Kinetic and thermodynamic studies on the removal of Cr (VI) ions from aqueous solution using n-ZVI

Department of chemistry, Faculty of Science, Benha University, Benha, Egypt, 13518
¹*Corresponding author Email. Eman.kamar@fsc.bu.edu.eg

Abstract
We have studied the removal of Cr (VI) ion from aqueous solution at different condition using n-ZVI. The n-ZVI was prepared via borohydrate reduction under inert atmosphere. The effect of temperature, concentration and loading quantities on kinetic and equilibrium of chromium ion removal using n-ZVI were thoroughly examined. The prepared n-ZVI was characterized by several techniques including X-ray diffraction (XRD), transmission electron microscope (TEM) and scanning electron microscope (SEM). The adsorption capacity was found to be 40 mg g⁻¹ at pH 3.9 and 300 K. The pseudo second order was found to be the best fitting kinetic model. The adsorption activation energy was calculated and given to be 41.56 kJ mol⁻¹. The thermodynamic parameters ∆G°, ∆H° and ∆S°, were also calculated. The results indicate the endothermic and spontaneous nature of the adsorption process.

Keywords: Zero valent iron, Chromium, Thermodynamic, Kinetic, Nanoparticles.

Received; 5 May 2018, Revised form; 14 Jun 2018, Accepted; 14 Jun 2018, Available online 1 July, 2018

1. Introduction

In recent decades, the rapid increase in levels of environmental contamination has resulted in increasing concern for both human health and global ecosystems. Inorganic contaminants are heavy metals because of their toxicity towards aquatic-life, human beings, and the environment. Water pollution caused by heavy metal ions, such as Ni (II), Cr (VI), Mo (VI), and Pb (II) in ground water, is one of the most serious environmental problems. Among the toxic metal oxyanions, chromium is widely distributed and exists in the waste coming from paint industry, metal finishing, textile dyeing, electroplating, and leather tanning [1]. Chromium mainly exists as trivalent Cr (III) and hexavalent Cr (VI) form in the natural environment. Because of the low solubility, mobility, and the weak ability to oxidize other species, the toxicity of Cr (III) is much lower than Cr (VI) [2]. In contrast, Cr (VI) demonstrates the higher toxicity, which can produce mutagenic, teratogenicity, and carcinogenic effects in biological systems by reacting with nucleic acids and other cellular components [3]. Due to the high toxicity of Cr (VI), applying efficient methods to remove Cr (VI) from waste water is of great importance. So far, various kinds of methods have been developed to reduce the harmful effects of Cr (VI), such as chemical extraction [4], reduction-precipitation [5], ion exchange [6], bioleaching process [7, 8], and biosorption [9, 10].

Chemical precipitation may cause secondary pollution, and the electrolysis method is energy consuming and economically unfavorable. A large amount of high purity organic solvents is needed for liquid–liquid extraction and liquid membrane separation, most of which are harmful to the environment and health. Among these methods, adsorption holds the significant position due to its high removal efficiency, low energy demand, and less chemical investment [11-13]. In the past years, researchers have applied various adsorbents to remove Cr (VI) from waste water, such as activated carbons [14], zeolites [15, 16], clays [17], and non-magnetic particles [18]. However, these adsorbents have many defects including low porosity, low surface area, and lack of functional groups [19], which is of great importance for an efficient adsorbent. Hence, adsorbents with high porosity, large surface area, and high functionality need to be developed for efficient removal of Cr (VI). Alternatively, Nano scale zero-valent iron (n-ZVI) has shown good potential to remove metal ions and other aqueous organic pollutants. Such as, its physicochemical properties and reductive capacity can facilitate rapid decontamination of polluted water and the removal rate is extremely high [20, 21]. Limited numbers of publications have been reported to illustrate the thermodynamics and activation energy calculations of the chromium ion adsorption using nZVI adsorbate [22, 23].

In this study, we have investigated the kinetic and adsorption isotherm models for chromium ion removal using nZVI. Different thermodynamic parameters and activation adsorption energy were calculated. Furthermore, the core shell model was verified manipulating the obtained results.

2. Materials and methods
All chemicals were of analytical grades and used as received. Deoxygenated deionized water (DDI) was used in the preparation of reagent solutions. However, the nitrogen atmosphere was maintained throughout the experiment process. FeCl₃, 6H₂O, NaBH₄, NaOH pellets, HCl, K₂Cr₂O₇, and dehydrated ethanol were supplied by
Sigma Aldrich. DDI water was prepared by passing pure nitrogen gas through DI water at a flow rate 100 ml per minute for 2 hours.

2.1 Preparation of n-ZVI
The black solids n-ZVI was prepared as previously reported [21]. Briefly, in 3 neck flask, 50 ml (0.02M) of NaBH₄ was added to 50 ml of (0.05M) FeCl₂·6H₂O dropwise, while the mixture was vigorously stirred by the aid of mechanical stirring at 400 RPM at room temperature. The n-ZVI was collected and washed with DDI water, followed by the dehydrated absolute ethanol. The prepared n-ZVI was dried under vacuum at room temperature in nitrogen atmosphere. Finally, it was stored in a vacuum desiccator.

2.2 Characterization
The surface morphology of n-ZVI was studied using field emission electron microscope (FE-SEM, JEOL6390) and high resolution electron microscope (HR-TEM, JEM2100).

2.3 Kinetic studies
Kinetic studies of Cr (VI) removal from aqueous solutions were carried out in different conditions of Cr (VI) concentration, loading amount of n-NZVI and at different temperatures.

Preliminary experiments were carried out to study the effect of pH. The results showed that the maximum removal is obtained at pH 3.9. Accordingly, all further experiments were carried out at pH 3.9. The loading effects of n-ZVI on the Cr (VI) kinetic removal were investigated using 0.03, 0.05 and 0.07 g added to 20 ml of Cr (VI) solution. The effect of different concentrations was studied using 75, 100, 150 and 200 ppm of Cr (VI). Samples were collected at different time intervals for Cr (VI) analysis. The adsorbed Cr (VI) concentration was measured using UV–Visible spectrophotometer, Jasco model V670. Adsorption isotherms were carried out at different Cr (VI) initial concentration 75,100,150 and 200 ppm and temperatures of 27,30 and 40 °C. The samples were collected after equilibrium and analyzed for Cr (VI) concentration.

The amount of Cr (VI) removal was estimated using the following equation,

\[ q_e = C_i - C_e \times \frac{V}{m} \]  (1)

Where; \( C_i \) and \( C_e \) is the initial and the concentration at time t, V is the volume of the solution (ml) and m is the mass of the solid n-ZVI (g).

2.4 Kinetic models
Different kinetic models are used to examine the experimental results of Cr (VI) removal. Pseudo first order, pseudo second order, and intraparticle diffusion models are utilized to reveal the adsorption kinetics process. The linear form of these models can be expressed as,

Pseudo first order
\[ \ln(q_e - q_t) = \ln(q_e) - k_1 \cdot t \]  (2)

Pseudo second order
\[ \frac{1}{q_t} = \frac{1}{K_2q_e^2} + \frac{1}{q_e^2} \]  (3)

Intraparticle diffusion
\[ q_t = K_f \cdot t^{0.5} + I \]  (4)

Where \( q_e \) and \( q_t \) (mg g⁻¹) the adsorption capacities at equilibrium and at time t (min), \( K_1 \) (min⁻¹) and \( K_2 \) (g mg⁻¹ min⁻¹) are the rate constant of pseudo first order and second order, respectively. \( K_p \) (g mg⁻¹ min⁻⁰⁵) is the intraparticle diffusion rate constant and I is the intercept.

2.5 Adsorption activation energy
Adsorption activation energy was calculated using Arrhenius equation (5) extracted from the pseudo second order model, the most fitted kinetic models. The plot of ln \( K_p \) against inverse temperature yields a straight line with slope \( -E_a/R \)

\[ K_p = K \cdot e^{\frac{-E_a}{RT}} \]  (5)

Where: K is the temperature independent constant (g mg⁻¹ min⁻¹), \( E_a \) sorption activation energy (KJ mol⁻¹), R the universal gas constant (8.312 J mol⁻¹ K) and T the absolute solution temperature.

2.6 Adsorption isotherm models
2.6.1 Langmuir isotherm
This type of isotherm postulate the adsorption occurred in a monolayer adsorption on a regular surface with confined a sorption sites. The linear equation of Langmuir isotherm is given by,

\[ \frac{q_e}{q_m} = \frac{C_e}{q_m} + \frac{1}{K_mC_m} \]  (6)

Where \( q_m \) is the maximum adsorption capacity (mg g⁻¹) and \( K_M \) is the Langmuir constant relate to the adsorption energy [24].

2.6.2 Freundlich isotherm
The Freundlich isotherm assumes monolayer and multilayer adsorption onto heterogeneous surface of an adsorbent [24]. The form of Freundlich equation is given by,

\[ \ln(q_e) = \ln(K_F) + \frac{1}{n} \ln(C_e) \]  (7)

Where \( K_F \) and \( n \) are isotherm constants related to adsorption capacity and adsorption intensity, respectively, and \( C_e \) is the equilibrium concentration (mg L⁻¹) [24].

2.6.3 Temkin isotherm
The linear form of Temkin isotherm is expressed as:

\[ q_e = \frac{R}{T}\ln K_T + \frac{R}{T}\ln C_e \]  (8)

Where b is the Temkin constant related to the heat of sorption (J mol⁻¹) and \( K_T \) is the Temkin isotherm constant (L g⁻¹) [24].

2.6.4 The thermodynamic parameters
The thermodynamic equilibrium constant \( K_a \) was used to calculate the thermodynamic parameters. \( K_a \) is given by,

\[ K_a = \frac{a_e}{a_i} = \frac{C_e}{C_i} \]  (9)

Where \( a_e \) the activity of the adsorbed ion, \( a_i \) the activity in solution at equilibrium, \( C_i \) and \( C_e \) are the corresponding activity coefficient. However, \( C_i \) is the Cr (VI) adsorbed on n-ZVI (m mol L⁻¹), and \( C_e \) is the concentration in equilibrium solution (m mol mL⁻¹).

However, \( G^0 \) (standard Gibbs free energy KJ mol⁻¹), \( H^0 \) (standard enthalpy change KJ mol⁻¹) and \( S^0 \) (standard entropy change J mol⁻¹ K⁻¹) were calculated using the standard Gibbs free energy equation (10),

\[ \Delta G^0 = -RT \ln K \]  (10)

\( K_0 \) was obtained from the slope of a linear plot of \( \ln \frac{C_e}{C_i} \) against \( C_e \). The slope of ln \( K_0 \) at different temperature
against $\frac{1}{T}$ allows calculating the standard thermodynamic parameters.

3. Results and Discussion

3.1 Characterization of n-ZVI

Figure (1) shows the XRD patterns of the prepared n-ZVI. It reveals the peak of zero valent iron at 44.76° in agreement with ASTM carb number 88-2324 [25], indicating the face centered cubic lattice structure.

3.2 Adsorption kinetics

Different parameters of adsorbent loading, Cr VI) concentrations, and temperature, were investigated. The figures 3-5 show the equilibrium is attained after 3.5 hours.

Pseudo first order, pseudo second order and intraparticle diffusion models have been used to evaluate the kinetic of the adsorption process.

The TEM analysis showing in fig (2a) revealing the formation of nanoparticles with particle size distribution between 15-25 nm. However, it is clear that limited agglomerate has been occurred. Surface morphology was characterized by SEM as shown in figure (2b). The SEM image shows dendritic structure. This can be attributed to the formation of an envelope of iron oxide and iron hydroxide according to the inner core structure of n-ZVI [26]. The SEM image shows a cave like structure due to the formation condition which controls the evolution of each n-ZVI particle [27].

Figure (2): TEM (a) and SEM (b) images for the synthesized nZVI particles

Figure (3): Variation of removal of Cr (VI) with time at different loading adsorbent

Figure (4): Effect of Cr VI concentration on the sorption kinetics by nZVI at 300 K and pH 3.9.

Figure (5): Effect of temperature on the % uptake of Cr(VI) using 0.05 g nZVI at different temperature and pH 3.9.
3.2.1 Pseudo first order

The slope and intercept of linear plots of ln (q_e - q_t) versus t were used to calculate the velocity (K_1) and the sorption capacity at equilibrium, as shown in figure (6) and table (1). According to the law value of R^2 the pseudo first order is not adequate to interpret the adsorption of Cr (VI) on n-ZVI [28].

3.2.2 Pseudo second order

The parameters of the pseudo second order were tabulated and given in table (1). The high linearity fitting R^2 obtained from the t/qt versus t plot figure (7) indicates the proper application of the pseudo second order to illustrate the adsorption kinetic of Cr (VI) using n-ZVI. Both values of K_2 and initial velocity indicate that the adsorption process has a chemical interaction. Similar manner has been reported for the adsorption using n-ZVI Figure (8, 9) [28].

Table (1): Kinetic parameters of pseudo first and pseudo second-order models of Cr (VI) removal using nZVI at pH 3.9 and 300 K.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Different loading at Cr (VI) 200 ppm</th>
<th>Different cons. (ppm) at 0.05 loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-ZVI</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pseudo first-order</td>
<td></td>
<td></td>
</tr>
<tr>
<td>qe (mg g(^{-1}))</td>
<td>32.61</td>
<td>17.4</td>
</tr>
<tr>
<td>k_1 x10^3 (min(^{-1}))</td>
<td>5.6</td>
<td>5.6</td>
</tr>
<tr>
<td>R^2</td>
<td>0.95</td>
<td>0.87</td>
</tr>
<tr>
<td>Pseudo second-order</td>
<td></td>
<td></td>
</tr>
<tr>
<td>qe (mg g(^{-1}))</td>
<td>58.14</td>
<td>38.61</td>
</tr>
<tr>
<td>k_2 x10^3 (min(^{-1}))</td>
<td>1.25</td>
<td>3.31</td>
</tr>
<tr>
<td>h (mg g(^{-1})min(^{-1}))</td>
<td>4.23</td>
<td>4.93</td>
</tr>
<tr>
<td>R^2</td>
<td>0.986</td>
<td>0.989</td>
</tr>
</tbody>
</table>

3.2.3 Intraparticle diffusion model

The adsorption process can be optimized through understanding the adsorption mechanisms to reveal the rate determine step. It can be accomplished through definite steps [24]: (1) film adsorption to the sorbent particles, (2) sorbent diffusion to the core of the sorbent.
Finally, adsorption to specific site by chemical or physical attraction.

The plot of \( q_t \) verses \( t^{0.5} \) figures (11, 12) show two steps. This proposes that the adsorption takes place in two steps. The first step is the faster one represents the film formation and the second step is the reduction step of Cr (VI) ion. The plots did not pass across the origin indicating that intraparticle diffusion is not the rate determining step, although it may take place in the adsorption process.

Table 2: The kinetic parameters of intraparticle diffusion of Cr (VI) removal using n-ZVI at pH 3.9 and 300 K.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Different loading at Cr (VI) 200 ppm</th>
<th>Different cons. (ppm) at 0.05 loading</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.03</td>
<td>0.05</td>
</tr>
<tr>
<td>n-ZVI K1 (mg g(^{-1})min(^{-1}))</td>
<td>5.15</td>
<td>5.04</td>
</tr>
<tr>
<td>C1 (mg g(^{-1}))</td>
<td>12.5</td>
<td>6.88</td>
</tr>
<tr>
<td>R²</td>
<td>0.996</td>
<td>0.985</td>
</tr>
<tr>
<td>n-ZVI K2 (mg g(^{-1})min(^{-1}))</td>
<td>1.53</td>
<td>0.563</td>
</tr>
<tr>
<td>C2 (mg g(^{-1}))</td>
<td>28.99</td>
<td>27.92</td>
</tr>
<tr>
<td>R²</td>
<td>0.986</td>
<td>0.989</td>
</tr>
</tbody>
</table>

3.4 Adsorption Isotherms

Different adsorption isotherms models Langmuir, Freundlich and Temkin were tested to analyze the adsorption of Cr (VI) ions by n-ZVI.

3.4.1 Langmuir Isotherm

The calculated Langmuir parameters \( q_m \) and \( K_L \) were obtained from the slope and intercept of \( C_e/q_e \) versus \( C_e \) figure (13) at different temperature and given in table (3). The \( R^2 \) are 0.99 at room temperature and decrease with increasing temperature to give 0.92 at 313 K. The Cr (VI) adsorption capacity on n-ZVI increase with increasing temperature. The calculated adsorption capacity is higher than that reported earlier [24].

3.4.2 Freundlich Isotherm

The different parameters of Freundlich isotherm were calculated and given at table (3). The \( K_f \) and \( n \) parameters are calculated from the intercept and slope of the linear plot of \( \ln q_e \) against \( \ln C_e \), as shown in figure (14). The values of \( n \) is more than unity representing the L-type isotherm characteristic of chemisorption adsorption type [24]. The values of \( K_f \) show an increase with increasing temperature reflect action of endothermic adsorption process.

3.4.3 Temkin Isotherm

The plot of Temkin adsorption isotherm figure (15) shows linearity at all the different temperatures studied.
The will fitting correlation linearity of value of 0.99 as shown in table (3) supporting the conclusion of an endothermic process of adsorption.

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Temperature</th>
<th>Parameters</th>
<th>n-ZVI perm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freundlich</td>
<td>300</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>303</td>
<td>05.57</td>
<td>1.93</td>
<td>0.999</td>
</tr>
<tr>
<td>313</td>
<td>10.06</td>
<td>2.55</td>
<td>0.980</td>
</tr>
<tr>
<td>Langmuir</td>
<td>300</td>
<td>64.10</td>
<td>5.50E-2</td>
</tr>
<tr>
<td>303</td>
<td>65.79</td>
<td>3.56E-2</td>
<td>0.981</td>
</tr>
<tr>
<td>313</td>
<td>67.11</td>
<td>2.85E-2</td>
<td>0.924</td>
</tr>
<tr>
<td>Temkin</td>
<td>300</td>
<td>0.243</td>
<td>167.06</td>
</tr>
<tr>
<td>303</td>
<td>0.330</td>
<td>170.89</td>
<td>0.989</td>
</tr>
<tr>
<td>313</td>
<td>0.773</td>
<td>203.61</td>
<td>0.959</td>
</tr>
</tbody>
</table>

4. Thermodynamic studies

The thermodynamic equilibrium constant $K_o$ at different temperature was estimated from the linear plots of $\ln (C_e/C_s)$ against $C_s$ as shown in figure (16). As the temperature increased the $K_o$ increased supporting the endothermic adsorption as indicated from the isotherm studies. The standard thermodynamic parameters were calculated and given in table (4). $G^0$ show negative values indicating spontaneous adsorption process. The $H^0$ and $S^0$ were evaluated from the plot of $\ln K_o$ versus $1/T$ as shown in figure (17). The positive $H^0$ values confirm the endothermic nature of Cr (VI) toward the n-ZVI nanoparticles. However, the affinity of n-ZVI for Cr (VI) was reflected through the positive value of the standard entropy [24].
Table (4): Thermodynamic parameters for Cr (VI) adsorption onto n-ZVI.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Kc</th>
<th>G°</th>
<th>H°</th>
<th>S°</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>1.50</td>
<td>-1.01</td>
<td>24.45</td>
<td>85.31</td>
</tr>
<tr>
<td>303</td>
<td>1.86</td>
<td>-1.54</td>
<td>24.45</td>
<td>85.31</td>
</tr>
<tr>
<td>313</td>
<td>2.33</td>
<td>-2.11</td>
<td>24.45</td>
<td>85.31</td>
</tr>
</tbody>
</table>

Fig (16): A plot of ln (Cs/Ce) versus Cs at various temperature of nVZVI.

Fig (17): A plot of ln K° versus 1/T at various temperature of nVZVI.

5. Summary and conclusion
In this study, the kinetics of adsorption of Cr (IV) using n-ZVI has been investigated by pseudo first and second order models. Also, the intraparticle diffusion model was tested. The calculations indicated that the pseudo second order is the most fitted model among the other models with high R² value. The adsorption isotherm was tested applying Langmuir, Freundlich and Temkin models. The Freundlich isotherm showed a best fit isotherm indicating the multilayer adsorption of Cr (VI) toward the n-ZVI surface. The kinetic and thermodynamic calculations and the adsorption activation energy proven that the overall adsorption process was spontaneous and endothermic in nature.

Reference
[13] B. Qiu, H. GU, X. Yan et al., Cellulose derived magnetic mesoporous carbon nanocomposites with


