

## Application of Magnetic Hydroxyapatite Nanoparticles for Removal of $\text{Cd}^{2+}$ from Aqueous Solutions

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### Expanded Abstract

#### Introduction

Environmental pollution by heavy metals is one of the most commonly-encountered problems in many areas in which biological controls have not been implemented. As these metals are non-biodegradable, they remain in the nature for a long time, and through deep percolation into underground water they can cause degradation of ecosystems. The uptake of these elements by plants and their inclusion in the chain of human and animal food is a great risk for the environment and the human being health. Due to non-biodegradable property of Cadmium and some other toxic heavy metals, these metals remain in the environment for a long time. Cadmium is one of the most toxic heavy metals and it has been reported to cause renal dysfunction, hyper-tension, lung insufficiency, bone lesions, cancer, and etc. The principal industrial sources of Cd in the environment are electroplating, smelting, alloy manufacturing, pigments, plastic, battery, mining and refining processes. In the recent years there have been some reports on the use of inorganic adsorbents for separating and removing heavy metals from aqueous solutions. Due to the availability, cost-effectiveness, stability against oxidation and reduction conditions and the possibility of recycling, inorganic adsorbents are economically viable. Traditional inorganic adsorbents with a low surface area lose their ability to absorb. Thus, making high capacity adsorbents for fast and easy removal of contaminants is a necessary step. One of the outstanding characteristics of fast-emerging nanotechnology studies is the high surface area to volume ratio of nanomaterials. Because of these outstanding features and other unique properties, nanoparticles may have potential to absorb pollutants from contaminated environments. So far, many technologies to remove heavy metals from aqueous solutions including chemical precipitation, ion exchange, membrane technologies, electrodialysis, and biosorption have been developed. Many of these methods have disadvantages such as high cost of operation, the high sludge, and secondary contamination. Nanoparticles with extremely small size and high ratio of surface-area to volume, provide better kinetics for the adsorption of metal ions from aqueous solutions. Hydroxyapatite as one of the major components of bones and teeth are widely used in biomedical and dental applications, drug delivery, and waste water remediation because of biocompatibility, low solubility, ion exchange and high sorption capacity of heavy metals. Magnetic separation technology as an efficient, fast and economical method for separating magnetic materials has been widely used in textile, biology, and environmental protection. In this study, magnetic hydroxyapatite nanoparticles were synthesized by co-precipitation method. The nanoparticles were characterized by x-ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), Fourier Transform Infrared spectroscopy (FT-IR), Vibrating Sample Magnetometer (VSM). Finally, the produced nanoparticles were used as adsorbents for the removal of cadmium ions from aqueous solutions. In batch experiments, the effects of pH, evaluation time and initial concentration of  $\text{Cd}^{2+}$  ions on adsorption were investigated.

#### Materials and Methods

$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{NH}_4\text{OH}$  (25%),  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{HPO}_4$  were purchased from Merck. All the solutions for the metal adsorption experiments were prepared using their nitrate salts. The amount of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (1.85 mmol) and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (3.7 mmol) was dissolved in 30mL of deoxygenated water under nitrogen atmosphere at room temperature, and then 10mL of  $\text{NH}_4\text{OH}$  solution was added to the resulting solution

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under vigorous mechanical stirring (300 rpm). A black precipitate was produced instantly. After 15 min, up to 50 mL of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (33.7 mmol) and 50 mL of  $(\text{NH}_4)_2\text{HPO}_4$  (20 mmol) solutions whose pH were all adjusted to 11 were drop wise added, simultaneously to the obtained precipitate solution for 30 min with mechanical stirring. The resulting puce suspension was heated at 110 °C for 2 h and then the mixture was cooled to room temperature and aged for 24 h without stirring. The obtained precipitate was separated by a magnet, washed repeatedly with deionized water till neutrality, dried in the drying oven at 110°C, and grinded with mortar. The final products were the prepared magnetic hydroxyapatite nanoparticles adsorbents. The adsorption behavior of the magnetic hydroxyapatite nanoparticles for  $\text{Cd}^{2+}$  ions was investigated by means of the batch experiments at  $24 \pm 1^\circ\text{C}$ . A known amount of magnetic hydroxyapatite nanoparticles was mixed with 50 mL of the corresponding  $\text{Cd}^{2+}$  solution over a period of time on a shaker at 150 rpm. After that, the aqueous phase was separated by magnetic decantation; the concentration of  $\text{Cd}^{2+}$  in the solution was determined by using an atomic absorption spectrometer. In order to determine the optimum of pH, 0.05 g of magnetic hydroxyapatite nanoparticles were added to 8 flask containing cadmium and under different pH conditions, the removal efficiency of cadmium ions by the adsorbent was detected. To evaluate the optimum dosage of magnetic hydroxyapatite nanoparticles adsorbent, 3–10 mg of freshly prepared magnetic hydroxyapatite nanoparticles was added to 50.0 mL of aqueous solution containing 50.0 mg/L  $\text{Cd}^{2+}$ . The results showed that increasing the amount of adsorbent, the adsorption efficiency of  $\text{Cd}^{2+}$  due to increased absorption of available sites, has increased the effect of contact time on the adsorption of  $\text{Cd}^{2+}$  by magnetic hydroxyapatite nanoparticles (pH of the solution: 5.5, amount of adsorbent: 0.1 g,  $\text{Cd}^{2+}$  concentration 50 ppm; temperature:  $25 \pm 1^\circ\text{C}$ ). Sorption isotherms were obtained by equilibrating magnetic hydroxyapatite nanoparticles with metal solutions of different initial concentrations: 10–300 mg/l for 30 min. After separation, the final concentrations of metal in the solutions were measured. The adsorption capacity was calculated according to the following equation:

$$q_e = (C_0 - C_e)V/m$$

The removal efficiency of lead ions was calculated by the difference of lead ion concentrations in aqueous solution using the equation expressed as follows:

$$R\% = (C_0 - C_e)/C_0 \times 100$$

where,  $q_e$  (mg/g) is the amount of lead ions adsorbed onto the unit amount of the adsorbent,  $C_0$  (mg/L) is the initial lead ion concentration,  $C_e$  (mg/L) is the final or equilibrium lead ion concentration,  $V$  (L) is the volume of the solution, and  $m$  (g) is the adsorbent weight in dry form. The Langmuir and Freundlich models were used to describe the relationship between the absorbed amount of  $\text{Cd}^{2+}$  and its equilibrium concentration in solution. To determine whether the  $\text{Cd}^{2+}$  adsorption process by magnetic hydroxyapatite nanoparticles is favorable or unfavorable for the Langmuir type adsorption process, the isotherm shape can be classified by a term "RL". RL values are ranged from 0 to 1 and indicate favorable adsorption, while  $RL > 1$ ,  $RL = 1$ , and  $RL = 0$  indicate unfavorable, linear, and irreversible adsorption isotherms. Phase composition of the samples were characterized using a X-ray diffractometer (XRD, Model pw-18/40, Philips, Germany) with  $\text{CuK}\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) incident radiation over the  $2\theta$  range of 10–80° at room temperature with a step size of 0.02°. The morphology of particles was investigated by scanning electron microscopy (SEM, Model VEGAII, XMU, Tescan, Czech Republic). To study the chemical structure of samples, Fourier Transform Infrared spectroscopy (FTIR, Model: EQUINOX55, Bruker, Germany) was used. For this, the samples prepared from 1:80 magnetic hydroxyapatite nanoparticles - KBr mixtures (by weight) were compacted into pellet form and then scanned from 4000 to 400  $\text{cm}^{-1}$ . The magnetization measurements were performed at room temperature using vibrating magnetometer. The concentration of  $\text{Cd}^{2+}$  in the solution was determined by using an atomic absorption spectrometer (Analytic jena-verio6).

## Conclusions

In this study, magnetic hydroxyapatite nanoparticles were synthesized by co-precipitation method, and the adsorption potential of nanoparticles for the removal of  $\text{Cd}^{2+}$  from aqueous solutions was investigated. The experimental results confirm that this adsorbent has the potential application for removal of  $\text{Cd}^{2+}$  from aqueous solution. The nanoparticles were characterized by x-ray diffraction, Field emission scanning electron microscopy, FTIR, and vibrating sample magnetometer. The effect of contact time, initial metal ions concentrations, pH, adsorbent dosage was discussed. The XRD patterns of samples confirm the hexagonal structure of hydroxyapatite and tetragonal structure of maghemite. This pattern indicates that the diffraction peaks are in agreement with the standard card (0566-074-01 ICSD) of hydroxyapatite and (0566-013-01 ICSD) of the tetragonal of maghemite. FESEM image of the nanoparticles showed almost spherical shape. The average size of nanoparticles was  $19 \pm 2$ . FTIR spectroscopy reveals expected bonds formation. Magnetic properties of nanoparticles prepared at room temperature were studied in the range of  $10000 \pm \text{Oe}$ . Hysteresis curves of nanoparticles showed that the saturation magnetization and coercivity of the nanoparticles was 2.8 emu/g and 0 Oe, respectively. The nanoparticles indicate super-paramagnetic behavior. The super-paramagnetic property of

the magnetic hydroxyapatite nanoparticles is critical for their application in industrial catalysis, environmental protection, biomedical and bioengineering field, which prevents them from aggregation and enables them to re-disperse rapidly when the magnetic field is removed. Finally, the produced nanoparticles were used as adsorbents for the removal of  $\text{Cd}^{2+}$  from aqueous solutions. In batch experiments, the effects of pH, evaluation time, adsorbent dosage and initial concentration of  $\text{Cd}^{2+}$  ions on adsorption were investigated. The highest removal efficiency of  $\text{Cd}^{2+}$  was in the range  $\text{pH} = 5-7$ . The removal efficiency increases with time in the first 30 min. Then, the adsorption curve reached equilibrium after this time. Removal efficiency increased as the adsorbent dosage was raised. When a dosage of 0.1 g was used, the removal efficiency reached 96%, indicating that the composite adsorbent magnetic hydroxyapatite nanoparticles showed strong affinity to  $\text{Cd}^{2+}$ . The adsorption was relatively fast and the equilibrium was established within 30 min to be considered the adsorption isotherm data could be well described by Langmuir equation. The  $R_L$  values in this study were in the range from 0.045 to 0.488 which indicated the favorable adsorption between  $\text{Cd}^{2+}$  and magnetic hydroxyapatite nanoparticles sorbent. Maximum adsorption capacities of  $\text{Cd}^{2+}$  were 84.746 mg/g. The results of adsorption experiments indicated that magnetic hydroxyapatite nanoparticles have high adsorption efficiency with short reaction time (30 min) and can be very effective to remove  $\text{Cd}^{2+}$  ions from aqueous solution. The most prominent advantage of prepared magnetic hydroxyapatite nanoparticles adsorbents with super-paramagnetism and adsorption capacities was the separation convenience from aqueous solutions.

**Keywords:** aqueous solutions, cadmium, co-precipitation method, hydroxyapatite, magnetic nanoparticles.

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