

BIORESOURCE TECHNOLOGY (BITE) (4.7 IMP)

A potential application of sludge based catalysts for the anaerobic bio decolorization of tartrazine dye

Sunil Athalathil ^a, Agusti Fortuny ^b, Josep Font ^a, Frank Stüber ^a, Cristophe Bengoa ^a,
Azael Fabregat ^{a*}

^aDepartament d'Enginyeria Quimica, ETSEQ, Universitat Rovira i Virgili, Av. Paisos Catalans 26, 43007 Tarragona, Catalunya, Spain

^bDepartament d'Enginyeria Quimica, EPSEVG, Universitat Politecnica de Catalunya, Av. Victor Balaguer s/n, 08800 Vilanova i la Geltru, Catalunya, Spain

***Corresponding Author:** Prof. Dr.: Azael Fabregat Llangostera, Departament d'Enginyeria Quimica, ETSEQ, Universitat Rovira i Virgili, Av. Paisos Catalans 26, 43007, Tarragona, Catalunya, Spain.

Tel: + (34) 977559643

Fax: + (34) 977559667

E-mail : azael.fabregat@urv.cat

Abstract

Two highly efficient (K_2CO_3 /sludge carbon and $ZnCl_2$ /sludge carbon) solids were prepared by chemical addition followed carbonization at 800 °C, and were tested for anaerobic reduction of tartrazine dye in a continuous packed bed reactor (UPBR), and their performance was compared to that of commercial activated carbon (CAC). The chemical and structural information of the solids were subjected to various characterizations in order to understand the mechanism for anaerobic decolorization, and efficiency for SBCZN800 and SBCPC800 materials was 87 % and 74 % respectively at a short space time (τ) of 2.0 min. A first-order kinetic model fitted the experimental points and kinetic constants of 0.40, 0.92 and 1.46 min^{-1} were obtained for SBCZN800, SBCPC800 and CAC respectively. The Langmuir and Freundlich model was successfully described the batch adsorption data. Based on these observations cost effective sludge based catalyst can produce from harmful sewage sludges for the treatment of industrial effluents.

Keywords: Sewage sludge; Carbonization; Biodecolorization, Tartrazine, Wastewaters

1. Introduction

Many industrial wastewater effluents, highly coloured, come from textile, paper processing, leather making unit and cosmetic industries, containing bio recalcitrants complex structure and toxic compounds. In Europe, 108 million tons of wastewaters are produced on a yearly basis, and about 36 million tons of chemicals, and other auxiliary substances must be

removed from the textile wastewaters (Valh et al., 2011). The majority of the textile industries are used about 60–70 % of synthetic azo dye throughout the textile processing steps (Carliell et al., 1995). In a study by Essawy group has estimated that approximately 20 % of dyes are discharged into industrial wastewaters, and the exact data on the amount of dyes discharged into the environment are not available.

Tartrazine dye is a part of azo dye family, containing azo chromophores (-N=N-) and widely used for several industrial applications. To date, many authors have realized that removing tartrazine from the water, and wastewater is a hard task because it is a stable molecule, not easy to hydrolyze, and also difficult to remove by an activated sludge process [Marmion et al., 1991 and Shaul et al., 1991]. At present only some authors have demonstrated the removal of tartrazine from the water and wastewaters, including, electrochemical bleaching [Fukatsu and Kokot, 2000, Gregory and Stead, 1978], anaerobic baffled reactor [Bell et al., 2000], and specific solid electrode [Jain et al., 2003]. Until now, most of the researchers focused on their study related to conventional physico-chemical techniques, which includes coagulation, ozonation, flocculation, membrane, nano- filtration and advanced oxidation processes for the removal of bio recalcitrants from the water and wastewaters [Chinwetkitvanich et al., 2000 and Petzol et al., 2007]. However, these oxidative reaction practices are greatly suffered from poor efficiency in practical applications. In this circumstances, biological treatment is one of the best tools, cost effective and attractive methods for removing the bio recalcitrants, which leads to complete detoxification, and avoiding the problems of sludge disposal, and it can effectively maximize the catalytic reaction. Currently available treatment methods are not enough to completely removing tartrazine dye from the water and wastewaters.

Activated carbon is a porous and amorphous material that remove a variety of organic pollutants from liquid and gases phases by adsorption. On the features and specific use of activated carbon are mainly its surface functionality, adsorptive, electrochemical, thermal stability and low environment impact. Many researchers have sought that activated carbon is best-suited materials for cleaning of wastewaters, but in the economic point of view, it is unsuitable for many developing countries.

On the other hands, sewage sludge disposal practice is one of the big problems for wastewater treatment plants (WWTPs) in the around world. Available disposal practices such as agriculture, incineration, landfill, fertilizer and other applications are still facing several environmental problems (Fytli, and Zabaniotou, 2008). This huge amount of sludge solid residues are available at low cost. If these sludge solid materials are converted into useful catalyst supporting materials they can be utilize for the treatment of bio recalcitrant compounds from the waste and waste waters. This sewage sludge basically contains complex mixture of organic, inorganic, volatile, bacterium and other substance that must be removed from the WWTPs. Unfortunately still there is no healthier solution for the proper sludge disposal methods. Since dewatering and drying of sewage biomass is costly practices, if those are converted into useful products can be solving the huge amount of sludge problems.

The Lebigue group has reported the solutions of healthier disposal, and produced inexpensive activated carbons from the sludge materials. Some researcher have reported the goodness of sludge assisted catalysts for the removal of pollutants from water and wastewaters [Okada et al., 2003; McKay et al., 1999; Martin et al., 2003; Otero et al., 2003a; Aksu, 2001; Kargi, and Ozmihci, 2004; Mahapatra et al., 2012]. The production of

solid adsorbents from the sewage sludges and utilized them for the mineralization of organic pollutants such as, Methylene blue and Reactive red [Li et al., 2011], 4-chlorophenol [Monsalvo et al., 2011] and Tartrazine [Eliana et al., 2001].

The Fabregat group recently reported the low-cost carbonaceous materials from sludge materials and their uses for anaerobic reduction of azo dye wastewaters in the continuous packed bed reactor system [Sunil et al., 2014]. Generally, anaerobic treatment methods are effective in the removal of azo-dyes, are environmentally safer and cost effective. The anaerobic reaction is non specific, micro consortia mediated extra-cellular process. This process is an enzymatic reaction between molecules of dyes and the cellular-reducing enzymes (Delee et al., 1998). The biological color removal methods from effluents containing dyes has been reported (Pandey et al., 2007).

The preparation of solids from the harmful sludge materials for the anaerobic reduction of tartrazine dye in a continuous UPBR reactor was investigated. The surface chemistry of solids was identified using various characterizations in order to understand the fundamental information for the anaerobic reduction of tartrazine dye in the packed bed reactor system. The mechanism of solid sludge catalysts for biological reduction of tartrazine dye is explained. The adsorption capacity of solid was performed in the batch adsorption equilibrium experiment. To our best knowledge, there is no more study conducted for the anaerobic reduction of tartrazine dye using sludge catalyst in the packed bed reactor system.

2. Materials and methods

2.1. Preparation of sludge based catalysts

Diagram 1 show the route for sludge based catalysts preparation from the sewage biomass. The anaerobic sludge biomass was dried in a furnace at 105 °C for 24 h. The dried product material was soaked in distilled water for 2 h followed by dried at 105 °C for 48h. The resulting dried sludge materials were grinding and sieving approximately mesh size ranges of 0.5 to 0.7 mm.

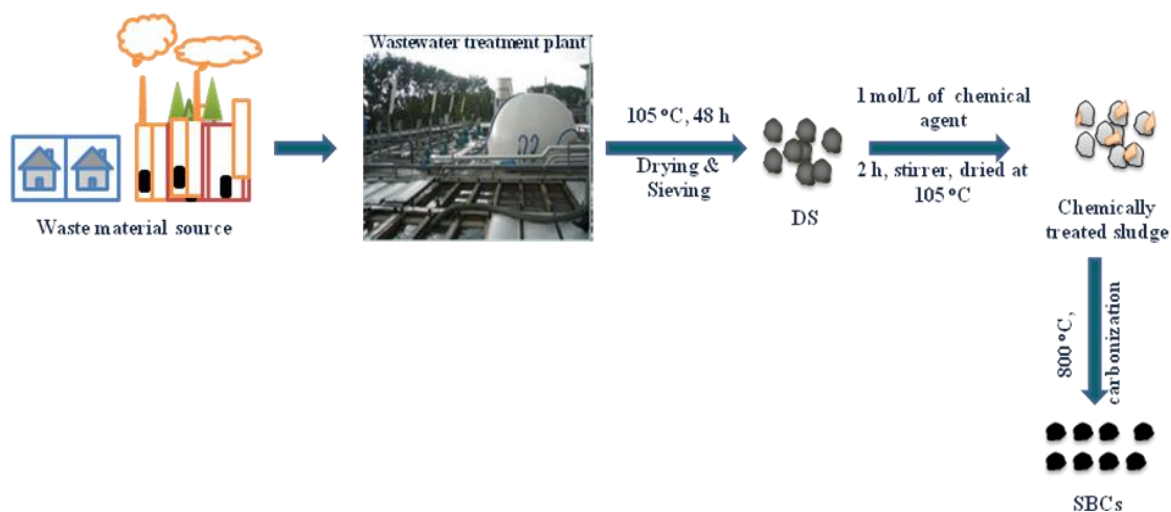


Diagram 1. Show the preparation of sludge based catalysts from the sewage sludge.

10 g of dried sludge (DS) was added in 25 mL of 1 mol/L K_2CO_3 (Sigma-aldrich) solution under stirring for 2 h at room temperature (24 °C). The impregnated solid material was dried at 105 °C for 24 h, and was placed in a quartz reactor (AFORA, Ref no: V59922) and heated at 800 °C with a fixed dwell time for 2 h. After the carbonization process, product material was washed several times with distilled water and dried at 105 °C for 24 h. The preparation procedure for SBCZN800 solid has been reported [26]. The commercial activated carbon was directly used throughout the experiment.

2.2. Countinous biological UPBR operation

The anaerobic mixed culture was pumped continuously through the solid in the UPBR reactor for a week. One reactor outlet is serially connected to other reactors so that maintained the same culture for all. In the reactor (15 mm in diameter with an available working volume of about 8 mL) was filled with a mixture of 10 g of carborandum granules (Carlo Erba Reagents), and 1 g of solid sludge catalyst used as the biological supporting materials. The mixed anaerobic culture within the reactor was maintained at a temperature of 35 °C. The feed solution contain tartrazine dye (85 %, Manuel Vilaseca, S.A), sodium acetate (Sigma-aldrich) and synthetic basal media [24], the feed solution bottle was kept in inert conditions through bubbling helium gas into the bottom. The concentration of azo dye tartrazine was measured by HPLC instrument. The Agilent (USA) system equipped with a gradient pump, a reversed-phase column C18 Hypersil ODS and a DAD (Diode Detector Array) detector at the specific wavelength of compound to be analyzed (245nm for tartrazine). The mobile phase consist of sulfuric acid buffer (pH 1.41) with milli-Q water (A) and methanol (B).

2.3. Batch adsorption experiments

Batch adsorption test was conducted with a set of eight 250 mL of Erlenmeyer flasks. 100 mL of azo dye tartrazine solutions with initial concentrations starting from 25 to 200 mg/L was taken in each flask. 100 mg of solids was added to each flask at room temperature (20 °C) and the pH of the solutions was originally without any control. The adsorption experiment was observed for 15 days to reach equilibrium isotherm and each day 30s normally shaken to maintain a uniform contact between solid catalyst and dye solution. The initial and final concentration of tartrazine dye was measured by HPLC.

2.4. Surface textures of sludge based catalysts

The ash content of the solids was determined by standard ASTM procedure (2002). The FTIR spectra was recorded in ATR mode used by the Perkin Elmer instrument in the frequency range between 4000 to 400 cm^{-1} . BET surface area of the samples was measured by using a QuadrasorbTM SI (Quantachrome Instruments). 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 X-ray (EDX) spectrum (Inca system, Oxford instruments) instrument. Thermo gravimetric analysis of samples using a TGA thermal analyzer (Perkin-Elmer TGA7) was carried out to investigate the weight loss. XRD spectra were obtained using a D/max-ra X – ray diffractometer (Bruker-AXS D8- Discover diffractometer) with CuK radiation at 40 kV and 40 mA over the 2 theta range of 5 - 70°. The data were collected with an angular step of 0.05° at 3s per step and sample rotation. Microsoft excel work sheet is used for the linear and non linear regression data process.

3. Results and discussion

3.1 Chemical and structural information of sludge catalysts

The surface porosity of new solid sludge catalyst was greatly improved after the chemical addition and higher heat treatment process. Since the starting material originated from sewage sludge and contain variety of impurities like ashes, bacterium, exhausted solids, chemical compounds and metal fractions. The surface textures of new materials, mostly meso pores, and BET surface area of SBCZN800 material was quite higher in comparison to SBCPC800. BET surface area measured for SBCPC800 and SBCZN800 materials were

106.0 m²/g and 202.0 m²/g respectively. The decolorization results show that surface porosity feature was influenced for the removal of tartrazine dye in the packed bed reactor system. The potential catalytic activity of solids was more active when they were introduced as a biological supporting catalyst in the continuous packed bed reactor than batch adsorption isotherms experiment.

The adsorption/desorption isotherms of the dried sludge and SBCs are shown in figure 1. The surface physical parameter was obtained from the N₂ adsorption isotherms, includes the BET surface area, total pore volume and pore diameter. Lower curve of each isotherm measurement was obtained by adsorption, and the upper curve was obtained by desorption. Isotherm results for both materials were close to each other, which indicated that the surface textures properties are quite similar. The isotherm patterns were followed Type IV adsorption isotherm model. Both materials showed the hysteresis loop phenomena. The adsorption isotherm curve shows the hysteresis as ferromagnetic and ferro electric nature. The adsorption/desorption isotherms observation that the solid materials mostly consist of meso-porosity.

Figure 1

The micro structure images of dried and SBCs are shown in figure 2. The images of dried sludge material has no detectable pores, and few inorganic particles were also present. After the treatment, the pore structure was clearly visible. Observation of surface porosity was agreed with N₂ adsorption and desorption isotherms. The surface of materials showed the chemical particles as potassium carbonate or zinc chloride particles were dispersed uniformly. SEM images are quite different for SBCZN800 and SBCPC800, mostly in the

pores arrangement. The surface image of SBCPC800 solid has grained cluster and several grooves are visible

Figure 2

Figure 3 shows the TG / DTG curves of the dried sludge and SBCs. The weight loss of samples was determined up to at 900 °C temperature. During this temperature range, almost all the compounds were decomposed. Since sewage sludge consists of several impurity such as organic, inorganic, exhausted solids, volatile matter, and metal fractions, after the carbonization at 800 °C, most of the substances were reduced or decomposed. The chemical fractions were joined with carbon matrix to form a cross-linked structure. Initially, the carbonization was performed at 800 °C most of the hydrates might decomposed. Alongside, the evidence which agreed with the surface characteristics information, and the results show that there is no much hydrates content in the catalysts.

Heat treatment, the carbonaceous content was shrunk, and the charred substances were occupied on the surface of solids. Highest weight loss was observed at 350 and 400 °C temperature range for dried sludge. Lower weight loss was observed for new materials due to the chemical particle incorporated in the interior wall and solid become hard. When the solids were applied in a packed bed reactor, it is necessary to have hardness of solids otherwise it can be powdering during the long-term operation.

Figure 3

The XRD (X-ray diffraction) technique is used to determine the crystalline contents of the materials. The results of XRD spectra are shown in figure 4. Higher amount of quartz ($\alpha\text{-SiO}_2$), considerable amount of calcite (CaCO_3) and lower amount of dolomite

(CaMg (CO₃)₂) was detected in the new solids. The presence of inorganic contents increases the mechanical strength of the solids. Higher amount of quartz, calcite, and less dolomite were detected in the DS material. After the heat treatment, calcite content level was significantly reduced. The presence of the hydrates in the catalyst was very low, which agreed well with the EDX measurement.

Figure 4

The chemical functional groups of the solids analyzed by FTIR, and spectra is shown in figure 5. The solid material had a broad peak at 3400 cm⁻¹ related to vibrations of OH groups, after the heat treatment obtained peak was reduced. The bands at 800 cm⁻¹ and 1200 cm⁻¹ in the solids were attributed to Si-O-Si and Si-O-Al bond. The IR peak at 800 cm⁻¹ corresponds to the quartz. The band at 2300 cm⁻¹ is mostly alkynes stretching bond. The sharp peaks at 1400 cm⁻¹ and 1700 cm⁻¹ belongs to oxygen and carboxylic groups respectively. The major chemical groups are presented in the catalysts, including -OH, C=C, NH, Si-O-C or Si-O-Al. The band at 1612 cm⁻¹ which is related to vibration of quinone and C=O molecule. The chemical groups are mostly configuration of aromatic and aliphatic compounds. The functional groups are also played an important role for the reduction of tartrazine molecules.

Figure 5

Ash content is an important factor which considers as an indicator for the quality of solid materials, but sometime it can reduce the efficiency of catalyst. Generally, ash consists of minerals such as silica, aluminum, iron, magnesium, and calcium. The presence of metal fractions in the SBCZN800 material was higher than that of SBCPC800 material.

SEM/EDX analysis is used to detect the metallic content of the samples are shown figure 1. The ash content for DS was 36 % and new solids were 40 % and 75 % for SBCNZ800, and SBCPC800 respectively. Carbon content is an important factor while considering the adsorption process and were measured 35, 19 and 42 % for DS, SBCPC800 and SBCZN800 respectively. A measurable amount of oxygen was also detected.

3.2. Adsorption isotherms results

Adsorption isotherm study explains dye molecule interact with sludge based catalyst, and it is necessary to optimizing the adsorption capacity of catalysts in order to understand the adsorption features. The amount of adsorbed tartrazine dye at equilibrium q_e (mg_{AOII}/g_{CM}) was calculated using equation 1.

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

where, C_o and C_e (mg/L) are the initial concentration of the dye and the equilibrium concentration of tartrazine dye, respectively. q_e is the amount of adsorbate adsorbed per unit mass of catalyst (mg/g), V is the volume of the solution (L) and W is the mass of catalyst used (g).

The equilibrium data analysis were using two different isotherm models: Langmuir and Freundlich models. The linearized Langmuir isotherm model describes the mono layer adsorption property of the catalysts, and the correlation coefficient of R^2 values was 0.98 and 0.98 for SBCZN800 and SBCPC800 solids, respectively. Results of Freundlich isotherm correlation coefficient of R^2 was 0.41 for SBCPC800 material. In case of SBCZN800 value is very low and was not fitted to Freundlich isotherm. The results of adsorption isotherm can explains the interactive features between the dye solution and

sludge catalysts. The linearized Langmuir (2) and Freundlich (3) models equation are below.

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

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (3)$$

Figure 6 shows the Linearized plots of the Langmuir and Freundlich models for the adsorption of sludge based catalysts.

Figure 6

Isotherm constants were obtained from the linearized models, obtained values are used to calculate the maximum adsorption capacity by using non linearized Langmuir (4) and Freundlich (5) isotherm equation.

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (4)$$

$$q_e = K_F C_e^{1/n} \quad (5)$$

From the data, Q_m (mg_{AOH}/g_{CM}) and K_L (L/mg) are Langmuir constants related to adsorption capacity and rate of adsorption, respectively. K_F and n are Freundlich constants. K_F (mg/g (L/mg)) is the adsorption capacity of the adsorbent which is defined as the absorption coefficient.

Adsorption isotherm data of tartrazine onto the solid is well fitted to the Langmuir isotherm, and the maximum monolayer adsorption capacity was 21.0 to 36.5 mg/g for SBCPC800 and SBCZN800, respectively. The adsorption capacity of SBCPC800 solid was

low. The observation of batch adsorption isotherms revealed that surface area was greatly influenced in the mono layer adsorption process.

3.3. Biological removal of tartrazine dye

The biological removal of tartrazine dye over the sludge based catalyst, and commercial activated carbons are shown in figure 7. The anaerobic reduction was performed with 100 mg/L of azo dye tartrazine solution at different space time operations (4, 2, 1, 0.5 and 0.25 min). The space time (τ) is calculated using equation 6.

$$\tau = \frac{m_c}{F_V \cdot P} \quad (6)$$

Where m_c (g) is the amount of sludge based catalysts, F_V (mL/min) is the volumetric flow rate and P (g/mL) is the density of the solution.

The experiment points were used to validate the first-order kinetic model by plotting the conversion as a function of space time (min). The experimental points were good fitted to first-order kinetic model, and kinetic constants were 0.40, 0.92 and 1.46 min⁻¹ for SBCZN800, SBCPC800 and CAC respectively. The SBCZN800 and CAC materials are the best suitable materials and well fitted to first-order kinetic model in the packed bed reactor system. Whereas, SBCPC800 material was unsuitable fit to first-order kinetic model.

The addition of chemical agents (1 Mol/L) greatly stimulated the azo dye reduction. In the presence of lower metal content could be avoid the anti-microbial effects. It has been reported that the higher concentration of metal content can diminished the microbial population [Petros et al., 2008]. The experimental result shows the new solids act as an effective biological supporting catalyst. The performance of catalyst using potassium carbonate shows lower conversion rates and the presence of zinc chloride catalyst obtained good conversion of 53 % at a space time in 1.0 min. The SBCZN800 material shows the greater degree of catalytic performance than the SBCPC800. In our previous, study has been also reported the goodness of SBCZN800 solid for the removal of acid orange II [26]. Only 25 % of dye removal was achieved for SBCPC800 catalyst. Dye removal is 98 % in 4.0 min and 87 % for SBCZN800 material at a space in 2.0 min operation. 91 % of dye conversion in 4.0 min and 74 % in 2.0 min was achieved for SBCPC800 compared to CAC. High dye removal of 99.95 % at 4.0 min, 92.20 % at 2.0 min, 73.24 % at 1 min, 58.14 % at 0.5 and 30.10 % at 0.25 min were measured for CAC respectively.

In batch experiment, the performance of sludge based catalyst was showed less adsorption capacity. High tartrazine dye removal was measured using catalysts origin from waste sludge biomass, even in a minutes of operation. The catalytic activity of SBCZN800 catalyst is only comparable to that of CAC. The experimental results revealed that performance of solids in the anaerobic reduction of tartrazine dye can dependent on the several factors including, chemical agents, carbonization, microbial population, chemical groups and surface chemistry.

Figure 7

Figure 8 shows the proposed mechanism for anaerobic reduction of tartrazine dye in the UPBR reactor system. The solid sludge catalysts and microbial population combine acted for the anaerobic reduction process of azo dye. Chemical particle such as potassium or zinc also enhanced the anaerobic reduction. The chemical groups such as quinone and C=O molecule was detected in the FTIR spectra. It is believed that the quinone molecule in the surface of sludge carbon material act as an immobilized redox mediator. The presence of microbial on the solid sludge carbon surface could act as an electron acceptor. Based on the all evidence, a possible anaerobic mechanism of sludge catalysts could be proposed. It is suggested that sludge carbon accepts the electron from the microbial activity and transfers the electrons to tartrazine dye molecule, further accelerating the biological reduction process to cleavage of -N=N- (azo bond) forms colorless amines. The several metal fractions, chemical groups and crystalline contents are identified in the solid material, which also enhanced the anaerobic reduction process. All the supporting evidence is equally contributed in the anaerobic reduction of azo dye tartrazine.

Figure 8.

The catalysts stability was checked during the 30 days continuous experiment in the UPBR reactor system. Figure 9 shows the reduction of tartrazine during the 30-days continuous operations at a space time in 2 min. The samples were collected at regular intervals of each day. During the 30-days continuous operation, nearly 10 samples were taken and analyzed the dye removal rates. The observation that the removal rates of tartrazine was almost similar trend in all the solids. Dye removal levels of 85, 73 and 92 % were achieved for SBCZN800, SBCPC800 and CAC respectively. The result shows the new solids have high

catalytic stability could be working for long term operation in packed bed reactor, even without any defects of surface textures.

Figure 9

The solid catalyst when they were introduced in the batch and continuous experiment was totally different. High removal level of tartrazine was achieved for continuous packed bed reactor operation. All the evidence suggested that the newly obtained solids have special synergistic activity when they were applied in the biological catalysts. There was very limited adsorption capacity observed in the batch experiment. The adsorption isotherm result shows that new solids have less adsorptive properties which acted only inert materials in the batch experiment. This work offers new paradigm opportunities for the environmentally acceptable reuse of harmful sludges and microbial population for the removal of hazardous pollutants from the water and wastewaters.

4. Conclusions

The performance of new solids for anaerobic decolorization of tartrazine dye was successfully investigated in continuous UPBR system. Almost complete biodecolorization of tartrazine dye was achieved at a very short space time. The results revealed that the surface textures, and catalytic performances of solids were highly impacted by chemical addition followed carbonization. Experimental points are well fitted to a first-order kinetic model that describes the behaviors of packed bed reactor operation. Based on these findings of new solids from the harmful sludge materials can be used as cost effective material for the removal of industrial effluents.

Acknowledgments

Financial support for this research was provided by the Spanish Ministerio de Educación y Ciencia and FEDER, projects CTM2008-03338 and CTM2011-23069. To acknowledge the doctoral fellowship from the Universitat Rovira i Virgili (Tarragona, Spain), for the financial support (2010BRDI/06–35). The author's research group is recognised by the Comissionat per a Universitats i Recerca del DIUE de la Generalitat de Catalunya (2009SGR865) and supported by the Universitat Rovira i Virgili (2010PFR-URV-B2-41).

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Fig.1. Nitrogen adsorption/desorptions isotherms of the dried sludge and sludge based catalyst.

Fig.2. SEM images of the dried sludge and sludge based catalyst.

Fig.3. TG-DTG curves of the dried sludge and sludge based catalyst.

Fig.4. XRD patterns of the dried sludge and sludge based catalyst.

Fig.5. FTIR spectra of the dried sludge and sludge based catalyst.

Fig.6. Linearized plots of the Langmuir and Freundlich models of sludge based catalysts.

Fig.7 Catalytic performances of the carbonaceous materials and commercial activated carbons.

Fig.8. Proposed mechanism for tartrazine dye in the UPBR reactor system.

Fig.9. Decolorisation of tartrazine during 30 days continuous operations at space time in 2 min

Figure 1

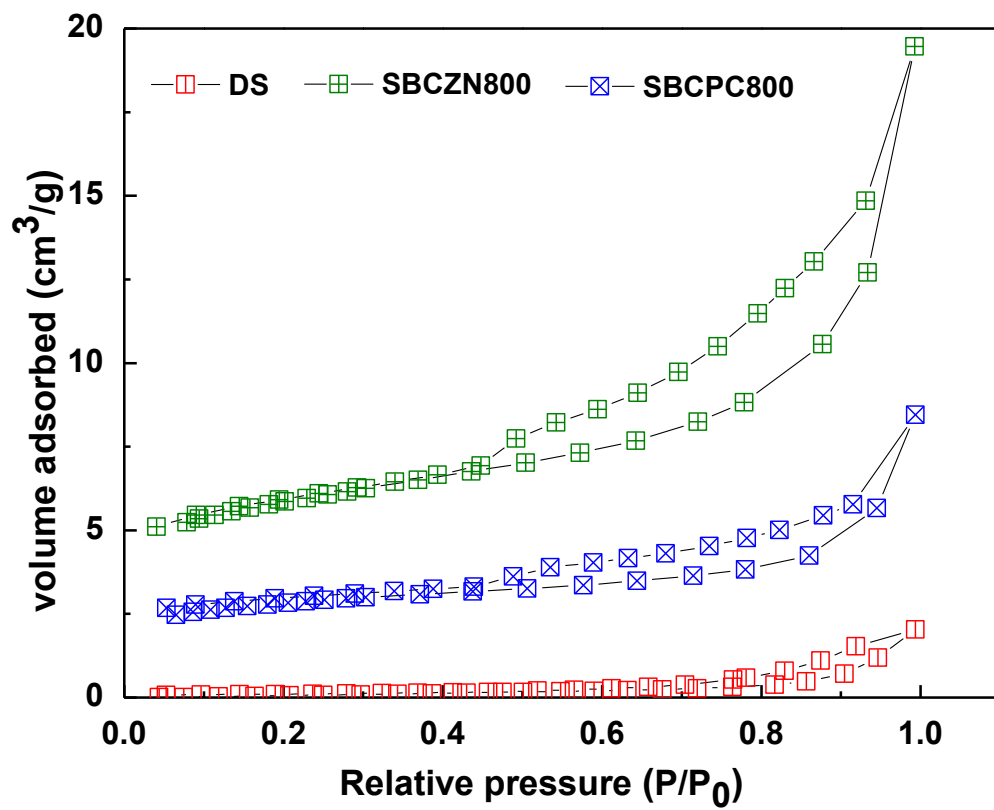


Figure 2

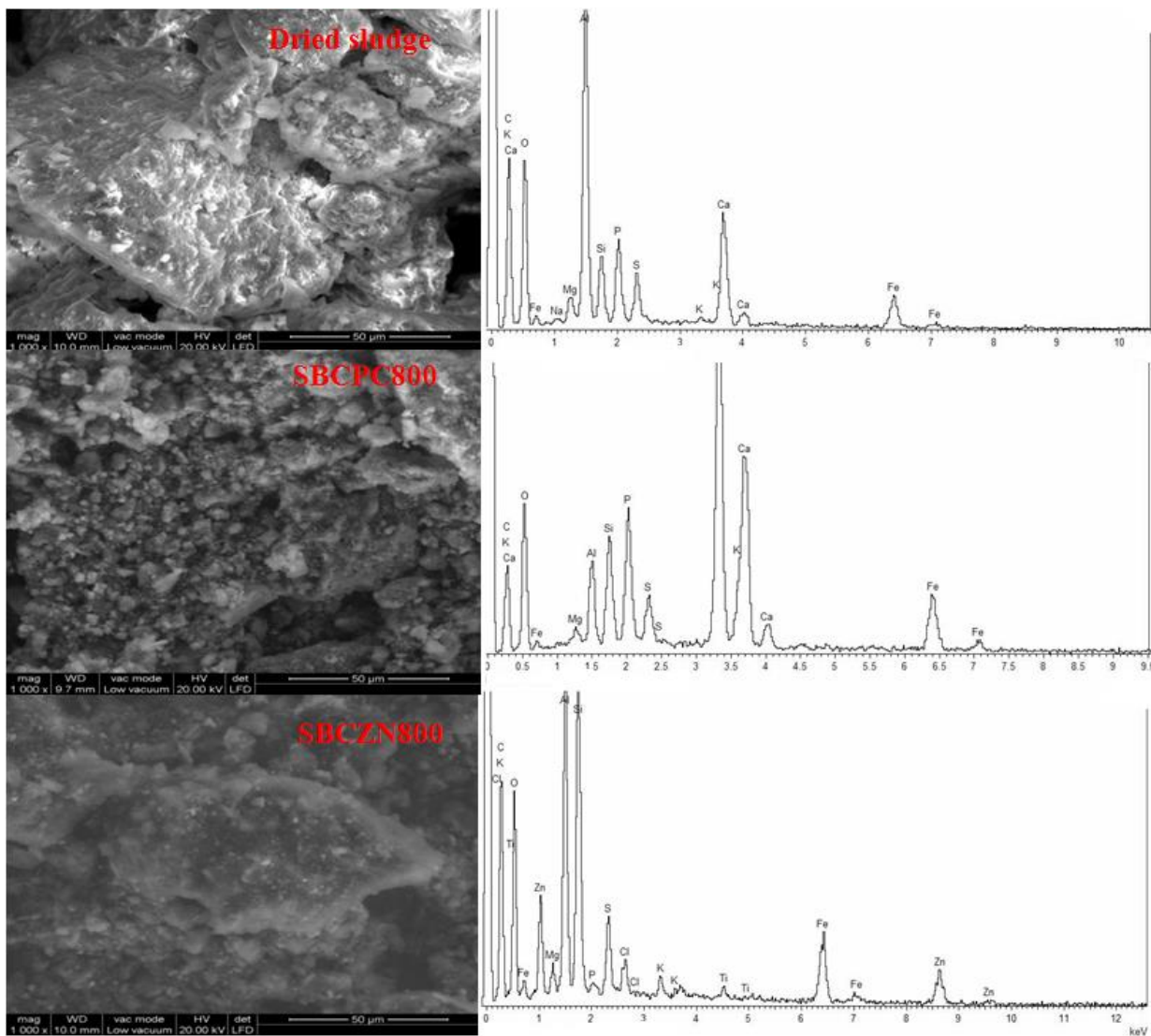


Figure 3

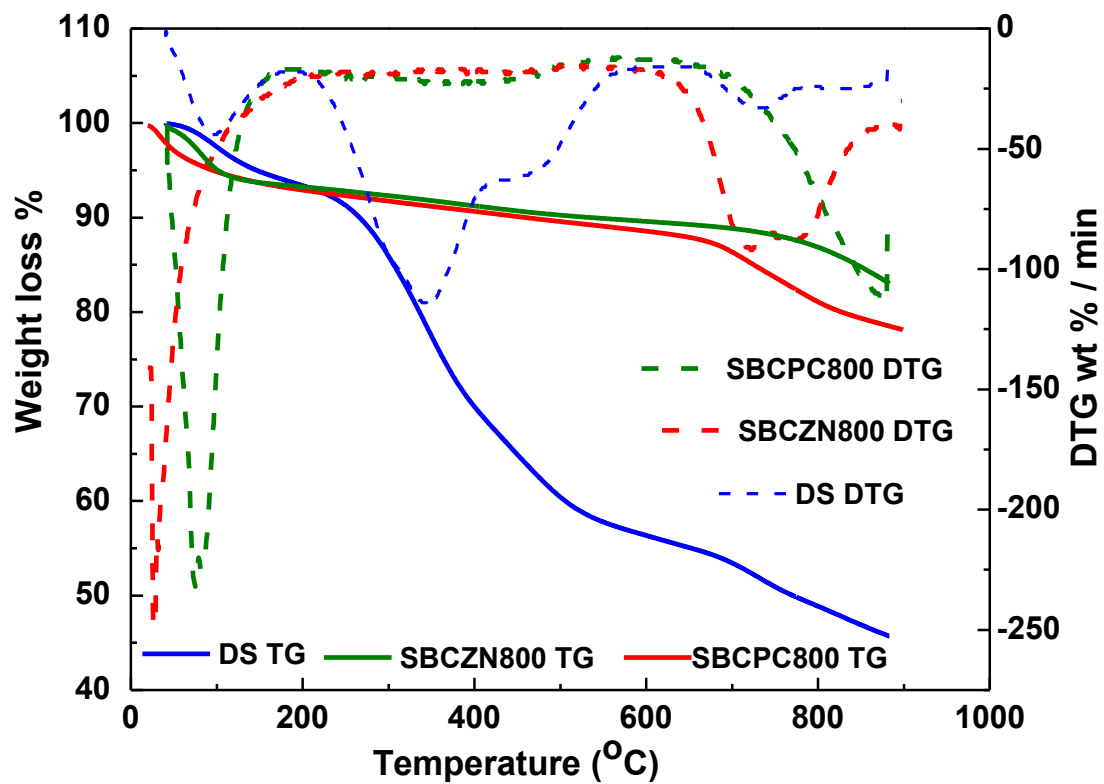
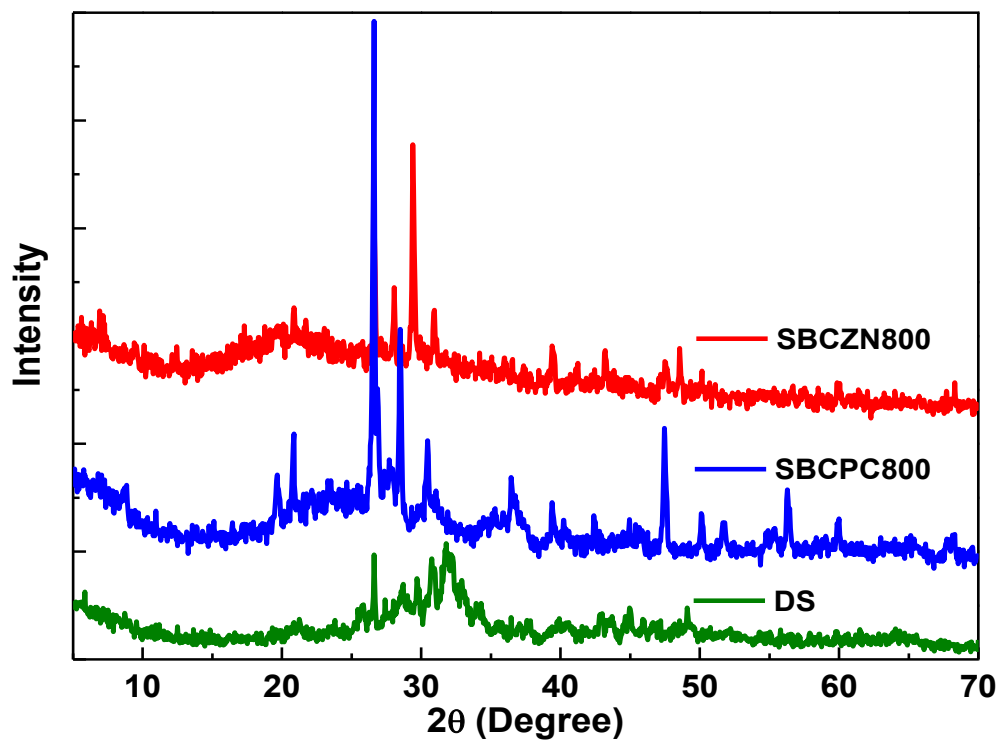


Figure 4



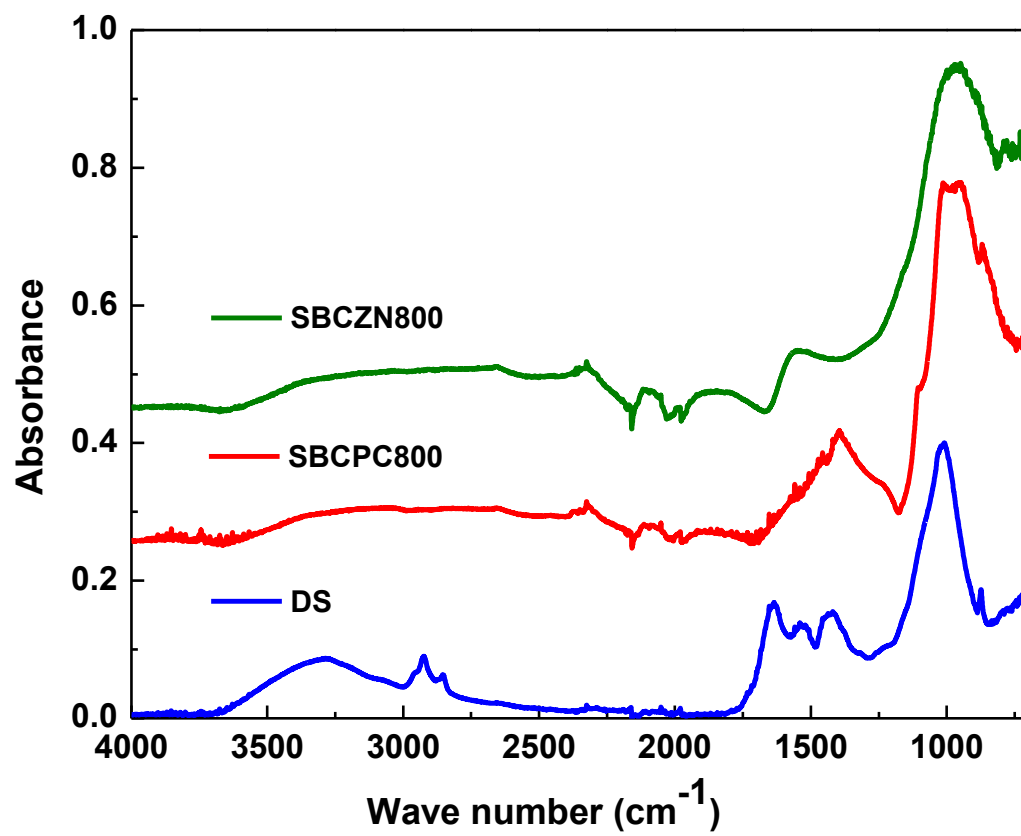


Figure 6

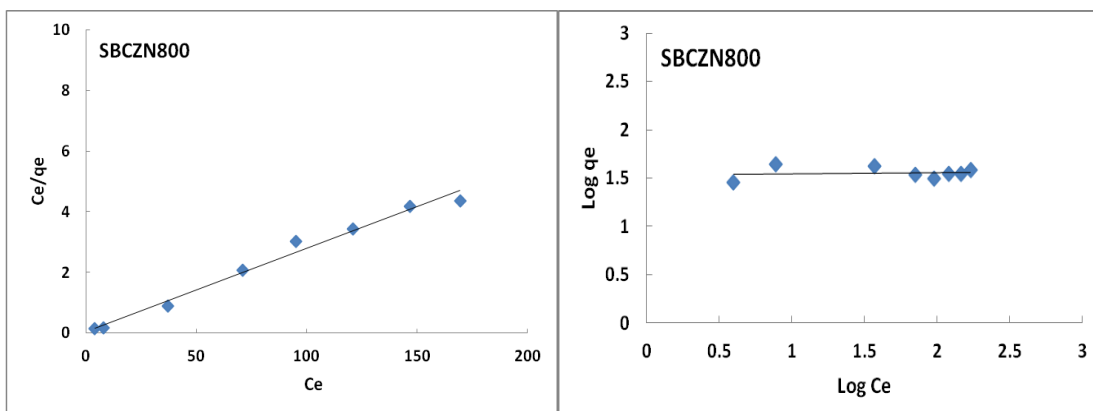
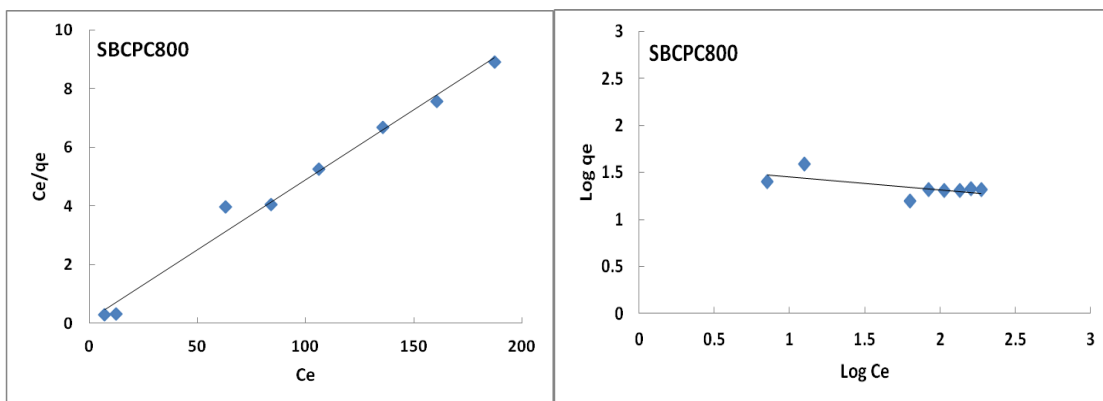


Figure 7

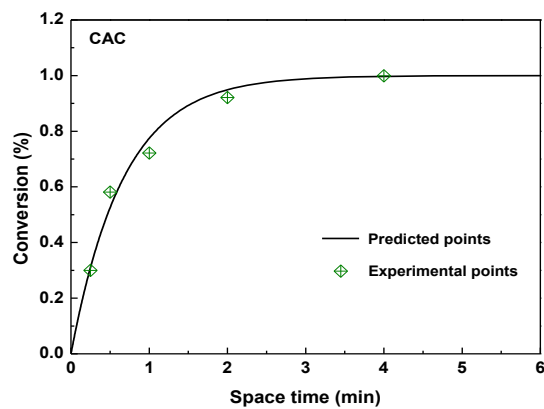
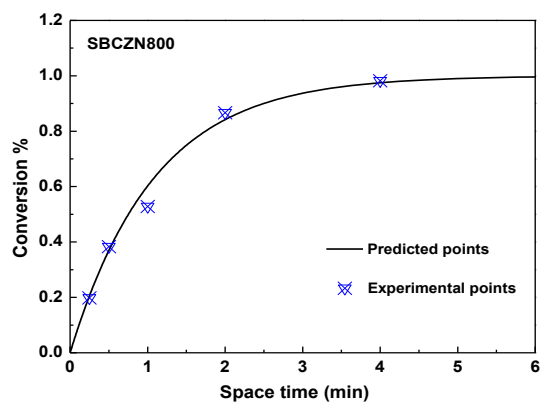
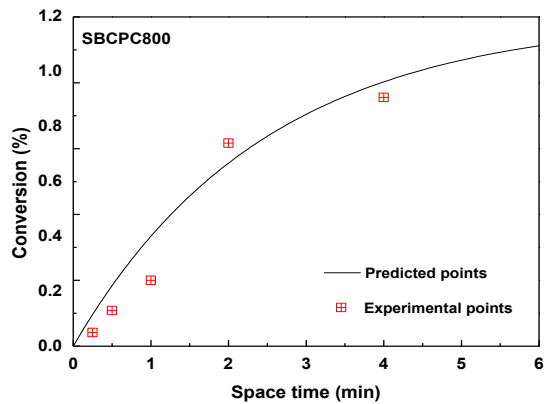


Figure 8

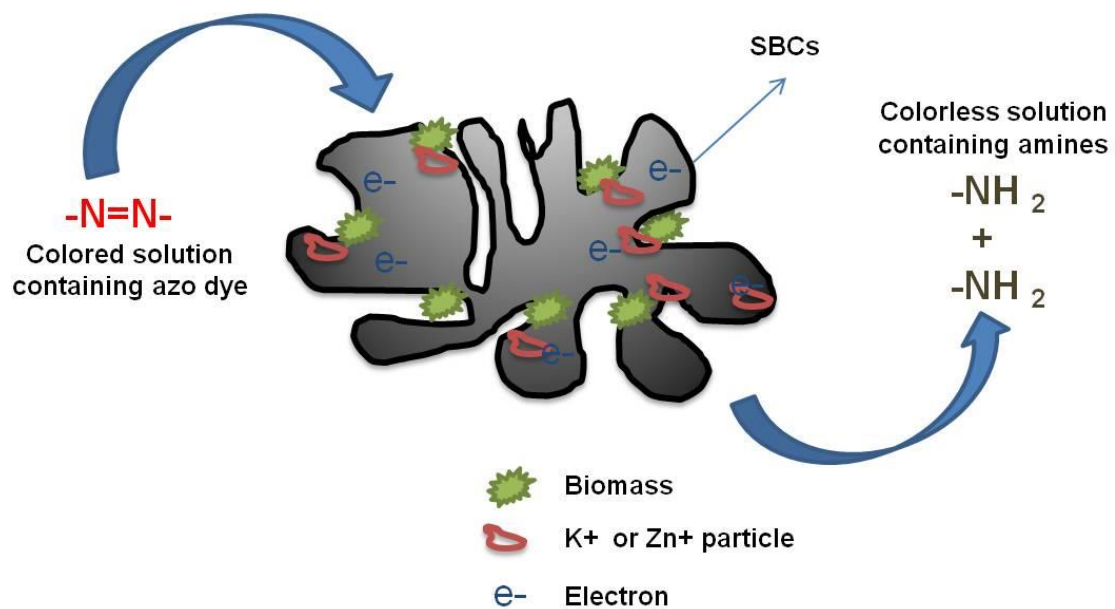
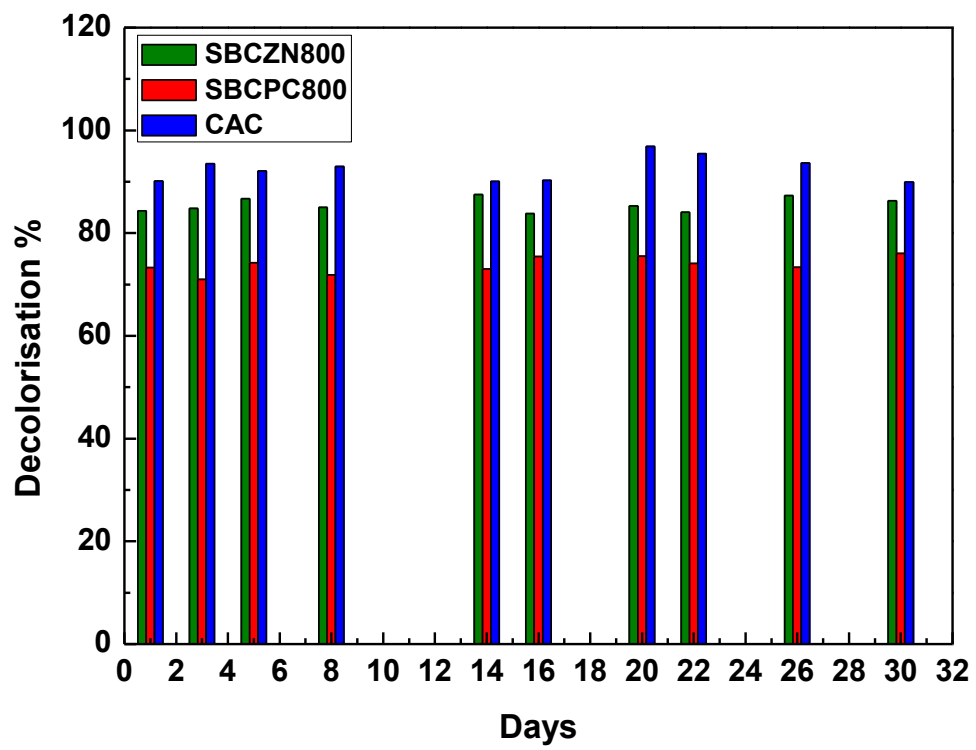


Figure 9



Highlights:

- Cost effective sludge based catalysts were prepared by simple method
- Solids were stable to adjust with anaerobic culture for long-term
- Langmuir isotherm with adsorption capacity of SBCZN800 was 38.0 mg/g
- High tartrazine removal was achieved at a very short space time.

Graphical abstract

