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Synthesis, characterization and adsorption properties of a novel biomagnetic composite for the removal of Congo red from aqueous medium

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ABSTRACT

A novel biomagnetic composite ($MnFe_2O_4$/PW) was synthesized and used for the removal of Congo red (CR) from aqueous solutions. Adsorption of CR on the composite adsorbent was studied as a function of time (5–300 min), initial CR concentration (100–200 mg/L), composite dose (0.05–0.1 g), pH (6–10), and temperature (25–55 °C). The properties of the biomagnetic composite were measured by BET, SEM, SEM–EDX, FTIR, XRD, and VSM techniques. The kinetics and isotherm studies were carried out under optimum removal conditions of CR by $MnFe_2O_4$/PW. The kinetics and equilibrium data fitted to the pseudo-first-order kinetics and Langmuir isotherm models. Using CR as model pollutant, the prepared composite adsorbent showed good adsorption capacity of 86.96 mg/g. Thermodynamic analysis showed that the adsorption was favorable, spontaneous and endothermic. The adsorbent could be regenerated using 50% of ethanol–water solution, remaining 87.36% of its original capacity after the first regeneration cycle and reaching 65.68% of the original capacity after the fifth cycle. This study shows that the synthesized biomagnetic composite could be utilized as an efficient and magnetically separable adsorbent for the dye removal applications.

1. Introduction

Congo red is seriously hazard to aquatic living organisms and can cause human carcinogen [1]. CR (disodium 4-amino-3-[[4-[4-[(1-amino-4-sulfonatonaphthalen-2-yl)diazenyl]phenyl] phenyl]diazenyl]-naphthalene-1-sulfonate) is a benzidine based anionic dye. It is the first synthetic dye produced that is capable of dyeing cotton directly. It is very sensitive to acids. This is red in the pH range of 5–10, and its sodium salt dyes cotton full red. The color changes from red to blue in the presence of inorganic acids (below pH 5). This blue color may be attributed to resonance among charged canonical structures [2]. It is generated from textiles, printing and dyeing, paper, rubber and plastics industry, among others. CR is known to metabolize into benzidine, which is known as a human carcinogen [3]. Therefore, it is necessary to remove residual CR from water sources before discharge to receiving water bodies.

Adsorption is highly effective, economical, promising and widely applied technique for the treatment of dye bearing wastewaters. However, for such an application, it is necessary to use a method for purification that does not generate secondary pollution that stem from the spent sorbent and involves materials that can be recycled and easily used on industrial scale [4].

Magnetic separation is considered as a quick and effective technique for separating magnetic particles. It has been used for many applications in biochemistry, analytical chemistry and mining ores [5]. Recently, magnetic separation has been one of the promising ways for an environmental purification technique because of producing no contaminants and having capability of treating large amounts of wastewater within a short time. Magnetic nano- or micro-particles of iron oxides have been widely used in the fields of separations and adsorption reactions [6].

Magnetic ferrite MFe_2O_4 (M denotes a divalent metal such as Fe^{II}, Mn^{II}, Co^{II}, Zn^{II}) nanoparticles possess special optical, electrical and magnetic properties, thus have storage, biosensing, disease diagnosis, catalysis and environmental analysis [7]. Spinel ferrite $MnFe_2O_4$, a well known magnetic bimetallic compound, has relatively high surface area, saturation magnetization and excellent chemical stability and often regulates free metal and organic matter concentration in soil or water through adsorption [8]. Manganese ferrite nanoparticles have proven to be useful in many applications, and they can provide a potential advantage for repeated magnetic separation purposes. Actually, manganese ferrite has been employed as catalysts in various reactions such as organic dehydrogenation, catalytic oxidation, Fenton reaction, and CO_2 reduction. Therefore, manganese ferrite may show a good combination of properties: high catalytic activity, good durability, and easy magnetic separation [9].

Until now, many researchers have studied on the development of low-cost biosorbents and activated carbon adsorbents from abundantly

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available by-products/waste materials for wastewater treatment applications because of having good potential to adsorb different types of contaminants; such as parsley stalk, cucumber peel, watermelon seed hull [10], grass waste [11], garlic peel [12], cherry sawdust [13], coffee husks [14], cotton waste [15], tomato waste [16], cocoa shell [17], and corncob [18]. Nowadays, interest has been growing in the use of magnetically separable low-cost adsorbents, thus the advantages of desirable adsorption capacity could be combined with magnetic separability.

The work presented here successfully recycled pomegranate waste into a low-cost adsorbent and further converted this into magnetically separable composite adsorbent. Pomegranate (*Punica granatum*) is considered to have originated in Iran and has been cultivated since ancient times [19]. Today it is widely cultivated throughout the Mediterranean region of Europe, and the Middle East. It is reported that India, Iran and Turkey are the most pomegranate grower countries around the world. Turkey is the third pomegranate producer country in the world with 315.150 tons annually [20]. Pomegranate is used in cooking, baking, juices, smoothies and alcoholic beverages, such as martinis and wine [21]. As pomegranate contains antioxidants, polyphenols, and vitamin C, it is among "functional foods". In 2013, 44 clinical trials were registered with National Institutes of Health to examine effects of pomegranate extracts or juice consumption on a variety of human disorders including prostate cancer, diabetes, atherosclerosis, aging, and pregnancy complications [22]. Therefore, pomegranate cultivation and consumption is rather high in world as well as in Turkey. Consequently pomegranate pulp is released as waste into the environment and does not have any economical value or industrial importance.

Many authors have studied the adsorptive properties of pomegranate wastes (peel, pulp, seed, husk, etc.) for the removal of various contaminants. For example, El-Ashtoukhy et al. [23] investigated the removal of lead and copper from aqueous solution using pomegranate peel as an adsorbent. Bhatnagar and Minocha [24] studied the feasibility of pomegranate peel as an adsorbent for the removal of 2,4-dichlorophenol pesticide from water. Adii et al. [25] used pomegranate peel as an adsorbent for the adsorption of Amaranth dye from aqueous solutions. Güzel et al. [26,27] studied the removal of Methylene blue dye and Cu (II) ions from aqueous solutions using pomegranate pulp as a new biosorbent. Amin [28] prepared new activated carbons from pomegranate peel for the removal of Direct blue 106 dye from aqueous solutions. El Nemr [29] used pomegranate husk carbon for the treatment of wastewater bearing Cr (VI). Ghaedi et al. [30] prepared low cost activated carbon by using pomegranate peel as a precursor for the adsorption of Congo red dye. Uçar et al. [31] also prepared activated carbon from pomegranate seeds and characterized. However, there is a lack of knowledge about the preparation of magnetically separable pomegranate waste (PW) as an adsorbent. This study is the first one to fabricate a magnetic composite from PW and use it as an adsorbent in CR removal.

The objectives of this study were i) to prepare a novel biomagnetic composite using a simple and economic method, ii) to characterize the prepared composite with various techniques, iii) to investigate its effectiveness in CR removal by studying the effects of adsorption variables on removal of CR, and iv) finally to evaluate the reusability of the prepared biomagnetic composite adsorbent.

2. Materials and methods

2.1. Materials

The raw PW was collected from Limkon Fruit Juice Factory in Adana, a city of Turkey. It was washed with distilled water and dried at 70 °C, then crushed in a grinder and sieved to 500 μm of particle size. The ground material was stored in desiccators until use. CR (formula: $C_{32}H_{22}N_6Na_2O_6S_2$, molecular weight: 696.67 g/mol, λ_{max}: 497 nm), manganese (II) chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$), ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) and NaOH were obtained from Sigma-Aldrich company. All the reagents were of analytical grade and used as received without further purification. All solutions were prepared with ultrapure water.

2.2. Preparation of $MnFe_2O_4$/PW composite

Coprecipitation method was used to prepare $MnFe_2O_4$/PW magnetic composite. A certain amount of PW was added into a 200 mL of solution containing 0.025 mol manganese (II) chloride and 0.05 mol ferric chloride at 60 °C. (The amount of PW was adjusted to obtain $MnFe_2O_4$/PW mass ratios of 1:1). Under vigorous magnetic-stirring and at 60 °C, 5 mol/L NaOH solution was added dropwise to raise the suspension pH to around 10 and the stirring was continued for 1 h. Afterwards, the suspension was heated for 4 h at 100 °C using a water bath. After being cooled, the prepared magnetic composite was repeatedly washed with distilled water to remove the impurities (e.g., Na^+, Cl^-). Then, the composite was dried in an oven at 110 °C and stored in glass bottles.

2.3. Characterization studies

Surface functional groups were detected using a Fourier transform infrared (FTIR) spectrometer (PerkinElmer spectrum 100, USA) in the scanning range of 4000–400 cm^{-1} for the spectra of raw $MnFe_2O_4$/PW and CR loaded $MnFe_2O_4$/PW.

The surface physical morphologies of raw $MnFe_2O_4$/PW and CR loaded $MnFe_2O_4$/PW were identified by using SEM technique and the elemental composition of the composite was determined from the SEM/EDX analysis (Jeol/jsm-6335F, USA).

N_2 adsorption–desorption isotherms on $MnFe_2O_4$/PW at 77 K were measured on a Micromeritics ASAP 2020, from which the Brunauer–Emmett–Teller (BET) surface area and Barrett–Joyner–Halenda (BJH) pore size distribution were calculated, respectively.

X-ray diffraction (XRD) measurements were performed on powdered samples in an X-ray powder diffractometer (Bruker, D8 Discovery EVA, Germany) measured using Cu Kα radiation at 40 kV and 40 mA over the range of 0° to 70° (2θ) at a scan speed of 6°/min.

A vibrating sample magnetometer (VSM; Lake Shore 7407) was used to measure the magnetic properties of $MnFe_2O_4$/PW. The specific magnetization curve of the composite was obtained at room temperature.

2.4. CR removal experiments

Batch adsorption experiments were carried out using a thermostated water bath shaker (Daihan-WSB-30, Korea). The effects of various operating parameters such as solution pH (6–10), adsorbent dosage (0.05–0.1 g), initial concentration (100–200 mg/L), contact time (5–300 min), and temperature (25–55 °C) on the adsorption were studied. The shaking rate was adjusted to 150 rpm for all experiments. The kinetics and isotherm studies were carried out under determined optimum conditions, namely with 0.07 g of the adsorbent, at natural pH of the dye solution and 150 rpm shaking rate. Then, under optimum conditions kinetics studies were carried out at 25 °C with different initial concentrations (100 and 200 mg/L) of CR solutions, and isotherm studies were carried out at different temperatures (25, 35, 45 and 55 °C) with different initial concentrations (25–340 mg/L) of CR solutions. After each experiment, the composite was separated from the solutions using a permanent magnet, and the initial and final dye concentrations were determined by a UV–vis spectrophotometer (Perkin Elmer-Lambda 25, USA) at 497 nm. The equilibrium adsorption capacity (q_e) was calculated according to the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where C_0 and C_e are initial and equilibrium concentrations, respectively (mg/L), V is solution volume (L), and m is the mass of adsorbent (g).