

Hexavalent Chromium Removal from Aqueous Solutions by Adsorption onto Synthetic Nano Size ZeroValent Iron (nZVI)

A.R. Rahmani, M.T. Samadi, R. Noroozi

Abstract—The present work was conducted for the synthesis of nano size zerovalent iron (nZVI) and hexavalent chromium (Cr(VI)) removal as a highly toxic pollutant by using this nanoparticles. Batch experiments were performed to investigate the effects of Cr(VI), nZVI concentration, pH of solution and contact time variation on the removal efficiency of Cr(VI). nZVI was synthesized by reduction of ferric chloride using sodium borohydrid. SEM and XRD examinations applied for determination of particle size and characterization of produced nanoparticles. The results showed that the removal efficiency decreased with Cr(VI) concentration and pH of solution and increased with adsorbent dosage and contact time. The Langmuir and Freundlich isotherm models were used for the adsorption equilibrium data and the Langmuir isotherm model was well fitted. Nanoparticle ZVI presented an outstanding ability to remove Cr(VI) due to high surface area, low particle size and high inherent activity.

Keywords—Adsorption, aqueous solution, Chromium, nZVI, removal.

I. INTRODUCTION

THE increasing contamination of urban and industrial wastewaters by toxic metal ions is a worrying environmental problem. One of the toxic and important heavy metals in wastewater is chromium. Industrial effluents from tanning, electroplating, paint, textile industries, etc [1] contains chromium species above the maximum contaminant level (MCL). Both trivalent and hexavalent forms of chromium exists in industrial wastewater. The toxicity caused by hexavalent chromium is high and therefore its removal from effluents is necessary. The hexavalent form has been considered to be more hazardous due to its carcinogenic properties [2]. Yet various methods used for removal of Cr(VI) from industrial wastewater include filtration, chemical precipitation, electro deposition and membrane systems or even ion exchange process [2].

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Chemical precipitation and reduction process needs other separation techniques for the treatment and disposal of high quantities of waste metal residual sludge produced [3]. The application of membrane systems for the wastewater treatment has major problems like membrane scaling, fouling and blocking. The disadvantage of the ion exchange process is the high cost of the resin while the electro deposition method is more energy intensive than other methods.

In recent years, for overcoming of these problems, investigations have been carried out for the effective removal of large quantities of Cr(VI) from wastewater using Chemicals [4]. Many reduction agents such as H_2S , Fe^{2+} , Fe^0 , etc. were employed for reduction of Cr(VI) which Fe^0 appear to be one of the most capable technologies. The mechanisms of Cr(VI) reduction by Fe^0 is a cyclic and consists of multiple reactions electrochemical corrosion [5]. In this process, the factors affecting such as iron metal type, Fe^0 area concentration and pH value on the rate of Cr(VI) reduction by Fe^0 were tested. Reactivity of ZVI can improve by decreasing of particle size in nanoscale zero-valent iron (nZVI) form [6, 7].

For that reason and in view of highly efficiency of nZVI, the main objective of present work was synthesis of nZVI and determination of its application in Cr(VI) removal from aqueous solutions. Also the influence of Cr(VI) and nZVI concentration, variations pH of solution and contact time on the efficiency of Cr(VI) removal was evaluated and the isotherm parameters were obtained by application of Langmuir and Freundlich models.

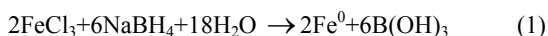
II. MATERIALS AND METHODS

2.1. Preparation of Cr(VI) solution and chemicals

All chemical reagents that used in this study were obtained from Merck (Germany). The solutions were prepared by dissolving the adequate quantities of the compounds in distilled water. Stock solution (1000 mg/l) of Cr(VI) was prepared by dissolving of $K_2Cr_2O_7$ into distilled water. Experimental solutions of the desired concentrations were obtained by successive dilutions and determined in 540 nm by UV/VIS spectrophotometer (Shimadzo-1700, Japan). 0.1 M NaOH or HCl was used to adjustment of pH and controlled by pH meter (Suntex model sp-701). Water was purified with a water distiller (Fater Electronic model 2104). The experiments were carried out at room temperature ($25 \pm 2^\circ C$). For all batch experiments, glassware and bottles were washed and rinsed before the use with HNO_3 and then by distilled water.

2.2. Synthesize of nZVI

nZVI was produced by reduction of ferric iron in the presence of sodium borohydrid. These particles were prepared freshly each day by adding 0.16 M NaBH₄ aqueous solution drop wise to a 0.1 M FeCl₃·6H₂O aqueous solution at ambient temperature and under atmospheric conditions [8-9]. The preparation of solutions involved the following steps: sodium borohydride (NaBH₄, 0.6053 g) solids were dissolved in 100 mL of 0.1 M NaOH solution (0.16 M NaBH₄ in 0.1 M NaOH solution), and then 2.7030 g of FeCl₃·6H₂O was dissolved into 100-mL pure water (0.1 M FeCl₃·6H₂O). NaBH₄ solution can be made either in water or NaOH solution, although NaBH₄ is unstable in water and can quickly result in a loss of reduction power. Addition of the NaBH₄ to the FeCl₃ solution in the presence of vigorous magnetic stirring resulted in the rapid formation of fine black precipitates as the ferric iron reduced to Fe⁰ and precipitated according to the equation (1): [6]



The particles were washed 3 to 4 times with a 10⁻⁴ M HCl (pH 4) solution and stored as a 5-mg Fe/mL concentrate at pH 4 and kept in a refrigerator at <4°C. The characterizations of solid-phase nZVI were carried out using XRD (Philips XRert) and SEM (Philips XL30).

2.3. Adsorption experiments

In each adsorption experiment, 100 ml of Cr(VI) solution of known concentration and pH was added to 0.25 g of nZVI in a 250 ml Erlenmeyer flasks. The beaker was mixed by magnetic stirrer (150 rpm) at room temperature for different time. After given period of time the sample centrifuged at 3000 rpm for 15 min. Then the solution filtered through 0.45 μm membrane filter and analyzed for Cr(VI). The residual Cr(VI) was analyzed by using 1,5- diphenylcarbazine and by a spectrophotometer at a wavelength of 540 nm [10]. The experiments were done by different concentration of nZVI (0.1, 0.25, 0.5, 1.0 g/100CC), initial Cr(VI) concentration (10, 20, 30 mg/L) and initial pH (3, 7, 10) in interval different time.

III. RESULTS AND DISCUSSION

3.1 Characterization of Fe⁰ Nanoparticles

The pristine samples collected from different crops synthesis of nZVI and were tested for characterization. Our result was similar to those reported in the literatures [7, 11]. The SEM micrograph of the Fe⁰ nanoparticles is shown in figure 1. Synthetic nZVI particle was in the size range of 10-100 nm as measured by SEM. This micrograph showed that the Fe⁰ nanoparticles do not appear as discrete particles but form much larger dendritic flocs whose size could reaches micron scale.

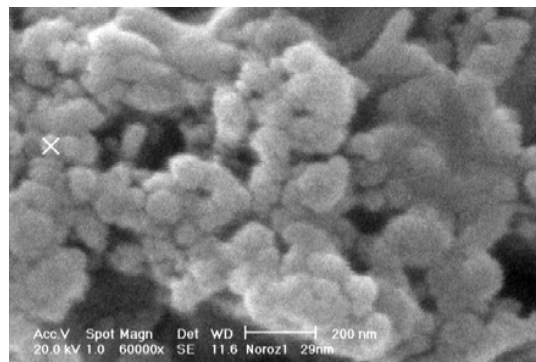


Fig. 1 SEM image of synthesized nZVI

The aggregation is attributed to the magnetic forces among the Fe particles. Similar phenomenon was observed by other researchers [6]. X-Ray diffraction of nZVI surface composition indicated that surface species of prepared nZVI is Fe⁰ and FeOOH (figure 2).

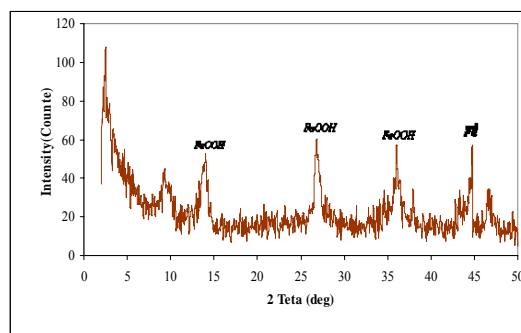


Fig. 2 X-Ray diffraction analysis of synthesized nZVI

3.2. Effect of pH on Cr(VI) removal

The effect of pH on the removal of Cr(VI) was studied by changing the initial pH (3-10) in interval different time. The relation between the initial pH of the solution and the removal efficiency of Cr(VI) is shown in Fig. 3. The percentage removal of Cr(VI) decreased from 99% to 67.3% with increasing the initial pH. Because at a low pH (pH=2), the dominant form of Cr(VI) is HCrO₄⁻ and the surface of the adsorbent is positively charged. By increasing of pH, the HCrO₄⁻ species shifts to other forms CrO₄²⁻ and Cr₂O₇²⁻. The decrease in adsorption of Cr(VI) by increasing the pH is due to the competition between the anions CrO₄²⁻ and OH⁻ [12]. Similar observations have been reported too [6].

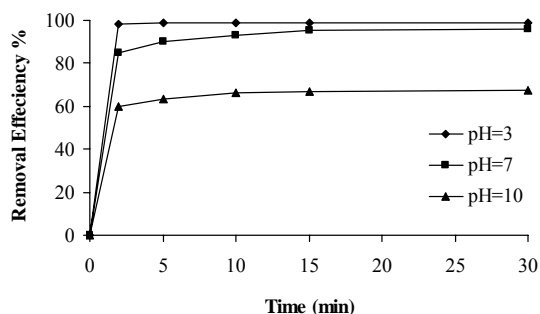


Fig.3 Effect of pH on the removal of Cr(VI) by synthesise of nZVI; (initial Cr(VI) concentration= 20 mg/L, nZVI= 0.25 g/100cc)

3.3. Effect of initial concentration of Cr(VI)

The relation between the initial concentration of Cr(VI) and removal efficiency of Cr(VI) is shown in Fig. 4. The results showed that the removal efficiency of Cr(VI) decreased from 99% to 71.3% with increasing the initial Cr(VI) concentration from 10 to 30 mg/L. The decrease in the percentage removal of Cr(VI) can be explained with the fact that the nZVI had a limited active sites, which would have become saturated above a certain concentration [5, 13].

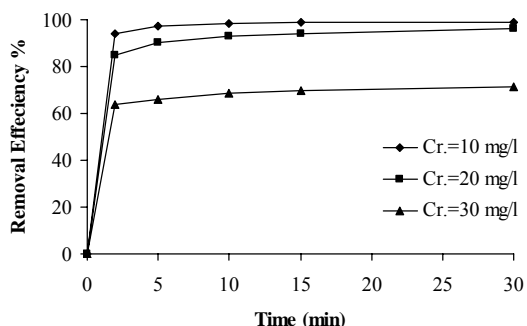


Fig. 4 Effect of initial Cr(VI) concentration on Cr(VI) removal by synthesise of nZVI; (pH=7, nZVI = 0.25 g/100cc)

3.4. Effect of nZVI concentration

The effect of nZVI concentration on the removal of Cr(VI) by nZVI was studied by changing the initial nZVI concentration (0.1, 0.25, 0.5, 1.0 g/100cc) in interval different time (Fig 5). The percentage removal of Cr(VI) increased from 46.2% to 99.99% with increasing the nZVI concentration from 0.1 to 1 g/100cc. The increase in Cr(VI) removal with an increase in the nZVI amount is due to the increase in surface area and adsorption sites available for adsorption [14]. Similar observations have also been reported [5, 15].

3.5. Effect of contact time

The effect of contact time on Cr(VI) removal by nZVI was studied by variation of the contact time (2 to 120 min), adsorbent concentration= 0.1 g/100CC and pH=7 for different initial Cr(VI) concentrations. The relation between the contact time and the removal efficiency of Cr(VI) is shown in Fig. 6. The percentage removal of Cr(VI) increased from 41.27% to

48.5% with increasing the contact time from 2 to 120 min for initial Cr(VI) concentration of 20 mg/L. The optimal removal efficiencies were obtained at 10 min.

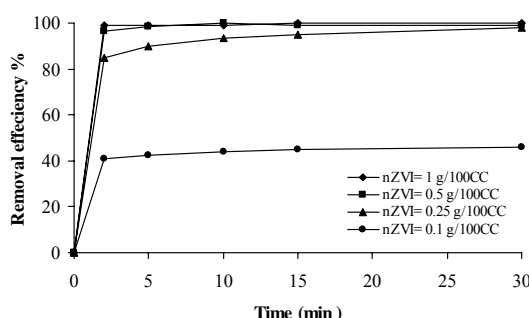


Fig. 5 Effect of nZVI on Cr(VI) removal by synthesise of nZVI; (pH=7, initial Cr(VI) concentration= 20 mg/l)

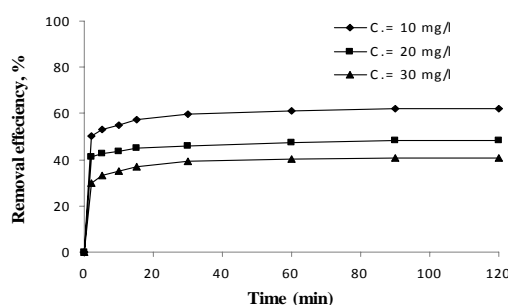


Fig. 6 Effect of contact time on Cr(VI) removal by synthesise nZVI; (pH=7, nZVI=0.1 g/100cc)

3.6. Equilibrium studies

Equilibrium studies were conducted in a series of 250 ml Erlenmeyer flasks filled with 100 ml of 20 mg/L Cr(VI) solutions with variation adsorbent concentration and pH=7.0±0.2. After 24 hr., the samples were separated and analyzed for their residual Cr(VI) concentration. The equilibrium adsorption capacity was calculated by equation (2) [16].

$$q_e = (C_0 - C_e) \times V / M \quad (2)$$

where q_e (mg/g) is equilibrium adsorption capacity, C_0 and C_e are initial and equilibrium concentrations (m/g) of Cr(VI), respectively. V (L) is the volume of solution and M (g) is the weight of the adsorbent.

The equilibrium data was fitted onto two common isotherm models, Freundlich and Langmuir.

The non-linear form of the Langmuir isotherm model for monolayer adsorption is expressed by equation (3) [1]:

$$q_e = \frac{q_m K_q C_e}{1 + K_a C_e} \quad (3)$$

The equation can be rearranged to the following linear form:

$$\frac{c_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m} c_e \quad (4)$$

where C_e is the equilibrium concentration (mg/L), q_e the amount of Cr(VI) ions sorbed per mass of adsorbent (mg/g), q_m is q_e for a complete monolayer (mg/g) and K_a is a sorption equilibrium constant (l/mg).

The non-linear form of the Freundlich equation is expressed by equation (5) [17].

$$q_e = K_f C_e^{1/n} \quad (5)$$

This equation is frequently used in the linear form by taking the logarithm of both sides.

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (6)$$

Where k_f and n are the isotherm constants.

The equilibrium data were fitted to the both Langmuir and Freundlich models. Plotting the experimental data using equations 3 and 5 in Fig. 7 indicates that both Freundlich and Langmuir models give good fit for the data. The isotherms constants were calculated and presented in Table 1. The comparison of correlation coefficients (r^2) indicates that adsorption was better described by Langmuir isotherm ($r^2=0.996$).

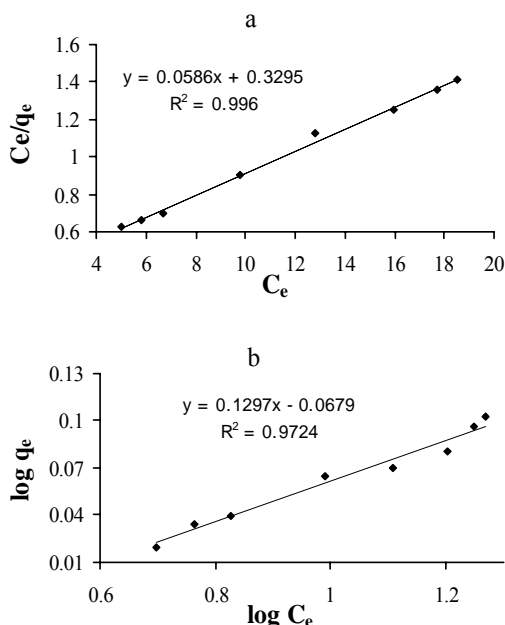


Fig. 7 Linear forms of Langmuir (a) and Freundlich (b) isotherms for Cr(VI) adsorption onto the synthesise of nZVI

TABLE I
ISOTHERM CONSTANTS FOR ADSORPTION OF Cr(VI) ONTO THE SYNTHESIZE OF nZVI

Langmuir constants			Freundlich constants		
Q_m (mg/g)	K_a (l/mg)	R^2	K_f	N	R^2
17.24	0.17	0.996	1.34	8.33	0.972

IV. CONCLUSION

- The experimental results indicated that the pH of the aqueous solution is crucial to the adsorption of Cr(VI) possibly because the presence of various Cr(VI) species

and the surface charge of adsorbent. The results showed that the removal of hexavalent chromium ion from aqueous solutions on synthesise of nZVI are effective for solution pH below 7.

- The Langmuir isotherm describes the experimental data better than Freundlich isotherm.
- Finally, the results show that the synthesise of nZVI can be used for the treatment of aqueous solutions containing chromium fasten and effective.

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