Journal of Environmental Chemical Engineering 3 (2015) 104–112

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

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

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

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ARTICLE INFO

Article history:
Received 23 January 2014
Accepted 1 July 2014
Available online 8 July 2014

Keywords:
Anaerobic reactor
Biodecolorization
Biofilm
Carbonaceous materials
Impregnation process

ABSTRACT

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

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 colored, 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, algae and bacteria) in the biological 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 algae 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].

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http://dx.doi.org/10.1016/j.jece.2014.07.002
2213-3437/

The biological treatment is one of the best options for the destruction of azo-dyes, considered as environmentally safe and cost effective methods [8]. Till 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.

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 sulfate ($FeSO_4{\cdot}7H_2O$) 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. 1 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 °C 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 (0.5–0.7 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 °C 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 6.0–7.0 and, finally, the product was dried in an oven at 105 °C for 15 h. 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™ SI Quantachrome 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 (PerkinElmer 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 °C). The pH of the solutions was maintained without any control and the flasks 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 Eq. (1):

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