Removal of Hexavalent Chromium from Aqueous Solution by Powdered Scoria—Equilibrium Isotherms and Kinetic Studies

Masoud Moradi, Lida Hemati, Meghdad Pirsaheb and Kiomars Sharafi

1Research Center for Environmental Determinants of Health, Kermanshah University of Medical Sciences, Kermanshah, Iran
2PhD Student of Environmental Health Engineering Faculty, Iran University of Medical Sciences, Public Health School, Tehran, Iran
3Department of Environmental Health Engineering, School of Public Health, Ilam University of Medical Sciences, Ilam, Iran
4PhD Student of Environmental Health Engineering Faculty, Tehran University of Medical Sciences, Public Health School, Tehran, Iran

Abstract: Heavy metals, particularly chromium are recognized as threatening pollutants leaving serious adverse effects on human health and environment due to their toxicity, un-biodegradable properties and high concentration in industrial effluent. The present study aimed to evaluate the Scoria powder efficiency, as an adsorbent, in removing chromium from aqueous solution. After preparing Scoria powder, batch experiments are performed in different times and adsorbent dosages (pH=7, heavy metals concentration = 50 mg/L and stirring/minute=200 rpm). Adsorption isotherm and kinetic reaction including Langmuir, Freundlich, Pseudo-first order and second-order model, Intra-particle diffusion and Elovich kinetics were applied to correlate the adsorption. The results indicated that chromium has low absorbs and its adsorption obeying Freundlich model. The correlation coefficients obtained from Freundlich model and Pseudo-second order kinetic were R²=0.996 and R²=0.999, respectively. So Freundlich expression and the kinetics of pseudo-second order gave a better fit to the experimental data of Scoria powder. Also, removing efficiency revealed significant increase after increasing the adsorbent dose and contact time (R²<0.001). According to obtained dimensionless constant separation term (RL) of Langmuir expression, the RL values for the adsorption of chromium onto Scoria powder range 1-0, indicating that the adsorption is a favorable process.

Key words: Hexavalent chromium • Isotherms and kinetic • Scoria powder

INTRODUCTION

Heavy metals, particularly chromium are recognized as threatening pollutants leaving serious adverse effects on human health and environment. High level concentration of heavy metals in industrial effluent is regarded as one of the most important environmental problems [1, 2]. These heavy metals are gradually accumulated in natural water ecosystems and their presence in ecological systems causes several adverse effects [3, 4]. Heavy metals pollution arise from various sources, such as nature and different industries including electroplating, battery, paint, stabilizers, metallurgical, chemicals, smelting of ores, paper, oil refineries and chemical fertilizers that discharge different heavy metals into the environment [5, 6]. Some of heavy metals are known to be toxic even in a little amount, such as chromium [7]. Removal of toxic pollutant, therefore, is needed to be set up according to standard limitation [8]. Among these, plating industries are particularly important...
due to heavy use of toxic metals. Accordingly, Farazmand et al., (2003) reported that the chromium concentration in plating effluent is 46.94± 3.84 mg/l [9].

Researchers have made use of several methods, such as ion exchange, ultra filtration, reverse osmosis, electrodialysis, chemical precipitation, evaporation, solvent extraction, membrane processes coagulation, flocculation, biological treatment, chemical oxidation and adsorption to remove or reduce heavy metals from aqueous solution [10, 11]. Indeed, effectiveness and inexpensiveness play an important role in selecting each of these removing methods. These factors, therefore, move researchers toward methods having low cost and high efficiency [11, 12]. Accordingly, each of these methods contain some advantages and disadvantages, depend on some issues, including: preparation of raw materials, flexibility, effectiveness of processes, cost, technical or maintenance problems, incomplete metal removal, facility requirement, expensive monitoring systems, large amounts of chemical and energy requirement, sludge and other wastes production [13].

In fact, to remove heavy metals from aqueous solutions, adsorption onto Scoria powder is proved to be an appropriate method according to its inexpensiveness and high availability. Thereby, several studies revealed that Scoria is a material with a porous structure and large surface area causing sorption onto this substance. So, the current research is an attempt to evaluate the Scoria powder efficiency, as an adsorbent, to remove chromium from aqueous solution. For the comparison purposes, adsorption isotherm which include Langmuir, Freundlich and Pseudo-first order, Pseudo-second order, Intra particle diffusion and Elovich kinetics are applied to the process.

**MATERIALS AND METHODS**

**Adsorbent Preparation:** Batch experiment was conducted as follows. At the beginning, Scoria granules, purchased from mines located in Kurdistan, were washed with distilled water and dried in an oven at 103°C for 6 hours to remove moisture. Thereafter, they were placed into a muffle furnace at 550°C for 1 hour to remove organic impurities. The Scoria granules were crushed and sieved through a 50 mesh sieve to achieved particle size of 0.297 mm.

**Procedure of Batch Experiments:** After adsorption, all synthetic solutions containing heavy metal (Cr\(^{+6}\)), with standard concentration (with regard to their concentration in industrial effluent (50 mg/l)), were prepared using stock solution purchased from Merck Company. Experiments were conducted using a batch reaction process and Scoria powder dosage of 2, 4, 6, 8 and 10 g weight. Then, 100 ml of a solution, containing 50 mg/l of heavy metal, was prepared. Also, predetermined amount of Scoria powder was added to this solution (100ml) in a 500 ml measuring flask. Then, it was placed on a magnetic stirrer with 200 rpm. Stirring was performed at different contact times (15, 30, 45, 60 and 75 minutes). The pH of all mixtures was set to 7.0 using HCL and HNO\(_3\). After this process, 50 ml of prepared solution was centrifuged at 2000 rpm for 15 min. Finally, metals concentration of solutions was determined using ICP 7300 DV (US).

**Adsorbent Characteristics:** The adsorbent characteristic is determined through FTIR, XRD and SEM. FTIR was performed using a spectrometer (WQF-510) that scans

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Fig. 1: FTIR spectra of Scoria powder
RESULTS

Effect of Adsorbent Dose on the Removal Process Efficiency: To determine the optimum dose of adsorbent, Scoria powder dosage ranges (2, 4, 6, 8 10 g) were considered as variable and other parameters as constant. The experiment revealed that the removal efficiency of chromium in a fixed contact time of 1 hour increases significantly from 76.98 to 100% (P<0.001) (Fig 3).

Effect of Contact Time on the Removal Process Efficiency: The optimum time has been determined as follows. At first, contact time ranges (15, 30, 45, 60, 75 minute) were regarded as variable and others as constant parameters. It was observed that through increasing contact time, the removal efficiency of chromium in predetermined optimum dose of Scoria powder (4g) increased significantly from 73.28 to 86.63 % (P<0.001) (Fig 3).

Studying Equilibrium Constant: In order to examine the equilibrium constant, a mixture solution of heavy metals with the same concentration (50 mg/l) was prepared. Considered volume in this experiment was 1000 ml with distilled water. 100 ml of this solution was transferred to a 500 ml measuring flask. After adding Scoria powder with dosage of 2, 4, 6, 8 and 10 g, they were placed on a magnetic stirrer with 200 rpm. The pH value of solution was set to 7.0. The process continued until achieving the process equilibrium state which took 60 minute. Also, the concentrations of heavy metals in adsorbent phase calculated using following equation (14) (Eq. 1).

Table 2: Effect of adsorbent dosage and contact time on the efficiency of chromium removal process

<table>
<thead>
<tr>
<th>Adsorbent (g)</th>
<th>15 min</th>
<th>30 min</th>
<th>45 min</th>
<th>60 min</th>
<th>75 min</th>
<th>P value</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>63.968</td>
<td>66.208</td>
<td>68.928</td>
<td>76.98</td>
<td>79.68</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>4</td>
<td>73.288</td>
<td>75.388</td>
<td>81.052</td>
<td>85.788</td>
<td>86.632</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>6</td>
<td>80.9</td>
<td>85.17</td>
<td>88.722</td>
<td>92.976</td>
<td>93.794</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>8</td>
<td>88.61</td>
<td>92.198</td>
<td>94.42</td>
<td>95.258</td>
<td>100</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>10</td>
<td>97.22</td>
<td>98.968</td>
<td>99.46</td>
<td>100</td>
<td>100</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>P value</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

Table 3: Langmuir separation factor of absorption process

<table>
<thead>
<tr>
<th>Rl, Factor</th>
<th>Absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>RL&lt;0</td>
<td>Irreversible</td>
</tr>
<tr>
<td>0&lt;RL&lt;1</td>
<td>Favorable</td>
</tr>
<tr>
<td>RL=1</td>
<td>Linear</td>
</tr>
<tr>
<td>RL&gt;1</td>
<td>Unfavorable</td>
</tr>
</tbody>
</table>

Table 4: Calculated parameters of isotherm models

<table>
<thead>
<tr>
<th>Adsorbed Heavy metal</th>
<th>Freundlich</th>
<th>Langmuir</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R²</td>
<td>l/n</td>
</tr>
<tr>
<td>Cr⁶⁺</td>
<td>0.9567</td>
<td>0.70028</td>
</tr>
</tbody>
</table>

Fig. 2: SEM photographs of Scoria powder

Table 1: Chemical composition of Scoria powder

<table>
<thead>
<tr>
<th>Composition</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>67</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>15.6</td>
</tr>
<tr>
<td>K₂O</td>
<td>5.4</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.1</td>
</tr>
<tr>
<td>Na₂O</td>
<td>3.7</td>
</tr>
<tr>
<td>CaO</td>
<td>3.9</td>
</tr>
<tr>
<td>MgO</td>
<td>0.2</td>
</tr>
<tr>
<td>etc.</td>
<td>3.1</td>
</tr>
</tbody>
</table>
Table 5: Calculated parameters of kinetic models

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Pseudo-first-order</th>
<th>Pseudo-second-order</th>
<th>Intraparticle diffusion</th>
<th>Elovich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K (min⁻¹)</td>
<td>R²</td>
<td>K (g mg⁻¹ min⁻¹)</td>
<td>R²</td>
</tr>
<tr>
<td>Cr⁺⁶</td>
<td>0.134</td>
<td>0.732</td>
<td>0.325</td>
<td>0.999</td>
</tr>
</tbody>
</table>

**Langmuir Isotherm:** The Langmuir isotherm is based on a hypothesis which estimates single-layer coating of adsorbent on the outer surface of the sorbent. Absorption rate is proportionate to driving force of the adsorbent on the surface area. Driving force and surface area are referring to concentration of solution and surface area available to the adsorbent, respectively [14]. Langmuir separation factor (R_L) is an important factor of Langmuir adsorption process which is in the range of (1-0) [15].

**Freundlich Isotherm:** Freundlich isotherm is based on monolayer absorption on heterogeneous surface of adsorbent containing unequal amount of energies. Not only it is not limited to a monolayer adsorption, but also it is applied for multi-layer absorption. Unlike Langmuir isotherm, temperature level of this isotherm decreases logarithmically. Linear equation model of Freundlich isotherm is as follows [16, 17].

**Kinetic Model of Adsorption:** The kinetic models evaluate the reaction rate that controls the equilibrium time [18]. These models are appropriate for designing and optimizing chemical processes that are based on removing pollutants from effluent. This study investigates kinetic reactions based on Pseudo-first-order and second-order model for adsorption mechanism. Therefore, to obtain kinetic model, contact time is a variable while other parameters are constant (adsorption rate of heavy metal in different times of 15, 30, 45, 60 and 75 min; fixed Scoria dose 6 g; and rpm=200).

**Intra-particle Diffusion Model:** Intra-particle diffusion kinetic model examines the mechanism of adsorption on porous adsorbent and determines the controlling level of adsorption rate which affects the adsorption process [19].

**Elovich Adsorption Kinetic:** The Elovich equation has been widely used in adsorption kinetics, which describes chemical adsorption (chemical reaction) mechanism in nature. The approaching equilibrium parameter of Elovich equation (R_e) was used here to describe the characteristic curves of adsorption kinetics [20].

Fig. 3: Effect of adsorbent dosage and contact time on efficiency of chromium removal process (Con=50 mg/l, PH=7, rpm=200)

\[ Q_e = \frac{(C_a - C_e)V}{m} \]  

Where:
- \( q_e \) is equilibrium concentration of heavy metals in adsorbent (mg/g)
- \( C_a \) and \( C_e \) are the concentration of heavy metals at initial and equilibrium states (mg/l)
- \( V \) is the volume of heavy metals solution (l)
- \( m \) is the weight of Scoria powder (g)

**Adsorption Isotherm:** Adsorption isotherm is principally significant to express how solutes interact with adsorbent and it is essential in optimizing the use of adsorbents. Creating appropriate interaction for equilibrium and optimizing in designing a surface adsorption system for removal of adsorbate is of critical importance. It should be noted that important adsorption isotherms include Langmuir and Freundlich.
DISCUSSION

Findings of the present study indicated that the highest removal rate of hexavalent chromium occurs at the initial 15 minutes. It means that wide adsorption sites of using adsorbent are available in a given initial time [21]. It was also found that the removal efficiency rate was relatively higher in term of increasing the adsorbent dose and contact time. Though, the removal efficiency rate was increased further due to increasing the adsorbent dose rather than increasing the contact time. The adsorption rate with increasing initial contact time in a given mass of sorbent is raised and then gradually reaches equilibrium because the adsorbing surfaces of a given particular mass of adsorbent involve particular sites to adsorb metal concentration of effluent. So, those sites would be occupied by adsorbate ions within short period of time due to increasing adsorbent dose and contact time. Adsorbed metal concentration carried out onto the pores of the adsorbent; consequently, the adsorption rate will be decreased [22]. However, metals adsorption highly depends on physicochemical characteristics of absorbent and adsorbate.

The results showed that the Scoria characteristics contain 67% and 15.6% of SiO$_2$ and Al$_2$O$_3$, respectively. In another study, Li et al., (2006) concluded that adsorbent size, pore distribution of adsorbent and chemical characteristics of their surface have a significant effect on removal efficiency [23]. In addition, Yenisoy-Karakas et al., (2004) indicated that the chemical characteristic of adsorbent surface plays a significant role in removing metals ions rather than adsorbent pore size [24]. Attempt made by previous researchers revealed that the presence of metal oxides in aqueous solutions considerably affect the adsorption process since it forms groups of agent factor on the surface area [1, 25]. While Scoria placed in water, its contained metal oxides would be covered by water molecules with the following formula [26-28] (Eq. 2 and Eq. 3).
where, $M_i$ is any alkaline or earth alkaline metal which is exchanged by metal ion of solution [15]. Some other researchers, such as Baradachky (2009), found that the removal efficiency of pollutants is related to hydroxyl groups attached to the silica structure [29]. In addition, other factors including electrostatic force and ion exchange are significant in adsorption of metals by Scoria. Also, physicochemical characteristics of adsorbate, such as metals hydrated radius, ion radius and pH level affect their adsorption rate.

Thus, with regard to above parameters and findings of previous experiments by other researchers, adsorption of hexavalent chromium by Scoria may be due to the following reasons. Given that, Scoria surface is negatively charged in pH=7 (pH that experiments was conducted in), heavy metals could be presented as hydrated complexes with water molecules in aqueous solutions [30]. Therefore, metals with larger ionic radius and smaller hydrated radius are further adsorbed by the adsorbent [1, 25, 31]. So removal efficiency of hexavalent chromium could be affected by its ionic and hydrated radius (small ionic radius (0.62 Å) and large hydrated radius (4.61 Å)). Also, at high pH level, hexavalent chromium changes to $\text{CrO}_4^{2-}$ which moves away from produced ion (SiO$_2^-$) of the adsorbent. Whereas, in acidic condition (low pH value) the hydrated radius (HCrO$_4$) are more and they are adsorbed by Si$^{4+}$ which is dominant in this condition. Hence the removal efficiency of chromium is considerable in low pH value [32]. In addition to hydrated and ionic radiuses of metals, metals could be adsorbed due to having electrostatic force with the adsorbent. Researchers such as Moracia et al., (2010) and Catalfouma et al., (2006) also reported metal removal results from ionic exchange process between alkaline and earth alkaline metals (Na$^+$, K$^+$, Mg$^{2+}$ and Ca$^{2+}$) or other available metals in solutes [8, 15].

The obtained isotherm adsorption data showed that the adsorption of hexavalent chromium obeyed the Freundlich model ($R^2=956$) and the adsorption process took place in multi-layered adsorbents. However, $n$ values [1-10] indicated the type of isotherm to be either favorable $n>1$ or unfavorable $n<1$. Thus, heterogeneous adsorbent surface is less important. Also adsorption intensity $0<(1/n)<1$ indicated that heavy metal adsorption is a favorable process [17, 33]. Therefore, considering RL, Scoria is an appropriated adsorbent for the removal of pollutants [34].

Analyzing kinetics of adsorption showed that data obeyed kinetic reaction with the following order: Pseudo-first order $<\text{Elovich}<\text{Intra-particle diffusion}<\text{second-order}$. It means that proper adsorption obeys the second-order kinetic model and absorption process is dependent on the adsorbent concentration because the second-order kinetic model is based on the capacity of absorption [35]. Also, linear equation of Intra-particle diffusion of kinetic indicated that it plays an important role in the adsorption process by Scoria powder [22].

**CONCLUSION**

According to obtained dimensionless constant separation term (RL) of Langmuir expression, the RL values for the adsorption of chromium onto Scoria powder range 1-0, indicating that the adsorption is a favorable process.

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**REFERENCES**


