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Color removal from anaerobic/aerobic treatment effluent of bakery yeast wastewater by polyaniline/beidellite composite materials

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ABSTRACT

The adsorption technique is widely applied for the removal of pollutants from wastewater, especially for toxic or non-biodegradable wastewater. In recent years, the production of alternative adsorbents to replace costly adsorbents has been paid more attention to in literature. Polyaniline/beidellite (PAn + Bei) composite material as an absorbent, which is efficient and low cost can easily be prepared via H_2SO_4, KIO_3 and aniline. This paper deals with color and total organic carbon (TOC) removal of biologically treated bakery yeast wastewater (BYW) using the PAn + Bei composite material by adsorption processes. The effects of experimental variables were chosen as the initial pH (pH_i), sorbent dosage (m_s), contact time (t_c) and mixing speed (s) by a batch sorption process. It was found that by increasing the adsorbent dosage (0.025–0.400 g/50 ml of composite dosage), contact time (2–240 min) and decreasing the pH_i (9–3) improved the color and TOC removal efficiencies. The optimum color and TOC removal efficiencies were obtained as 88.7% and 63.3% at 0.400 g/50 ml of adsorbent dosage, a pH_i of 3, 240 rpm, and 240 min. In addition, a pseudo-second order kinetic model was proposed to correlate the experimental data. To understand the removal mechanism and characterize the surface of the PAn + Bei composite material, size exclusion chromatography (SEC), BET surface analysis, fourier transform infrared spectroscopy (FTIR) analysis, scanning electron microscope (SEM), thermal gravimetric analysis (TGA), and differential scanning calorimetry (DSC) were employed. As a consequence, the proposed mechanism for the removal by PAn+Bei composite material seems to be driven by an ion exchange process.

1. Introduction

Baker's yeast production by fermentation uses molasses as a raw material which is a by-product of the sugar industry. Due to the molasses, baker's yeast wastewater (BYW) has a high organic content and dark brown color. Melanoidins are the source of this dark brown color in BYW which is resistant to biodegradation. Melanoidins restrict the sunlight and make a reduction in the natural photochemical process for self-purification of the surface waters [1,2].

Various treatment methods such as a biological process (anaerobic, aerobic), physico-chemical treatment (adsorption, membrane process, reverse osmosis, coagulation/flocculation, electrocoagulation) and oxidation processes (ozone, Fenton) have been performed for the treatment of BYW [3,4]. Nowadays biological treatment of BYW is realized by combinations of anaerobic digestion and aerobic systems that successfully reduce BOD and COD to acceptable limits, but do not deal effectively with the dark color and limits the reuse/recycling of the process water.

Treatment by oxidation technology is generally effective on the color, but not COD, membrane filtration processes are prone to fouling [5,6], and reverse osmosis generates a high salinity that presents disposal difficulties [7]. Coagulation removes color and COD effectively, but possesses a number of drawbacks such as necessities for high quantity of inorganic coagulants. Decolorization through chemical treatment by ozone, Fenton's reagent and H_2O_2/UV lead to temporary color reduction because of the transformation of the chromophores [8–11].

For these reasons, the BYW requires an alternative treatment technology which is relatively simple and effective in the removal of color before its safe disposal into the environment. Adsorption techniques are widely used to remove pollutants from the water, especially those that are toxic and not easily biodegradable. The studies focused on the production of alternative adsorbents to replace the costly ones reported in literature. Attention has focused on composite materials which are generally produced with various natural solids such as beidellite, cheap natural clay, and polymeric materials like polyaniline (PAn) for the effective removal of

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pollutants when compared with other polymeric materials. PAn has a large variety of advantages such as high removal efficiencies, low cost, easy synthesis, both chemically (powder form) and electrochemically (a film), and environmental stability. Thus, studies have focused on the production of PAn coated different composite materials recently [12,13]. In literature, sawdust [14–17], rice husk and saw dust of *Eucalyptus camaldulensis* [18], palygorskite [19], montmorrillonite [20], silica gel [21] were coated by polyaniline for the removal of pollutants from water/wastewater.

The novelty of this study is the production of a new composite material by coating beidellite with aniline to use it for color and TOC removal of biological treated baker's yeast wastewater for the first time. The effects of the variables such as initial pH (pH_i), sorbent dosage (m_s), contact time (t_c) and mixing speed (s) on the adsorption were examined by using a batch method. Several kinetic mechanisms were applied on data and molecular weight distributions (MWDs) were monitored during treatment by SEC. SEM, TGA, BET surface analysis, DSC, and FTIR were used to characterize the PAn + Bei composite materials.

2. Materials and methods

2.1. Preparation of beidellite/polyaniline composite

Beidellite is a dioctahedral smectite named after Beidell, CO, USA. Large deposits of beidellite minerals were explored in different locations of Turkey [22]. It was used for daily cleaning processes in the Black Sea region of Turkey. PAn is a poly aromatic amine that can be easily synthesized chemically from Brønsted acidic aqueous solutions. It is one of the most potentially conducting polymers and has obtained considerable attention in recent years. Chemical polymerization of aniline in aqueous acidic media (Brønsted acid) can easily be performed by the use of chemical oxidizing agents such as $(NH)_4S_2O_8$, KIO_3 and $K_2Cr_2O_7$ as shown in Fig. 1 [23]. There are a few studies regarding the production of polyaniline composites material in which different coated material, oxidizer, acid types and production processes were used. Ansari [14] and Ghorbani et al. [24], have produced different polyaniline composite materials by similar production processes with this study. Ghorbani et al. [24], produced the polyaniline and polypyrrole composites material for treatment of a real wastewater, paper mill wastewater, and the results showed that polyaniline/polypyrrole composite material have an important potential for using pollutants from real wastewater. In this study, preliminary studies were realized according to literature, then the production conditions of Ansari [14] and Ghorbani et al., were modified for production of PAn + Bei composite materials. For preparation of composite materials, 1 g of beidellite was added to 100 ml H_2SO_4 (1 M) solution and the solution was mixed at a stirring rate of 500 rpm [25]. Then, 1 g KIO_3 was added at room temperature and 1 ml of aniline monomer was injected slowly. The polymerization was carried out at room temperature for 2 h. In order to remove the unreacted monomers and oxidants, the final product was washed thoroughly with 500 ml of deionized water. Then, the product was dried at 60 °C for 24 h. The beidellite was used as received without any pretreatment.

2.2. Experimental set-up and analytical methods

The anaerobic-aerobic treated wastewater was obtained from the baker yeast production industry in Turkey and batch adsorption tests were carried out in a NUVE ST-402 model shaker. TOC levels were determined through combustion of the samples at 680 °C using a non-dispersive IR source (Shimadzu, TOC-L model). The pH of the sample was adjusted with H_2SO_4 or NaOH and measured by a pH meter (WTW Inolab pH 720) and the color of the wastewater was measured utilizing a UV–Vis spectrophotometer at 475 nm (PerkinElmer 550 SE).

JEOL 6.060 type scanning electron microscopy (SEM) was used to obtain SEM images. The FTIR spectra of the beidellite and PAn + Bei composite material were recorded on a PerkinElmer Spectrum 100. The TGA curves were performed on a Mettler Toledo TGA 1 Star Sytem at a heating rate of 15 °C/min from room temperature to 1000 °C. For DSC analysis, a Mettler Toledo DSC1 instrument was used. The BET surface area was measured from the N_2 adsorption/desorption isotherms with a Micromeritics ASAP 2010 analyzer (US).

The MWD was determined using HPSEC with a Hewlett–Packard HPLC 1100-series system equipped with a refractive index (RI) detector, a diode array detector (DAD) and two ultrahydrogel (Waters, Product Number: WAT011535 and WAT011525) columns. RID measures change in refractive index and its unit was called "Refractive Index Units (nRIU)". DAD is a type of UV–vis detector and its unit was named as absorbance unit (AU) at any wavelength. Deionized water at a flow rate of 1 ml/min was used as the mobile phase. The results were calibrated using 1 g/l of polyethylene oxide with different molecular weights (25.3, 44.0, 78.3, 152.0 and 326.0 kDa). The weight-average molecular weight (M_w) and number-average molecular weight (M_n) were calculated from the data using the following equations [26] and these calculations were processed by ChemStation software.

$$M_w = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i} \quad (1)$$

$$M_n = \frac{\sum_i n_i M_i}{\sum n_i} \quad (2)$$

M_i and n_i are the molecular weight and the height of each ith fraction eluted at the ith volume in the chromatogram, respectively. The polydispersity index (PDI) or heterogeneity index, is a measure of the distribution of molecular mass in a given polymer sample. PDI is calculated from M_w/M_n.

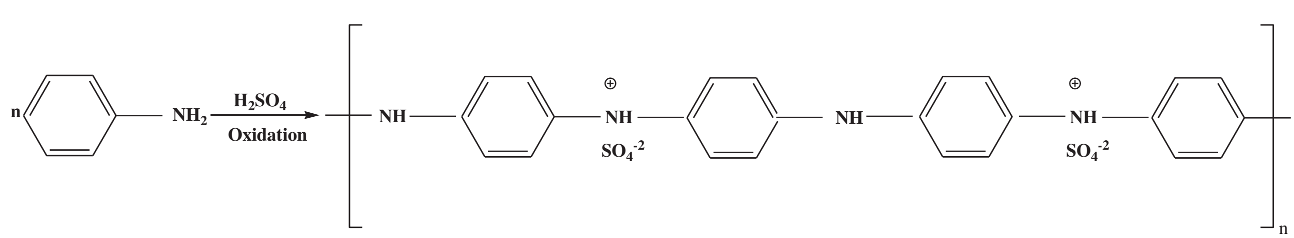

Fig. 1. Overall polymerization reaction of polyaniline [23].