Synthesis of magnetic alginate hybrid beads for efficient chromium (VI) removal

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ABSTRACT

Recently magnetic bio-composites have attracted the attention of scientists because of their unique characteristics like selectivity and high sorption capacity. In the present study, Fe3O4@Alg-Ce magnetic composite beads were developed by incorporating Fe3O4 particles onto alginate (Alg) biopolymer followed by cross-linking with Ce3+ ions. The synthesized magnetic beads were characterized using FTIR and SEM with EDAX analysis and utilized for chromium (VI) removal in batch mode. A comparative adsorption performance of Fe3O4 particles, calcium alginate (CaAlg) composite and Fe3O4@Alg-Ce magnetic hybrid beads was made. The magnetic alginate beads possess an enhanced SC of 14.29 mg/g than CaAlg composite and Fe3O4 particles which possess SC of 9.45 and 9.72 mg/g respectively. The various sorption influencing parameters like contact time, pH, challenger anions, initial chromium concentration and temperature were optimized. The adsorption process was explained using Freundlich and Langmuir isotherms. The sorption kinetics was fitted well with the pseudo second order and intra particle diffusion model. The calculated thermodynamic parameters indicate the nature of chromium sorption is spontaneous and endothermic.

1. Introduction

The dissolution of minerals and rapid industrialization has led to increased disposal of heavy metals into the environment which is of special concern because of their persistency and biomagnifying property. One such hazardous heavy metal is chromium. Chromium compounds will produce toxic, mutagenic, and carcinogenic effects in the biological systems [1]. The exposure of hexavalent chromium compounds lead to DNA damage, lung cancer, skin rashes, respiratory problems, damage to immune systems and also affects the kidney and liver [2]. Numerous methods are available to remove toxic chromium from water which includes reduction [3], adsorption [4,5], electro-coagulation [6], membrane separation [7], etc. Among them, adsorption is an efficient technique imparting great interest towards chromium removal [8].

Copious materials could be utilized as adsorbents for removing toxic ions and the challenges are mechanical strength, cost, abundance and sorption capacity of adsorbents. Biosorption is environmentally sound technique has increasingly received more attention because of its relatively low-cost, abundant and effective in removing metal ions. Therefore the usage of the biopolymers has gained more importance [9–11]. Alginate is one of the natural polymers which possess advantages like high molecular-weight, non-toxic, selective, efficient and inexpensive [12]. The sodium alginate (NaAlg) is water soluble and less stable and hence it cannot be used for adsorption process directly. In order to overcome this difficulty, numerous attempts were carried out to increase its stability and sorption capacity by synthesizing polymeric composites [13] and cross-linked with different higher valence metal ions [14,15]. Several reports are available indicating the efficiency of alginates in the removal of various heavy metals by coupling it with materials like carbon nanotubes [16] and activated carbon [17]. In recent days, magnetic particles received more attention because of its high surface area and selectivity, which results in increased adsorption. Many researchers have utilized the magnetic particles to enhance the uptake capacity [18,19]. Recently the adsorbents with rare earth elements are being paid more attention because of their selectivity, high adsorption capacity, minimum pollution and easy operation [20]. Hence in the present study, Ce(III) was utilized as cross-linking agent which makes the materials more stable and also improves the uptake capacity.

The present investigation was aimed to synthesize the magnetic alginate polymeric beads and its application towards chromium
Magnetic Fe₃O₄ particles were dispersed over the alginate polymeric matrix and cross-linked with cerium ions resulting in the generation of new magnetic hybrid beads. Synthesized Fe₃O₄@Alg-Ce magnetic beads were utilized for Cr(VI) sorption under batch process. The magnetic beads were characterized by FTIR, SEM and EDAX analysis. To obtain the maximum sorption capacity (SC), the experiments were optimized by varying diverse factors like pH, different initial Cr(VI) concentrations and temperature. Sorption data have been fitted to various isotherms and kinetic models. The thermodynamic parameters viz., ΔS°, ΔH° and ΔS° have also been calculated to find the nature of sorption.

2. Materials and methods

2.1. Materials

Sodium alginate with a molecular weight of 70,000–80,000 was purchased from Himedia (India). Diphenyl carbazide, ferrous chloride, ferric chloride, sodium hydroxide, hydrochloric acid, cerium (III) sulphate, acetic acid and all other chemicals used were of AR grade, for solution preparations double distilled water was used.

2.2. Synthesis of Fe₃O₄ particles

Fe₃O₄ particles were prepared by chemical co-precipitation method. About 0.06 mol of FeCl₃·6H₂O was dissolved in 100 mL double distilled water and stirred well for 2h. About 0.03 mol of FeCl₂·4H₂O was dissolved separately in 100 mL double distilled water and it was slowly added to the above solution with constant stirring. Then, 100 mL of 10 M NaOH was added drop wise to the above mixture and stirred well for 4h at 50 °C to obtain Fe₃O₄ particles. The magnetic particles was filtered and washed with water followed by ethanol and acetone. Finally, the magnetic (Fe₃O₄) particles were dried in hot air oven at 50 °C for 24h.

2.3. Synthesis of Fe₃O₄@Alg-Ce magnetic beads

About 10 g of sodium alginate was added to 200 mL double distilled water and stirred vigorously for 1 h. About 2 g of synthesized Fe₃O₄ particles was added with constant stirring at 60 °C using a magnetic stirrer for 10 h. Then the above mixture was added dropwise in 2% cerium (III) sulphate (w/v) solution for cross-linking to get Fe₃O₄@Alg-Ce magnetic beads. The obtained magnetic alginate beads left undisturbed in Ce(III) solution for 24 h for complete cross-linking. Finally, the magnetic alginate beads was filtered, washed with distilled water and dried in hot air oven at 50 °C for 24 h. The dried magnetic beads were sieved to uniform size and then used for sorption studies.

2.4. Chromium sorption studies

Sorption experiments were determined by batch process in duplicate. About 0.1 g of Fe₃O₄@Alg-Ce magnetic beads were added to the conical flask containing 50 mL of chromium solution with 100 mg/L as initial concentration. The contents were shaken thoroughly using a thermostated shaker rotating at a speed of 200 rpm and the filtrate was analyzed for chromium. The experiments were optimized for maximum SC by varying various parameters viz., contact time, initial chromium concentration, pH and the presence of other ions which are normally present in water. The influence of pH on the sorption of Cr(VI) was studied by varying the pH of the solution in the range of 3–11 using 0.1 M HCl/NaOH solution. Samples were taken at prefixed time intervals for the analysis of Cr(VI) concentration in the solution until sorption equilibrium was reached. Temperature studies were carried out with different initial Cr(VI) concentrations viz., 80, 100, 120 and 140 mg/L at different temperatures 30, 40 and 50 °C by keeping the mass of sorbent as 0.1 g and volume of the solution as 50 mL. The solution was then filtered and the residual Cr(VI) ion concentration was measured.

2.5. Analysis

The chromium ion concentration was determined using UV-Visible Spectrophotometer Spectroquant- Pharo 300 (Merck, Germany) at 540 nm with diphenyl carbazide as complexing agent [21]. The pH measurements were carried out with Thermo Orion Benchtop multiparameter kit (VERSA STAR 92) using pH electrode.

2.6. Instrumental analysis

Fourier transform infrared (FTIR) spectra of the materials were carried out using JASCO-460 Plus spectrophotometer in the range of 400–4000 cm⁻¹ using KBr pellets. The surface morphology of the composite beads was imaged by scanning electron microscopy (SEM) – Joel model: JSM 6390. The SEM facilitates the direct observation of the surface microstructures of the fresh and Cr(VI) sorbed Fe₃O₄@Alg-Ce magnetic beads. Elemental spectra of the Fe₃O₄@Alg-Ce magnetic beads were obtained using an energy dispersive X-ray analyzer (JSM 6390, USA) during SEM observations which allows a qualitative detection and localization of elements in the beads.

2.7. Statistical tools

The computations were done using Microcal Origin (Version 8.0) software. The goodness of fit and best model was discussed using error bar plot, regression correlation coefficient (r), chi-square analysis (χ²) and standard deviation (sd).

3. Results and discussion

3.1. Characterization of Fe₃O₄@Alg-Ce magnetic beads

FTIR spectra of NaAlg, Fe₃O₄@Alg-Ce magnetic beads and Cr(VI) sorbed Fe₃O₄@Alg-Ce composite beads are shown in Fig. 1. In the FTIR spectra of NaAlg, the two bands at around 3434 and 1028 cm⁻¹ were assigned to –OH and C–O stretching vibrations respectively.
which indicates the presence of hydroxyl groups. The bands at 1608 and 1412 cm\(^{-1}\) corresponding to \(\text{C} = \text{O}\) asymmetric and symmetric stretching vibrations of the carboxyl groups. The FTIR spectra of \(\text{Fe}_3\text{O}_4@\text{Alg}-\text{Ce}\) beads shows these two bands gets shifted to 1613 cm\(^{-1}\) and 1418 cm\(^{-1}\) respectively, revealing the occurrence of cross linking between cerium ions and carboxyl group of sodium alginate. In addition to this a new absorption band at 561 cm\(^{-1}\) in FTIR spectra of \(\text{Fe}_3\text{O}_4@\text{Alg}-\text{Ce}\) beads indicates the presence of \(\text{Fe}_3\text{O}_4\). The broadening of band at 3420 cm\(^{-1}\) in the FTIR spectra of Cr(VI) sorbed \(\text{Fe}_3\text{O}_4@\text{Alg}-\text{Ce}\) composite beads indicates the electrostatic attraction between the \(\text{HCrO}_4^-\) ions and the beads. The shifting of band from 1415 to 1424 cm\(^{-1}\) also indicates the electrostatic attraction. In addition, a new band at 572 cm\(^{-1}\) corresponds to the Cr–O bond which indicates the presence of Cr(VI) in the chromium sorbed magnetic beads [22].

The digital images of wet and magnetic properties of dry \(\text{Fe}_3\text{O}_4@\text{Alg}-\text{Ce}\) beads are shown in Fig. 2a and b respectively. The SEM image of the overall shape of \(\text{Fe}_3\text{O}_4@\text{Alg}-\text{Ce}\) composite bead is shown in Fig. 2c. The close view SEM images of \(\text{Fe}_3\text{O}_4@\text{Alg}-\text{Ce}\) composite beads and Cr(VI) sorbed \(\text{Fe}_3\text{O}_4@\text{Alg}-\text{Ce}\) composite beads are presented in Fig. 2d and e respectively. Rough and uneven bumps in the beads reveal the good condition for adsorption of Cr(VI) over \(\text{Fe}_3\text{O}_4@\text{Alg}-\text{Ce}\) composite beads. The change in the SEM micrographs of the beads before and after chromium treatment indicates the sorption of Cr(VI) onto the beads. The EDAX spectra of \(\text{Fe}_3\text{O}_4@\text{Alg}-\text{Ce}\) and chromium sorbed \(\text{Fe}_3\text{O}_4@\text{Alg}-\text{Ce}\) magnetic beads were shown in Fig. 2f and g. The Cr(VI) sorption has occurred on \(\text{Fe}_3\text{O}_4@\text{Alg}-\text{Ce}\) magnetic beads which were confirmed by the presence of chromium peaks in the EDAX spectra of chromium sorbed \(\text{Fe}_3\text{O}_4@\text{Alg}-\text{Ce}\) magnetic beads.

3.2. Effect of contact time on Cr(VI) sorption

For optimizing the maximum chromium SC, sorption experiments were carried out by varying contact time between 10 and 120 min with 100 mg/L as initial Cr(VI) concentration and 0.1 g as adsorbent dosage at solution pH (4.82). Fig. 3 shows that the sorption of chromium by \(\text{Fe}_3\text{O}_4\) particles, CaAlg composite and
Fe₃O₄@Alg-Ce magnetic beads reaches saturation at 100 min and hence 100 min was fixed as period of contact for the subsequent experiments. The magnetic alginate beads possess an enhanced SC of 14.29 mg/g than CaAlg composite and Fe₃O₄ particles which possess SCs of 9.45 and 9.72 mg/g respectively. Further studies were restricted to Fe₃O₄@Alg-Ce magnetic beads as it possesses the maximum SC than CaAlg composite and Fe₃O₄ particles.

3.3. Influence of pH

The sorption process is always pH dependant and the SC varies with pH medium. So sorption experiments were done at five different pH levels, viz. 3, 5, 7, 9 and 11 respectively with 100 mg/L as initial Cr(VI) concentration and by keeping all other parameters as constant. Fig. 4 shows that the maximum sorption was observed at acidic pH rather in basic pH. The SC declines in alkaline pH, which may be due to influence of hydroxide ions, which occupies the actives sites of the magnetic beads and it competes with HCrO₄⁻ ions during sorption [23]. The maximum SC was observed at pH 5 and hence the actual solution pH was maintained for the subsequent studies.

3.4. Effect of challenger co-ions on Cr(VI) sorption

The SC of the magnetic alginate beads in the presence of other ions which are commonly present in water, viz. Cl⁻, NO₃⁻, HCO₃⁻ and SO₄²⁻ was investigated at room temperature with a fixed initial concentration of 200 mg/L for these ions and 100 mg/L as initial Cr(VI) ion concentration and maintaining all other parameters as constant. Fig. 4 shows that the SC of the magnetic beads was slightly influenced in the presence of the challengers anions like Cl⁻, NO₃⁻ and SO₄²⁻ ions. On the other hand, the SC was decreased in the presence of HCO₃⁻ ions due to the increase in the solution pH which simultaneously reduced the active sites of the magnetic beads. Further it may also be due to the similarity in ionic radius of HCrO₄⁻ and HCO₃⁻ ions [24].

3.5. Sorption isotherms

The SC of Fe₃O₄@Alg-Ce magnetic beads was quantified by using Freundlich [25] and Langmuir [26] isotherms. The linear plot of log qₑ vs. log Cₑ indicates the applicability of Freundlich isotherm. The values of 1/n, n and kₑ of composite beads are given in Table 1. The favorable condition for adsorption is confirmed by the values of 1/n lying between 0 and 1 and n values between 1 and 10. The higher values of r indicate its applicability of Freundlich isotherm. The linear plot of Ce/qₑ vs Ce indicates the applicability of Langmuir isotherm. The values of b and Qₑ can be calculated from the intercept and slope of the plot Ce/qₑ vs Ce. The values of Qₑ for the sorbent were found to increase with the increase in temperature, which further confirms the endothermic nature and temperature dependence of the sorption process. The Rₛ values lying between 0 and 1 indicated that the conditions were favorable for adsorption. The lower χ² values indicate that the adsorption follows Freundlich isotherm.

3.6. Thermodynamic parameters

The effect of temperature is a major influencing factor in the sorption process. The sorption of Fe₃O₄@Alg-Ce magnetic beads was monitored at three different temperatures 30, 40 and 50 °C under the optimized condition and thermodynamic parameters viz., standard free energy change (∆G°), standard enthalpy change (∆H°) and standard entropy change (∆S°) were calculated. The calculated values of thermodynamic parameters are shown in Table 1. The negative values of ∆G° indicate the spontaneous nature of chromium sorption onto the composite. The value of ∆H° is positive indicating that the sorption process is endothermic. Similarly, the positive value of ∆S° shows the increased randomness at the solid/solution interface during chromium (VI) sorption.

3.7. Sorption kinetics

To understand Cr(VI) sorption, two types of kinetic models viz., reaction-based and diffusion-based models were applied to test the fitness of experimental data. The sorption process is analyzed by using reaction-based models, including pseudo-first-order [27] and pseudo-second-order models [28]. The linear plots of log (qe – qt) against t give straight line indicating the applicability of pseudo-first-order model. The slope of the straight line plot of log (qe – qt) against t at different temperatures viz., 30, 40 and 50 °C gives the value for pseudo-first-order rate constant (kₑ) and r values which are listed in Table 2. The pseudo-second-order equation can be found out experimentally by plotting t/qt against t. The values of qₑ, k, h and r for pseudo-second-order model obtained from the plots of t/qt vs. t for Cr(VI) sorption at different temperatures viz., 30, 40 and 50 °C by the composite beads are presented in Table 2. It reveals that the qₑ values of Fe₃O₄@Alg-Ce magnetic beads
of chromium sorbed Fe₃O₄@Alg-Ce magnetic beads confirms the sorption of chromium onto the magnetic alginate beads.

4. Conclusions

The developed low cost, eco-friendly and mechanically stable Fe₃O₄@Alg-Ce magnetic beads exhibits its applicability towards efficient Cr(Ⅵ) removal. The magnetic alginate beads were characterize using FTIR and SEM with EDAX analysis. The SC was influenced by pH medium and in the presence of bicarbonate ion. The sorption follows Freundlich isotherm and the nature of Cr(Ⅵ) removal was spontaneous and endothermic. The kinetic studies revealed that the pseudo-second-order and intra particle diffusion models are fitted well. The mechanism of Cr(Ⅵ) sorption was governed mainly by electrostatic adsorption. The prepared magnetic alginate beads will overcome the brittleness, poor mechanical strength and pressure drop during field studies.

References