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Calcium alginate–bentonite–activated carbon composite beads as highly effective adsorbent for methylene blue

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HIGHLIGHTS

- An activated carbon–bentonite–alginate (ABA) composite was synthesized facilely.
- ABA showed a prominent existence of exchangeable cations.
- ABA was proven to be an extraordinary adsorbent for the removal of model dye methylene blue.
- The regenerated ABA was successfully employed several times for the adsorption.

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ABSTRACT

Three adsorbents, namely, bentonite–alginate beads, activated carbon–alginate beads, and activated carbon–bentonite–alginate beads (ABA) were prepared for the adsorption of methylene blue (MB). The effects of solution pH (3–11), temperature (30, 40, and 50 °C), initial concentration (25–500 mg/L), and contact time were investigated. Results showed that the maximum monolayer adsorption capacity of ABA beads for the adsorption of MB was 756.97 mg/g at 30 °C. Furthermore, the adsorption kinetics illustrated the suitability of employing the pseudo-second-order kinetic model. The equilibrium adsorption data fitted the Freundlich isotherm well. In addition, the ABA composite exhibited more than 70% adsorption uptake capacity after six regeneration cycles. The outcomes of this study suggest the potential of ABA composite for cationic dye removal.

1. Introduction

Dyes are broadly utilized in various industries, such as textile, paper, food, cosmetics, pharmaceuticals, and others. The effluents from these industries usually contain dyes, which cannot be removed by conventional processes. Some of the most commonly used dyes and their metabolites are carcinogenic and possess a potential health hazard to all forms of life. These compounds, without correct treatment, can be stabilized and remain in the water for a long time. For these reasons, colored effluents are a serious environmental problem, and thus, proper treatment processes need to be developed [1]. Several methods of wastewater treatment such as coagulation [2], aerobic or anaerobic digestion [3], advanced oxidation process [4], adsorption [5,6], and others have been effectively applied for the removal of various dye stuff from aqueous solutions. All these methods have advantages and disadvantages in terms of their effectiveness, cost, and environmental impact [7]. Adsorption has been vastly reported as the most widely used technique for the removal of toxic organic and inorganic micropollutants from wastewater because of its performance and ease of operation [8,9].

Activated carbon is an extensively used adsorbent applied for the removal of pollutants because of its high specific surface area and surface reactivity [10]. The main problem associated with activated carbon involves the costs of preparation and raw materials; however, this drawback can be alleviated by utilizing low-cost materials. Good operation techniques alone cannot ensure system sustainability if raw material supply is not perpetual. For these reasons, several revealing research works have highlighted the removal of different pollutants by several activated carbons produced from low-cost precursors [11].

Clay minerals have also been recognized as very good adsorbents because of their amazing textural properties, abundance,

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and inexpensiveness [12,13]. Errais et al. [12] extensively described the efficiency of raw clay minerals to uptake anionic dyes from a liquid solution. The Algerian bentonite-type clay has been widely used in catalysis [14], sorption of dyes [15], herbicides [16], metals, and drilling of oil wells for its rheological properties. A key issue in this context is that neat clay minerals are not very efficient in removing micropollutants from water compared with activated carbon because of their low surface area. Furthermore, the difficulty experienced in recovering clay particles from solutions after adsorption process makes them even less attractive as adsorbents for industrial water treatment. This problem ultimately makes regeneration of these colloidal particles quite difficult. In addition, clay minerals have a poor affinity for organics because the hydration of clay mineral surface tends to reduce the accessibility of the interlayer spaces to aromatic molecules. Thus, these clay minerals lose a substantial amount of their adsorption capacity when they are regenerated for reuse.

Alginates are natural polysaccharides that are produced by brown algae. Based on the exact nature of the seaweed species, they represent 10–45 wt.% of dry matter [17]. Their high bioavailability and easy extraction process explain their low cost. Alginates are widely used in many different applications because of their versatile properties that can be monitored according to different stimuli (concentration, temperature, pH, etc.). In aqueous solution, alginates are usually employed as thickening agents to increase the viscosity of the medium [18]. In the presence of cations (usually divalent or trivalent), they can produce a hydrogel according to a complexation mechanism. The transformation is known under the designation "ionotropic gelation." Given its biocompatibility, Ca^{2+} is the most applied and studied gelling agent [19]. Calcium alginate is widely used in immobilizing activated carbon [20], carbon nanotubes [21], titania nanoparticles [22], and magnetite nanoparticles [23] to create different adsorbents to remove wastes like dyes, pigments, and metals from aqueous solutions.

The individual features of activated carbon, bentonite, and alginate toward adsorption are not always very promising and identical; thus, the idea of combining them to make an effective composite material for dye removal was conceptualized. Moreover, the inherited problems linked with the individual adsorbents might be minimized by combining them. In this study, commercial powdered activated carbon named 'hydrodarco C' was used as activated carbon, which was produced by steam activation of lignite coal under carefully controlled conditions. Therefore, the objectives of this study were as follows: first, to prepare a variety of composite beads from the combination of bentonite–alginate beads (BA), activated carbon–alginate beads (AA), and activated carbon–bentonite–alginate beads (ABA) via a simple fabrication method; second, to compare and verify the best composite among the prepared samples; third, to evaluate the best composite as an adsorbent for the removal of the model dye methylene blue (MB) from aqueous solution; finally, to implement an easy regeneration technique and application to recover composite beads from solutions after adsorption.

2. Materials and methods

2.1. Chemicals

The bentonite clay was supplied by the Enterprise Nationale des Substances Utiles et des Produits Non Ferreux, Hammam Boughrara, Algeria, it was grinded to a particle size that ranges from 20 μm to 45 μm. Sodium alginate and calcium chloride were purchased from R&M Chemicals, R&M Marketing Essex, UK, and hydrodarco C was obtained from Norit Nederland. Methanol and methylene blue (chemical formula: $C_{16}H_{18}N_3SCl$, molecular weight: 319.85 g/mol, solubility in water: 40 g/L) were supplied by Merck Chemical Company. All other chemicals were used without any further purification. Deionized water was used for the preparation of all the required solutions.

2.2. Preparation of the ABA adsorbent

A 2% (w/v) sodium alginate solution was prepared by mixing 2 g of sodium alginate in 100 mL deionized water with stirring for 1 h, and then 2 g of bentonite clay and 2 g of hydrodarco c were added. The mixture was stirred overnight. When the mixture became homogeneous, it was dropped through a burette into 4% (w/v) calcium chloride to form beads with vigorous stirring. The excess unbounded calcium chloride from the bead surface was removed by washing many times with deionized water. The washed beads were then dried for 48 h at room temperature and stored in a clean bottle. The same method was employed for the preparation of BA and AA composites.

2.3. Characterization of adsorbents

The scanning electron microscope (SEM) micrographs of the adsorbents were obtained using Zeiss (Model Supra 35 VP, Germany). Brunauer–Emmett–Teller (BET) surface area was determined by N_2 adsorption–desorption method using an automated Micromeritics ASAP 2020 surface area analyzer at 77 K. The sample was degassed at 200 °C for 2 h before BET analysis.

Fourier transform infrared spectroscopy (FTIR) analysis of the adsorbent before and after adsorption was carried out in KBr pellets in the range of 4000–400 cm^{-1} with 4 cm^{-1} resolution using Perkin–Elmer Spectrum GX infrared spectrometer.

The point of zero charge (pHpzc) was determined according to the method described by Auta and Hameed [24]. In brief, the initial pH (pHi) of aqueous solutions (200 mL) were adjusted to a pH range of 2–12 using 0.1 M HCl or NaOH. Then, 0.2 g of adsorbent was added to each sample. The dispersions were stirred for 48 h at 30 °C, and the final pH of the solutions (pHf) was determined. The point of zero charge was obtained from a plot of (pHf − pHi) versus pHi.

2.4. Selection of the best composite as an adsorbent

The percentage removal of MB at 100 mg/L of the initial concentration in 30 °C were 84.35%, 83.22%, and 95.71% for AA, BA, and ABA composites, respectively, and all other adsorption parameters were kept constant as described in Section 2.5. Based on the preliminary assessment of the different composites in terms of the percentage removal of MB, ABA was the best adsorbent among the samples tested. Therefore, all further experiments were performed using the ABA composite.

2.5. Batch adsorption studies

Batch experiments were performed with 200 mL of MB solutions of predetermined initial concentration (25–500 mg/L) in an array of 250 mL flasks. Exactly 0.2 g of adsorbent was added to each flask, and the solution was agitated in a preselected temperature-controlled (30, 40, and 50 °C) water bath shaker set at 130 rpm until equilibrium was attained. After that, the MB solutions were collected from the flasks at the end of the experiment and analyzed using SHIMADZU UV/Vis 1601 spectrophotometer at $\lambda_{max} = 665$ nm.

The adsorption capacity of MB by the adsorbent at equilibrium q_e (mg/g) was calculated according to the following equation:

$$q_e = \frac{(C_o - C_e)v}{W} \tag{1}$$