Removal of $\text{Sr}^{2+}$ from aqueous solutions by adsorbent activated carbon of almond shell

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ABSTRACT: In this paper, removal of $\text{Sr}^{2+}$ from aqueous solutions with prepared adsorbent activated carbon of almond shell was investigated. The prepared adsorbent were characterized by scanning electron microscopy (SEM) and BET surface area analysis. The kinetic and isotherm of $\text{Sr}^{2+}$ adsorption were studied. The effects of operational parameter such as pH, adsorbent dosage and contact time on the process were studied and optimized. The experimental results showed that $\text{Sr}^{2+}$ adsorption onto adsorbent followed Langmuir isotherm. Adsorption kinetics of $\text{Sr}^{2+}$ onto the adsorbent followed the pseudo-second-order kinetic model.

Keywords: Removal, Adsorption, Isotherm model, Almond shell

INTRODUCTION

$\text{Sr}^{2+}$ is one of the most common radionuclides present in radioactive liquid wastes which are produced inevitably during preparation and application of the nuclear material (Chen and Wang 2012). The chronic toxicity of $\text{Sr}^{2+}$ to humans and the environment has been well documented. For example, high concentration of $\text{Sr}^{2+}$ causes cancer of lungs, nose and bone. It is essential to remove $\text{Sr}^{2+}$ from industrial wastewater before being discharged (Chen et al., 2008; Chegrouche et al., 2009). Pollutant removal from wastewater using adsorption process is interested because different adsorbents are able to concentrate specific substances from solution onto their surfaces (Mahmoodi 2013). Specified amounts of metal ions are lost in the process of manufacturing and utilization and often cause environmental pollution problems. The discharge of wastewaters in the ecosystem has been problematic due to their toxicity and resistance to biodegradability. Among different techniques for pollutant removal, the traditional ones, such as adsorption, ultra-filtration, coagulation–flocculation, ozonation, $\text{H}_2\text{O}_2$ oxidation, photo-oxidation, and combination of several techniques have been applied (Gong et al., 2005; Madaeni and Mansourpanah 2004; Guibal and Roussy 2007). The cell walls of almond shell consist of cellulose, silica, lignin, carbohydrates which have hydroxyl groups in their structures. In this paper, the potential of almond shell, an agro-based adsorbent, has been explored for the removal of $\text{Sr}^{2+}$ from water. The prepared adsorbent were characterized by SEM and BET analysis. The kinetic and isotherm of $\text{Sr}^{2+}$ adsorption were studied. The effects of operational parameter such as pH, adsorbent dosage and contact time on the process were studied and optimized.

MATERIALS AND METHOD

MATERIALS

In this study, activated carbon obtained from almond shell was used to removal $\text{Sr}^{2+}$ from the aqueous solutions. The aqueous solutions of $\text{Sr}^{2+}$ with initial concentration of 50 mg L$^{-1}$ $\text{Sr(NO}_3)_2$ from the Merck Company in Germany and also twice distilled water were used. Other chemicals used in the project were purchased from the Merck Company (Germany).

Preparation of Activated Carbon

First, 50 g of almond shell was added to 1 L of distilled water and was boiled for 5 h. After filtration, the action was repeated once more. The moist almond shell was put in a vacuum oven for 8 h in 105 °C. The resulted dried almond shell was put in furnace with inert nitrogen for 5 h under the temperature of 350 °C. The obtained carbon was passed through the standard sieve of ASTM with 100 mesh. The resulted active carbon was washed
and cleared for several times using distilled water and when the pH solution (pH = 7) the active carbon drying in a vacuum oven for 3 h in 105 °C.

**Apparatus**

For analyzing the morphology and adsorbent surface, scanning electron microscope (SEM) model Philips XL30 was used and BET method the base to nitrogen adsorption/desorption isotherms measured at 77 K. UV/VIS Spectrophotometer, Jenway (6505) was employed for measuring absorbance using glass cells of path length 1 Cm.

**Adsorption procedure**

Batch adsorption experiments were carried out in Erlenmeyer flask (250 mL), where solution of Sr²⁺ (200 mL) with initial Sr²⁺ concentration of 50 mg L⁻¹ was placed. The effects of solution pH values, adsorbent dosage and contact time on Sr²⁺ removal were investigated. The solution pH values (2-12) were adjusted at the desired level using dilute NaOH 0.1M or H₂SO₄ 0.1M (the pH values were measured with Horiba M12 pH meter). The Sr²⁺ adsorption was done by mixing of adsorbent in flask for 60 min. The solution samples were taken at certain time intervals (0-60 min.) and adsorbent was separated by centrifuged at 160 rpm for 10 min. . The change on the absorbance of all solution samples was monitored and determined at certain time intervals during the adsorption process. At the end of the equilibrium period, the Sr²⁺ concentration was determined by using a spectrophotometer (UV-vis spectrophotometer, Jenway (6505) at λmax = 513 nm. The kinetics and isotherm of Sr²⁺ adsorption were studied by contacting 200 mL of Sr²⁺ solution with initial Sr²⁺ concentration of 50 mg L⁻¹ at room temperature (25 °C) for 60 min at a constant stirring speed of 160 rpm at different adsorbent dosages. Different amounts of adsorbent (0.06–0.24 g) was applied to removal Sr²⁺. The amount of Sr²⁺ adsorbed at equilibrium \( q_e \) (mg g⁻¹) was calculated by following equation:

\[
q_e = \frac{(C_0 - C_e)V}{m}
\]

where \( C_0 \) (mg L⁻¹) is the initial Sr²⁺ concentration, \( C_e \) (mg L⁻¹) the Sr²⁺ concentration at equilibrium, \( V \) (L) the volume of the solution and \( m \) (g) is the mass of the adsorbent. The amount of Sr²⁺ adsorbed at time \( t \) \( q_t \) (mg g⁻¹) was calculated by following equation:

\[
q_t = \frac{(C_0 - C_t)V}{m}
\]

where \( C_0 \) (mg L⁻¹) is the initial Sr²⁺ concentration, \( C_t \) (mg L⁻¹) the Sr²⁺ concentration at any time \( t \), \( V \) (L) the volume of the solution and \( m \) (g) is the mass of the adsorbent.

**RESULTS AND DISCUSSION**

**The Characterization of adsorbent activated carbon**

Figure 1 shows the SEM image of adsorbent activated carbon. Regarding the specified scale in the Figure 1, the size of particles is nanometer. Specific surface areas are commonly reported as BET surface areas obtained by applying the theory of BET to nitrogen adsorption/desorption isotherms measured at 77 K. The BET surface area of adsorbent was 462 m² g⁻¹, respectively.
Adsorption kinetics

The controlling mechanism of the adsorption process, kinetic models are used to analysis the experimental data. The rate of adsorption process can be identified with the kinetic adsorption data. Many kinetic sorption models studied for test the experimental data in adsorption process. Using the correlation coefficients ($R^2$), confirms the experimental data with the model. If the higher value is closed to unity, it means that model used for the kinetics is justified. In this research, we choose two kinetic models, pseudo- first-order kinetic model and pseudo-second-order kinetic model, are tested to find the best fitted model for the experimental data. The pseudo-first-order kinetic model (Lagergren 1898) is generally shown as follows:

$$\frac{dq_i}{dt} = k_1(q_e - q_t)$$  \hspace{1cm} (3)

where $q_t$ and $k_1$ are the amount of Sr$^{2+}$ adsorbed at time $t$ (mg g$^{-1}$) and the rate constant of pseudo-first-order kinetics (min$^{-1}$), respectively. Integrating Eq. (3) with the boundary conditions ($t=0$ to $t=\tau$ and $q_t=0$ to $q_t=q_e$) show the linear equation as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 \tau$$  \hspace{1cm} (4)

or

$$q_t = q_e [1 - \exp(-k_1 \tau)]$$  \hspace{1cm} (5)

A plot of $\log(q_e-q_t)$ versus $\tau$ presents a linear relationship from which $k_1$ and $q_e$ are the slope and the intercept, respectively. The pseudo-second-order kinetic model (Ho 1995) applied to adsorption kinetic, can be written as follow:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2$$  \hspace{1cm} (6)

where $k_2$ is the rate constant of pseudo-second-order kinetics (g mg$^{-1}$ min$^{-1}$). Integrating Eq. (6) with the boundary conditions ($q=0$ to $q=q_e$ and $t=0$ to $t=\tau$) show the linear equation as follows:

$$\frac{\tau}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t$$  \hspace{1cm} (7)

or

$$q_t = \frac{k_2 t q_e^2}{1 + (k_2 q_e^2)}$$  \hspace{1cm} (8)

If the second-order kinetics is applicable, the plot of $t/q_t$ versus $t$ will be a linear relation. The values of $k_2$ and $q_e$ will be determined from the intercept and the slope of the plot. Kinetic constants obtained by linear regression (Figure 2. SEM image of adsorbent activated carbon).
and 3) for the two models are listed in Table 1. The correlation coefficients ($R^2$) for the pseudo-first-order kinetic model are relatively low. For the pseudo-second-order kinetic model, the $R^2$ value is 0.9955 the second-order model to describe the adsorption process of Sr\textsuperscript{2+} onto the adsorbent.

Figure 2. Pseudo-first-order kinetic of adsorption of Sr\textsuperscript{2+} onto adsorbent (concentration of Sr\textsuperscript{2+} = 50 ppm, adsorbent dosage= 0.24 g, contact time=50 min, pH= 7, T=25 °C).

Figure 3. Pseudo-second-order kinetic of adsorption of Sr\textsuperscript{2+} onto adsorbent (concentration of Sr\textsuperscript{2+} = 50 ppm, adsorbent dosage= 0.24 g, contact time=50 min, pH= 7, T=25 °C).
Table 1. Adsorption kinetic parameters of Sr\textsuperscript{2+} adsorption onto the adsorbent.

<table>
<thead>
<tr>
<th></th>
<th>Pseudo-first-order</th>
<th></th>
<th>Pseudo-second-order</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$ (min\textsuperscript{-1})</td>
<td>0.0826</td>
<td>$q_\text{e,cal}$ (mg g\textsuperscript{-1})</td>
<td>9.10</td>
</tr>
<tr>
<td>$q_\text{e,exp}$ (mg g\textsuperscript{-1})</td>
<td>16.877</td>
<td>$R^2$</td>
<td>0.9068</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9955</td>
<td>$k_2$ (g mg\textsuperscript{-1} min\textsuperscript{-1})</td>
<td>0.3275</td>
</tr>
<tr>
<td>$q_\text{e,cal}$ (mg g\textsuperscript{-1})</td>
<td>17.12</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Adsorption isotherm**

Adsorption isotherm demonstrates the relationship between equilibrium concentrations of adsorbate in the solid phase, and in the liquid phase at the constant temperatures. The adsorption isotherms are often obtained in the laboratory using batch tests in which the equilibrium data are attempted by various isotherm models. There are the initial experimental tests that determine feasibility of adsorption treatment. There are many different isotherm models have been suggested for the adsorption of solutes in a liquid solution onto a solid surface. In this study, the Langmuir and Freundlich isotherms were used to describe the equilibrium adsorption. The Langmuir isotherm model assumes monolayer coverage of adsorbate over a homogenous adsorbent surface with a finite number of identical sites, and there is no interaction between the adsorbate molecules. The Langmuir model can be described as follows (Langmuir 1918):

$$q_e = \frac{bq_mC_e}{1 + bC_e}$$  \hspace{1cm} (9)

A linear expression for the Langmuir isotherm can be expressed as following:

$$\frac{C_e}{q_e} = \frac{1}{C_m} + \frac{C_e}{q_m}$$  \hspace{1cm} (10)

where $C_e$ is the equilibrium concentration of Sr\textsuperscript{2+} solution (mg L\textsuperscript{-1}), $q_e$ the equilibrium capacity of Sr\textsuperscript{2+} on the adsorbent (mg g\textsuperscript{-1}), $q_m$ is the monolayer adsorption capacity of the adsorbent (mg g\textsuperscript{-1}), and $b$ is the Langmuir adsorption constant (L mg\textsuperscript{-1}) and related to the free energy of adsorption.

The empirical Freundlich adsorption isotherm is obtained on the assumption that the sorption takes place on a heterogeneous adsorbent surface, where the sorption energy distribution decreases exponentially. This equation is also applicable to multi layer adsorption and is expressed by the following equation (Freundlich 1907):

$$q_e = K_f C_e^{1/n}$$  \hspace{1cm} (11)

where $K_f$ and $n$ are the Freundlich constants which represent the adsorption capacity and adsorption intensity of the sorbent, respectively. Eq (11) can be linearized by taking logarithms as:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$  \hspace{1cm} (12)

From which the Freundlich constants can be determined.

To study the applicability of the Langmuir and Freundlich isotherms for the Sr\textsuperscript{2+} adsorption onto adsorbent linear plots of $C_e/q_e$ against $C_e$. In $q_e$ versus $\ln C_e$ are plotted (Figure 4 and 5). The values are shown in Table 2. The $R^2$ values show that the Sr\textsuperscript{2+} removal isotherm does not follow the Freundlich isotherm (Table 2). The linear fit between the $C_e/q_e$ versus $C_e$ and the calculated $R^2$ values for Langmuir isotherm model show that the Sr\textsuperscript{2+} removal isotherm can be approximated as Langmuir model. This means that the adsorption of Sr\textsuperscript{2+} takes place at specific homogeneous sites and a one layer adsorption onto adsorbent surface.
Figure 4. Langmuir model for adsorption of Sr$^{2+}$ onto adsorbent (concentration of Sr$^{2+}$ = 50 ppm, adsorbent dosage= 0.24 g, contact time=50 min, pH= 7, T=25 °C).

Figure 5. Freundlich model for adsorption of Sr$^{2+}$ onto adsorbent (concentration of Sr$^{2+}$ = 50 ppm, adsorbent dosage= 0.24 g, contact time=50 min, pH= 7, T=25 °C).

Table 2. Adsorption isotherm parameters of Sr$^{2+}$ adsorption onto the adsorbent.

<table>
<thead>
<tr>
<th>q_m (mg g$^{-1}$)</th>
<th>b (L mg$^{-1}$)</th>
<th>R$^2$</th>
<th>Kf (mg g$^{-1}$)</th>
<th>n</th>
<th>R$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.871</td>
<td>3.717</td>
<td>0.9806</td>
<td>2.63</td>
<td>1.96</td>
<td>0.8138</td>
</tr>
</tbody>
</table>

**Effect of adsorbent dosage**

Figure 6 plots the effects of different adsorbent dosages (g) on Sr$^{2+}$ percent removal. The increase in Sr$^{2+}$ removal with adsorbent dosage can be attributed to an increase in the adsorbent surface, which increased the availability of adsorption sites. This figure indicates that in the presence of adsorbent, 99.3% of Sr$^{2+}$ was adsorbed with 0.24 g of adsorbent. However, if the adsorption capacity (mg g$^{-1}$) decreased with the increasing amount of adsorbent. The decreased is due to adsorption sites remaining unsaturated during the adsorption process (Chao-
Yin et al., 2008). Another reason for this result may be the overlapping of adsorption sites due to overcrowding of adsorbent particles.

Figure 6. Effect of adsorbent dosage on Sr$^{2+}$ removal by adsorbent (concentration of Sr$^{2+}$ = 50 ppm, contact time=50 min, pH=7, T=25 °C).

**Effect of contact time**

The effect of contact time on Sr$^{2+}$ percent removal the adsorbent is shown in Figure 7. The percent removal increase during the initial adsorption stage and then continue to increase at a relatively slow speed with contact time until a state of equilibrium is attained in 50 min. This phenomenon is attributed to the fact that a large number of vacant surface sites are available for adsorption at the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases.

Figure 7. Effect of contact time on Sr$^{2+}$ removal by adsorbent (concentration of Sr$^{2+}$ = 50 ppm, adsorbent dosage= 0.24 g, pH=7, T=25 °C).
Effect of pH

The pH of a \( \text{Sr}^{2+} \) solution is an important influencing factor for the adsorption of \( \text{Sr}^{2+} \) onto adsorbent. Figure 8 shows the percent removal of \( \text{Sr}^{2+} \) onto adsorbent at different pH from 2 to 12, which clearly shows that the best results were obtained in acidic solution, \((\text{pH} = 7)\). The charge of adsorbent, its surface is presumably positively charged in acidic solution and negatively charged in alkaline solution. For adsorbents with bases as agents, the adsorbent surface charge varies with pH changes. In low pH, the \( \text{H}_3\text{O}^+ \) ions accumulate near the surface ligands and cause the adsorbent surface charge to increase (Xuan et al., 2006). As shown in Figure 8, the more pH increases the more adsorbing covalence of the absorber decreases. Based on the theory of surface complexation, this decrease can be due to the increased competition between \( \text{OH}^- \) and adsorbing varieties for active sites as well as the increase in negative charge of the surface (Krishnani et al., 2008).

![Figure 8](image_url)

**Figure 8.** Effect of pH on \( \text{Sr}^{2+} \) removal by adsorbent (concentration of \( \text{Sr}^{2+} = 50 \text{ ppm} \), adsorbent dosage= 0.24 g , contact time=50 min, \( T=25^\circ \text{C} \)).

CONCLUSIONS

In this study, adsorbent activated carbon of almond shell synthesized for removal \( \text{Sr}^{2+} \) in water solution. The prepared adsorbent were characterized by SEM and BET analysis. The effects of operational parameter such as pH, adsorbent dosage and contact time on the process were studied and optimized. The results showed that \( \text{Sr}^{2+} \) adsorption onto adsorbent followed Langmuir isotherm. Adsorption kinetics of \( \text{Sr}^{2+} \) followed the pseudo-second order kinetic model.

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