carbon complex and absorbs onto it, after that the reaction products desorb from the surface of catalysts.

Figure 6

Adsorption isotherm results

Adsorption isotherm is described by two non-linearized isotherm models: the Langmuir (2) and Freundlich (3) isotherm models. The adsorption capacity of new materials is calculated

from the linearized isotherm equation and the obtained values are used to calculate the maximum adsorption capacity by using non-linearized isotherm equation. Adsorption capacity of catalysts increases with the initial concentration of AOII dye solutions. The maximum adsorption capacity was reached at low concentrations of AOII dye.

The Langmuir isotherm equation is given as:

$$q_e = \frac{Q_m K_L C_e}{1+K_L C_e} \quad (2)$$

The Freundlich isotherm equation is given as:

$$q_e = K_F C_e^{1/n} \quad (3)$$

where, q_e (mg/g) is the amount of catalysts adsorbed per unit mass of adsorbent (mg/g). C_e (mg/L) the equilibrium concentration of AOII dye solution. Q_m (mg_{AOII}/g_{CM}) and K_L (L/mg) are Langmuir adsorption capacity and constants respectively.

Freundlich isotherm is to determine the heterogeneous surface on the surface of impregnated materials. K_F and n are Freundlich constants. K_F (mg/g (L/mg) $^{1/n}$) is the adsorption capacity of the adsorbent. Adsorption capacity of impregnated catalysts depends on the nature of catalyst, charges of metal, electron affinity and surface functional groups. The higher adsorption capacity was measured 172 mg/g for SBCNi600 catalyst. Table 4 presents the isotherm models fitting of AOII dye over different catalysts.

Table 4

The isotherm data was well fit to Langmuir isotherm model. Figure 7 shows the Langmuir isotherms and the predicted results of AOII dye over different catalysts.

Figure 7

Anaerobic reduction of AOII dye

The anaerobic reduction of AOII dye was carried out at different space times (4, 2, 1, 0.5 and 0.25 min) in the continuous UPBR system. In the reactor operation, steady state was reached within one-day continuous operation.

Figure 8 (A) show the continuous operation of 5 days in UPBR reactor for SBCNi600 catalyst. Nearly 98 % of dye conversion was achieved for SBCNi600 catalyst and the amount of produced sulfanilic acid (SA) level increases up to 57 mg/L in 4.0 min.

Figure 8 (A) & (B)

Only 20 % dye removal measured for SBCZn600 catalyst during the 5 days in 0.25 min continuous operation (Figure 8 B). The results show that the production of sulfanilic acid was very low.

Figure 9 shows removal of AOII dye and the amount of produced SA during the 100-days continuous UPBR reactor operation at a space time of 4.0 min for SBCFe600 catalyst. Removal of AOII dye was higher level without loss of catalyst stability and the growth of bio film on the catalyst is steady. For SBCFe600, 97 % of AOII dye conversion was measured, and the amount of SA levels increases up to 55 mg/L during the operation. It is important to say that the catalysts have a good life span in the reactor for long time operation without powdering the materials. In a continuous operation, dye conversion levels steady up to 40-days and after that, level was slightly decreased.

Figure 9

In UPBR system, the almost complete removal was achieved at very short space times (τ). AOII dye conversion 78 % was measured for SBCZn600, 57 % for SBCFe600; 55 % for SBCNi600 and 10 % for SBCCo600 respectively in 1.0 min operation. Our previous study

has reported about 98 % dye removal was achieved for CAC in 1.0 min. The dye removal of SBCCo600 catalyst was 20 % in 1.0 min as compared to other impregnated catalysts. The dye removal of SBCFe600, SBCNi600 and SBCZn600 catalysts were 40 %, 37 % and 48 % respectively in 0.5 min. Only 10 % dye removal is for SBCCo600 in 0.5 min that cannot consider as good removal. The AOII removal of SBCFe600, SBCNi600, SBCZn600 and SBCCo600 was 27 %, 26 %, 19 % and 6 % respectively in 0.25 min. In case of commercial AC about 44% AOII dye, removal was achieved in 0.25 min. The dried sludge carbon, DS, cannot be used for catalytic experiments because its mechanical properties make it inadequate to avoid the plugging of the reactor. Figure 10 shows the conversion of AOII dye over SBCs at various space time operation in UPBR bioreactor.

Figure 10

The addition of metal particles to carbonaceous materials increases the catalyst mobility, electro negativity and electro affinities; those are influenced in the catalytic reduction process, which leads to higher level of AOII dye removal. The cobalt metal impregnated catalyst shows the lowest removal because the presence of Co inhibits the growth of biomass, hence the ability of the catalyst performs was very poor. Other selected metal particle such as Ni, Zn, and Fe stimulates the growth of biomass in the catalysts. The metal particles on the catalyst interact with the immobilized biomass forming a bio film. The presence of metal stimulates the growth of biomass in the bio reactor, which leads to highest AOII dye uptake. The catalysts abilities depend on the different metal, impregnated catalysts and the catalysts SBCZn600, SBCFe600 and SBCNi600 are the best materials due to the Zn, Fe and Ni metals are more adequate for the growth of biomass [36]. The SBCCo600 catalyst shows the lowest removal because the presence of Co inhibits the growth of biomass, hence the ability of the

328 catalyst perform was very poor. In fact, the Co metal impregnated catalyst was toxic to the
329 anaerobic culture. Figure 11 shows the schematic diagram of the sludge based catalyst and
330 the mechanism of the reduction of azo dye under anaerobic conditions. This new solid
331 supporting catalyst for the reduction of azo dyes in anaerobic conditions in which biology,
332 chemistry and physics aspects combine to get synergistic effects in the solid materials surface
333 for the biodecolorization of azo dyes and the product obtained mainly sulfanilic acid and the
334 1-amino-2-naphthol.

335 **Figure 11**

336 Figure 12 shows the decolorized AOII dye and the amount of produced SA under anaerobic
337 conditions. The amount of produced SA molecules is directly proportional to decolorize AOII
338 dye molecule. The amount of produced SA is an almost steady state throughout the anaerobic
339 reaction but sometimes SA degrades in the presence of anaerobic biomass. In the reactor,
340 during the 100-day continuous operation few amounts of SA molecule degrade by
341 immobilized biomass. Overall results noticed that anaerobic reduction of AOII dye
342 influenced by the metal particle in the catalyst. The sludge based catalysts produced from the
343 harmful sludge materials proved to be the most cost effective material and better choices for
344 the treatment of contaminated dye solutions from textile industries.

345 **Figure 12**

346 **4. Conclusions**

347 The present work investigated the preparation of new sludge based carbonaceous materials
348 impregnated with different metals for anaerobic reduction of AOII dye in a packed bed
349 reactor. The SBCs exhibited several peculiarities, including cost effective, good surface
350 texture, and environmentally acceptable conditions. The addition of metal particle to harmful

exhausted solid sludge followed by heat treatment of the carbonaceous materials relatively high surface area (194 m^2/g) and enhances the AOII dye removal in batch adsorption and continuous bio reactor experiment. The immobilized anaerobic biomass on the catalyst in the anaerobic reactor greatly influences the heterogeneous catalytic reaction and without loss of catalyst stability. For SBCFe600, 97 % of AOII dye removal was measured, and the amount of SA levels increases up to 55 mg/L during the 100-day operation. Overall results indicate that the new materials possess excellent surface textures and removal rate of AOII dye is extremely high. The adsorption isotherm data of AOII are properly described by Langmuir isotherm model. The higher adsorption capacity was measured 172 mg/g for SBCNi600 catalyst. The SBCs performs closer capacity to commercial activated carbon, and they have remarkable physic-chemical properties, can introduce into various fields of catalytic reaction in the chemical reaction engineering. The addition of metal particle to carbonaceous materials further heat treatment is an excellent valorization option for converting harmful exhausted sludge into useful and inexpensive carbonaceous catalysts for treating textile effluents.

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476 activated sludge and on other aerobic microorganisms: a review, J. Hazard. Mater.
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481 Table 1 Operating conditions of continuous UPBR reactor during the experiments.

Variables	Values
Mass of catalyst, g	1.0
Inert support material (Carborundum), g	10.0
Reactor working volume , mL	8.0
Reaction temperature, ^{o}C	35.0
pH inlet	6.8 - 7.4
Flow rate, mL min^{-1}	15 to 240
Redox Potential (Ag^{+}/AgCl electrode), mV	- 400 to - 500
AOII Concentration, mg/L	100
Sodium acetate concentration, mg/L	200

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Table 2 The carbonaceous yield, ashes content and main chemical composition of dried sludge and SBCs

Weight (%)	DS	SBCZn600	SBCFe600	SBCNi600	SBCCo600
Carbonaceous yields	--	70.6	63.5	66.5	65.2
*Ash content	35.0	36.33	62.44	46.76	52.52
**Elemental analysis					
C	35.0	49.81	39.16	45.5	44.68
Si	2.32	7.78	6.29	5.82	5.64
O	40.24	23.05	29.29	21.7	24.2

**Dduplicates analysis, ** Triplicate analysis*

505 Table 3 The specific surface area and total pore volume of dried sludge and SBCs

Sample Code	BET surface area (m^2/g)	Total Pore Volume Vt (Cm^3/g)
DS	6.0	0.02
SBCZn600	111	0.20
SBCFe600	107	0.15
SBCNi600	194	0.24
SBCCo600	161	0.20

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518 Table 4 Adsorption isotherm fitting data of AOII dye over SBCs

Sample code	Langmuir isotherm			Freundlich isotherm		
	K_L (L/mg)	Q_m (mg/g)	R^2	K_F (mg/g $(L/mg)^{1/n}$)	1/n	R^2
SBCZn600	0.22	96	0.99	0.41	1.1	0.79
SBCFe600	0.03	156	0.96	0.54	1.0	0.96
SBCNi600	0.10	172	0.89	0.41	1.4	0.98
SBCCo600	0.10	154	0.98	0.6	1.1	0.90

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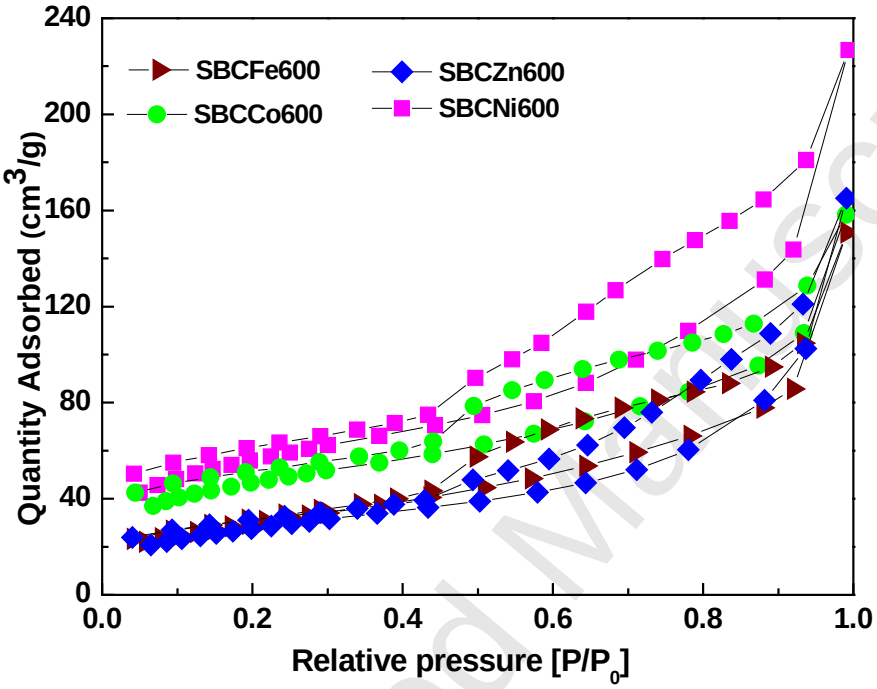

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524 Fig. 1 Nitrogen adsorption/desorptions isotherms of SBCs.

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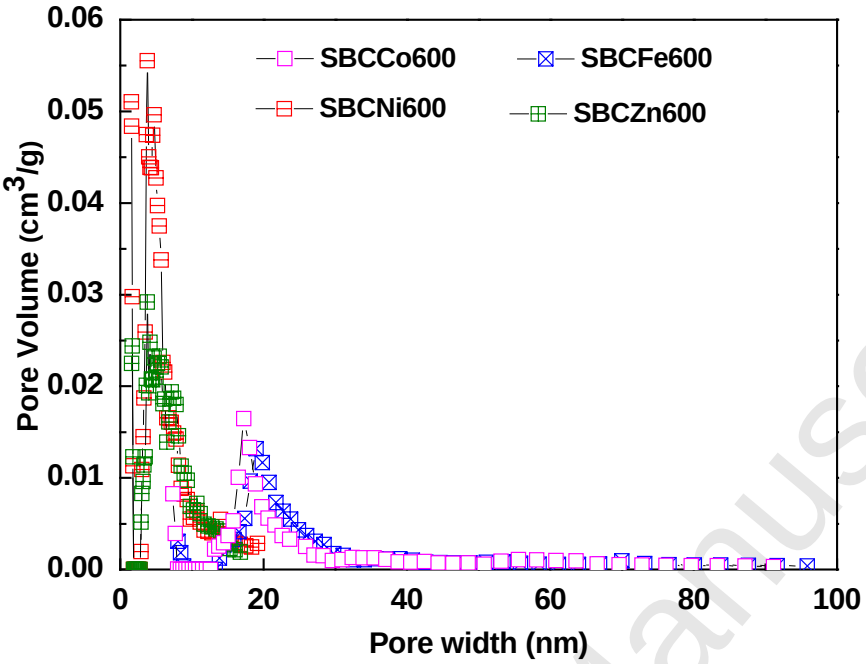
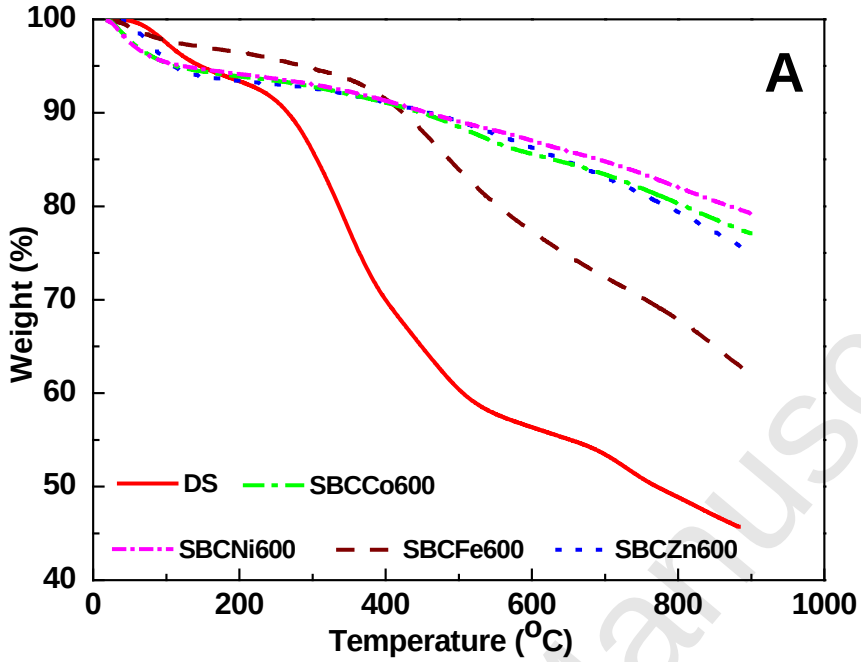


Fig. 2 Pore size distribution curves of SBCs.



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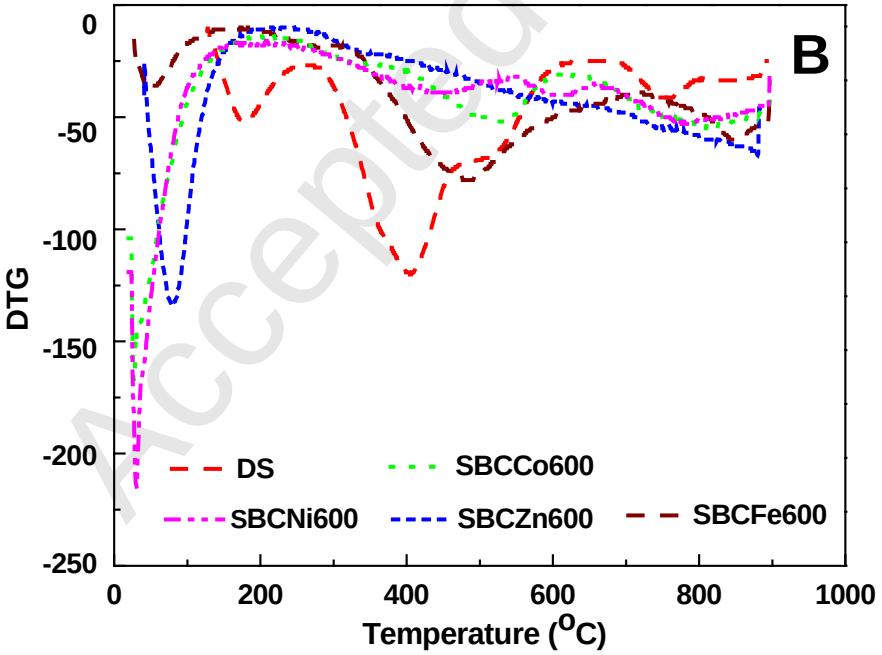

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540 Fig. 3 (A) TGA and (B) DTG curves of the dried sludge and SBCs.

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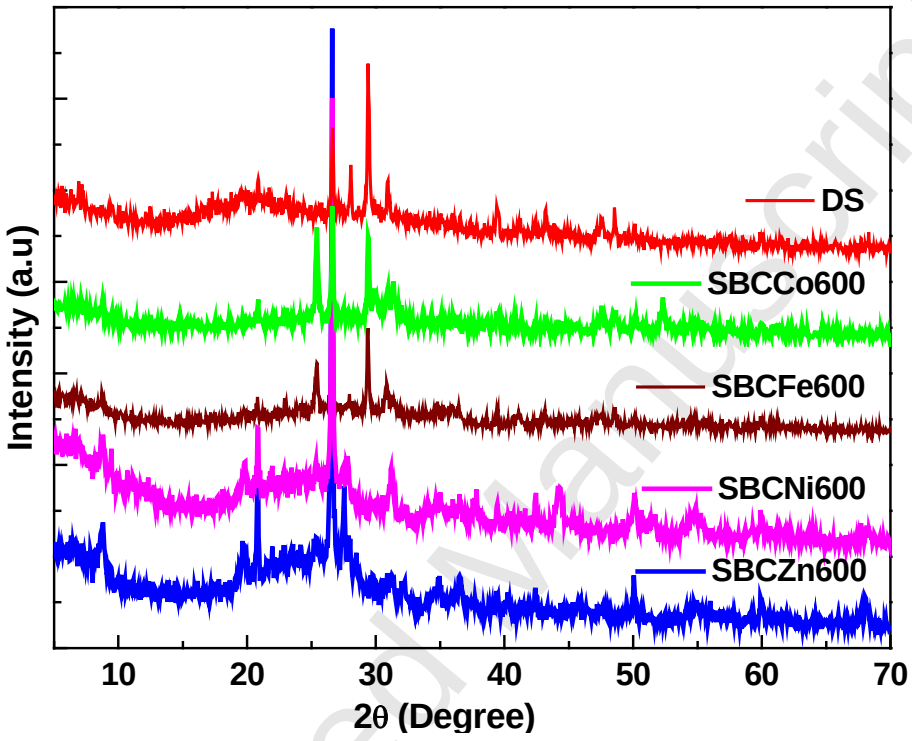

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543 Fig. 4 XRD patterns of dried sludge and SBCs.

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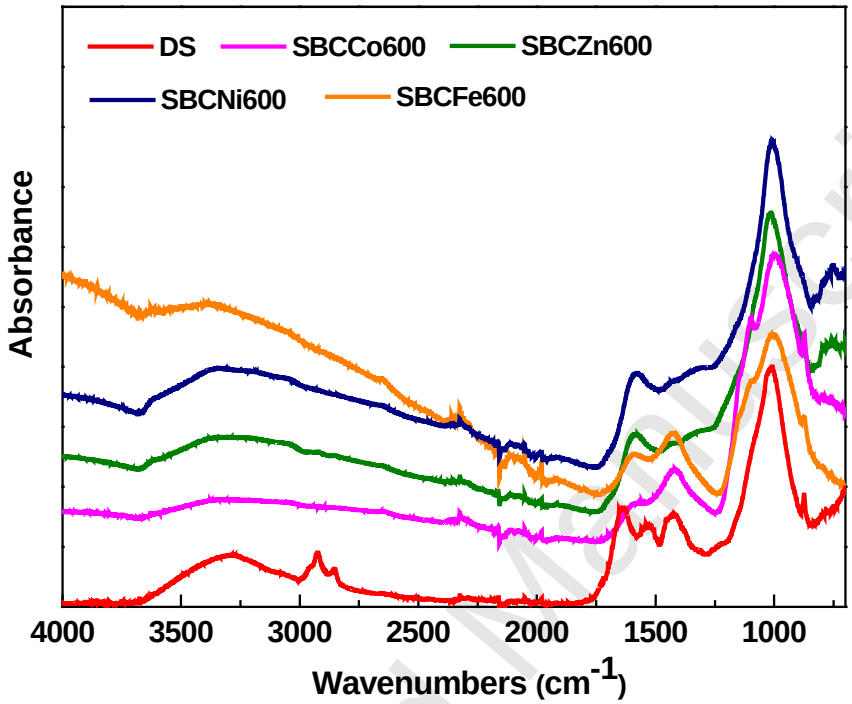

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553 Fig. 5 FTIR spectra of the dried sludge and SBCs.

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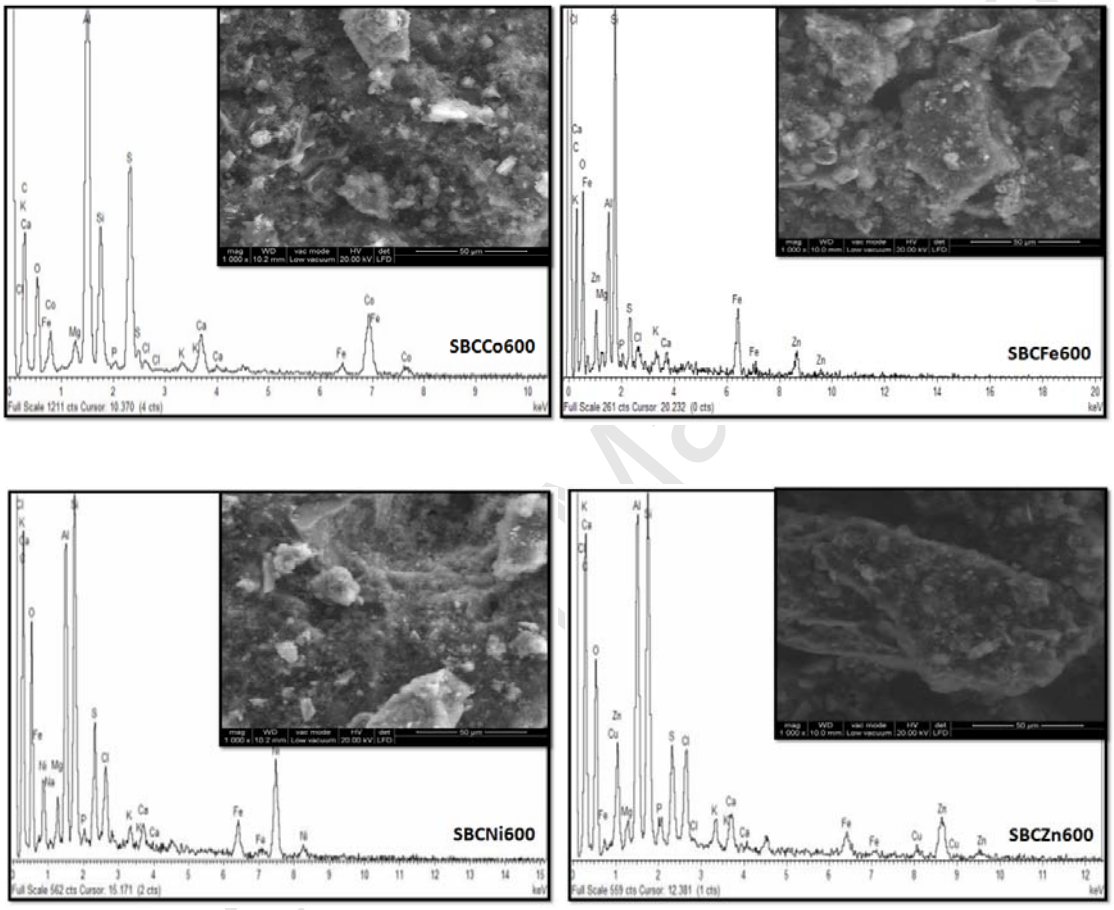

Fig. 6 Microstructure images and EDS spectra of the SBCs.

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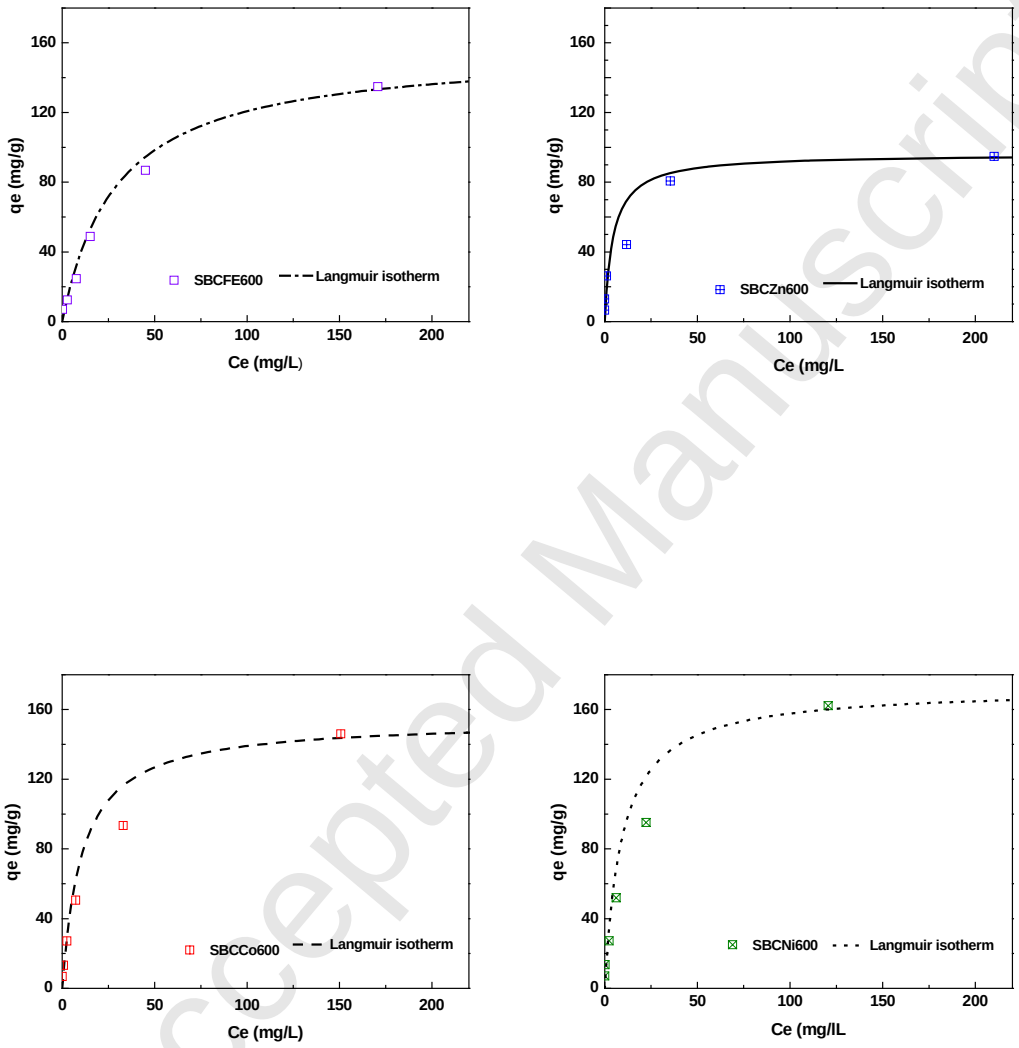

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579 Fig. 7 Langmuir isotherm of AOII dye over SBCs; Ambient room temperature: 20 °C;

580 Catalysts amount: 0.100 g; Amount of AOII dye solution: 50 mg/L; Observation duration: 15

581 days.

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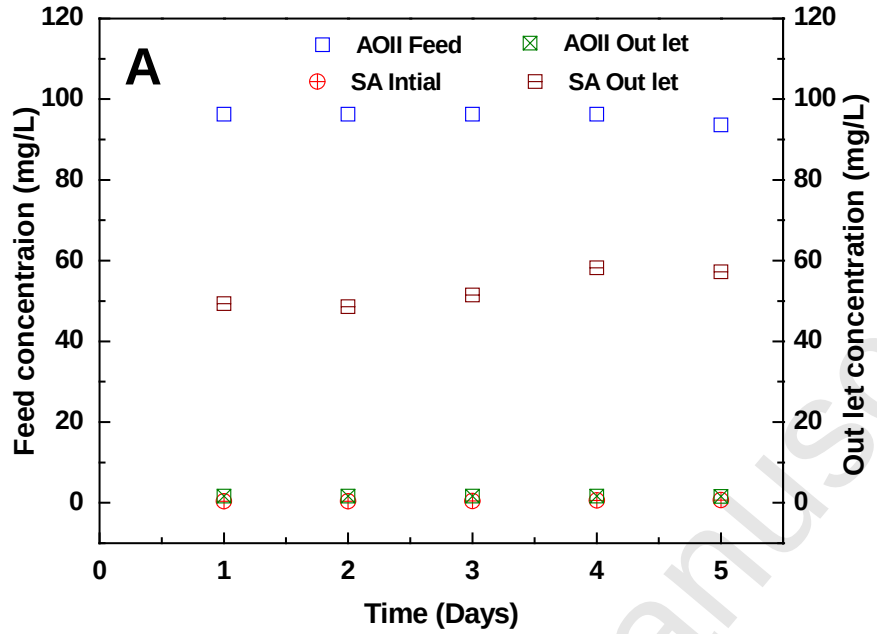

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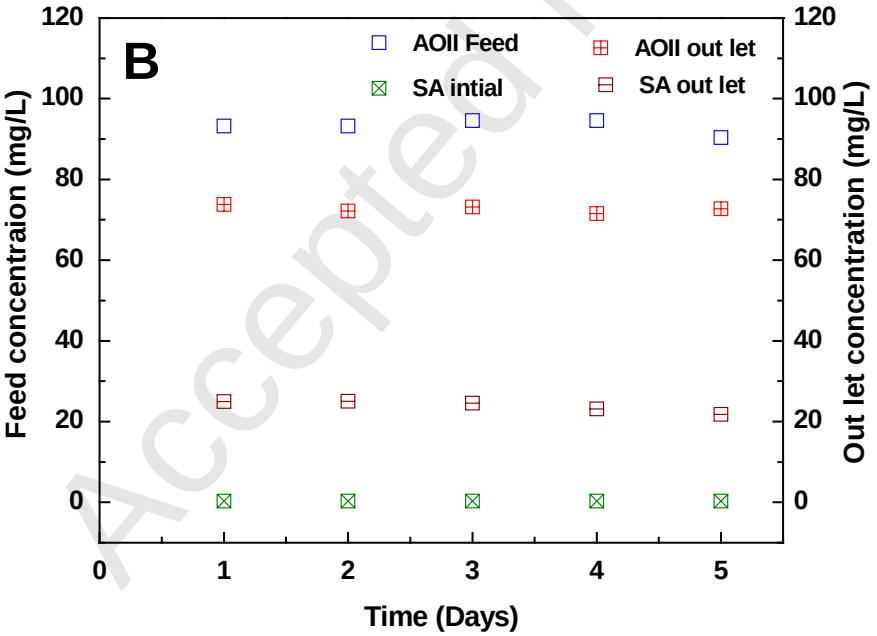

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585 Fig. 8 AOII and sulfanilic acid (SA) initial and out let concentration during 5 days steady
586 state operation at various space time: (A) 4.0 min; (B) 0.25 min, in an anaerobic UPBR
587 reactor system.

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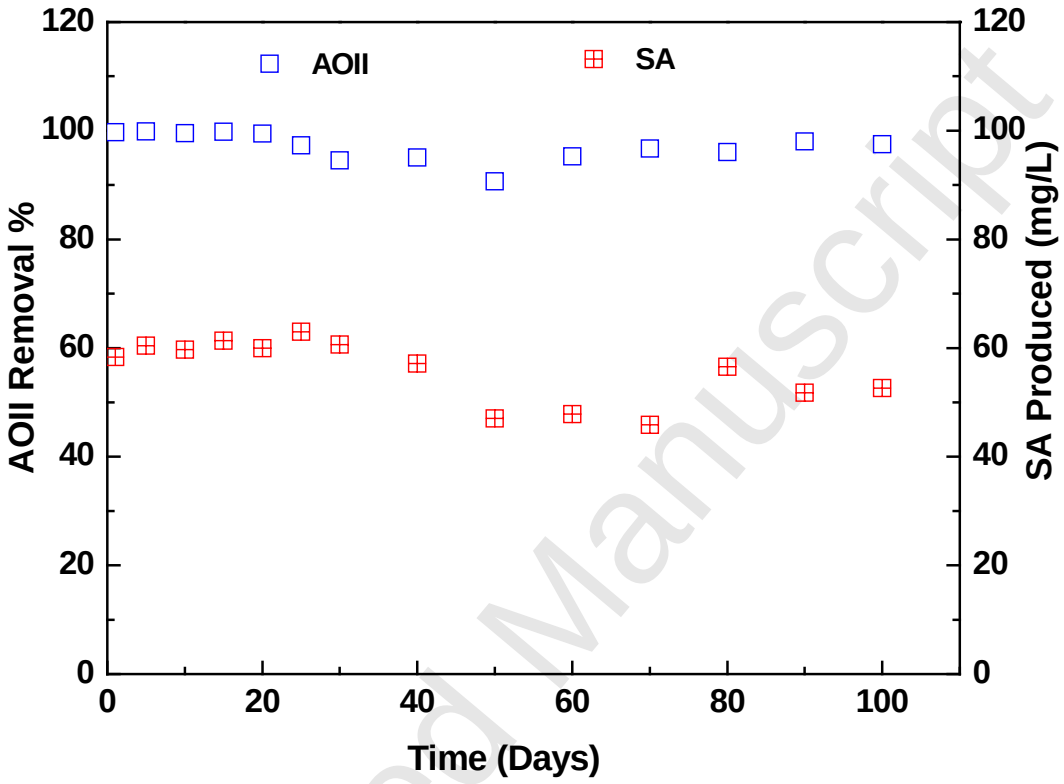

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591 Fig. 9 AOII removal and sulfanilic acid production during 100 days operation at space time

592 of 4 min; AOII dye feed concentration: 100 mg/L; Catalyst: SBCFe600.

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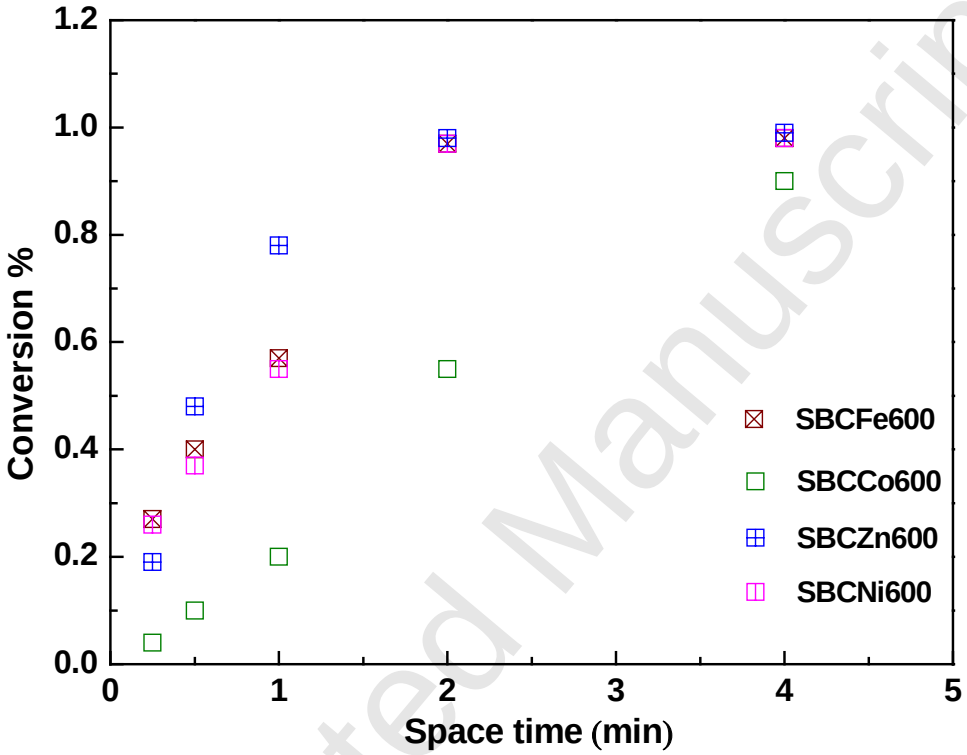

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603 **Fig.** 10 Conversion of AOII dye over SBCs at various space time operation in UPBR

604 bioreactor.

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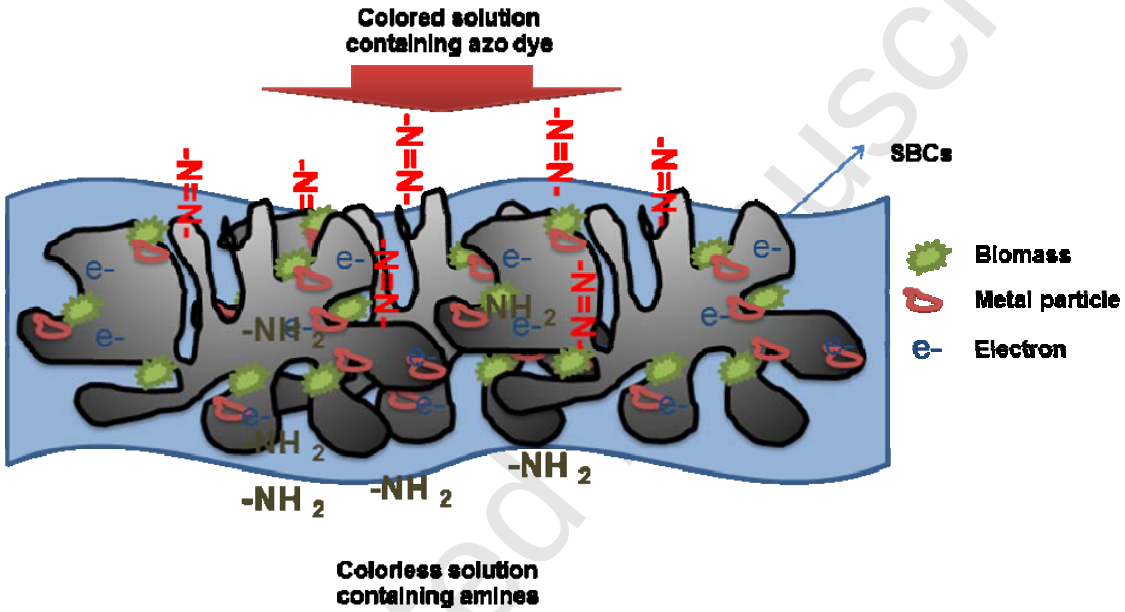

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615 Fig. 11 Schematic diagram of the sludge based catalyst and the mechanism of the reduction

616 of azo dye under anaerobic conditions.

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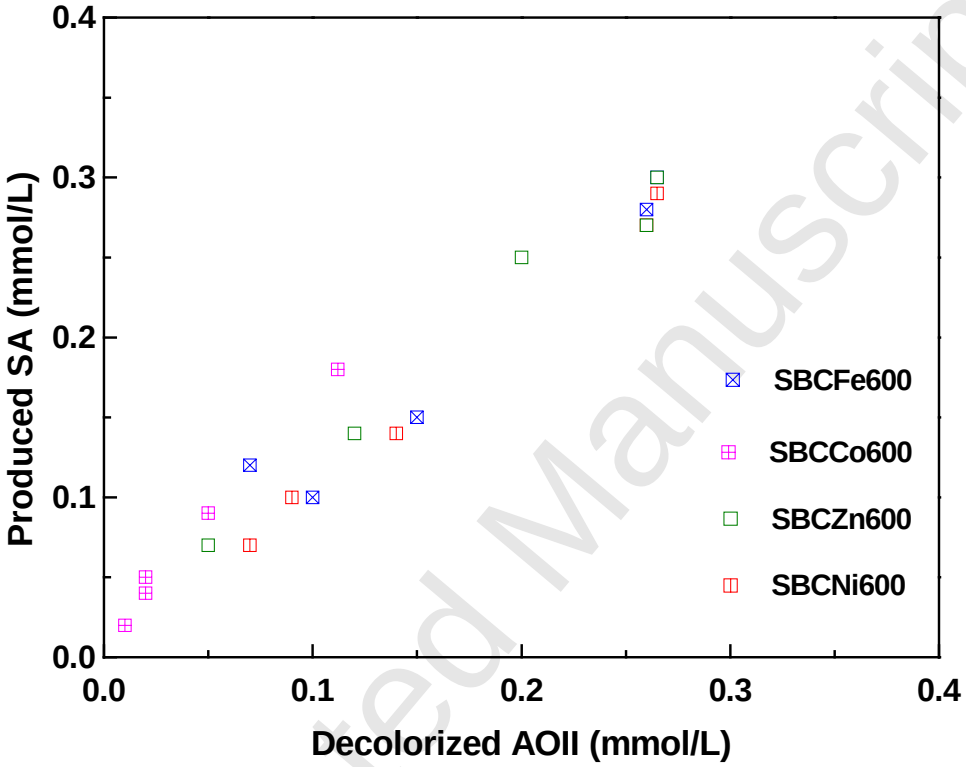

Fig. 12 Decolorized AOII dye and the amount of produced SA under anaerobic conditions.