The removal of Cr (VI) from aqueous solution by dried powder of activated sludge: kinetic and equilibrium studies

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Abstract

**Background:** Nowadays, different methods are applied for the removal of heavy metals from the aqueous resources that the adsorption process is one of them. The chromium VI is one of the most prevalent contaminants which create serious difficulties; so, it should be removed from the contaminated waters by an effective method before being leaved into the environment. The present research investigated the use of dried powder of activated sludge of Kavirite wastewater treatment plant as biob sorbent for removal of chromium (VI).

**Methods:** In the present experimental study, the effects of pH, adsorbent dose, primary concentration of metal and contact time on the removal of chromium (VI) from the aqueous solutions were studied. Then, the equations of isotherm and adsorption kinetic were specified based on the optimal conditions. The absorbent features were analyzed by SEM and EDX techniques.

**Results:** The maximum efficiency of the removal of chromium (VI) at pH 2, optimal dose of 5 g/L, contact time of 60 min and with primary concentration of 15 mg/L was reported 99.83 percent. The study of relation of the isotherm and kinetic in the reaction revealed that the process of adsorptions of chromium follows the Freundlich model \((R^2=0.90)\) and the pseudo- second order kinetic model \((R^2= 1)\), respectively.

**Conclusions:** The dried powder of activated sludge can be applied as a proper adsorbent for the removal of Chromium VI from the aqueous resources.

**Keywords:** Bio-sorbent; Wastewater; Adsorption; Chromium(VI); Isotherm

1. Introduction

The access to the healthy, reliable and without contaminant freshwater is of the early needs of human being to have a dynamic and sustainable society. The increasing growth of population and the improvement of life level, the development of industries and the technology transfer would be resulted in the increase of water consumption and wastewater production. The heavy metals are of the most important contaminants which are produced by these kinds of units and enter into the environment (1). The high toxicity of these metals has concluded that even the entrance of few concentrations of these materials create serious problems for the natural ecosystems (2). One of the most dangerous kinds of these metals is chromium used in dyeing, leather tanning and metal plating industries (3). The chromium generally exists in the aqueous environment in two categories such as (III) and (VI) capacities; chromium (VI) is one of the harmful oxidants and of group A of the carcinogen materials (4). The most important problems of this contaminant, it can be referred to the capability of bioaccumulation in liver, renal syndrome and death in the concentrations above 0.1 mg/L.
(5). The United States Environmental Protection Agency (VSEPA) has determined the permissible limit of the chromium (VI) in the standard of discharge into the surface waters 0.1mg/L and for the drinking waters 0.05mg/L (6).

So far, numerous methods have been applied by different researchers for the removal of heavy metals ions of the aqueous solutions such as adsorption, osmosis reverse, electrochemical treatment, concentrative vaporization, solvent extraction, ion exchange, biological exclusion, coagulation and continuous separation process (7). But applying these methods is not possible because of imperfect removal of metal, need to high energy and special chemical materials, costly equipment and production of toxic sludge inside and outside the country (8). At the present, many researches have been done for the purpose of applying new, cheap and reprisal methods in the removal of chromium of which it can be referred to the use of absorbents such as granule active carbon, cartridge shell, biological wastes and agriculture wastes (9, 10). The adsorption is an effective process and has different applications and it is nowadays considered to be an economical and efficient method for the removal of heavy metals from the aqueous solutions. Generally, the adsorption is the process of accumulation of materials in the interface between two phases (10). Of different adsorbents, it can be referred to the dried powder of activated sludge which has attracted very attention because of rapid and perfect removal of most of metals, easy access to the needed primary material sand high versatility (11). The study of bio-sorption of heavy metals on the sludge of treatment plants such as activated sludge, disposal sludge and the aerobic and non-aerobic granule and the wastewater sludge is regarded as a proper biomass for the bio-sorption studies because of microorganism heterogeneous mass. So far, numerous studies have been done in regard the removal of chromium (VI) by use of cheap adsorbents in Iran and the other countries; for example, a study was done by Fooladifard and Ebrahimi (2010) on the efficiency of disposal activated sludge for removal of nickel and cadmium from aqueous environments. The results of this study revealed that the sludge powder had high capacity of adsorption for cadmium in comparison to nickel (12). AlonoroSoko et al. (2013) carried out a study in the regard of application of coal ash for absorption of nickel and copper. The results of this research showed that the coal ash is proper absorbent for the nickel and copper removal (13). Hamani et al. (2006) did a study about the application of powder of activated sludge in the removal of copper, cadmium, lead, nickel and zinc from the aquatic solutions. The results of this research revealed that the optimal pH for the adsorption of copper, cadmium and lead was 4 and for nickel and zinc was 5 (14). Netaji et al. (2013) prepared and identified the activated sludge of the corncob covered with the nanoparticles of iron for the removal of chromium (VI). The results indicated that the highest level of adsorption has been occurred in pH 2 (15). The purpose of present research was the study of the potential of removal of chromium (VI) by the dried powder of activated sludge, effect of different factors such as pH, amount of adsorbent, primary concentration of chromium and contact time in the aqueous solutions. The isotherm, reaction kinetics and also the optimal parameters of this adsorbent was investigated in the removal of chromium (VI).

2. Methods

2.1. Preparation of adsorbent:

For the purpose of preparation of dried powder of the sludge needed for the tests, the dry sludge was collected from the sludge- drying beds of wastewater treatment plant of Kavirtire factory of Birjand city and was washed with the distilled water to be transferred to the laboratory and was dried in the temperature of 103-105 °C inside the lagoon for 24 hours. Then, the dried sample was powdered by the cracker mill and was granulated by the Mesh 50-120.

2.2. Preparation of solution:

For the preparation of stock solution of chromium (VI), Potassium dichromate (K2Cr2O7) with mass number 294.19g/mole and absoluteness degree of 99 percent was solved in the distilled water.

The most important variables studied in this test are as following: the primary pH of solution with scale 2–9 (2,3,4,5,6,7,8,9), adsorbent dose of 1-10 (1,2,5,7,10) g/l, mixing time of 5-180min (5,10,20,30,60,90,120,180), and initial concentration of contaminant 5-50 (5,10,15,35,50) mg/l.

For the performance of rests, at first, 100cc of the sample with specific concentrations were taken by the graduated cylinder and poured inside the Erlenmeyer; the 1N HCL and NaOH was used for the regulation of pH. Then, the specific dose of adsorbent was weighed and added to the sample inside the Erlenmeyer and was put rapidly on the shaker that its speed had been regulated previously. After the intended contact time, the sample was taken from the shaker and was
filtered by Whatman filter paper 0.45 micron. The filtered sample was used for evaluating the level of remained chromium (VI).

It should be explained that all the tests has been done in batch method and the laboratory temperature of 24 to 26 °C and mixing of 200 rpm. For determining the optimal situation in the removal of chromium (VI), the One- Factor- at- a-Time method (OFAT) is applied that one of the parameters is regarded variable and the other ones stay fix.

In this test, all the variables of chromium VI was evaluated with 540nm wavelength and by UV/VIS Spectrometer T80+ (Metering Mode) and Diphenylcarbazide- 1,5 as reagent. All the materials used in this test, were product of Merck KGaA Company in Germany and the analysis of data was done by Excel software.

The level of adsorption of chromium (VI) (R%) and its adsorption capacity (qₑ) were calculated as following:

Relation 1:

\[ \%R = \frac{(C₀ - Cₑ)}{C₀} \times 100 \]

C₀ and Cₑ are the initial and final concentration based on mg/lit, respectively.

Relation 2:

\[ qₑ = \frac{V}{M} \times (Cₘᵢₙ - Cₜₕₜ) \]

qₑ: equilibrium adsorption capacity based on mg/g
V: solution volume based on l
M: absorbent mass based on g
Cₘᵢₙ and Cₜₕₜ are the initial and outcome concentration based on mg/l

2.3. Adsorption experiments:

The Langmuir and Freundlich models were used for the analysis of results of adsorption. The Langmuir isotherm is based on the single- layer and uniform adsorption of the adsorbent with a fix power on all the levels on the adsorbent. In spite of Langmuir model, the Freundlich isotherm is based on multi- layer adsorption of the absorbed matter on the adsorbent.

Relation 3:

\[ \frac{x}{m} = \frac{abcqe}{1 + bCₑ} \]

\[ \frac{c}{q} = \frac{1}{k₁} + \frac{c}{k₂qₑ} \]

That in which:

\[ qₑ = \frac{X}{m} \]

is the amount of adsorbed matter in the unit of adsorbent mass based on mg/g, Cₑ is the concentration of the absorbed matter in liquid phase after equilibrium based on mg/g, qₑₓₘ is the maximum adsorption capacity based on mg/g and Kₑ is the Langmuir constant. a and b are the empirical constants determined for each specific system.

The capacity of adsorption of heavy metals by the biosorption with the use of one non-dimensional parameter (Rₑ) that is derived from the Langmuir equation is also evaluable. The adsorption can be non-reversible (Rₑ= 0), favorable (Rₑ< 1<0), linear (Rₑ= 1) or unfavorable (Rₑ> 1).

Relation 4:

\[ \log qₑ = \log \frac{1}{m} + \frac{1}{n} \log cₑ \]

That in which \( \frac{1}{m} \) and \( cₑ \) have the same definitions. n and kₑ are the Freundlich constants which are calculated for the specific adsorption system.

The kinetic equations study the transfer of the particles of absorbed matter at the unit of time and determine the speed of the reaction, too. The Pseudo- first and Pseudo- second order kinetics would be investigated in the present study.

Relation 5: Pseudo- first order linear equation

\[ \ln(qₑ - qₜ) = \ln qₑ - k₁t \]

Relation 6: Pseudo- second order linear equation

\[ \frac{t}{qₜ} = \frac{1}{K₂qₑ²} + \frac{c}{qₑ} \]

3. Results

3.1 Characteristic of biosorbent

The results of SEM image of surface of the adsorbent before and after the adsorption process have been presented in figure1. Before the adsorption process, the surface of adsorbent had very pores which are proper for trapping different species such as metal ions. The level of dispersion of ingredient particles in the heterogeneous adsorbent bed is an amorphous and mass form and has a specific level of disorder (figure 1- A). According to Figure 1-B, when bio absorbent was conducted with the chromium, its homogeneity was increased but the dispersion was decreased. This matter revealed that the adsorbent bed has a charge opposed to the ion of chromium the adsorption of which has been resulted in the reduction of level of
dispersion and formation of mass on the surface of absorbent bed.

The Energy Dispersive X-ray spectroscopy (EDX or EDS) is an analytical method which is applied for analyzing the structure or the chemical features of one sample. This method relies on the study of interaction between the excitation resource of X-ray and a sample. The EDX spectrum is a chart which has been drawn based on the reception of energy X from each level of energy. Each of the peaks presented in this chart is related to one atom and is indicative of one element. The peaks with more heights in the spectrum mean higher concentration of the intended element in the sample.

The results of spectrum of EDX of dried powder of the activated sludge before and after the contact with chromium (VI) has been presented in figure 2. According to these pictures, the prepared sample adsorbent shows the absence of any kind of absorbed ion (figure 2-A). After the process of adsorption, chromium VI has been absorbed in sample adsorbent and a part of elements existing in the dried powder of sludge has been activated (figure 2-B).

3.2. Effect of pH and mechanism of Cr(VI) biosorption:

The pH of solution showed a special effect in the adsorption of the chromium. By the increase of pH, the adsorption of the chromium (VI) was considerably decreased; in such a way that the efficiency has changed from 100 percent at pH 2 to 54.8 percent at pH 9. Also, the kind of charge of surface of adsorbent can be determined well by the use of pH\textsubscript{pc}. At under pH\textsubscript{pc} (zero point charge), the charge of surface of adsorbent is positive and at above pH\textsubscript{pc}, the charge of surface of adsorbent is negative (Fig 2). So, the pH 2 was used for the rests of tests.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figures/figure1.png}
\caption{SEM images, A) bio-sorption before contact with chromium B) bio-sorption after contact with chromium}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figures/figure2.png}
\caption{EDX image of dried powder of activated sludge A) bio-sorption before contact with chromium B) bio-sorption after contact with chromium}
\end{figure}
3.3. Effect of adsorbent dose:
The Fig 3 shows the effect of adsorbent dose on the efficiency of removal of chromium. As it is observed in the chart, the efficiency of removal has been increased from 80.2 percent to 100 percent by the increase of absorbent dose from 1 to 10 g/L. The amount of optimal adsorbent was selected 5g/L with 100 percent efficiency.

3.4. Effect of initial concentration and contact time:
The effect of contact time and primary concentration of chromium on the efficiency of removal process has been presented in Fig 4. In this step, the time and initial concentration of chromium was regarded variable and the other parameters were considered constant. The amount of adsorption of chromium was evaluated with the concentrations 5, 10, 15, 35 and 50 mg/L, at the times 5, 10, 20, 30, 60, 90, 120 and 180 minutes, with the pH and amount of optimal adsorbent determined in the previous steps. The results revealed that the efficiency of removal is reduced by the increase of concentration from 5mg to 50mg/L and the equilibrium concentration for chromium VI is 15mg/L. Also, by increasing the contact time more than 60 minutes, no considerable change is observed in the process of removal of chromium (VI) by the intended adsorbent. The amount of removal of chromium (VI) at the contact time 60 min and concentration of 15mg/L was evaluated 99.83 percent.

3.5. Kinetic and isotherm experiments:
Table 1 shows the results related to the data obtained of the equilibrium isotherms of process of adsorption of chromium by the dried bio-sorbent of activated sludge. The maximum adsorption capacity (qmax) based on the Langmuir isotherm method was obtained 16.67mg/L and also, the regression coefficient for the Langmuir and Freundlich models was calculated 0.80 and 0.90, respectively. In the Freundlich isotherm, the amount of n (1 to 10) indicates the proper process of adsorption that was 2.64 for this metal.

The amounts of kinetic parameters of process of adsorption of chromium (VI) have been presented in table 2. The results of study of kinetic equations of the adsorption showed that the computational adsorption capacity for the pseudo- first order and pseudo- second order kinetic models has been 0.71 and 1, respectively; while the empirical adsorption capacity obtained from the tests has been 3.10mg/g.
Ahmadi Ghohaki M et al

Figure 4: Effect of reaction time and primary concentration of chromium VI on efficiency of removal process by dried bio-sorption of activated sludge (pH=2, adsorbent concentration= 5g/L, rpm= 200)

Table 1: Parameters of adsorption isotherms

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Langmuir constants</th>
<th>Freundlich constants</th>
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</thead>
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<tr>
<td></td>
<td>$q_{max}$ (mg/g)</td>
<td>$K_L$ (l/mg)</td>
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<tr>
<td>Chromium VI</td>
<td>16.67</td>
<td>5.973</td>
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</table>

Table 2: Parameters of kinetic models

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$C_0$ (mg/L)</th>
<th>$K_1$ (min$^{-1}$)</th>
<th>$q_1$ cal (mg/g)</th>
<th>$R^2$</th>
<th>$K_2$ (g/mg min)</th>
<th>$q_2$ cal (mg/g)</th>
<th>$R^2$</th>
<th>$q_{exp}$ (mg/g)</th>
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</thead>
<tbody>
<tr>
<td>Chromium VI</td>
<td>5</td>
<td>0</td>
<td>0.18</td>
<td>0.16</td>
<td>17.53</td>
<td>1</td>
<td>1</td>
<td>1.10</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.01</td>
<td>0.33</td>
<td>0.49</td>
<td>0.71</td>
<td>2.01</td>
<td>1</td>
<td>2.10</td>
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<tr>
<td></td>
<td>15</td>
<td>0.01</td>
<td>0.54</td>
<td>0.71</td>
<td>0.23</td>
<td>3.03</td>
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<tr>
<td></td>
<td>35</td>
<td>0.01</td>
<td>1.40</td>
<td>0.97</td>
<td>0.05</td>
<td>6.75</td>
<td>1</td>
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<tr>
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<td>0.01</td>
<td>1.11</td>
<td>0.89</td>
<td>0.08</td>
<td>8.53</td>
<td>1</td>
<td>8.64</td>
</tr>
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4. Discussion

In the research done about the removal of chromium (VI) from aqueous solutions by the use of dried powder of activated sludge, it was specified that the PH of solution has a very effect on the amount of adsorption of anion, in such a way that in most of cases, the amount of adsorption of ion of chromium solution is considerably decreased by the increase of PH (in the range of neuter to alkali). The change of PH is effective in the adsorption of chromium; because it determines the ion species kind of chromium and the charge of surface of the absorbent. If the surface charge of the absorbent be positive, its capacity for the adsorption of anions would be increased and the electrostatic adsorption would be happened. So, the solution PH affects both the charge of surface of the absorbent and the charge of chromium specie and this situation controls the adsorption of chromium. As it is revealed in chart 2, the PH$zpc$ for the dried bio-sorbent of activated sludge is 7 and it is clear that the absorbent charge is neuter. The protons existing on the surface of the absorbent are easily isolated in the acetic PHs; therefore, the surface of adsorbent would have the negative charges that this matter increases the amount of adsorption of chromium because of creation of electrostatic attractive force (16). In addition, because of existence of positive ions released from the surface of absorbent in the acetic PHs, a repellant force is created between these ions and the ions of chromium that would be resulted in the removal of chromium and reduction of efficiency. But, because the electrostatic attractive force created on the surface of the absorbent is powerful than the repellant force of the positive ions released in the environment, this affair would cause the increase of...
amount of removal of chromium VI in the acetic pHs (17). The efficiency of removal of chromium is reduced in the alkali PHs, because the concentration of ion OH is increased in the solution and the OH groups existing on the surface of the adsorbent has no tendency to be released. So, the adsorption is done in a few amounts. Also, in higher PHs, the Hydroxyl ions are increased in the solution and compete with the ions of chromium for the adsorption on the active sites of the absorbent and the adsorption of chromium is decreased (18).

Jain et al. (2013), in their study, obtained the similar results in the removal of chromium by the pod of sunflower seeds and evaluated the optimal pH 2 for the removal (19). Also, the results of research done by Naseh et al. by the use of natural adsorbent of green pod of peanut and its ash in the removal of chromium VI from the aqueous solutions revealed that the most amount of removal of chromium has been happened in pH 2 (15).

According to the results obtained of these tests, the removal of chromium (VI) is increased by the increase of amount of bio- sorbent. In different studies which have been done about the adsorption of solution ions of heavy metals by different adsorbents, the amount of used adsorbent as one of the factors effective in the process of adsorption of heavy metals was introduced and its effect was investigated. By the increase of amount of adsorbent (from 1 to 10 g/L), the amount of adsorption of chromium was increased from 80.2 to 100 percent. But this procedure is continued with a specific amount of the adsorbent in a specific concentration of chromium and then the amount of adsorption would stay nearly fix, by the increase of the adsorbent. So, according to the obtained results, the optimal amount of the adsorbent was selected 5g/L. Jain et al. (2013) and Taghizade et al. (2012) concluded the similar results in this regard (19 & 9).

The results of determination of effect of the contact time and the equilibrium concentration have been presented in Fig 4. The results of present research revealed that the efficiency of removal of chromium (VI) and the primary concentration have inverse relation with each other; the reason is that the adsorbents have few active places which are saturated at high concentrations. Therefore, the amount of metal ions existing in the solution is reduced with the decrease of primary concentration of chromium and consequently, the absorbent absorbs a higher percentage of the metal ions (20). At the first minutes, the amount of adsorption is high for the reason of existence of vacant places on the surface of the adsorbent; but these vacant places is filled by the chromium ions with the passage of time and the speed of adsorption is reduced (21). The amount of adsorption of the metal from the solution is reduced by the saturation of surface of the adsorbents and in fact, the solid and liquid phases are almost equilibrated and hence are resulted in staying constant the amount of adsorption (22). Table 1 shows the results related to the data derived from the equilibrium isotherms of process of adsorption of chromium by the dried bio-sorbent of the activated sludge. The regression coefficient for the Langmuir and Freundlich models was obtained 0.80 and 0.90, respectively. With regard to the correlation coefficients (R²), it can be resulted that the equilibrium data of process of adsorption of chromium VI obey the Freundlich isotherm better than the Langmuir isotherm; it means that the adsorption has been in a multilayer form and the structure of the adsorbent has been heterogeneous. The 1/n is indicative of absorption power in the Freundlich isotherm that is observed 0.38 for chromium and this indicative of a favorable and profitable adsorption. The equilibrium parameter and factor in the process of adsorption of Chromium (VI) was obtained 0. The equilibrium parameter obtained from the Langmuir model is 0 (RL=0) and indicative of irreversible adsorption system of this model. The amounts of qmax of the Langmuir isotherm indicate the metal ions needed for the single-layer adsorption and express that 16.67 g/L chromium is needed for the complementation of the adsorption layers. Selvarani et al. (2012) in a study titled removal of chromium (VI) by magnetic nanoparticles of zero iron concluded that the adsorption of chromium by the studied absorbent follows the Freundlich model that corresponds to the results of present research (23). The amounts of pseudo- first and pseudo- second order kinetic parameters were presented in table 2. According to the results obtained, the correlation coefficients in the pseudo- first and pseudo-second order kinetics are 0.71 and 1, respectively. This matter indicates the similarity of process of adsorption of chromium to the pseudo- second order adsorption kinetic that corresponds to the results of studies done by Meena et al. in the regard of the adsorption of ions of chromium VI (24).

5. Conclusion

In the present research, the dried powder of the activated sludge was used as an adsorbent for the removal of chromium (VI) from the aqueous solutions. The results of this survey are indicative of this matter that the adsorption of ion of
solution of chromium depends on pH of the solution. Also, it was observed that the dried powder of the activated sludge could remove the chromium (VI) with 15mg/L concentration and adsorbent dose of 5g/L in pH= 2, (% 99.83) at the contact time of 60 minutes and 200 rpm. The results of adsorption isotherm revealed that the adsorption of chromium follows the Freundlich isotherm and the pseudo-second order kinetic. The general results obtained of this study showed that the dried absorbent powder of the activated sludge could be used as a cheap and efficient adsorbent with very high capacity for the removal of chromium from the aqueous solutions. Although the use of this adsorbent for the actual samples of aqueous resources may be relatively difficult, but more studies are needed to be done in this regard.

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