# Characterization and performance of carbonaceous materials obtained from exhausted sludges for the anaerobic biodecolorization of the azo dye Acid Orange II

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## ABSTRACT

This work presents the preliminary study of new carbonaceous materials obtained from exhausted sludge, their use in the heterogeneous anaerobic process of biodecolorization of azo dyes and the comparison of their performance with one commercial active carbon. The preparation of carbonaceous materials was conducted through chemical activation and carbonization. Chemical activation was carried out through impregnation of sludge-exhausted materials with $ZnCl_2$ and the activation by means of carbonization at different temperatures (400, 600 and 800 °C). Their physico chemical and surface characteristics were also investigated. Carbonaceous materials SBC400, SBC600 and SBC800 present values of 13.0, 111.3 and 202.0 $m^2/g$ of surface area. Biodecolorization levels of 76 % were achieved for SBC600 and 86 % for SBC800 at space time ($\tau$) of 1.0 min, similar to that obtained with commercial activated carbons. The experimental data fit well to the first order kinetic model and equilibrium data are well represented by the Langmuir isotherm model. Carbonaceous materials show high level of biodecolorization even at very short space times. Results indicate that carbonaceous materials prepared from sludge-exhausted materials have outstanding textural properties and significant degradation capacity for treating textile effluents.

*Keywords*: Azo dye; Biological carbonaceous material; Biodecolorization; Sewage exhausted materials.

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## 1. **Introduction**

Sewage sludge is an unavoidable byproduct of the treatment of wastewaters and exists in a huge amount around the world. In the European Union alone, the annual production of dry solid sludge exceeds 10 million tons [1]. These huge amounts of waste materials, consequently, cause major handling and disposal problems [2], and are hence available almost free of cost to be used in other forms for various applications. Usually these materials are reutilized in agriculture, incineration, land filling, compost manufacture, bio gas production, manufacture of adsorbents, etc.; some of which will be forbidden in the next future. If the solid wastes are used as low cost adsorbents (LCAs), it will provide a twofold environmental advantage . First, the amount of waste materials is partially reduced and secondly the low-cost adsorbent, if developed, can reduce the contaminants in wastewater at a reasonable cost.

The sludge-exhausted material is carbonaceous in nature and rich in organic materials. Hence, it has the potential to be converted into carbonaceous material if it is pyrolyzed under controlled conditions or through the addition of some chemical agents like zinc chloride and potassium hydroxide in order to increase the surface area and pore volume [3-5]. Activated carbon has been reported to be adsorptive, electrochemical and catalytic in nature. They have the important characteristic property of adsorbing organic compounds in their porous structure, depending on their surface functionality and the content of mineral matter [6-7]. Although many efforts have successfully been devoted to obtaining activated carbons from sewage sludge, even with a very large surface area, the high cost associated with their preparation has pushed researchers to focus their attempts on developing novel efficient, low cost adsorbent materials from sewage sludge [8-20]. Even, a research work patented the preparation of low cost adsorbent from sludge materials [21]. Usually, $ZnCl_2$ is used as a dehydrating reagent [22] and as a tar-formation suppressant [23] as it essentially promotes the aromatization of carbon skeleton and helps to develop a well porous structure [24]. For $ZnCl_2$ activation and carbonization, the reported optimum procedure involves dwell times of 650 °C for 2 h and 550 °C for 1 h respectively [25]. Depending on the conditions of chemical activation involved in the various mechanisms for $ZnCl_2$ activation, good textural properties of porosity and surface area could be developed [26-27]. Since the carbon constituents are converted to tar at high temperatures while burning them off, the sludge material becomes hard and porous in nature. The carbonaceous material is then activated with $ZnCl_2$ and is finally washed with hydrochloric acid solution to remove the extraneous reaction products and un-reacted $ZnCl_2$ particles. Even after the acid-washing of activated carbon, zinc content is still 10 times higher than that in the raw sludge [28]. The adsorption capacity of any carbonaceous material depends on the type of its organic molecule and its micro porosity. However, certain experimental studies reveal that small molecules such as phenol can access micro pores; natural organic matter can access mesopores; and bacteria can access macro pores [29].

On the other hand, textile wastewater pollution mainly comes from the textile processing unit, pigments units, paper industries, and waste water treatment plant. The textile industry presents a global pollution problem owing to the dumping discharge of dye contaminated water into water bodies, which is having a major impact on the quality and hazardous of water resources. The worldwide annual production of dyes is more than 7 x 105 tonnes reported by Joo et al., 2001 [30]. In the past years, many researchers have reported various physico-chemical methods for removing colored compounds from textile wastewater. These methods include coagulation, adsorption, oxidization, electro-chemical and ultra-filtration [31-32]. In fact, all these methods are costly and need additional set up or arrangement to remove the byproducts. Most physicochemical methods can remove dyes efficiently but are not feasible due to their high cost and limited versatility [33]. Alternately, biological treatment methods may present a relatively inexpensive way to remove the effluents from wastewater [34-35]. Biologically activated carbons (BAC), explored in recent researches, encourages anaerobic degradation resulting in improved efficiency of wastewater treatment process [36-37]. The effective degradation of azo dyes in wastewater effluents have already been successfully studied with selected microorganisms [38-39]. Many bacterial, fungal and algal species can absorb or degrade azo-dye molecules. Some studies have demonstrated that the bacterial biodecolorization of azo dyes can take place under aerobic or anaerobic conditions [40-41]. Biodecolorization of water-soluble azo-dyes from dye house effluents, which can influence the environmental parameters, have been achieved with bacterial cultures [42]. These biological methods are friendly from an environmental point of view, which can complete mineralization of organic pollutants at low cost. However, treatments of wastewater containing dyes are still a technical challenge.

Our previous work demonstrated the feasibility of the anaerobic, catalytic reductive azo-dye degradation mechanism using commercial active carbons, so it offers an effective and promising treatment in the reduction of azo dyes. It was also reported that the biological consortia present in this BAC yielded high biodecolorization rates at short space times [43]. In this work, we focus on the preparation, characterization and catalytic performance of carbonaceous materials from exhausted-sludge materials. The strength of this new approach is to use these new materials for the reaction of azo dyes in anaerobic conditions in which biology, chemistry and physics act in a synergistic way to obtain the reactive biodecolorisation at environmental acceptable conditions. The effective biodecolorization of Acid Orange II (AOII) was carried out in a continuous anaerobic UPBR system. Thus, this work describes for a comparison of different carbonaceous materials with commercial AC (CAC) in the biodecolorization of AOII. This work also highlights the significance of chemical activation agents, carbonaceous materials yield, ash content and chemical compositions and also first order kinetic rate modelling and equilibrium isotherm are included. In addition, surface area, pore size distribution, thermal gravimetric analysis, functional groups and surface images are shown.

## 2. Methods and materials

## *2.1. Dye and chemicals*

Acid Orange II (dye content 87 %) and sulfanilic acid (min. 99%), sodium acetate (99 %,), zinc chloride (min. 99%), acetic acid (99.8%) and hydrochloric acid (> 37 %,) were purchased from Sigma-Aldrich Company. Activated carbon (Merck, 1.5 mm granules, ref. 1025141000) was crushed and sieved into 0.5 to 0.7 mm in size. Carborundum granule obtained from Carlo Erba Reagents Company was used as inert diluents for the supporting catalyst. The basal media contained the following chemical compounds (mg $L^{-1}$): $MnSO_4.\cdot H_2O$ (0.155), $CuSO_4\cdot 5H_2O$ (0.285), $ZnSO_4\cdot 7H_2O$ (0.46), $CoCl_2\cdot 6H_2O$ (0.26), $(NH_4)\cdot 6MO_7O_{24}$ (0.285), $MgSO_4\cdot 7H_2O$ (15.2), $CaCl_2$ (13.48), $FeCl_3\cdot 6H_2O$ (29.06), $NH_4Cl$ (190.9), $KH_2PO_4$ (8.5), $Na_2HPO_4\cdot 2H_2O$ (33.4), and $K_2HPO_4$ (21.75). These chemicals were obtained from Sigma–Aldrich Company.

## *2.2. Preparation of carbonaceous material*

Anaerobic sludge materials, obtained from the municipal wastewater treatment plant of Reus (Spain), were used to prepare the carbonaceous materials. Slurry sludge was first dried in an oven at 105 ± 1 °C for 24 h and, then solid material was soaked in distilled water for 2 h. The filtered solid material was dried at 105 ± 1 °C for 48 h. The recovered dried material was subsequently crushed and sieved into 0.5 to 0.7 mm in size. 10 g of dried sample was impregnated into 25 mL (deionized water) of 1 M zinc chloride solution stirred (300 rpm) for 2 h at room temperature. The $ZnCl_2$ impregnated solid separated from the solution and the sample was dehydrated in an oven at 105 ±1 °C for 15 h. The impregnated solid material was placed in a quartz reactor (AFORA, Ref no: V59922) and carbonized in a furnace at different stages of temperatures (400, 600 and 800 °C) with a fixed dwell time for 2 h. After the carbonization, the material was washed three times with 5 M hydrochloric acid solution and finally with distilled water until the solution reached to pH 6-7. After that, the material was dried at 105 ± 1 °C in an oven for 15 h and weighed to calculate the yield. The $ZnCl_2$ impregnated material was placed in a plastic bottle at a room temperature for further studies and materials were designated as SBC400, SBC600 and SBC800.

The yield was calculated for the carbonaceous materials hence produced. The carbonaceous material yield (X) was estimated by eq. 1.

$$X = \left(\frac{C_m}{S_m}\right) \times 100 \quad (1)$$

where $C_m$ is the weight of produced carbonaceous materials and $S_m$ is the weight of sludge material.

### 2.3. *Experimental setup and methods*

The laboratory experimental set up for anaerobic continuous upflow packed-bed reactor (UPBR) with biological carbonaceous material is shown in Fig. 1. The reactor of 15 mm in diameter with an available working volume of about 8 mL was filled with a mixture of 10 g of carborandum granules and 1 g of carbonaceous material used as catalyst. To prevent the washing out of CMs, filters were placed onto the top and bottom of the reactor. To prepare the mixed culture, filtered anaerobic sludge was continuously pumped through the reactor for five days. One reactor outlet is serially connected to other two reactors so that maintained the same culture for all. During this period, mixed culture grown immobilized on the carbonaceous material surface. Through this reactor, a solution containing AOII, basal media and sodium acetate as the carbon source was then fed continuously. The mixed culture within the reactor was maintained at a temperature of 35±1 °C. In the feed bottle, helium gas was continuously bubbled to maintain the anaerobic condition and the pH was adjusted between 6.8 and 7.4 (with acetic acid 10 %). The outlet of the reactor was connected to a redox meter to monitor the redox potential, which was maintained below -500 mV. Experimental points were taken as the average values from triplicate tests for each space time operation.

### *2.4. Characterization of carbonaceous materials*

Surface images of samples were obtained with the electronic scanning microscopy (ESEM)(FEI Quanta 600) using an accelerating voltage of 15 to 20 kV, the elemental composition was obtained by energy dispersive spectrometer (EDS) (Inca system, Oxford instruments) the functional groups of samples were determined using a Fourier transform infrared spectrometer (FT-IR), X-ray diffraction (XRD) spectra were obtained using a D/max-ra X–ray diffract meter (Bruker-AXS D8- Discover diffractometer) with CUk radiation at 40 kV and 40 mA over the $2\theta$ range of 5-70$^{o}$, the thermal analysis using a TGA analyzer (Perkin-Elmer TGA7) was carried out to investigate the weight loss of the materials and theporosity of the carbonaceous materials was characterized by nitrogen adsorption isotherm. In the $N_2$ physisorption analysis, adsorption/desorption isotherms at 77 K were measured using a Quadrasorb$^{TM}$ SI (Quantachrome Instruments). The surface area was determined by the BET (Brunauer-Emmett-Teller) method.

### *2.5. Dye biodecolorization analysis*

Acid Orange II, sulfanilic acid (main product of biodecolorization of the AOII), and sodium acetate were analyzed by High Pressure Liquid Chromatography (HPLC) using an Agilent (USA) system equipped with a gradient pump, which impulsed a methanol–water mobile phase at a flow rate of 1 ml min$^{-1}$ through a C18 Hypersil ODS column. A DAD (Diode Array Detector) detector was used to identify the compounds. The analysis for specific wavelengths of each compound yielded 487 nm for Acid Orange II, 252 nm for sulfanilic acid and 210 nm for acetate.

### *2.6. Adsorption isotherm experiments*

Adsorption tests were conducted on a set of six 250 mL Erlenmeyer flasks containing 0.100 g of adsorbent and 50 mL of AOII solutions within the initial concentrations starting range of 12.5 to 400 mg/L. The adsorption experiment was kept for 15 days at ambient room temperature (23 °C) and, each day, 30 s of shaking allowed to maintain a uniform contact between materials and dye solutions. The pH of the solutions was left without any control. The amount of adsorbed dye was measured from the concentrations in the dye solution initial and final adsorption. The amount of adsorbed dye at equilibrium $q_e$ ($\text{mg}_{\text{AOII}}/\text{g}_{\text{CM}}$) was calculated using eq. 2.

$$q_e = \frac{(C_o - C_e)\, V}{W} \tag{2}$$

where, $C_o$ and $C_e$ (mg/L) are the initial and the equilibrium concentrations of dye, respectively. $q_e$ is the amount of adsorbent adsorbed per unit mass of adsorbent (mg/g), $V$ is the volume of the solution (L) and $W$ is the mass of carbonaceous adsorbent used (g). The experiment results reported the average values from duplicate runs.

### *2.7 Adsorption isotherms modeling*

The equilibrium data were then fitted using two different isotherm models, namely the Langmuir and Freundlich models. Langmuir isotherm assumes monolayer adsorption on the catalyst surface. The Langmuir isotherm equation (3) gave an accurate information of the experimental data.

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \tag{3}$$

where $Q_m$ ($\text{mg}_{\text{AOII}}/\text{g}_{\text{CM}}$) is the maximum adsorption capacity corresponding to complete monolayer coverage, $C_e$ (mg/L) is the final equilibrium dye solution concentrations, and $K_L$ (L/mg) is the equilibrium constant. The experimental data were also analyzed by using Freundlich isotherm equation (4). It is well described about the non ideal adsorption process.

$$q_e = K_F C_e^{1/n} \tag{4}$$

where, $C_e$ is the equilibrium concentration of the dye solution (mg/L), $K_F$ and $n$ are Freundlich constants. $K_F$ (mg/g (L/mg) $^{1/n}$) is the adsorption capacity of the adsorbent which can be defined as the absorption coefficient.

# 3. RESULTS AND DISCUSSION

## *3.1. Textural characterization of carbonaceous materials*

The physical properties of anaerobic mesophilic sludge were tested according to standard methods [44]. The result showed that the sewage sludge was consisted of 22.7±0.3 of volatile matter, 7.60±0.49 of total carbon, 8.34±0.14 of ashes and pH range of 7.75±0.34. The carbonization yields of the CMs was 83.4 ± 0.1, 69.7 ± 0.5 and 60.4 ± 0.6 wt % for the SBC400, SBC600 and SBC800, respectively. The carbonization temperature does have much influence on the weight loss. The overall weight loss was found to increase with higher carbonization temperature. Increase of temperature also enhances the shrinkage of carbon constituents present in the material, which results in a decrease of the yield of CMs.

Infrared spectroscopy was used to obtain the information on the chemical structure and functional groups on the surface of the DS and the CMs and the results are shown in Fig. 2. Significant changes have occurred in the different carbonization conditions, and some peaks appeared as slightly deviated. The major adsorption bands of dried sludge appears at 3286, 2924, 2853, 2051, 1980, 1635, 1539, 1419, 1022 and 873 cm$^{-1}$. These peaks correspond to alkenes, ester, aromatic, ketones, alcohol, hydroxyl and carboxyl bonds. The carbonaceous materials prepared at 400 °C and the dried sludge did not give any significant difference in the peak positions. Consequently, the dried sludge and SBC400 material present the same functional groups on the surface. The band frequency at 3286 cm$^{-1}$ is due to the adsorption of water molecules. The band appearing at 2924 cm$^{-1}$ corresponds to ethyl and methylene groups [45] and those at 3200 and 3381 cm$^{-1}$ are attributed to alcohols and phenols. The band range 1981 to 1920 cm$^{-1}$ is assigned to the vibration of C≡N. In the band range of 1400 to 1750 cm$^{-1}$ appears the amides. The band at 1539 cm$^{-1}$ is due to the vibration of aromatic-carbon stretching. The peaks between 1100 to 1200 cm$^{-1}$ are related to alcoholic, phenolic and carboxylic groups [46]. The peaks describe either the Si-O or C-O stretching in alcohol and ether groups [47].

The XRD technique measures the presence of inorganic materials, like quartz and calcite, and also metal oxides (ashes) on the surface of DS and CMs and Fig. 3 shows the experimental results obtained. For the dried sludge, XRD spectra shows a great peak of quartz (Q). This peak reduces with temperature. The presence of calcite (C) is greater in SBC600 and SBC800 than in DS and the presence of dolomite is very low in all cases.

Results of thermal analysis of DS and CMs are shown in Fig. 4. The initial weight loss of dried sludge, 14.1 % in the interval 20-300 °C, shown on the TGA curve, was mainly due to the desorption of physically adsorbed water [48]. The TGA curve for the DS also shows an overall weight loss of 54.3 % once reached 900 °C. The dried materials thermal curve was shown the highest weight loss rate at temperature between 350 and 400 $^{o}$C. In the case of SBC400, SBC600 and SBC800 materials, the initial weight loss was of 6.3 %, 7.4 % and 8.0 % weight loss respectively, in the interval 20-300 °C. For SBC400, SBC600 and SBC800, total weight losses of 35.0 %, 24.2 % and 17.0 % were observed at 900 °C, respectively. It can be thus noticed that the weight loss of DS is higher than any of the prepared CMs.

SEM images of the DS and the CMs can be seen in Fig. 5. The micro structure of dried sludge shows homogeneous porous and loosely arranged in space. The surface of prepared carbonaceous materials was loose and shows pores of different size, which can hinder the dye-molecule transfer and prevent the catalytic reduction on the material surface.

Energy dispersive spectra analysis permits to measure the weight percentage of carbon and metals, Mg, Al, Fe, Na, K, P, Co, Zn and Ti in the CMs. The results obtained from the chemical analysis data are presented in the Table 1. The percentage of carbon in CMs was in the range of 41-53, higher than that in dried sludge (35 %). All the results reported were obtained from triplicate analysis.

Nitrogen adsorption /desorption isotherms are used to determine the surface area, total pore volume and pore diameter, which provide systematic information on the adsorption mechanism and porous structure. Fig. 6 shows the nitrogen adsorption/desorption isotherms of DS and CMs. The lower curve of each isotherm measurement was obtained by adsorption, and the upper curve was obtained by desorption. The isotherm results of catalysts are close to each other, that indicated the surface textures are almost similar and isotherms also follows Type - IV adsorption model. The pore diameters of the CMs obtained were in the range of 3.4 to 5.4 Å and the mean pore diameter of dried sludge was 101 Å. The pore size distribution curve for the DS and CMs are shown in Fig. 7. The average pore diameter of the materials obtained is in the sequence of DS>SBC400>SBC600 >SBC800.

Table 2 shows the surface area, total pore volume and average pore diameter of the DS, CMs and CAC. The specific surface area is often the primary role in an understanding the structure, which is the key characteristics, capable of affecting the quality and value of the materials. A very low surface area (6.0 $m^2/g$) and pore volume (0.02 $cm^3/g$) was observed for the CMs prepared at 400 ºC. This may be due to the insufficient heat transferred at its low carbonization temperature, and also due to the absence of volatile substance release, which is required for the development of pores. Low temperatures for carbonization are not adequate to dehydroxylate the inorganic acids and to fully carbonize the organic matter [49]. Also some evidence has suggested [50] that the temperature at 550 °C is enough to attain the required decomposition of the sewage sludge. But below this temperature, sintering and hence a drop in the BET surface area occurs.

The specific surface area of 111.3 and 202.0 $m^2/g$ was obtained for the prepared carbonaceous materials SBC600 and SBC800, respectively. As the temperature is increased up to 600 or 800 °C, many substances decompose. Therefore, the surface area and pore volume of carbonaceous material greatly increase. It is well determined that, with increasing the carbonization temperature, the percentage of inorganic particles, especially Zn metal ions, that leached from the chars are reduced [51]. The higher temperature carbonization induces the conversion of inorganic fraction into mineral compounds. It produces the encapsulation of metals within the carbon phase. Therefore, both the organic and inorganic structures are more reactive to acids. The surface porosity results summarized that the chemical activation and low temperature carbonization created more micro pores than higher temperature activation. However, it has been demonstrated that it is possible to prepare an efficient carbonaceous material through minimal temperature carbonization.

### *3.2. Adsorption isotherms of carbonaceous materials*

Adsorption isotherm is an important method to determine the relation between the dye molecule (adsorbate) and the carbonaceous materials (adsorbents). The correlation of equilibrium data is essential for fundamental understanding the adsorption mechanism. In this study, Langmuir and Freundlich isotherm models were developed. The detailed parameters of these two different forms of isotherm models are presented in Table 4. The Langmuir isotherm model fitted well to AOII with a maximum adsorption capacity of 4.5, 96 and 98 $mg_{AOII}/g_{CM}$ for SBC400, SBC600 and SBC800 materials respectively. Whereas for SBC600 and SBC800, it was observed that the maximum adsorption capacity was found to be similar trend, the SBC400 adsorption capacity was very poor. Figure 8 shows the Langmuir isotherms for AOII onto carbonaceous materials. The adsorption isotherm of our materials was considered, the SBC600 and SBC800 materials shows similar performance. In case of Freundlich isotherm constants from Table 3, it was observed that isotherm constant $K_F$ was found to be similar for SBC600 and SBC800, 0.41 and 0.39, respectively.

### *3.3. Catalytic performance of carbonaceous materials*

Effective biodecolorization of AOII was carried out in a continuous anaerobic upflow packed bed reactor. The biodecolorization of Acid Orange II dye (Feed concentration: 100 mg/L) onto CMs was checked in an anaerobic continuous up-flow packed bed bioreactor (UPBR) system working at 35 ± 1°C. The catalytic performance of CMs was checked at different space-times of 4, 2, 1, 0.5 and 0.25 min. At the test start, biodecolorization is high due to the adsorption of dye onto the CMs, until a pseudo steady state is attained. Usually, the surface area is an important factor for the adsorption of organic compounds, since larger surface area results in higher adsorption The comparison was based on the different carbonization temperatures of the prepared sludge materials with commercial AC. In an UPBR bio reactor, better conversion is achieved even though at short space time (τ) when compared to commercial AC. The results show that the catalytic performances of the CMs are good for dye biodecolorization. AOII conversion about 100% at 4.0 min, 99.9% at 2.0 min, 98.3% at 1 min 74% at 0.5 and 44% 0.25 min were achieved in commercial AC. The achieved biodecolorization of our preparation materials concerned, viz., SBC600 and SBC800, were very similar, but the catalytic performance of SBC400 was observed to be very low. It must be noted that 99% biodecolorization of AOII was obtained with both SBC600 and SBC800 at a space time of 4.0 min operation. The degradation efficiency was 86% in 1 min and 64% in 0.5 min for SBC800. For SBC600, the biodecolorization efficiency is moderately less, being 76% in 1 min and 48% in 0.5 min. The dye removal efficiency of SBC800 and SBC600 is 30% and 20% respectively in 0.25 min. This compares well with the removal efficiency for SBC400, 25 % in 4.0 min and 15 % in 1 min. Only 10 % dye removal is for SBCCo600 in 0.5 min that cannot consider as good removal.

The concerning the decolorization of azo dye mechanism the biomaterial is involved in the complex process which associated with biology, chemistry, and physics to get synergistic effects for the removal of AOII dye. It seems the electron transport linked to azo dye molecules in the biomass extra cellular environment and other option is that the metal species can exhibit in the bio materials as doubly positively charges. The electrons are liberated from the biomaterial by the enzymatic or chemical process. In the complex nature of the biomaterials has increases the catalyst mobility, electro negativity and electro affinity, which is greatly influenced in the reduction of AOII dye molecule. The conjugated double bond of azo dye molecule are transported over the biomaterial surface, where they are can make direct contact with either the azo dye molecules or redox supported biomaterials. In such combined action to be linked to establishing, the electron localized on the bio material surface. This combined action is turned into breaking the azo bond (-N=N-) resulting the formation of hazardous colorless aromatic amines of sulfanilic and the1-amino-2-naphthol. Figure 11 shows the removal of AOII and the amount of produced sulfanilic acid (SA) under anaerobic condition. The amount of produced SA molecule is directly proportional to decolorize AOII dye molecule.

The experimental results indicate that the efficiency of solid material in the anaerobic reduction of azo dye molecule is dependent on its carbonization temperature and chemical treatment, but comparable to commercial activated carbons.

Table 4 shows the kinetic constants of first-order kinetic data model for AOII in UPBR bioreactor. The experimental data fitted well to the first-order kinetic model. The predicted result of AOII decolorization in bioreactor was favorable for short space time operation. The results show that the SBC400 material is not suitable for packed bed reactor operation. The representations for first order kinetic modeling are shown in Fig. 9.

## 4. Conclusions

In the current work, a continuous up-flow packed bed reactor was used to check the performance of new materials obtained from the exhausted sludge materials for the anaerobic decolorization of AOII in continuous UPBR system at various space time operations.

We observed that the addition of chemical agent to carbonaceous materials can increase the catalyst activity and the surface textures, which is greatly influenced in the catalytic reduction of AOII dye molecules.

A better surface texture is developed on the material surface after the acid washing. BET surface area, total pore volume and pore diameter, relatively improved after the heat treatment. Equilibrium data were fitted to Langmuir and Freundlich isotherms, although the equilibrium data were best represented by the Langmuir isotherm model. Good conversion rate of AOII dye was achieved in a very short space time. The catalytic performance of CMs was found similar to the commercial activated carbon. Overall results show that these materials are suitable for packed bed reactor operation for azo dye AOII. In this countinous treatment of AOII dye in the reactor have not found any loose of catalytic textures or activity during the operation.

Therefore, it is possible to develop an efficient sludge based carbonaceous material for the treatment of textile effluents, utilizing the potentially useful adsorbents from solid waste materials, which offers significant advantages over currently available expensive commercial activated carbons.

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## FIGURE CAPTIONS

**Figure 1.** Schematic diagram of the experimental setup of continuous anaerobic upflow packed-bed bio reactor, UPBR.

**Figure 2.** FTIR spectra of DS and the CMs.

**Figure 3.** XRD patterns of DS and the CMs. Band labeling: Q, Quartz: C, Calcite: D, Dolomite.

**Figure 4.** Thermal analysis curves of DS and the CMs.

**Figure 5.** SEM images of DS and the CMs.

**Figure 6.** Nitrogen adsorption/desorptions isotherms of the DS and the CMs.

**Figure 7.** Pore size distribution curves of DS and the CMs.

**Figure 8.** Langmuir isotherms for AOII onto CMs.

**Figure 9.** First order kinetic modeling of AOII anaerobic decolorization in UPBR results for fitting of CMs and commercial activated carbons.

**Figure 10.** Removal of AOII dye and the amount of produced sulfanilic acid.

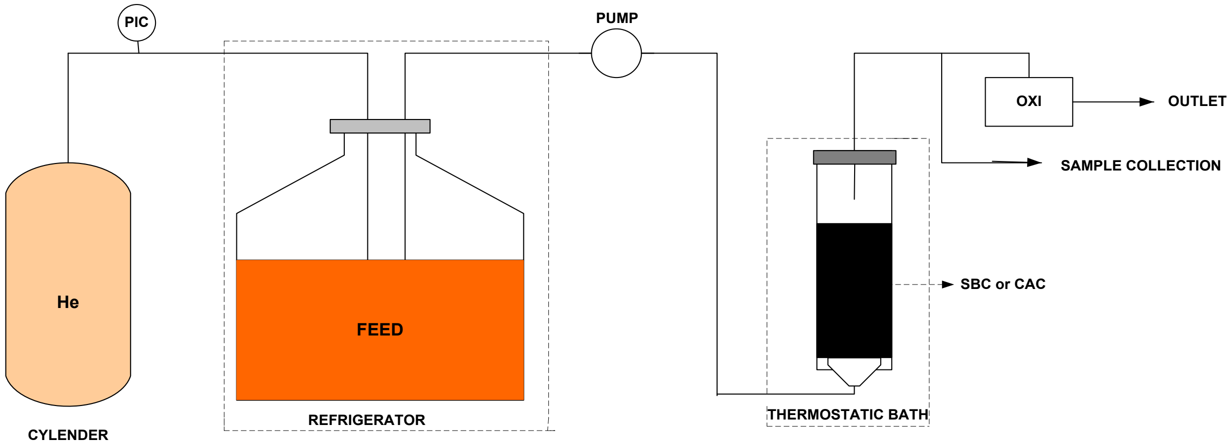

PIC
PUMP
OXI
OUTLET
SAMPLE COLLECTION
He
FEED
SBC or CAC
CYLENDER
REFRIGERATOR
THERMOSTATIC BATH

**Figure 1.**

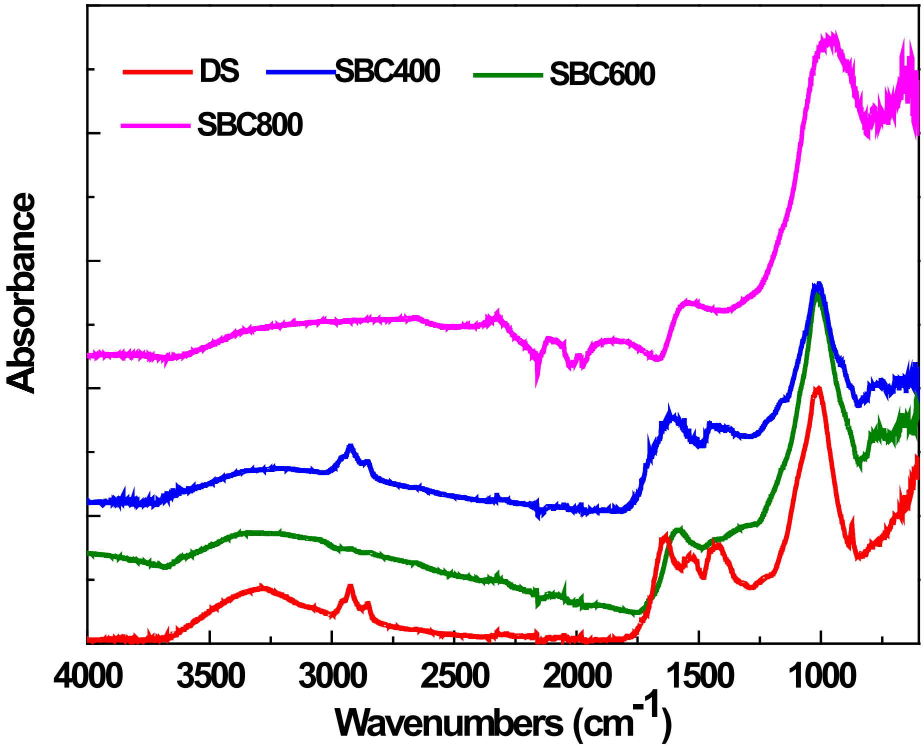

DS
SBC400
SBC600
SBC800
Absorbance
4000
3500
3000
2500
2000
1500
1000
Wavenumbers ($cm^{-1}$)

**Figure 2.**

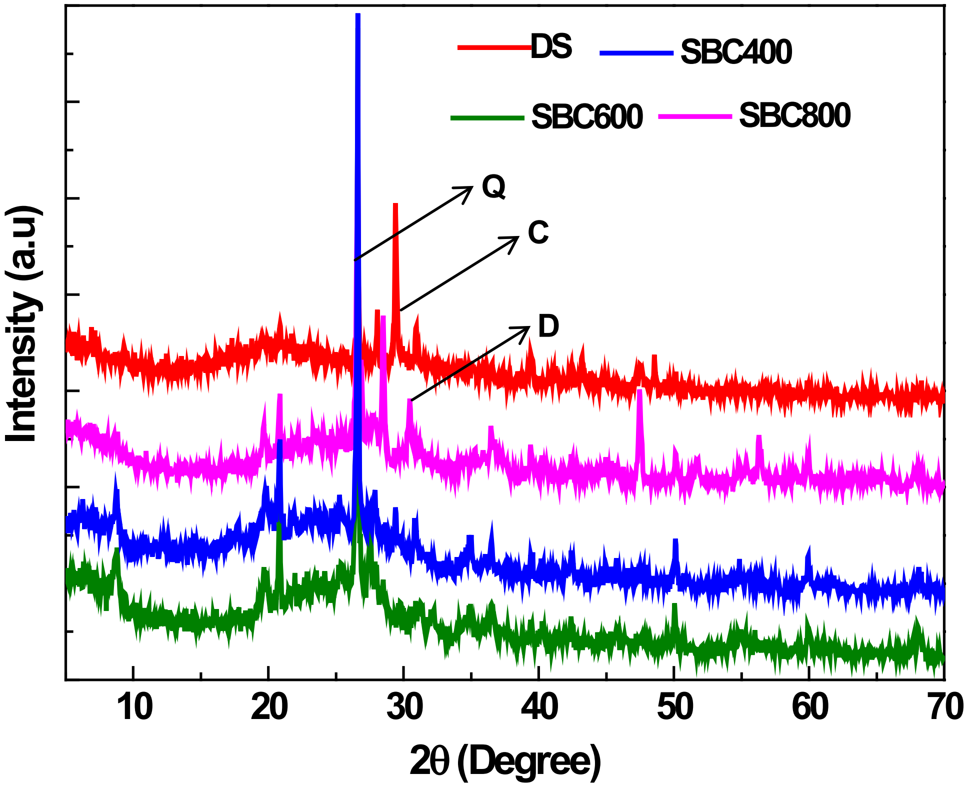

DS
SBC400
SBC600
SBC800
Q
C
D
Intensity (a.u)
10
20
30
40
50
60
70
2θ (Degree)

**Figure 3.**

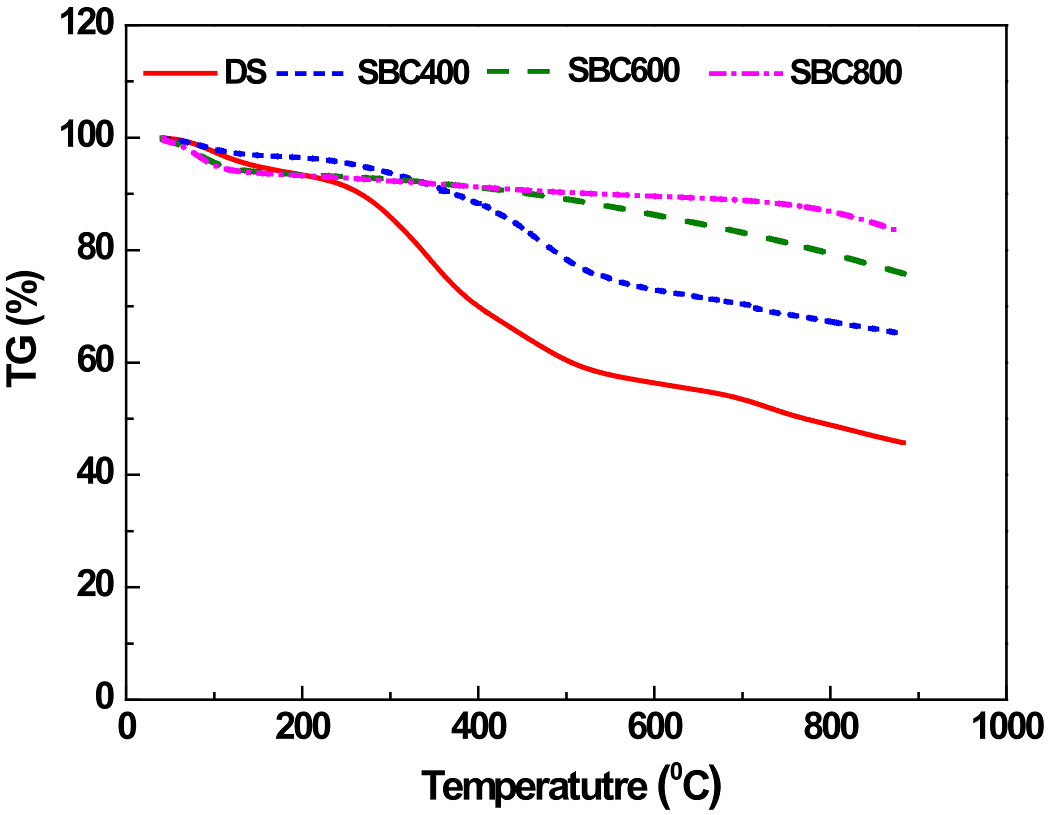

DS
SBC400
SBC600
SBC800
TG (%)
0
20
40
60
80
100
120
0
200
400
600
800
1000
Temperatutre ($^0$C)

**Figure 4.**

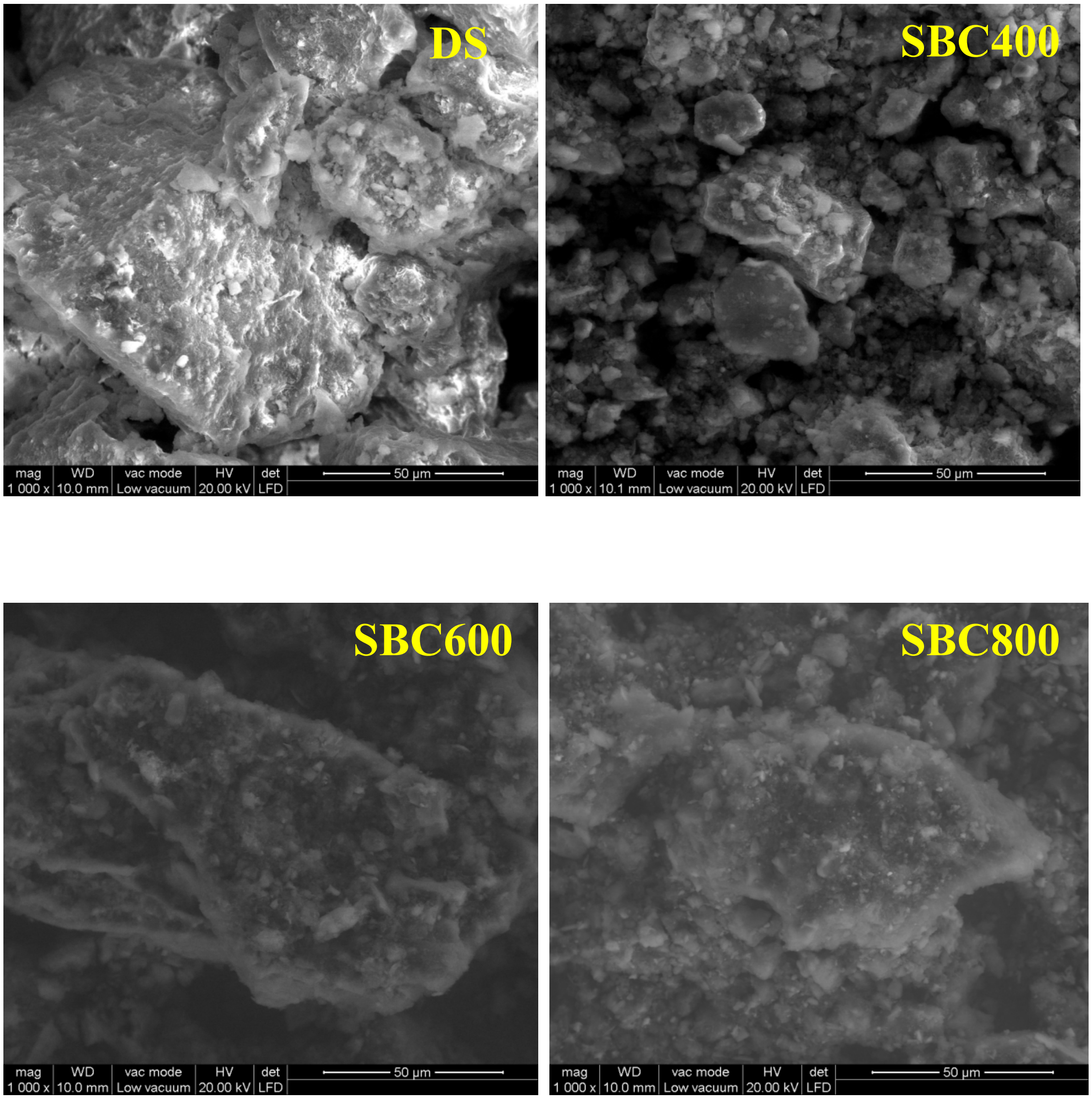
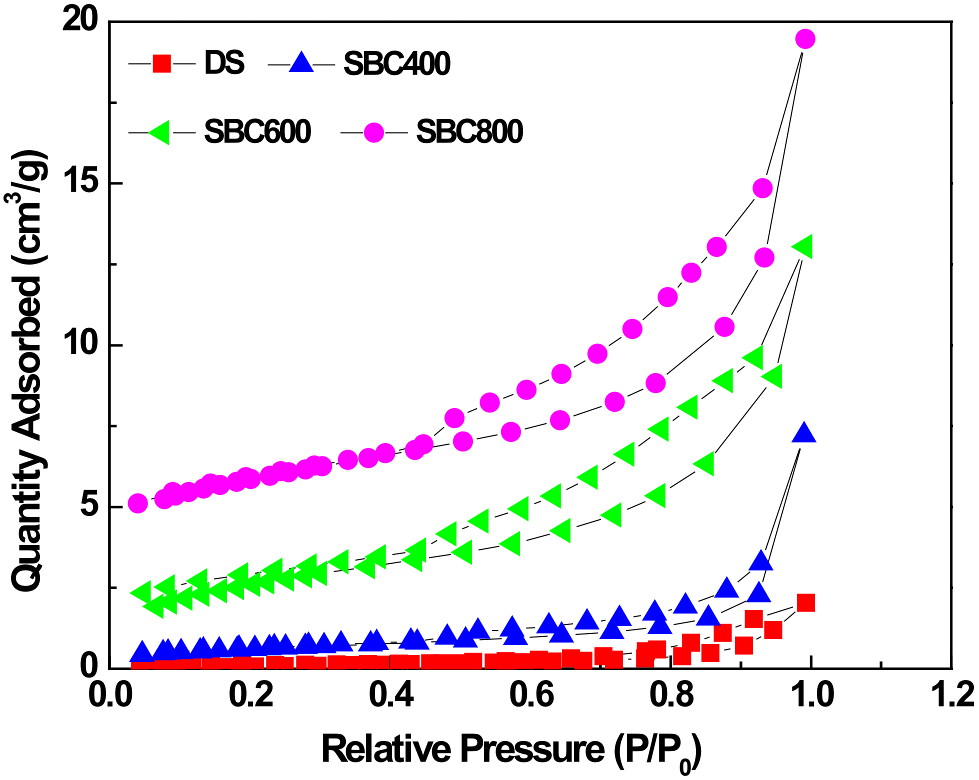
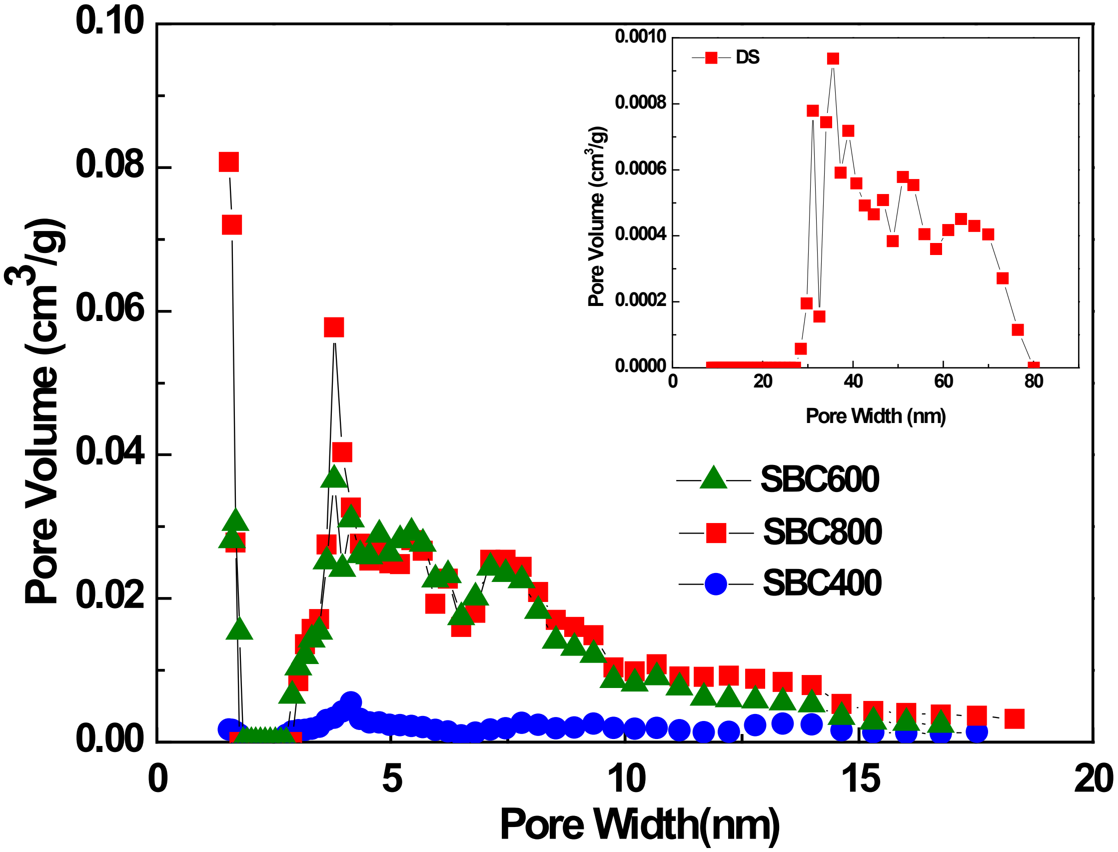

DS
SBC400
SBC600
SBC800
mag 1 000 x
WD 10.0 mm
WD 10.1 mm
vac mode Low vacuum
HV 20.00 kV
det LFD
50 µm

**Figure 5.**



20
15
10
5
0
Quantity Adsorbed (cm$^3$/g)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
Relative Pressure (P/P$_0$)
DS
SBC400
SBC600
SBC800

**Figure 6.**



Pore Volume (cm$^3$/g)
0.10
0.08
0.06
0.04
0.02
0.00
0
5
10
15
20
Pore Width(nm)
SBC600
SBC800
SBC400
DS
Pore Volume (cm$^3$/g)
0.0010
0.0008
0.0006
0.0004
0.0002
0.0000
0
20
40
60
80
Pore Width (nm)

**Figure 7**

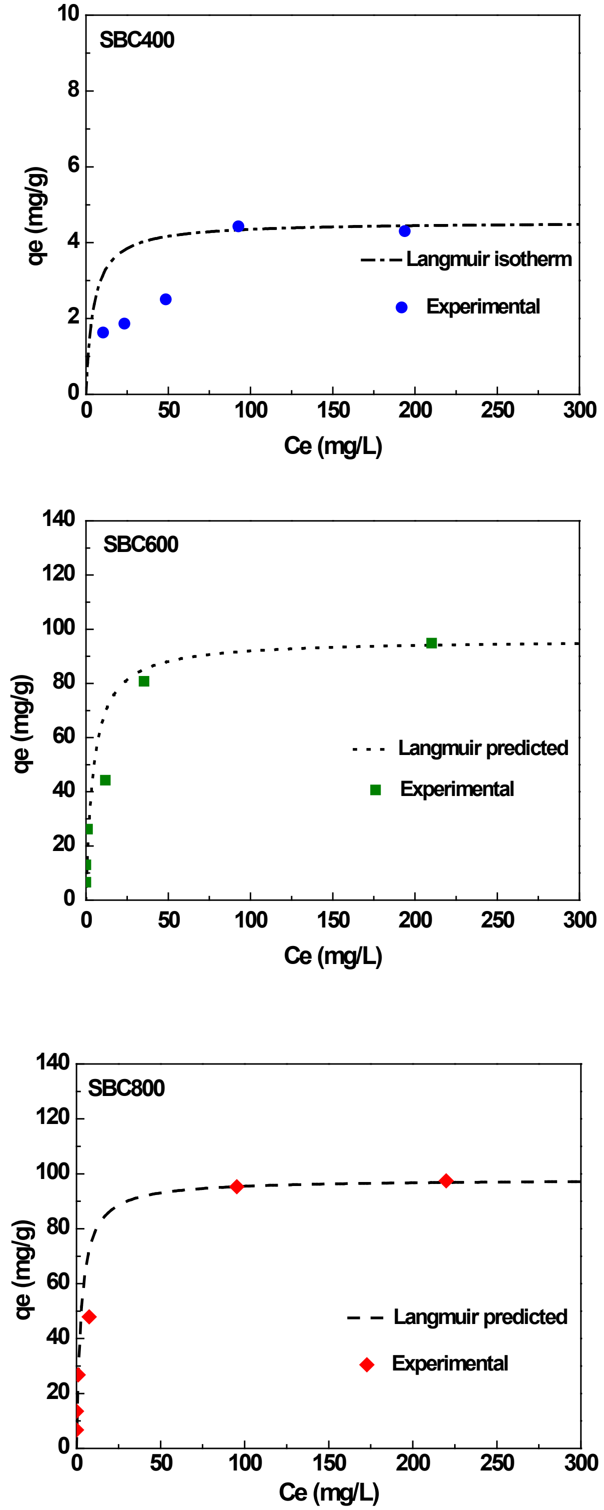

SBC400
qe (mg/g)
0
2
4
6
8
10
0
50
100
150
200
250
300
Ce (mg/L)
Langmuir isotherm
Experimental
SBC600
qe (mg/g)
0
20
40
60
80
100
120
140
0
50
100
150
200
250
300
Ce (mg/L)
Langmuir predicted
Experimental
SBC800
qe (mg/g)
0
20
40
60
80
100
120
140
0
50
100
150
200
250
300
Ce (mg/L)
Langmuir predicted
Experimental

**Figure 8.**

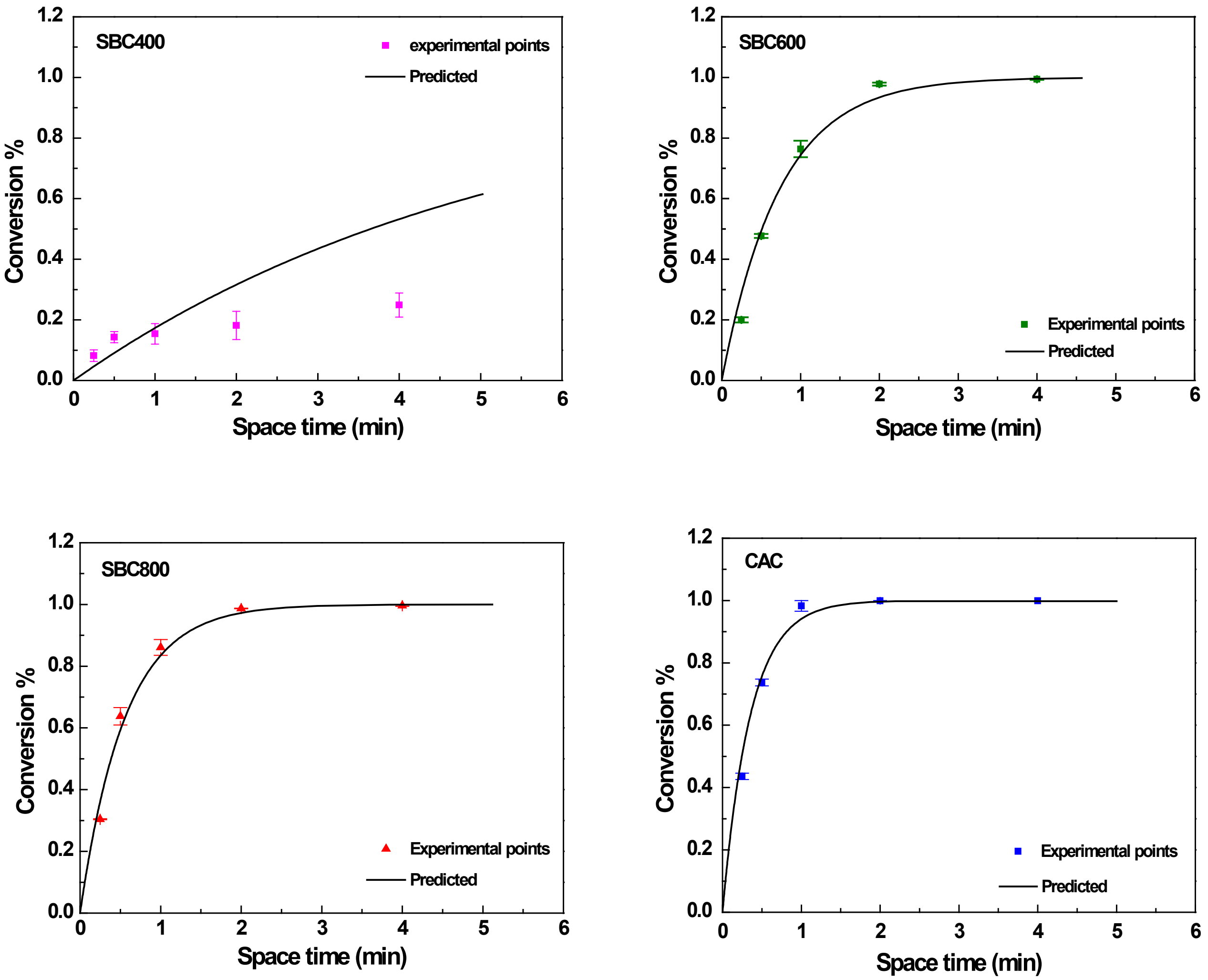

SBC400
experimental points
Predicted
Conversion %
Space time (min)
SBC600
Experimental points
Predicted
Conversion %
Space time (min)
SBC800
Experimental points
Predicted
Conversion %
Space time (min)
CAC
Experimental points
Predicted
Conversion %
Space time (min)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
0
1
2
3
4
5
6

**Figure 9.**

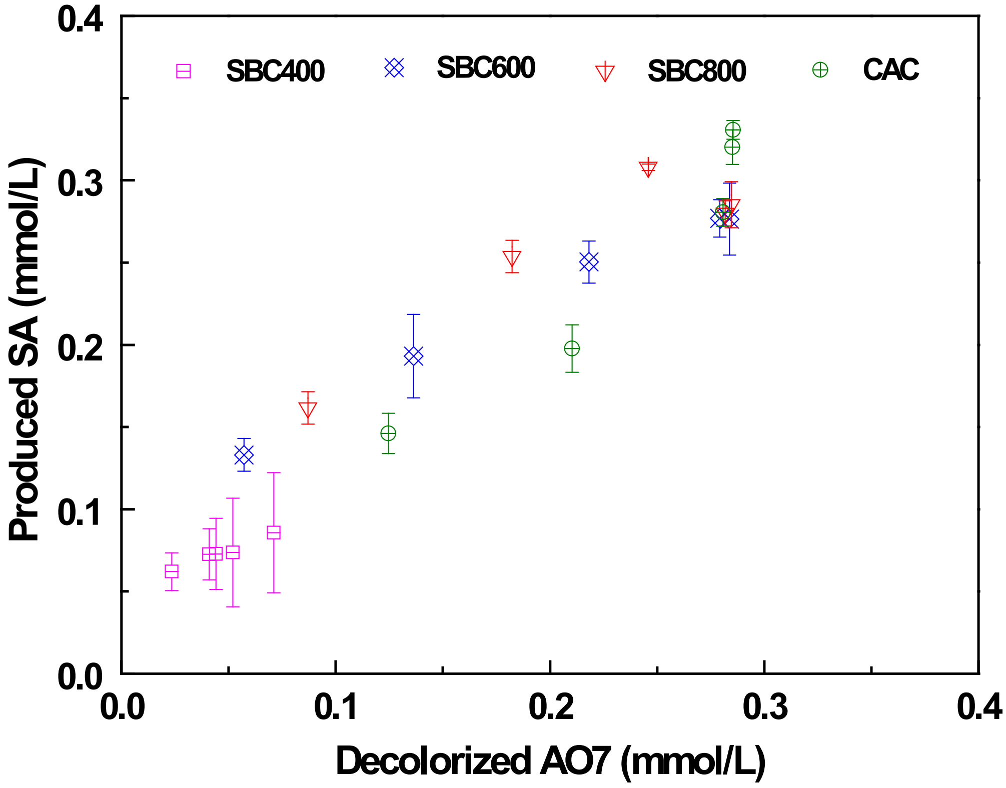

SBC400
SBC600
SBC800
CAC
Produced SA (mmol/L)
0.0
0.1
0.2
0.3
0.4
Decolorized AO7 (mmol/L)
0.0
0.1
0.2
0.3
0.4

**Figure 10.**

## TABLE CAPTIONS

**Table 1.** Ash content and the main elemental compositions of DS and the DMs ( Mean value ± standard deviation is presented, n=3 and *n=2 ).

**Table 2**. Specific area, total pore volume and average pore diameter of the DS, CMs, and CAC.

**Table 3.** Different isotherm model parameters and correlation coefficient for CMs on AOII dye.

**Table 4.** First order kinetic model for anaerobic AOII in UPBR bio reactor (Mean value ± standard deviation is presented, n=5 )

.

**Table 1.**

| Samples | Ashes* | C | O | Na | Mg | Al | Si | P | S | Cl | K | Ca | Fe | Cu | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| DS | 35.34±0.91 | 35±1.55 | 40.24±1.97 | 0.26±0.03 | 0.6±0.14 | 3.56±3.45 | 2.32±0.1 | 3.62±0.18 | 2.29±0.07 | --- | 0.28±0.13 | 6.93±0.83 | 4.59±0.59 | --- | --- |
| SBC400 | 34.53±0.09 | 53.03±2.26 | 25.16±0.77 | 0.31±0.32 | 0.38±0.13 | 3.05±0.57 | 7.76±1.72 | 0.59±0.29 | 1.85±0.15 | 1.86±0.03 | 0.6±0.05 | 0.74±0.22 | 1.53±0.14 | 0.76±0.23 | 2.38±0.23 |
| SBC600 | 36.34±0.12 | 49.81±2.75 | 23.05±0.24 | 0.57±0.12 | 0.41±0.03 | 5.72±3.9 | 7.78±0.87 | 0.46±0.14 | 1.77±0.23 | 2.15±0.38 | 0.81±0.32 | 0.51±0.23 | 1.39±0.24 | 0.8±0.41 | 4.77±1.38 |
| SBC800 | 40.43±0.08 | 41.85±4.14 | 25.33±1.48 | 0.66±0.05 | 0.92±0.24 | 7.8±4.27 | 6.19±1.68 | --- | 2.11±0.22 | 1.3±0.34 | 0.37±0.08 | 0.9±0.71 | 5.97±1.15 | --- | 6.6±0.84 |

**Table 2.**

| Sample code | Temperature ($^oC$) | BET surface area ($m^2/g$) | Total pore volume $V_t$ ($cm^3/g$) | Average pore diameter $D_p$ (Å) |
|---|---|---|---|---|
| DS | 105 | 6.0 | 0.02 | 101.3 |
| SBC400 | 400 | 13.0 | 0.03 | 5.4 |
| SBC600 | 600 | 111.3 | 0.20 | 4.0 |
| SBC800 | 800 | 202.0 | 0.24 | 3.4 |
| CAC | -- | 1100.0 | 0.73 | 13.4 |

**Table 3.**

| Sample code | Langmuir isotherm | | | Freundlich isotherm | | |
|---|---|---|---|---|---|---|
| | $K_L$ (L/mg) | *Qm* (mg/g) | $R^2$ | $K_F$(mg/g (L/mg)$^{1/n}$) | *1/n* | $R^2$ |
| SBC400 | 0.21 | 4.55 | 0.96 | 0.33 | -- | 0.89 |
| SBC600 | 0.22 | 96.15 | 0.99 | 0.41 | 1.13 | 0.79 |
| SBC800 | 0.37 | 98.03 | 0.99 | 0.39 | 1.16 | 0.79 |

*-- the experimental value has no physical sense*

**Table 4.**

| Samples | *Kinetic constants (min-$^{1}$) |
|---|---|
| SBC400 | 0.198±0.12 |
| SBC600 | 1.364±0.36 |
| SBC800 | 1.801±0.36 |
| CAC | 2.844±0.93 |

* $r_{AOII} = -k.C_{AOII}$ *(First order equation), n=5*

# GRAPHICAL ABSTRACT