



Chitosan–alunite composite: An effective dye remover with high sorption, regeneration and application potential



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ABSTRACT

This study was undertaken to prepare a novel and environmentally friendly composite for the use in the wastewater treatment process. This composite was produced by immobilizing alunite with a glucosamine biopolymer, chitosan. Batch and dynamic flow mode decolorization potential of the chitosan–alunite composite (CAC) was systematically evaluated in Acid Red 1 (AR1) and Reactive Red 2 (RR2) contaminated media. pH, sorbent dosage, contact time and flow rate were screened through the sorption experiments. Equilibrium sorption experiments indicated that CAC has very high sorption potential for RR2 and AR1 dyes with the maximum sorption capacities of 462.74 and 588.75 mg g⁻¹, respectively. Good regeneration and reuse potential in 20 consecutive cycles are other important advantages of this composite. More importantly, CAC could also be used in the treatment of real wastewater without performance decrease. Overall, this study suggests that CAC is a promising sorbent for the removal of anionic dyes from aqueous solutions.

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1. Introduction

Pollution of the natural water sources by synthetic dye contaminants through the uncontrolled discharge of the colored effluents is a worldwide environmental problem. These types of effluents are generally considered to be highly toxic to the living systems. In addition to their potential toxicities, dye molecules in the aquatic media reduce the photosynthetic reactions and exhibited a great resistance to treatment. Therefore, efficient decolorization of contaminated effluents and water recycling are of great importance for the protection of human health and environmental quality (Vakili et al., 2014).

Different processes for decolorization of dye containing wastewaters typically include physical, chemical, electrical and biological origin. However, their uses are restricted because of high cost, low selectivity, sludge production, operational difficulty and potential toxic by-products. Moreover, the use of only one treatment process alone cannot be sufficient to completely remove the dye from wastewater. For this reason, a combination of these processes is necessary to achieve the desirable goal (Hao, Kim, & Chiang, 2000).

Among the wastewater treatment methods, adsorption has been recognized as one of the effective, convenient and most straightforward techniques for the removal of organic and

inorganic contaminants (Liu, Zeng, et al., 2015). It utilizes the different natural, pretreated and immobilized forms of sorbent materials (Asgher & Bhatti, 2010; Bayramoglu & Arica, 2011; Bayramoglu, Adiguzel, Ersoy, Yilmaz, & Arica, 2013; Bulgariu & Bulgariu, 2015; Dural, Cavas, Papageorgiou, & Katsaros, 2011; Sari, Tuzen, Citak, & Soylak, 2007). The use of immobilized sorbent materials in the treatment process provides some advantages over the corresponding natural and free forms of sorbents such as enhanced mechanical strength, good regeneration potential and ease of separation. Therefore, increased efforts were observed in the studies on the development of immobilized sorbents in recent years. In this context, different kinds of polymeric materials including polyacrylamide (Yi & Zhang, 2008; Zhou et al., 2011), polysulfone (Khalid et al., 2015; Vijayaraghavan & Yun, 2008), polyvinyl alcohol (PVA) (Tsekova, Todorova, Dencheva, & Ganeva, 2010), alginate (El-Sherbiny, Abdel-Hamid, Rashad, Ali, & Azab, 2013) and Kappa-carrageenan (Salgueiro, Daniel-da-Silva, Girão, Pinheiro, & Trindade, 2013) have been used as immobilization matrix for preparation of composite sorbent materials.

Chitosan is a natural polycationic biopolymer and attracts considerable attention because of its excellent properties such as hydrophilicity, non-toxicity, biocompatibility, and biodegradability. Chitosan and its derivatives offer properties with great potential for many fields, such as food, cosmetic, medicine and environment. Owing to active amine and hydroxyl groups present in its structure, chitosan is also characterized as potential sorbent for synthetic dyes and heavy metals (Jiang, Sun, Liu, Wang, & Tian, 2014; Kyzas, Lazaridis, & Kostoglou, 2013; Liu, Yang, Zhang, &

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Huang, 2015; Petrova, Pestov, Usoltseva, & Neudachina, 2015; Wan Ngah, Teong, & Hanafiah, 2011). Alunite is a kind of jarosite group mineral and is not soluble in aquatic media. This mineral containing approximately 50% of SiO₂, formed as a result of hydrothermal alteration of tuff. It is mainly used for the production of aluminum sulfate, potassium sulfate, potassium alum and alumina and evaluated as adsorbent in a few adsorption study (Akar, Tosun, Ozcan, & Gedikbey, 2010; Kavak, 2009; Özacar & Şengil, 2003; Özacar, 2003; Tunali, Özcan, Özcan, & Gedikbey, 2006).

Polymer/layered silicate composites are known to combine the physical and chemical properties of both inorganic and organic material (Zeng et al., 2015). In the present study we aimed to investigate the decolorization performance of the one composition of alunite and chitosan. To date, although the numbers of investigations have been documented on the formation of composites between chitosan and silica materials, to our knowledge, there is no report in the literature on the removal of AR1 and RR2 dyes by alunite-chitosan composite (CAC) material. IR spectroscopic and electron microscopic techniques were used for the characterization of the new sorbent and adsorption process. Batch mode decolorization process was evaluated by kinetic and isotherm models. We further showed through dynamic flow mode studies that CAC has high potential for use in large scale treatment.

2. Experimental

2.1. Dye solutions

Commercial textile dyes, Acid Red 1 (AR1) and Reactive Red 2 (RR2) were used in this study for target sorbates. They were purchased from Sigma–Aldrich and used without further purification. 1000 mg L⁻¹ stock solutions of AR1 and RR2 dyes were prepared by dissolving known amounts of dyes in deionized water. The concentrations of working solutions were obtained by diluting the stock solutions. 0.1 M HCl or 0.1 M NaOH solutions were used to adjust pH of the solutions.

2.2. Preparation of chitosan/alunite composite

Alunite mineral was provided from Kütahya, Turkey and crushed, ground using a laboratory mill and sieved to particle size of 150 µm. The powdered alunite was calcined at different temperatures of 400, 500, 600, 700 and 800 °C and calcined alunites were used for the preparation of composite material.

Chitosan was obtained from Sigma–Aldrich (CAS-No: 9012-76-4; deacetylation: ≥75.0%; viscosity: 20–300 cps; low molecular weight). Calcined alunite powders were ultrasonically dispersed in 60 mL of 5% (v/v) acetic acid solution. Alunite-chitosan (mass ratio: 1:2) suspension was injected into 500 mL of 0.50 M NaOH solution. Phase separation of the two components upon addition into NaOH was prevented by continuously stirring on a magnetic stirrer since alunite is insoluble in water and/or base solutions. In order to remove the excess NaOH, the wet beads were rigorously washed with distilled water, separated from the aqueous phase by filtration and dried in an oven. Dried beads were ground into powder by using a laboratory mill and sieved to constant particle size using an ASTM sieve (<300 µm). The final composites were weight and composite yields higher than ~85% were obtained. This small decrease in the composite yield could be attributed to the solid loss during the washing procedure.

2.3. Instrumentation

The surface morphology of the unloaded and dye loaded sorbent materials was studied using Park Systems XE-100 atomic force

microscope (AFM). For imaging, a freshly cleaved glass surface was used as substrate. The drop deposition method was used for sample preparation and 30 µL of sorbent suspension was employed. The prepared samples were allowed to rest at 25 °C for a few hours in a desiccator until imaging. The measurements were performed by non-contact mode with 300 kHz frequency and 0.50 Hz scan rate in air at room temperature. A silicon cantilever which has a spring constant of 40 N/m was used. An energy-dispersive X-ray analysis (JEOL 5600 LV SEM) was used to determine the elemental composition of the adsorbent. A zetasizer Nano ZS (Malvern Instruments, UK) was used for zeta potential measurement of the composite. IR spectral analysis was performed on a Bruker Tensor 27 IR spectrophotometer using KBr disk technique. UV/vis spectroscopy (Shimadzu UV-2550) was used to determine dye concentrations in the solutions.

2.4. Adsorption procedure

In batch adsorption studies, 25 mL of dye solutions with an initial concentration of 100 mg L⁻¹ of AR1 and RR2 was treated with a known amount of composite powder. During the adsorption experiments, the dyes were contacted with composite at room temperature and stirred at 200 rpm. The optimum adsorption conditions (initial pH, adsorbent dosage, contact time) were determined in the batch system. Adsorption isotherm studies were conducted in the solutions containing 5.0 and 10 mg adsorbent with AR1 and RR2 dyes, respectively. Initial dye concentrations were ranged between 25 and 500 mg L⁻¹. After a suitable time for adsorption equilibrium, mixtures were centrifuged at 4500 rpm, the supernatants were separated from solid phase and used to determine the dye concentration by UV spectrometry. The adsorbed amounts of dye onto per gram of adsorbent were calculated by the following relationship:

$$q_e = \frac{V(C_i - C_e)}{m} \quad (1)$$

where C_i and C_e are the initial and equilibrium concentrations (mol L⁻¹), m is the weight of composite (g) and V is the dye solution volume (L).

Column experiments were conducted for the adsorption of AR1 and RR2 dyes using a glass column (9 mm internal diameter) at optimum pH 3.0. Alunite/chitosan composite was packed between two layers of glass wool to provide a uniform solute flow in the column. The effects of bed height and flow rate on the adsorption of dye were investigated to optimize the process parameters.

Desorption performance of the composite was examined using 0.01 M NaOH as regeneration agent. Dye adsorption/desorption cycles were repeated for 20 times.

Desorption yield values at the end of each cycle were calculated as follow;

$$\text{Desorption yield (\%)} = \frac{\text{Desorbed dye concentration}}{\text{Adsorbed dye concentration}} \times 100 \quad (2)$$

3. Results and discussion

3.1. Characterization of alunite/chitosan composite

EDX (energy dispersive X-ray) analysis of the composite sorbent indicated that CAC has the following elemental composition; C: 34.87%, O: 46.50%, Mg: 1.16%, Ca: 0.72%, Na: 1.51%, K: 1.12%, S: 4.48%, Al: 3.36%, Si: 4.24%, Fe: 2.05%.

IR spectra of CAC before and after decolorization process are shown in Fig. 1(a). As can be seen from these figures CAC has complex surface structure. The absorption bands in the spectrum of CAC at the wavenumber region of 3480–3515 cm⁻¹ can be ascribed to overlapping of –OH and –NH stretching vibrations. The peak at

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