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Enhanced hexavalent chromium removal from aqueous solution using a sepiolite-stabilized zero-valent iron nanocomposite: Impact of operational parameters and artificial neural network modeling

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ABSTRACT

The efficiency of zero-valent iron nanoparticles (ZVINs) for the removal of chromium Cr(VI) from solutions is strongly decreased due to particle agglomeration. To solve this problem, a sepiolite-stabilized ZVIN (S-ZVIN) composite was made using a liquid-phase method and then characterized employing scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectrometer (EDS). Batch experiments were also conducted to (1) investigate the influence of various experimental variables on the removal efficiency of Cr(VI), (2) compare the removal efficiency of bare ZVIN and S-ZVIN treatments and (3) evaluate the capability of the artificial neural network (ANN) technique to model the Cr(VI) removal. The Cr(VI) removal efficiency was enhanced by increasing S-ZVIN dosage while a considerable decrease was observed by increasing the initial Cr(VI) concentration. The acidic and neutral pH values were appropriate for Cr(VI) removal. The enhancement was observed in Cr(VI) removal by increasing chloride concentration. Additionally, pseudo first-order showed better performance than pseudo second-order kinetic model to fit the experimental data of Cr(VI) removal. The ANN model could predict the experimental data of Cr(VI) removal with a determination coefficient of 0.9803. The relative significance of each input variable on the removal of Cr(VI) was calculated.

1. Introduction

Nowadays, the growth of industrialization and the abrupt increase in population have led to the production of high amounts of pollutants. Chromium is considered a contaminant which is found in various industrial wastewaters such as those of electroplating, leather tanning, dye industries, and metal processing [1]. The human exposure to the chromium may cause diseases like asthma [2] and tubular damage [3]. An increase in concentration of chromium in water resources also leads to spoiling of sperm in males and breast cancer in females [4,5]. The Environmental Protection Agency (EPA) of the United States has set 0.05 mg/L and 0.01 mg/L as the maximum permissible concentration of chromium in potable water and inland water, respectively [6]. However, the common concentration of chromium in contaminated aqueous sources is considerably higher than the permissible limit. Consequently, the high concentration of chromium should be reduced to meet the limit. Therefore, removal of excess amount of chromium from water supply sources has been a great concern for environmentalists.

In order to remove metals from contaminated solutions, several conventional techniques including ion exchange [7], adsorption [8], biosorption [9], electrocoagulation [10], and photo catalysis [11] have been utilized to remove metals from contaminated solutions. However, the aforementioned conventional techniques either cost a lot or have some operational restrictions. Hence, application of novel technology in order to remove Cr(VI) with low-cost and high efficiency is a priority.

In the past decade, the application of zero-valent iron (Fe^0) in treatment of polluted groundwater has attracted the attention of environmental researchers. The passive remediation technology was performed using microscale zero-valent iron in permeable reactive barriers (PRBs). However, particle size introduces a critical limitation regarding the reactivity of particles with target contaminants.

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To overcome the problem, zero-valent iron nanoparticles (ZVINs) with higher surface areas, which potentially provide more reactivity with contaminants, were widely used to remove a wide variety of pollutants such as nitrate (NO_3^-) [12,13], Pb^{2+} [14], Cr(VI) [15], nitrobenzene [16], and polychlorinated biphenyls (PCBs) [17] from soil and water media. The removal of Cr(VI) using ZVIN has been ascribed to: (1) the reduction of Cr(VI) as an electron acceptor via ZVIN as an electron donor to trivalent chromium and (2) the precipitation of Cr(III) onto the surfaces of ZVIN. Eqs. (1)–(3) express the above-mentioned mechanisms ($0 < x < 1$) [18,19]:

$$2Fe^0 + {Cr_2O_7}_{(aq)}^{2-} + 14H^+ \rightarrow 2Fe_{(aq)}^{3+} + 2Cr_{(aq)}^{3+} + 7H_2O \quad (1)$$

$$xCr^{3+} + (1-x)\,Fe^{3+} + 3H_2O \rightarrow (Cr_xFe_{1-x})\,(OH)_3 + 3H^+ \quad (2)$$

$$xCr^{3+} + (1-x)\,Fe^{3+} + 2H_2O \rightarrow Cr_xFe_{1-x}OOH + 3H^+ \quad (3)$$

Although ZVIN shows a great ability to remove environmental pollutants, their application in remediation technology has some restrictions. It has been shown that bare ZVINs tend to agglomerate rapidly in aqueous solutions and reach the micro-meter size [20,21]; as a consequence, their surface area and efficiency to react with environmental pollutants decreases. Therefore, to enhance the colloidal stability and surface area of ZVIN, a large number of stabilizers like polyacrylic acid [22], guar gum [23], starch [24], and polyvinylpyrrolidone [25] have been used.

The porous materials have recently been replaced with polyelectrolytes to stabilize ZVIN suspension and to improve their dispensability [26]. Shi et al. [27] used bentonite-supported ZVIN to remove Cr(VI) from wastewater and showed that the application of bentonite significantly decreased ZVIN agglomeration. Kaolinite was also used to increase Pb^{2+} removal efficiency by ZVIN through keeping them dispersed and stabile in the suspension [28]. Sepiolite is a low-cost mineral which is potentially a suitable adsorbent to treat polluted groundwater because of the high surface area and its exclusive structure [29,30]. Although several types of minerals have been employed to improve colloidal stability of ZVIN, there are few studies which have used sepiolite as a stabilizer in the synthesis procedure of ZVIN. Beside the intrinsic nature of ZVIN, chemical compositions and pH of groundwater can play an important role in ZVIN efficiency. The presence of luxury amounts of anions like nitrate, phosphate and chloride may lead to a renewal of surface reactive sites and life-time of ZVIN [31].

Another point of the present work is finding the suitable artificial neural network (ANN) model to predict the reductive removal of Cr(VI) from aqueous solutions using S-ZVIN. The ANN is intrinsically a novel and promising data-based approach that has been applied for modeling the contaminant removal process. The employment of ANN approach to eliminate the difficulties of environmental engineering has been considered as a brilliant subject of numerous review articles. To the best of our knowledge, although ANN was applied to model a couple of processes (*i.e.* biosorption [32], adsorption [33], photoelectron-Fenton [34] and photocatalysis [35]), the artificial neural network modeling of reductive removal of Cr(VI) using ZVIN was not discussed well.

The aims of this study are to synthesize sepiolite-supported ZVIN and investigate the removal efficiency of Cr(VI) form aqueous solutions using S-ZVIN under the influence of initial pH of aqueous solution, dosage of S-ZVIN application, initial concentration of Cr(VI), and chloride ion (Cl^-) concentration. ANN approach has been used to model the experimental data of Cr(VI) removal using S-ZVIN.

2. Materials and methods

2.1. Materials and chemicals

The natural sepiolite used in this study was prepared from Daneshbonyad Farapooyan Isatis Co., Yazd, Iran. The mineral was ground using ball mill and then passed through a 0.053 μm sieve. All chemical reagents, ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$), sodium borohydride ($NaBH_4$), potassium dichromate ($K_2Cr_2O_7$), 1,5 diphenylcarbazide, acetone, concentrated hydrochloric acid (12N HCl), sodium hydroxide (NaOH), and potassium chloride (KCl) used in this study were of analytical grade with no pretreatments. The chromium solution was prepared by dissolving enough amounts of $K_2Cr_2O_7$ in a specific volume of distilled water. In addition, all solutions were kept in 4 °C prior to the experiments.

2.2. Synthesis of ZVIN

The bare-ZVIN was synthesized using liquid-phase method [36]. In brief, 20 mL of $NaBH_4$ solution (1.05 M $NaBH_4$) was added together with the constant flow of 3 mL/min into 100 mL of ferrous sulfate (0.065 M $FeSO_4$) using dropping funnel under N_2 atmosphere. The reaction was performed until the end of dropping of $NaBH_4$ solution, when the color of suspension became dark. Afterwards, in order to miniaturize the size of particles, suspension was stirred for another 30 min. The ferrous sulfate was reduced based on Eq. (4) [37]:

$$2Fe^{2+} + BH_4^- + 2H_2O \rightarrow 2Fe^0 + BO_2^- + 4H^+ \quad (4)$$

After observing black precipitated particles in suspension, a strong magnet was applied to separate particles from the suspension. The filtered particles were washed with deionized water and acetone sequentially and were vacuum dried in a desiccator for 24 h.

For the synthesis of S-ZVIN, 100 mL of 0.065 M $FeSO_4$ was mixed with 100 mL of sepiolite suspension (10 g/L) using a magnetic stirrer. Then 20 mL of 1.05 M $NaBH_4$ aqueous solution was carefully added into the solution. The subsequent steps for the synthesis of S-ZVIN were similar to the ones in the previous section.

After the synthesis of ZVIN, the size and morphology of ZVIN and sepiolite were examined using scanning electron microscope (SEM) (Hitachi S 4160 model, Japan) and LEO-906E transmission electron microscope (TEM), respectively. Furthermore, elemental composition of synthesized particles and sepiolite were determined using energy dispersive X-ray spectroscopy (EDS) technique.

2.3. Colloidal stability of ZVIN

To assess the colloidal stability of synthesized ZVINs, 0.25 g/L ZVIN suspension was prepared in a cell of spectrophotometer. The changes in absorbance of suspension during 180 min were monitored at 508 nm using a UV-Visible spectrophotometer (Unico, USA) at quiescent conditions and at room temperature (25 ± 2 °C). The pH of suspension was set to 3, and 0.1 mM NaCl solution was used to provide ionic strength [38].

In addition to spectroscopic method, direct observation method was also used to evaluate the colloidal stability of ZVINs. Based on this, 0.25 g/L of ZVIN suspension was prepared and colloidal stability of suspensions were monitored from the photos taken using a digital camera in different time intervals during a period of 180 min.

2.4. Batch experiments for Cr(VI) removal

To study the Cr(VI) removal from aqueous solutions, batch experiments were conducted in plastic bottles at room temperature. To compare the ability of bare ZVINs and S-ZVINs for the removal of Cr(VI), 0.01 g of each adsorbent was added to plastic bottles containing 20 mL of 100 mg/L Cr(VI). The pH of solutions was adjusted to 3 and the bottles were shaken using rotary shaker at 120 rpm for 5, 10, 15, 30, 45, 60, 75 and 90 min. Moreover, to obtain the optimum pH of Cr(VI) removal, similar experiments were conducted at equilibrium contact time (determined from the kinetic experiments) in the pH range of 3–10. The pH of aqueous solutions was adjusted using 0.1 M HCl and 0.1 M NaOH.