Full paper/Mémoire

A novel magnetic biosorbent prepared using an oak shell waste material as an efficient adsorbent for consecutive removal of Pb^{2+}, Ag^+, Ba^{2+}, Sr^{2+}, and CrO_4^{2-} from aqueous solutions

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ABSTRACT

In this research, the performance of a new biosorbent prepared using low-cost oak shell waste materials for consecutive removal of particular cations and chromate anions from aqueous solutions was studied. The adsorbent impregnated with Pb^{2+}, Ag^+, Ba^{2+}, and Sr^{2+} was used to remove chromate anions by the formation of an appropriate insoluble precipitate. The biosorbent was characterized by FTIR, XRD, SEM, TG-DTG, and VSM techniques. The adsorption capacities of 133.84, 53.12, 50.12, and 40.39 mg g^{-1} were obtained for chromate for the samples containing Pb^{2+}, Ag^+, Ba^{2+}, and Sr^{2+} cations, respectively. The chromate uptake was inversely proportional to the k_{sp} of the chromate precipitate and increased with the cation content of the adsorbent. The adsorption process was kinetically fast and the equilibrium was established within 10 min. The experimental data were analyzed by the Langmuir, Freundlich, Sips, and Redlich-Peterson isotherm models. The data were fitted to the Langmuir isotherm, indicating that chromate was adsorbed homogeneously on the adsorbent surface.

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1. Introduction

With increasing industrial activities, a large amount of waste and run-off from the industries enters the environment and causes serious health problems. Chromium is one of the hazardous element that is widely released into the environment from leather tanning, cement, plastic, metallurgical, textile, batteries, refractories, pigment, welding, stainless steel, ceramic, catalysis, wood preservatives, electroplating, photography, galvanometric, metal cleaning, and mining industries [1,2]. Although chromium has several oxidation states, from −2 to +6, Cr(VI) it is more soluble, toxic, carcinogenic, and non biodegradable. Moreover, as a mutagenic agent, it causes serious health problems such as dermatitis, allergic sensitization, stomachache, nausea, vomiting, severe diarrhea, hemorrhage, epigastric pain liver, kidney and respiratory damages, and gastrointestinal ulcers [3–5]. Based on the pH of the solutions, Cr(VI) exists as different species such as chromates (CrO_4^{2-}), dichromates ($Cr_2O_7^{2-}$), and bichromates ($HCrO_4^-$) [6].

Various conventional techniques have been employed to remove chromium from wastewaters including precipitation [7], ion exchange [8], ultrafiltration [9], flotation [10], reverse osmosis [11], electrochemical [12], and coagulation [13]. These methods generally suffer from disadvantages such as cost, production of chemical sludge [14], and harmful chemicals as a secondary pollutant [15]. Adsorption is the most favorite and feasible technique for the separation of pollutants owing to its high efficiency, selectivity, low-cost, and easy handling [16].

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Different adsorbents such as resins [17], goethite [18], zeolite [19], MCM-41 [20], clay [21], and gamma Al$_2$O$_3$ [22] have been employed for the removal of chromates. The use of biosorbents has been enhanced in recent days in plant species such as walnut shells [23], pine cone [24], oak shell [25], and maize spatha [26].

Nevertheless, many concerns have arisen for the discharge of toxic metals from industries into the environment such that intensive studies are underway to develop cost-effective adsorbents using environmentally friendly biomaterials for the removal of heavy metals from liquid wastes.

Many researchers developed production of activated carbons to reduce the preparation cost of the adsorbent. Activated carbons (AC) have unique properties such as high porosity, large surface areas, and functionalized surface. They are prepared economically and their efficiency can be readily improved via the chemical modification [27,28]. Although the reactivity of the nano-sized adsorbents is higher than their micro-sized counterparts, their separation from the solution is incomplete, tedious, and time-consuming. One way to eliminate the separation difficulties is to consider the magnetization of adsorbents by iron oxide.

In this research, a biosorbent was prepared using an oak shell obtained from local agricultural waste materials. It was magnetized using Fe$_3$O$_4$, functionalized with dithizone, and then impregnated with particular cations. The cation-loaded adsorbents were used for the removal of chromate anions from aqueous solutions under different experimental conditions.

2. Experimental

2.1. Materials and methods

Analytical grade reagents were provided from Merck Company. Stock solutions of cations were prepared by dissolving appropriate amount of nitrate salt in de-ionized water. The chromium stock solution was prepared by dissolving accurately weighed amount of potassium dichromate into deionized water. Characterization of the samples was performed by using different techniques including a scanning electron microscope (MIRA3LMU model, TESCAN Company), X-ray diffraction system (PANalytical model X'Pert PRO), Fourier transforms infrared spectrometer (FTIR Perkin—Elmer 65), and thermal analyzer (TG-DTG) (NETZSCH STA 409 PC/PG), VSM (LDJ Electronics Inc., Model 9600). The concentration of cations was measured using an atomic absorption spectrometer (Shimadzu Elmer Perkin devices 300 Analyst model A). Chromate concentration was measured using the HPLC method by using an Agilent Technologies 1200 Series instrument with a Quaternary pump, column XDB-C18 ($L = 25$ cm, id $= 4.6$ mm and particle size$= 5$ μm, Injected and detected volumes: 5 μL, flow rate: 1 mL min^{-1}).

2.2. Preparation, magnetization and functionalization of activated carbons

Activated carbon (AC) was prepared by the carbonization of oak shell waste materials collected from Zagros forests, Kohmareh Sorkhi region, Fars, Iran. The process was executed in a quartz tube furnace under a N$_2$ atmosphere. The AC was then treated, respectively, with hydrochloric acid, and nitric acid to remove remaining organic matters and to increase the surface functional groups. The acid treated sample was denoted as AC-COOH. The acid treated AC was magnetized using Fe$_3$O$_4$ nanoparticles synthesized in the presence of activated carbon under alkaline conditions and inert atmosphere. 0.21 g of FeSO$_4$·7H$_2$O and 0.31 g of FeCl$_3$·6H$_2$O were dissolved in 8.0 mL of de-ionized water and 1.0 mL of ammonium hydroxide solution (25%, w/v) was added dropwise to the solution. 1.0 g of AC—COOH was then added and the mixture was vigorously stirred for 30 min at 80 °C. The mixture was cooled down to room temperature and the solid was removed and washed repeatedly with distilled water until the pH of filtrate was 5—6. The magnetized activated carbon (AC—Fe$_3$O$_4$) was dried and stored in desiccators [29]. To increase the selectivity and capacity of the adsorbent, the magnetic adsorbent was functionalized using dithizone. For functionalization, AC-Fe$_3$O$_4$ was first reacted with thionyl chloride to produce acyl chloride (AC-COCL) which then was reacted with dithizone solution. The functionalized adsorbent (AC-Fe$_3$O$_4$-DTZ) was magnetically separated, thoroughly washed with DMF, ethanol and diethyl ether, respectively, and dried at 70 °C for 8 h [25,30].

2.3. Confinement of AC-Fe$_3$O$_4$-DTZ with Pb^{2+}, Ag$^+$, Ba^{2+} and Sr^{2+} cations

To study the performance of AC-Fe$_3$O$_4$-DTZ for consecutive removal of the studied cations and chromate anions, the adsorption capacity of the sorbent towards the cations was firstly measured, and then the cation-loaded adsorbents were employed for the removal of chromate from aqueous solutions. To evaluate the capability of the adsorbent for the uptake of cations, in a series of experiments 0.1 g of the functionalized adsorbent was equilibrated with 25 mL of Pb^{2+}, Ag$^+$, Ba^{2+}, Sr^{2+} solutions having different concentrations (100—5000 mg L^{-1}). The pH of the solution was adjusted to 6.5 and the mixture was shaken for 7 min until the equilibration was established. The adsorbent was separated by a magnet bar placed outside of the reaction vessel and the concentration of the cation in the remaining solution was measured by an atomic absorption method. The amount of the adsorbed cation was calculated by the following equation:

$$Q = \frac{(C_0 - C_e) \times V}{m} \tag{1}$$

where Q is the equilibrium adsorption capacity (mg g^{-1}), C_0 is the initial concentration of the metal ion (M), C_e is the equilibrium concentration (mg L^{-1}), V (L) is the volume of the solution, and m (g) is the mass of adsorbent. For each cation, four samples with different cation contents were prepared and denoted accordingly (Table 1). As indicated in Fig. S2, the adsorption capacity of the functionalized adsorbent towards the studied cation was higher than the other adsorbents. Therefore, the magnetized activated