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Removal of Acid Orange 7 from aqueous solution using magnetic graphene/chitosan: A promising nano-adsorbent

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ABSTRACT

Magnetic graphene/chitosan (MGCh) nanocomposite was fabricated through a facile chemical route and its application as a new adsorbent for Acid Orange 7 (AO7) removal was also investigated. After synthesis, the full characterization with various techniques (FTIR, XRD, VSM, and SEM) was achieved revealing many possible interactions/forces of dye–composite system. The results showed that, benefiting from the surface property of graphene oxide, the abundant amino and hydroxyl functional groups of chitosan, and from the magnetic property of Fe_3O_4, the adsorbent possesses quite a good and versatile adsorption capacity to the dye under investigation, and can be easily and rapidly extracted from water by magnetic attraction. The maximum absorption capacity was reached at initial pH 3 and 120 min contact time. The batch adsorption experiments showed that the adsorption of the AO7 is considerably dependent on pH of milieu, amount of adsorbent, and contact time. The adsorption kinetics and isotherms were investigated to indicate that the kinetic and equilibrium adsorption were well-described by pseudo-first order kinetic and Langmuir isotherm model, respectively. The adsorption behavior suggested that the adsorbent surface was homogeneous in nature. The study suggests that the MGCh is a promising nano adsorbent for removal of anionic azo dyes from aqueous solution.

1. Introduction

The treatment and disposal of dye-contaminated wastewater is one of the most serious environmental problems faced by the textile, papermaking, printing, and related industries [1]. Dyes are among the most hazardous materials found in industrial effluents, which needs to be treated, because its presence in water bodies reduces light penetration, precluding the photosynthesis of aqueous flora and fauna [2], besides being aesthetically objectionable for drinking and other purposes [3]. In addition, some of the organic dyes and their products have mutagenic or carcinogenic influence on human beings [4].

Various treatment processes such as biological treatment [3], coagulation/flocculation [5], ozone treatment [6], chemical oxidation [7], membrane filtration [8], ion exchange [9], photocatalytic degradation [10] and adsorption [11], have been developed to remove these compounds from colored effluents. However, high energy consumption, complicated design and multiple operations have limited applications of those techniques in industry. In this regard, adsorption appears to be an attractive method for treatment of dye effluents due to its low-cost, simplicity of operation, as well as the availability of a wide range of adsorbents [12,13]. In recent years, a considerable number of studies have focused on low-cost alternative materials for the removal of dyes by adsorption method [14–16].

All the conventional physical and chemical methods used for the adsorption are often cost prohibitive, while biosorption method is eco-friendly as well as economic [17]. Nowadays, one of the most promising adsorption methods for the removal of dyes is the application of chitosan. Chitosan, β-(1-4) acetyl-D-glucosamine, is a linear biopolymer of glucosamine. It can be produced commercially by chemical deacetylation of chitin, a major component of the exoskeleton of crustaceans such as crabs, lobster and shrimp. Chitosan is the second most abundant polymeric material in nature after cellulose [18]. It can be used as a bio-adsorbent to remove cationic and/or anionic dyes due to the simultaneous presence of amino and hydroxyl groups, which can serve as active/adsorption sites [19]. The performance of chitosan as adsorbent can be improved by: (i) the use of cross-linking reagents, which stabilize chitosan in acid solutions and enhance its mechanical properties

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and (ii) derivatization with grafting functional groups onto the chitosan backbone, which improves its adsorption capacity [20]. Recently, different kinds of substances have been used to form composites with chitosan such as graphene oxide and magnetite. These composites have been affirmed to present better adsorption capacity and resistance to acidic environment. Some works in literature dealt with highlights of the application of chitosan composites as adsorbents, including synthesis, mechanisms and other factors, which can affect adsorption capacity of these composites [21,22]. Graphene oxide (GO), a precursor in the formation of graphene layers, has been studied as an adsorbent and its ability to remove cationic dyes has been demonstrated [4,23]. From a structural point of view, GO is a highly-oxidized planar material containing 25–33% oxygen with good adsorption between layers. For this reason, it has been reported that GO based nanocomposites can serve as a dye remover in aqueous solutions [12]. Compared with conventional adsorbents, the merits of GO as adsorbents are its structure types and diverse compositions, tunable pore size, large surface area, and coordinatively unsaturated or saturated metal sites to regulate the adsorption ability [24–26].

The aim of this study was to prepare and explore the potential of a promising nano-adsorbent material namely magnetic graphene/chitosan (MGCh) for the removal of the Acid Orange 7 (AO7) [*p*-(2-hydroxy-1-naphthylazo) benzene sulfonic acid]. It is to be noted that AO7 is a popular water-soluble dye, which is used for dyeing a variety of materials such as nylon, detergents, cosmetics, wool, and silk. Like most other azo dyes, it tends to be disposed of in industrial wastewater, a practice which poses a severe health threat to humans [27]. The effect of various experimental parameters on adsorption, such as the initial dye concentration, contact time, and solution pH were studied in detail. In addition, the adsorption isotherms and kinetics parameters were evaluated.

2. Materials and methods

2.1. Materials

Chitosan (degree of deacetylation 85.0 wt%, viscosity > 200 cps) was purchased from Sigma–Aldrich (Germany). Commercial graphite flakes were supplied by Sigma–Aldrich (Germany) with a particle size of 150 mesh and purity of 99.9%. Acid Orange 7 (AO7, index color no. 15510), as adsorbate, was obtained from Alvand Sabet Company (Iran). Its molecular weight and maximum wavelength (λ_{max}) were 328 g/mol and 497 nm, respectively. All other solvents and materials were of analytical grade, commercially available, and were used without further purification. Deionized water was used throughout the experiments for solution preparations.

2.2. Synthesis of graphene oxide

Graphene oxide was prepared according to the Staudenmaier method [28]. First, H_2SO_4 (18 mL) and HNO_3 (9 mL) were added into a 500 mL flask and cooled by immersion in an ice bath, and then graphite powder (1.0 g) was added under vigorous stirring. After the graphite powder was well dispersed, potassium chlorate (11.0 g) was added slowly over a 2 h period to avoid sudden increase in temperature, and the mixture was allowed to stir for 96 h at room temperature. On completion of the reaction, the mixture was poured into deionized water (100 mL) and filtered. The graphite oxide was re-dispersed and washed in a 5% solution of hydrochloric acid. Then, the product was washed repeatedly with deionized water, until the pH of the filtrate was neutral, and finally vacuum dried.

2.3. Synthesis of magnetic graphene/chitosan nanocomposite

Preparation of graphene/Fe_3O_4/chitosan nanocomposite material was carried out in a solvothermal system using $FeCl_3{\cdot}6H_2O$ as iron source and ethylene glycol as the reducing agent. In brief, graphite oxide (0.50 g) was ultrasonicated in ethylene glycol (70 mL) for 3 h to produce a clear solution. The chitosan (0.65 g) previously dissolved in acetic acid was added and the mixture were mixed with vigorous stirring for 30 min. Subsequently, $FeCl_3{\cdot}6H_2O$ (0.8 g) was added into the solution and ultrasonicated for 15 min. Consequently, $NaOAc{\cdot}3H_2O$ (3.1 g) was added with vigorous stirring for 20 min. The mixture was sealed in a Teflon-lined stainless steel autoclave and maintained at 185 °C for 6 h, and then cooled to room temperature. The black product graphene/Fe_3O_4/chitosan was washed with ethanol and deionized water for several times, and dried in vacuum.

2.4. Characterization methods

Magnetic property of MGCH was measured on a vibrating sample magnetometer (VSM) (Meghnatis Daghigh Kavir Co., Kashan, Iran) at room temperature. The FTIR analysis of the MGCh nanocomposite was conducted in a Bruker spectrophotometer, model Tensor 27, using the transmittance method with wavelength between 400 and 4000 cm^{-1} at a resolution of 4 cm^{-1}. X-ray diffraction (XRD) patterns were recorded on a Philips PW1800 diffractometer with Cu Kα radiation for crystalline phase identification. The sample was scanned from 0° to 80°. Morphological structures of samples were examined by scanning electron microscopy (SEM) with a SEM TESCAN (model WEGA-II), operating at an accelerating voltage of 15.0 kV.

2.5. Preparation of dye solutions

The stock solution of dye was prepared by dissolving 1 g of analytical grade dye in 1000 mL of distilled water. All experiments were carried out at room temperature (25 ± 1 °C) using a constant agitation speed of 100 rpm. The pH of each solution was adjusted to the required value with diluted or concentrated H_2SO_4 (N 4) and NaOH (1 N) solutions before contacting the sorbent. Experimental solutions of the desired concentrations were prepared by successive dilutions. All the experiments were carried out in a batch system in order to evaluate the effects of different operational variables.

2.6. Batch experiments

Dyes concentrations were determined using absorbance values measured before and after the adsorption spectrophotometer (Varian Cary Bio 100 UV–vis Spectrometer, Australia) at the wavelength corresponding to the maximum absorbance of 497 nm. The maximum wavelength (λ_{max}) was recorded by UV–vis spectrophotometer. In all cases, a proper dilution was necessary to obtain a well measurable absorption. The pH of the solutions during the studies was determined by a pH meter. The adsorption capacity, q_t, at time (t) was calculated from the mass balance, given by Eq. (1):

$$q_t = \frac{(C_0 - C_t)}{M} \times V \quad (1)$$

where q_t is the amount of dye taken up by the adsorbent (mg/g), C_0 is the initial dye concentration (mg/L), C_t is the concentration of dye (mg/L) at time t, V is the volume of dye solution (L) put in contact with the adsorbent, and M is the mass (g) of the biosorbent.