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A highly selective sorbent for removal of Cr(VI) from aqueous solutions based on Fe_3O_4/poly(methyl methacrylate) grafted Tragacanth gum nanocomposite: Optimization by experimental design

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ABSTRACT

In this work, poly(methyl methacrylate) grafted Tragacanth gum modified Fe_3O_4 magnetic nanoparticles (P(MMA)-g-TG-MNs) were developed for the selective removal of Cr(VI) species from aqueous solutions in the presence of Cr(III). The sorbent was characterized by Fourier transform infrared (FTIR) spectroscopy, transmission electron microscopy (TEM), a vibrating sample magnetometer (VSM), and thermo-gravimetric analysis (TGA). A screening study on operational variables was performed using a two-level full factorial design. Based on the analysis of variance (ANOVA) with 95% confidence limit, the significant variables were found. The central composite design (CCD) has also been employed for statistical modeling and analysis of the effects and interactions of significant variables dealing with the Cr(VI) uptake process by the developed sorbent. The predicted optimal conditions were situated at a pH of 5.5, contact time of 3.4 h, and 3.0 g L^{-1} dose. The Langmuir, Freundlich, and Temkin isotherm models were used to describe the equilibrium sorption of Cr(VI) by the absorbent, and the Langmuir isotherm showed the best concordance as an equilibrium model. The adsorption process was followed by a pseudo-second-order kinetic model. Thermodynamic investigations showed that the biosorption process was spontaneous and exothermic.

1. Introduction

Heavy metal contamination is one of the most worldwide environmental problems of this century [1,2]. Among the various heavy metals, chromium (Cr) is one of the most toxic contaminants generated by the electroplating, leather tanning, metal finishing, steel fabrication, and textile industries. Cr exists in several chemical forms displaying oxidation numbers from 0 to VI, however, the higher oxidation states of Cr are of interest due to the toxic and mutagenic nature of these states. Only two species of Cr, trivalent and hexavalent Cr, are stable enough in aqueous environment. Cr(VI) is highly toxic than Cr(III) due to its high water solubility and mobility [3–5]. The toxicity of Cr(VI) originates from its oxidizing property and formation of free radicals inside the cell during the reduction of Cr(VI) to Cr(III) [6,7]. Therefore, the development of methods for selective removal of Cr(VI) in the presence of Cr(III) is of great importance. The US Environmental Protection Agency (USEPA) has laid down the maximum contaminant level (MCL) for Cr(VI) in domestic water supplies to be 0.05 mg L^{-1}, while total Cr is regulated to be discharged below 2 mg L^{-1}.

For this sense, various methods have been developed to remove Cr(VI) from the industrial wastewater including chemical precipitation [8], ion-exchange [9,10], reduction [11], electrochemical precipitation [12], solvent extraction [13], and membrane separation [14,15]. These conventional chromium elimination processes are costly or ineffective in most cases, and may also lead to environmental problems from the point of view of waste disposal. Compare to the traditional methods, the adsorption method has been used as one of the most promising methods in the removal process of Cr(VI) due to high efficiency, easy handling, and the effectiveness of various adsorbents. In recent years, biosorption has been focused on using readily available bioresource, low-cost, non-toxic, and effective adsorbents [16,17].

Nowadays, natural polymers such as chitosan [18], alginate [19], guar gum [20], gum Arabic [21], and cellulose [22,23] have been used in the removal of Cr(VI) from wastewaters. These biodegradable compounds enable the formation of a complex with various metal ions. This property can be improved by modification of these compounds with suitable functional groups through esterification [24], oxidation reactions [25], or crosslinking techniques [26]. Grafting is a simple technique to introduce different functional groups onto the polymers to prevent dissolution of hydrophilic polymer chains in aquatic media and provides new binding sites. However, low surface area and drawback in separation of natural polymers from aqueous phase limit their use in practical applications.

Magnetic separation is a promising method for solid–liquid phase separation technique, enabling the treatment of a large amount of

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sample within a short time. The Fe_3O_4 magnetic nanoparticles have unique properties such low cost synthesis, low toxicity, and relatively high surface area. Therefore, it is expected that the introduction of Fe_3O_4 into natural polymers would not only enhance the chemical and colloidal stability but also improve the separation ability of adsorbents from aqueous solution with the help of an external magnetic field [27–29].

Tragacanth gum (TG) is one of the most abundant biopolymers and eco-friendly natural polysaccharides. TG is an exudate gum from shrubby locoweeds native to arid regions of the eastern Mediterranean and southwestern Asia and desert highlands of northern and western Iran, particularly the Zagros Mountains region [30]. It is an anionic carbohydrate which has stability against heat and a wide range of pH and consists of major water soluble and insoluble fractions of D-galactose, D-galacturonic acid and L-rhamnose with traces of ketohexose [31]. The chemical modification of TG has been performed using crosslinking and grafting techniques to produce accessible binding sites in this biopolymer and to enhance its stability and sorption capacity [32].

In this work, a new magnetic adsorbent was developed by the surface modification of Fe_3O_4 nanoparticles with poly(methyl methacrylate) grafted TG for selective removal of Cr(VI) in the presence of Cr(III). A possible mechanism for the adsorption of Cr(VI) by the proposed adsorbent has been discussed. The response surface methodology (RSM) using a full factorial design was used to explore the region of interest of the effective variables and find the optimum condition.

Up to now, no previous work on graft polymerization of magnetic TG with methyl methacrylate (Fe_3O_4/P(MMA)-g-TG) for removal of Cr(VI) has been reported. Therefore, the objective of the present study was to prepare a new magnetic natural adsorbent for removal of Cr(VI) and employ RSM in the optimization process of Cr(VI) by the proposed adsorbent.

2. Experimental

2.1. Chemicals

Potassium chromate (K_2CrO_4), methyl methacrylate (MMA), ascorbic acid (AA), acetone, 1,5-diphenylcarbazide, HNO_3, and potassium persulfate ($K_2S_2O_8$) were all of analytical grade and provided from Merck (Darmstadt, Germany). Tragacanth gum (TG) was given from local natural resources. Stock solution of Cr(VI) was prepared by dissolving an appropriate amount of K_2CrO_4 in deionized water.

2.2. Instrumentation

The developed adsorbent (Fe_3O_4/P(MMA)-g-TG) was characterized by transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), thermo-gravimetric analysis (TGA), and a vibrating sample magnetometer (VSM). TEM micrographs were obtained by a Carl Zeiss model Em10 transmission electron microscope (Jena, Germany) operating at 80 kV to investigate the morphology of the nanoparticles. The FTIR spectra (400–4000 cm^{-1}) of the adsorbent dispersed in KBr pellets were recorded by a VERTEX 70 FT-IR spectrophotometer (Bruker, Munich, Germany). Thermo-gravimetric analysis (TGA) was performed on Shimadzu TGA-50 (Tokyo, Japan) in N_2 atmosphere. The magnetic properties of P(MMA)-g-TG-MNPs and the naked MNPs were investigated by a Lake-Shore VSM model 4700 (Westerville, Ohio, USA) vibrating sample magnetometer. Deionized water was obtained by an AquaMax water purification system (Younglin, Anyang, Korea). The pH measurements were carried out using a digital pH meter Corning 125 equipped with a combined glass electrode. The pH values were adjusted by the addition of 1 M HCl or NaOH solution. The concentration of Cr(VI) was measured using the diphenyl carbazide method by a Shimadzu 2501 UV–Vis. spectrophotometer (Tokyo, Japan).

2.3. Synthesis of poly(methyl methacrylate) grafted TG immobilized on magnetic nanocomposite (P(MMA)-g-TG-MNPs)

Magnetic nanoparticles were prepared according to the previous work [28]. P(MMA)-g-TG-MNPs was fabricated by a one step polymerization method. Briefly, 1.0 g intact Tragacanth gum was dissolved in 250 mL deionized water at 70 °C in a Pyrex bottle. Then, 2.0 g of Fe_3O_4 nanoparticles was added to the solution under stirring at 1200 rpm. Subsequently, 6 mL of methyl methacrylate (MMA) and 1.35 g of ascorbic acid (AA) were added, and the reaction mixture was stirred for 30 min. Afterwards, 1.35 g of $K_2S_2O_8$ was added and the reaction was allowed to continue for 1 h at room temperature. Finally, the resulting nanocomposites were separated from any homopolymer with acetone, collected by an external magnetic field and dried in a vacuum oven to reach a constant weight.

2.4. General procedure for removal of chromium (VI)

Adsorption experiments were performed in batch wise adsorption mode in 50 mL polyethylene bottles; each containing 30 mL of Cr(VI) solution by varying the initial Cr(VI) concentration from 1 to 50 mg L^{-1} and 3.0 g L^{-1} P(MMA)-g-TG-MNPs dose at 25 °C were stirring for 3.4 h at 200 rpm. After the equilibrium was reached, the adsorbent was collected under a strong external magnetic field and the supernatant was collected. The initial (C_i) and equilibrium (C_e) concentrations of Cr(VI) ions were determined by diphenylcarbazide reagent spectrophotometrically at 542 nm. The uptake of Cr(VI) ions by the adsorbent was evaluated by the removal efficiency (R%) according to Eq. (1):

$$R(\%) = \frac{C_i - C_e}{C_i} \times 100. \tag{1}$$

To investigate the effect of the pH, 10 mL of 10 mg L^{-1} Cr(VI) or Cr(III) with the pH ranging from 2.0 to 8.0 was mixed with 10 mg of the naked MNPs, or P(MMA)-g-TG-MNP adsorbents at 25 °C for 2 h. The pH values were adjusted by the addition of HNO_3 or NaOH solutions.

For the kinetics investigation, batch studies were conducted in a temperature-controlled shaker using a fixed adsorbent dose of 3.0 g L^{-1} and the Cr(VI) solutions at 10, 20 and 30 mg L^{-1} concentrations (pH 5.5). At various time intervals (0–240 min), samples were collected by an external magnetic field and the remaining Cr(VI) were determined spectrophotometrically.

2.5. Optimization

A full factorial design consisting of 16 experimental runs with 6 runs at the center point was used for screening and modeling of the important process variables. Four variables in the experiment process viz. sample pH (A; 5–6), adsorbent dose (B; 1.0–3.0 mg mL^{-1}), initial concentration (C; 10–30 mg L^{-1}), and contact time (D; 2–4 h) were selected to be analyzed, aiming to figure out their influence on the removal of Cr(VI) by the adsorbent. Two other variables, i.e. temperature and stirring rate were kept constant at 25 °C and 200 rpm, respectively, during the experiments. A half normal plot was used for choosing the important process variables. Then, the analysis of variance (ANOVA) was performed to validate the model. However, the related models are somewhat limited to only two levels in these types of designs. Thus, a second-order model (response surface design) which provides more than two levels for fitting of a full quadratic model [33] is necessary to find the best conditions for removal of Cr(VI). Finally, an experiment was again performed under the obtained optimal conditions to validate the defined model. The Design Expert Trial Version 8.0 software was used to develop the experimental plan for RSM.