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Preparation of dye waste-barium sulfate hybrid adsorbent and application in organic wastewater treatment

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ABSTRACT

A new hybrid material was developed by the template-free hybridization of weak acidic pink red B (APRB, C.I. 18073) with $BaSO_4$. The composition and structure of the material were determined and characterized. In contrast to conventional sorbents, the hybrid material has a specific surface area of 0.89 m^2/g, but it contains lots of negative charges and lipophilic groups as the basis of specific adsorption. The efficient removal of cationic dyes and persistent organic pollutants (POPs) indicates that it has an improved adsorption capacity and selectivity with a short removal time less than 2 min; while the hybrid sorbents fit the Langmuir isotherm model, and follow the octanol–water partition law. Instead of using APRB reagent, an APRB-producing wastewater was reused to prepare the cost-effective sorbent, and the equilibrium adsorption capacities of which reached 222 and 160 mg/g for EV and BPR, respectively. The sorbents was then used to treat three wastewater samples with satisfactory results of over 97% decolonization and 88% COD-decreasing. In addition, the hybrid sorbent was regenerated from sludge over five cycles, and its adsorption capacity was not appreciably changed. This work has developed a simple and eco-friendly method for synthesizing a practical and efficient sorbent.

1. Introduction

Recently, global economic prosperity has caused rapid growth and extensive development of the textile industry. Over 100,000 dyes have been synthesized worldwide, and more than 700,000 tonnes are produced annually. More than 10,000 dyes are commercially available, but over 5% is discharged into aquatic environments by plants and users [1]. During the dye production and use, highly concentrated dye wastewater is drained into environmental water without being effectively treated, especially in developing countries. For example, many dye-producing and -using plants are located throughout the Yangtze Delta Area of China, the drinking water sources of the Yangtze River and Taihu Lake. These water bodies have been greatly harmed, badly disrupting both the normal lives of people in this region and local economic development [2,3]. Dyes are classified as follows: anionic/direct, acidic and reactive; cationic/basic; and non-ionic disperse dyes, over 80% of which are of the aromatic azo type. Such dyes are frequently used for fabrics; therefore, they are expected to be adherent, long lasting and resistant to sunlight and chemical processes. Moreover, fabric dyes should not fade through oxidation during normal washing. Therefore, such dyes are usually stable in acidic and alkaline media and resistant to temperature, heat, light and microbes [4], and that gives them the potential for persistence and long-term accumulation in the environment. Most azo dyes are toxic, carcinogenic and mutagenic, causing allergies, dermatitis, skin irritation, cancer and mutations in humans [5]. Therefore, regulation of dye discharge and dye-polluted or -colored wastewater has become increasingly stringent in many countries.

The removal, decolorization, mineralization and decomposition of azo compounds in dye wastewater are very important. In recent years, conventional abiotic techniques have been widely developed and applied in the treatment of azo dye wastewater. These techniques can be divided into separative treatments, including adsorption, flocculation, ion exchange and membrane filtration; and destructive treatments, including electrolysis, oxidation and reduction. Some of them have proved effective, but they often have serious limitations. For instance, activated carbon is the most efficient and popular adsorbent, so it is often used to treat variable wastewater [6]. However, chemical and thermal regeneration of spent carbon are both expensive and impractical on a large scale; also, they produce additional effluent and result in considerable adsorbent loss. Natural substances have also been used as sorbents, *e.g.* wood dust, bentonite and waste solids [7–10]. Adsorption by conventional sorbents generally depends on the specific surface area, so low adsorption capacity, poor selectivity, slow

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Abbreviations: APRB, weak acidic pink red B; EV, ethyl violet; MB, methylene blue; WAG, weak acidic green GS; BPR, basic pink red B; ABB, acidic brilliant blue 6B; CBR, cationic brilliant red 5GN; POPs, persistent organic pollutants; Phe, phenanthrene; Flu, fluorene; Bip, biphenyl; BPA, biphenol A.

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adsorption rate and difficult reproduction [11] restrict the extensive use of most sorbents. Furthermore, membrane filtration is slow and entails a high cost of use, while flocculation entails several problems, including color reversion of treated water and disposal of sludge with high water content; and destructive treatments with high cost often cause secondary pollution. Thoughtfully, the "using waste to treat waste" paradigm in the treatment of wastewater is often adopted because waste reuse is an optimal solution [12]. Recently, some wastes have been reused and applied in the treatment of dyes wastewater, such as fly ash [10,13], de-oiled soya [14], wheat husk [15] and so on [8,16], which do significant contributions to the pollution control and resource reuse partly.

There has been a great deal of interest in the design and synthesis of inorganic/organic complex materials to achieve specific properties. Various synthesis techniques developed during the last few years have given us access to functional materials with characteristics such as surface modification, inorganic/organic hybridization and functional ligand-loading [17,18]. These materials have been widely applied in various fields such as films, catalysts and pharmaceutical products [19–21]. A dye with a functional group that absorbs visible light is often used to prepare hybrid materials for application to solar cells and sensors [22,23]. However, these synthesis methods often require complicated procedures, strict conditions and high purity reagents [24].

Adsorptive precipitation was discovered during the mid 20th century and applied mostly in analytical chemistry [25]. The classical co-precipitation method has been extensively applied to the enrichment of metal ions [26] and the synthesis of functionalized materials [24]. As a conventional dyes, weak acidic pink red B (APRB) shows good electrophilicity and hydrophobicity, due to containing two negative sulfonic acid groups and a long hydrophobic alkyl chain. It attracted us whether a novel absorbent can be synthesized through co-precipitation hybrid of APRB with some appropriate inorganic skeleton. If feasible, a new idea is inspired: based on the selective of co-precipitation to some extent, concentrated APRB-producing wastewater should also be reused as a reactant to prepare a more cost-effective sorbent applicable to the treatment of organic wastewater. In this work, both of clean and waste APRB were applied as the active species and $BaSO_4$ as the skeleton to construct novel adsorbents successfully. The removal of cationic dyes and POPs indicated that it has a high adsorption capacity caused by charge attraction and hydrophobic stack. Moreover, recurrent regeneration of the sorbent by acidifying sludge was tested for reuse.

2. Experimental

2.1. Materials

The APRB reagent (content > 98%) and an APRB-producing wastewater were provided by the Zhejiang Shuanghong Chemical Plant. The dyes: ethyl violet (EV, C.I. 42600), methylene blue (MB, C.I. 52015), weak acidic green GS (WAG, C.I. 61580), basic pink red B (BPR, C.I. 50240) and acidic brilliant blue 6B (ABB, C.I. 42660) (purity > 95%) and the POPs: phenanthrene (Phe), fluorene (Flu), biphenyl (Bip) and biphenol A (BPA) (purity > 99.9%) were purchased from Sigma. The MB and cationic brilliant red 5GN (CBR, C.I. 48016) wastewaters were sampled from two dye plants, and the POPs wastewater was taken from a chemical plant. Inorganic substances, including the skeleton reactants $BaCl_2$ and Na_2SO_4, were purchased (A.R. grade) from the Shanghai Medical Group.

2.2. Synthesis of the materials

The $BaSO_4$–APRB hybrid sorbent liquid was prepared in the addition sequence: SO_4^{2-}–APRB–Ba^{2+}, with molar ratios 1.5:0.2:1. Using the same method, the $BaSO_4$–APRB surface-modified material was prepared in the sequence ethanol–SO_4^{2-}–Ba^{2+}–APRB, and the $BaSO_4$-only liquid was prepared in the absence of APRB. The solid contents of the liquids and the concentrations of APRB, Ba^{2+} and SO_4^{2-} in the material solids were determined by spectrophotometry, Inductively coupled plasma optical emission spectrometer (ICP-OES) and ion chromatography (IC) after the solids were dissolved in ethylene diamine tetraacetic acid and ammonia (EDTA–ammonia). The thermal gravity analysis (TGA) data, X-ray diffractometer (XRD) curves and scanning electronic microscopy (SEM) images of the material powders were collected, and ζ-potentials and size distributions were determined. Transmission electronic microscopy equipped with energy dispersive X-ray spectroscopy (TEM-EDX) was used to determine the distributions of different elements in the hybrid material. BPR was used to measure the isoelectric point and K_d of the hybrid material. Instead of the commercial APRB reagent, the APRB-producing wastewater was reused to prepare a cost-effective hybrid sorbent, which was used in this work to treat the wastewaters.

2.3. Adsorption of dyes and POPs

Five dye solutions, WAG, ABB, EV, MB and BPR, were treated with the material. Their rates of removal were calculated and compared with those of the corresponding untreated dye solutions. As representative cationic dyes, EV and BPR were selected for investigating the mechanism of adsorption by the material. The molar amounts of EV and BPR bound to the material were calculated. A conventional sorbent, activated carbon powder, was compared with the hybrid sorbent. The effects of pH, ionic strength and temperature on the adsorption of EV were also determined. The POPs, Phe, Flu, Bip and BPA, were used to investigate the adsorption of hydrophobic organic substances by the sorbent. The treated supernatant was measured by spectrofluorometry and the rates of POPs removal were calculated. Furthermore, their K_{pw} values were calculated, and the relationship between the K_{ow} and K_{pw} of the POPs was established.

2.4. Treatment of wastewaters and reproduction of the sorbent

Two typical MB and CBR wastewaters were sampled from two cationic dye plants and one chemical plant. The $BaSO_4$–APRB hybrid sorbent directly prepared from the APRB-producing wastewater was used to treat them. The chromaticity and chemical oxygen demand (COD) of the dye wastewaters were determined, and their rates of removal were calculated and compared. The adsorption of POPs from the chemical wastewater was evaluated by high-performance liquid chromatography (HPLC) [27]. In addition, the sludge produced during treatment of the wastewaters was collected in a strongly acidic medium to regenerate the hybrid sorbent. Five cycles of adsorption–precipitation–recovery were performed, and the efficacy of the regenerated absorbent in treating both the dye wastewaters was examined.

The details on the experimental procedures and characterization with a more detailed description have been summarized in Supporting Information (SI) File.

3. Results and discussion

3.1. Optimization of the synthesis conditions

The reactants were added in different sequences (Fig. S1 in SI). The first addition sequence, SO_4^{2-}–Ba^{2+}–APRB, was found to result in the lowest amount of APRB captured. This is because $BaSO_4$ particles were formed before the APRB was added, so APRB could only be adsorbed on the outer surface of the $BaSO_4$ particles.