Removal of Silver (I) from Aqueous Solutions by Natural Bentonite

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Abstract. The aim of the present work is to investigate the ability of commercial natural bentonite (untreated) (NB) to remove silver ions from aqueous solution. Specific surface area of the sample was determined as a result of N\textsubscript{2} adsorption-desorption at 77 K using BET method. X-ray powder diffraction (XRD) was used to characterize the (NB). Towards this aim, batch adsorption experiments were carried out and the effect of various parameters on this removal process has been investigated. The effects of pH, adsorption time, silver ion concentration, bentonite doses, Temperature and the NB treatment (calcinations and washing) on the adsorption process were examined. The optimum pH for adsorption was found to be 4-8. It was found that NB treatment has a substantial effect on the metal uptake. In adsorption studies, residual silver ions concentration reached equilibrium in a short duration of 15 min. The paper discusses the thermodynamic parameters of the adsorption (the Gibbs free energy, entropy, and enthalpy). Adsorption of Ag\textsuperscript{+} on NB appeared to follow Langmuir isotherm. Our results demonstrate that the adsorption process was spontaneous and endothermic under natural conditions. Additionally, a pseudo-second-order rate model was adopted to describe the kinetics of adsorption. In desorption experiment, an approximately (15%) desorption yield was obtained for silver ions.

Introduction

The removal of metal ions from industrial wastewaters using different adsorbents is always of great interest\cite{1,2}. Because, industrial wastewaters often contain considerable amounts of metal ions that would endanger public health and the
environment if discharged without adequate treatment. High concentrations of the metals in solution affect humans, animals and vegetation. The pollution of water and soil with metal cations increases proportionally with the expansion of industrial activities [3, 4]. In order to minimize processing costs for these industrial wastewaters, most of the last investigations have focused on the use of low cost adsorbents [5, 7]. In the last years, utilization of clay minerals such as bentonite to control the pollution due to the effluents polluted with heavy metal ions has increased. Bentonite has ion-exchange capability to remove unwanted metal ions and this property makes bentonite favorable for wastewater treatment. Beside this, price of bentonite is considered very cheap [8, 9].

Silver is a very useful raw material in various industries due to its excellent malleability, ductility, electrical and thermal conductivity, photosensitivity and antimicrobial properties. Significant amounts of silver are lost in the effluents discharged from such industries and due to the toxicity of silver to living organisms, the removal of this metal from wastewaters is an important concern. The presently available technologies for the removal of silver include precipitation, electrolysis, solvent extraction, use of ion-exchange resins, chelating agents, etc. These processes can be profitably used on a large scale when the metal concentrations in effluents are sufficiently high, i.e., above 100 ppm [10, 11].

Taking into account all the above, we have considered it of great interest to assess the ability of commercially available commercial bentonite (untreated, NB) for the removal of silver ions from aqueous solution and optimization of conditions for its maximum adsorption. To increase the efficiency of metal removal and to maximize the amount of silver recoverable from solution the effects of various parameters (especially pH of the medium; bentonite dose; heat treatment and washing of bentonite) on the Ag⁺ removal process have been investigated. Also, the thermodynamics of the Ag⁺ adsorption and desorption of Ag⁺ have been investigated.

Materials and Methods

Chemicals

Silver nitrate (I) (AgNO₃) was used in the adsorption experiments. pH adjustments were carried on using 0.1N hydrochloric acid (HCl) and 0.1N sodium hydroxide (NaOH). All Ag⁺ solutions were prepared with ultra-pure water (specific resistively of 18 MW. Cm) obtained from an E-pure (Barnstead, USA) purifier system. Super purity nitric acid (SpA, 68%) purchased from ROMIL Ltd., UK was used for sample preparation. Single element ICP Standard solutions from MV Laboratories INC. (USA) were used for system calibrations.
**Adsorbent**

The commercial natural bentonite (untreated) (NB) was obtained from a local supplier (Bariod Saudi Arabia Limited) was used. It was characterized by X-ray diffraction (XRD) and chemical analysis. The chemical composition of the tested samples was as follows (Wt%) SiO2 40.43, Al2O3 15.87, CaO 2.80, K2O 0.14, Na2O 2.02, Fe2O3 10.86, MgO 3.32.

Comparative XRD patterns of the natural commercial bentonite clay are shown in Fig. 1. The XRD patterns of this clay indicate that the dominant component is montmorillonite (68.74 %). The remaining components are, K-feldspar (15.72%) and Calcite (15,723%).

![Fig. 1. The XRD patterns of the NB.](image)

**Characterization of Adsorbent**

Commercial natural bentonite (untreated) (NB), grey in color, particles size ranged between 0.0375 - 0.25 mm, was used. Bentonite sample was divided into three parts: First part used in the adsorption studies as received and labeled by NB; the second part was washed with distilled water several times with deionized water to remove any particles adhering to the surface, salt and any water-soluble impurities. The washed sample was oven-dried at 60 °C under vacuum over night for several hours before use in the adsorption studies. The dried bentonite was grounded, sieved the washed sample labeled by WB and stored in sealed polypropylene bottles., and the third part was calcined in a
furnace at 700°C for 24 h. The hot sample was cooled down to room temperature over silica gel then ground and passed through sieves. The calcinations bentonite was labeled by CB and stored in sealed polypropylene bottles.

The specific surface area of Commercial natural bentonite (untreated) (NB) was determined by applying the BET (Brunauer, Emmet, Teller) equation. The resulted surface area of commercial natural bentonite (untreated) (NB), \( S_{NB} = 45.9 \text{m}^2 \text{g}^{-1} \) This values are lower than those expected for montmorillonite\(^{[12]}\), but it may be due to the lack of treatment. In fact, Bourg et al. 2007 and Goldberg 2002 have measured, for a montmorillonite without pretreatment, specific surface areas of 23.9 and 18.6\( \text{m}^2 \text{g}^{-1} \)^\( [13,14]\): It is possible that \( \text{N}_2 \) molecules can not penetrate easily the interlayer regions between the layer sheets, involving an underestimation of specific surface areas\(^{[15,16]}\).

**General Procedure**

Adsorption of silver with commercial bentonite (untreated ) (NB), NB was carried out in a batch reactor. 2000 mg/L of silver stock solution was prepared by dissolving 3.14 g of AgNO\(_3\) in 1 L deionized water. Standard silver solutions ranging between 40 and 2000 mg/L were prepared by diluting the stock solutions. 0.5gm of bentonite mixed with 50mL of silver solution with different concentrations (40-2000 mg /l) were applied in the shaker. 162 rpm stirring rate and 25°C temperature were applied in the shaker. The concentration of silver remained in the solution after shaking 1h was analyzed by using a Perkin-Elmer Optima 5300 DV ICP optical emission spectrometer coupled with peristaltic pump and AS-93 plus auto sampler unit. In the study, the effects of several factors such as pH, concentration of solution, bentonite doses, heat treatment, washing of commercial natural bentonite (untreated) (NB) and contact time on silver removal efficiency were examined.

**Adsorption Models**

Equilibrium isotherms for Ag\(^+\) were obtained by performing batch adsorption studies. The adsorbed silver amount (\( q_e \)) per unit absorbent mass was calculated as follows:

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

Where \( C_o \) is the initial Ag\(^+\) concentration, \( C_e \) is the concentration of Ag\(^+\) at equilibrium (mg/L), \( m \) is the clay mass (mg) and \( V \) is the solution volume (L).
Calculations were made by using these data and adsorption curves were obtained.

**Kinetic Studies**

The kinetic experiments were conducted in batch mode on NB. The experimental details were as follows: 0.5g NB was added to 50mL Ag\(^+\) solution. The corresponding Ag\(^+\) concentration was 200 mg/L. The suspension was shaken for a period between 5 and 1440 min with a rotary shaker at a speed of 162 rpm. After being centrifuged, Ag\(^+\) was analyzed by a Perkin-Elmer Optima 5300 DV ICP optical emission spectrometer. All experiments were carried out in duplicate.

**Effect of pH**

pH is one of the most important parameters while assessing the adsorption capacity of an adsorbent for metal ions sequestering from aqueous solution [17, 19]. The pH of the system controls the adsorption capacity due to its influence on the surface properties of the adsorbent and ionic forms of the silver in solutions. The influence of pH in the range of 2-8 was studied keeping all other parameters constant (silver concentration = 500 and 1000mg/l; stirring speed = 162 rpm; contact time = 1h, adsorbent dose= 0.5g, temp. = 25°C). The pH of silver solution was adjusted after adding the adsorbent. The pH of the solution was adjusted by using a dilute NaOH and HCl solutions. Also the pH of bentonite suspension measured before and after Ag\(^+\) adsorption on NB surface.

**Effect of Adsorbent Dose**

The adsorption percent (%) of Ag\(^+\) on NB was studied at different adsorbent doses [0.1- 5gm /50 ml silver solution] at silver concentrations (500 and 1000 mg/l), keeping stirring speed (162 rpm), temperature (25 °C) and contact time (1 hr) constant.

**Effect of Temperature**

The effect of temperature on adsorption isotherms was conducted under isothermal conditions at 293, 313, and 333 k by maintaining the mixtures in a water circulation shaker bath whose temperature varied within ±0.5°C. The experimental procedures employed for studying the effect of temperature on the adsorption isotherm were the same as those described in the section above and the temperature was controlled. In order to assume maintaining thermal equilibrium, the bottles were first put into the temperature controlled shaker bath for about 1 h prior to the experiment.
Desorption Experiment

Desorption experiments were performed in order to estimate the metal releasing capacity of NB with silver. NB saturated with different adsorbed amount silver ions were dried at 60°C and then 0.5g of these samples were added in a glass reactor containing 50mL deionized water under constant temperature of 25°C. The resulting bentonite suspension was mechanically agitated for 1h with a stirring rate of 162 rpm and several samples were analyzed for their silver ions content with a Perkin-Elmer Optima 5300 DV ICP optical emission atomic spectrometer.

Results and discussion

Kinetics of Adsorption

The adsorption kinetics, yielding the solute uptake rate, are the most important determinant of the adsorption efficiency of commercial bentonite (untreated) (NB) and therefore, its potential application. Figure 2 presents the effect of the contact time on the Ag^{+} adsorption rate at 200mg/L. According to Figure 2 silver sorption was very fast. The slopes of the lines joining the data points in the figure reflect the adsorption rates. As it is seen, high adsorption rates were observed at the beginning and then plateau values were reached within 15 min. The adsorption rate obtained with the NB seemed to be very satisfactory. Due to the preference of short adsorption times for the minimum energy consumption, NB can be accepted as an efficient adsorbent for Ag^{+} removal when its short adsorption time is considered. Taking into account these results, a contact time of 2h was chosen for further experiments. It must be remarked that when both systems reached equilibrium, final pH also remained constant.

The kinetics of silver uptake can be described by pseudo-first-order and pseudo-second-order model [20, 22].

The pseudo-first-order model is given as:

\[
\ln (q_e-q_t) = \ln q_e - K_1 t
\]  

The pseudo-second-order model is expressed as:

\[
\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}
\]

\[
h = K_2 q_e^2
\]
where $K_1$ is the rate constant of pseudo-first-order adsorption ($\text{min}^{-1}$), $K_2$ ($\text{g/mg min}$) the rate constant of pseudo-second-order adsorption, $h$ the initial adsorption rate ($\text{mg/g min}$) and $q_e$ and $q_t$ are the amount of adsorbed $\text{Ag}^+$ on adsorbent ($\text{mg/g}$) at equilibrium and at time $t$, respectively.

These models were evaluated from the experimental data to evaluate the rate of adsorption of $\text{Ag}^+$ onto the NB. The adsorption kinetic constants and linear regression values are given in Table 1. From the Table 1., we can see that the degree of fit $r^2$ for the pseudo-second-order kinetic model ($r^2 = 1$) is very higher than those of the pseudo-first-order model ($r^2 < 0.42$). Accordingly, the pseudo-second-order kinetic model is applicable, and the plot of $t/q_t$ versus $t$ shows a linear relationship (Fig. 3, a and b). Also, the $q_e$ calculated values fit the experimental data. This suggests that the pseudo-second-order adsorption mechanism is predominant and that the overall rate of the $\text{Ag}^+$ adsorption process appeared to be controlled by the chemical process \[^{[23]}\]. The calculated $q_e$ values of the first-order model do not give reasonable values, which are obviously different from the experimental $q_e$ values. So, adsorption of $\text{Ag}^+$ onto NB is not a pseudo-first-order process.

![Graph](image-url)

**Fig. 2.** Effect of contact time on $\text{Ag}^+$ adsorption rate by NB (silver concentration 200 mg/L, 25°C and NB dose = 10/L.).
Fig. 3. Pseudo-first order (a) and pseudo-second order (b) reaction kinetics for the adsorption of Ag⁺ on NB surface.

Table 1. Parameters for adsorption of Ag⁺ onto NB derived from the pseudo-first- and second-order kinetic models and their compatibility to the associates.

<table>
<thead>
<tr>
<th></th>
<th>Pseudo-first-order</th>
<th></th>
<th>Pseudo-second-order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>qₑ (mg/g)</td>
<td>K₁ (min⁻¹)</td>
<td>R²</td>
</tr>
<tr>
<td></td>
<td>1.9</td>
<td>-0.016</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Effect of Solution pH

The pH dependence of Ag\(^{+}\) adsorption onto NB surface is shown in Figure 4. Experiments were carried out using Ag\(^{+}\) ion concentrations, 1000 mg/ L at different pH values. As it is seen in Fig. 4, adsorbed amount of silver (\(q_e\)) is low at low pH values. The value of \(q_e\) is increased by increasing the pH value and reaches a plateau at a pH value of 6.0. It is apparent that using solutions at pH values between 4.0 and 6.0 gives the highest \(q_e\) values. So, we can carry out this Ag\(^{+}\) adsorption process not only at a certain pH value, but also in a wide range of pH values. The surface charge of bentonite is a strong function of the pH. In this work the point of zero charge of NB particles at pH 4 = 0. Therefore at low pH (below the point of zero charge), the exchange sites on the bentonite particle become positive, the silver cations compete with the H\(^{+}\) ions in the solution for the active sites and consequently lower adsorption \[^{24}\]. At high pH values (above point of zero charge), surface of the bentonite has a higher negative charge which results in higher attraction of cations (Ag\(^{+}\)). These data are in agreement with the results obtained by several earlier workers for metal adsorption on different adsorbent \[^{25-29}\]. Hence adsorption of Ag\(^{+}\) onto NB is at optimum in the pH range 4-8.

![Fig. 4. Effect of pH on Ag\(^{+}\) removal by NB [at initial silver concentrations 1000 mg/L, bentonite dose = 10 g/L.].](image)

Measuring the pHs of the NB suspension before and after silver adsorption can give good information for revealing the above comments. Figure 5 shows the pH values of NB suspension before and after silver adsorption. As can be seen from this figure, increase in the final suspension pH after silver adsorption may be attributed to the replacement of alkaline and alkaline earth metals (Na\(^{+}\), K\(^{+}\), Ca\(^{2+}\), Mg\(^{2+}\)) located in the exchange sites of commercial bentonite (untreated) (NB) with silver ions existed in the solutions. Furthermore, carbonate, presented in the commercial bentonite (untreated) (NB) structure, may also be dissolved.
Effect of Bentonite (NB) Dosage

Adsorption % of Ag⁺ on NB was studied at different adsorbent doses [0.1, 0.3, 0.5, 0.7, 1, 2, 3, and 5 g/50ml, respectively] keeping initial silver concentration (500 and 1000 mg/l), temperature (25°C) and contact time (1h) constant. The results showed that with increase in the adsorbent dose, adsorption % of Ag⁺ was increased and the maximum removal was observed with adsorbent dose (Fig. 6). Increase in the percentage adsorption with adsorbent dose may be due to the increase in adsorbent surface area and availability of more adsorption sites [30]. But unit adsorption (adsorbed amount ,mg/g) was decreased with increase in adsorbent dosage (Fig.7.) As the adsorbent dose was increased the unit adsorption was decreased. This may be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles [31].

Adsorption Isotherm

Figure 8 plots the adsorption amount of Ag⁺ adsorption by NB adsorbent at various temperatures (293, 313 and 333 K). It was observed with temperature increase the adsorbed amount of silver on NB surfaces increased. This change occurs because of increasing kinetic energy of the of the silver ions, which increases the frequency of collisions between the NB and silver ions and thus enhances adsorption of silver on the surface of the NB. All batch experimental data were fitted to the isotherm models of the well-known Langmuir and Freundlich using the method of least squares and an optimization algorithm. There models are represented mathematically as follows.
Fig. 6. Effect of commercial bentonite (untreated) (NB) dose on adsorption % of Ag\(^+\) at different silver concentration (500 and 1000mg/L) and constant temperature = 25\(^\circ\)C.

Fig. 7. Effect of commercial bentonite (untreated) (NB) dose on the adsorbed amount of Ag\(^+\) at different silver concentration (500 and 1000mg/L) and constant temperature = 25 \(^\circ\)C.

Fig. 8. Adsorption isotherms of Ag\(^+\) onto NB adsorbent at different temperatures.
The Langmuir isotherm model is obtained by combining the adsorption and desorption rate equations\[32\].

\[
\frac{d\theta_t}{dt} = k_{ad}C_t N (1 - \theta_t) - k_d N \theta_t
\]

Where \( N \) is the maximum number of adsorption sites occupied by the Ag\(^+\) and \( \theta_t \) is the dimensionless surface coverage ratio (\( \theta_t = q_t/q_m \)). When the sorption process reaches equilibrium, Eq. (2) yields

\[
q_e = \frac{K_L q_m C_e}{1 + K_L C_e}
\]

Where \( K_L = k_{ad}/k_d \) is the Langmuir constant; \( q_m \) is the maximum adsorption capacity (mg g\(^{-1}\)) and \( q_e \) is the adsorbed amount of Ag\(^+\) (mg g\(^{-1}\)) at equilibrium. Rearranging Eq. (3) yields the Langmuir parameters:

\[
\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}
\]

The Freundlich isotherm model show the relationship between the amount of Ag\(^+\) adsorbed by the NB adsorbent (\( q_e \), mg g\(^{-1}\)) and the equilibrium concentration of Ag\(^+\) (\( C_e \), mg l\(^{-1}\)) in solution\[33\].

\[
q_e = K_F C_e^{1/n}
\]

Where \( K_F \) and \( n \) are Freundlich constants that are related to the adsorption capacity and adsorption intensity, respectively.

Figure 9 and 10 display linear plots of \( C_e/q_e \) versus \( C_e \) and \( \ln q_e \) versus \( \ln C_e \) at 293, 313 and 333 K. For Langmuir isotherm in Fig. 9, the values of \( q_m \) and \( K_L \) were determined from experimental data by linear regression. According to Freundlich isotherm (Fig. 10), the values of \( K_F \) and \( n \) were obtained similarly. The data in Table 2 presents the results, along with associated correlation coefficients (\( R^2 \)). The data in Table 2 reveals that the Langmuir model yields a better fit than the Freundlich model, according to the correlation coefficients.
Fig. 9. Linearized Langmuir isotherm models for Ag$^+$ adsorption by the NB adsorbent at (a) 293 K, (b) 313 K and (c) 333 K (adsorbent dosage, 10 g/L and shaking time, 2 h).
Fig. 10. Linearized Freundlich isotherm models for Ag⁺ adsorption by the NB adsorbent at (a) 293 K, (b) 313 K and 333 K (adsorbent dosage, 10 g/L and shaking time, 2 h).
Table 2. Parameters of Langmuir and Freundlich adsorption isotherm models for Ag⁺ on NB adsorbent at different temperature.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>qₑₑ (mg/g)</th>
<th>Kₑₑ (L/mg)</th>
<th>Kₑₑ (L/mol)</th>
<th>R²</th>
<th>Kᶠ</th>
<th>n</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>53</td>
<td>0.040</td>
<td>4280</td>
<td>0.989</td>
<td>0.66</td>
<td>1.98</td>
<td>0.919</td>
</tr>
<tr>
<td>313</td>
<td>57</td>
<td>0.036</td>
<td>3852</td>
<td>0.977</td>
<td>0.87</td>
<td>2.15</td>
<td>0.915</td>
</tr>
<tr>
<td>333</td>
<td>69</td>
<td>0.033</td>
<td>3531</td>
<td>0.980</td>
<td>0.51</td>
<td>1.85</td>
<td>0.946</td>
</tr>
</tbody>
</table>

**Adsorption Thermodynamics**

The thermodynamic parameters of the adsorption, i.e. the standard enthalpy ΔH°, Gibbs free energy ΔG° and entropy ΔS° were calculated using the equations:

\[ \Delta G = -RT \ln k_L \]  \hspace{1cm} (9)

\[ \ln k_L = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \]  \hspace{1cm} (10)

Where R is the ideal gas constant (kJ mol⁻¹ K⁻¹), K_L = k_ads/k_d is the Langmuir constant and T is the temperature (K). ΔH° and ΔS° values can be obtained from the slope and intercept of Van’t Hoff plots of ln Kₑₑ(from the Langmuir isotherm) versus 1/T \[^{34,35}\].

The results of these thermodynamic calculations are shown in Fig. 11 and Table 3. The negative value for the Gibbs free energy for silver adsorption shows that the adsorption process is spontaneous and that the degree of spontaneity of the reaction increases with increasing temperature. The overall adsorption process seems to be endothermic (ΔH = 5.3 kJ mol⁻¹). This result also supports the suggestion that the adsorption capacity of NB for silver increases with increasing temperature. Table 3 also shows that the ΔS value was positive. This occurs as a result of redistribution of energy between the adsorbate and the adsorbent. Before adsorption occurs, the heavy metal ions near the surface of the adsorbent will be more ordered than in the subsequent adsorbed state and the ratio of free heavy metal ions to ions interacting with the adsorbent will be higher than in the adsorbed state. As a result, the distribution of rotational and translational energy among a small number of molecules will increase with increasing adsorption by producing a positive value of ΔS and randomness will increase at the solid–solution interface during the process of adsorption. Adsorption is thus likely to occur spontaneously at normal and high temperatures because ΔH > 0 and ΔS > 0.
Fig. 11. Plot of the Langmuir isotherm constant ($\ln K_L$) vs. temperature ($1/T$). The thermodynamic parameters in Table 4 are determined from this graph.

Table 3. Thermodynamic constants for the adsorption of Ag$^+$ on commercial bentonite (untreated) (NB) at various temperatures

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$\ln K_L$</th>
<th>$\Delta G$ (kJ/mol)</th>
<th>$\Delta H$ (kJ/mol)</th>
<th>$\Delta S$ (kJ/mol K)</th>
<th>R ((kJ/mol K)$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>5.4</td>
<td>5.55</td>
<td>-9.65</td>
<td>-10.49</td>
<td>4.15</td>
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<tr>
<td>313</td>
<td>5.55</td>
<td>5.6</td>
<td>-11.69</td>
<td>4.15</td>
<td>0.05</td>
</tr>
<tr>
<td>333</td>
<td>5.6</td>
<td>5.6</td>
<td>-11.69</td>
<td>4.15</td>
<td>0.05</td>
</tr>
</tbody>
</table>

**Desorption**

In metal ion removal process, it is important to study the desorption of the adsorbed metal ions under suitable conditions. In the desorption studies deionized water was used as desorption agent. The NB samples loaded with different adsorbed amount of Ag$^+$ ions (initial silver concentration = 500, 1000 and 2000 mg/L) were placed in 50 ml deionized water and the amount of silver ions desorbed within 1 h measured. Figure 12 shows the data of the adsorbed and desorbed amount Ag$^+$ ions. The data show that there is about 12.5, 11.6 and 14.7% of Ag$^+$ ions desorbed from NB surface loaded by 36.3, 46.5 and 50.3 mg/g.
Fig. 12. Adsorbed and desorbed amount of Ag\(^{+}\) at three initial silver concentrations (500, 1000 and 2000 mg/L) and temperature 25°C.

**Effect of Bentonite Treatment**

Figure 13 shows the maximum adsorbed amount of silver ions on NB, WB and CB at initial silver concentrations, 1000 mg/L. The adsorbed amount of Ag\(^{+}\) on WB was higher than NB and CB. This result may be due to removal of dissolved and excess salts located in the exchange sites of commercial bentonite (untreated) (NB) upon washing. Therefore, the exchange sites on bentonite surfaces increased and consequently become available for more adsorption of silver ions from solution. Also in this figure decreasing of the adsorption capacity of CB was very lowered compared to NB. Depending on many investigators, the heat treatment of clay leads to dehydration and dehydroxylation of the bentonite, cation exchange capacity and surface area decreased and consequently the adsorption capacity decreased \([19, 36, 37]\).

Fig. 13. The adsorbed amount of Ag\(^{+}\) on natural bentonite (NB), calcined bentonite (CB) and washed bentonite (WB).
Conclusions

The following conclusions can be drawn from this investigation:

1. This study proved that Ag\(^+\) could be adsorbed and thus higher significant amounts removed by NB from aqueous solutions.

2. In batch mode adsorption studies, removal % of Ag\(^+\) increased with the increase of contact time, amount of adsorbent and pH.

3. The equilibrium data could be described by the Langmuir and Freundlich isotherm equations. However, the Langmuir model better represented the sorption process than the Freundlich model.

4. Kinetic modeling results showed that the pseudo second-order equation was appropriate for the description of this type of adsorption and removal.

5. High adsorption capacity of washed bentonite (WB) compared to Natural bentonite (NB) and calcined bentonite (CB).

6. About 11-14 % of Ag\(^+\) desorbed from NB surfaces indicating less affinity between NB surfaces and Ag\(^+\) ions.

7. Depending on the negative value of \(\Delta G\), the adsorption of Ag\(^+\) on NB surfaces was spontaneous and the adsorption was endothermic process.

References


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إزالة الفضية (I) من المحاليل المائية
باستخدام البنتونايت الطبيعي

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المستخلص. تهدف الدراسة الحالية إلى التحقق من مقدرة البنتونايت الطبيعي التجاري (غير المعالج) في إزالة أيون الفضية من المحاليل المائية. تم في هذا البحث تقدير المساحة السطحية المحددة للعينة كنتيجة لامتصاص أمطار غاز النيتروجين عند درجة حرارة 77K باستخدام طريقة BET. أطياف أشعة سين للتشتت (XRD) ثم 77K

للوصول لهذا الهدف فقد تم استخدام تجربة الامتصاز ومنها تم الحصول على آثار الظروف المعملية المختلفة على عملية الإزالة. كما تم اختيار أكثر كل من ال pH وزمن الامتصاز وتركيز أيون الفضية وكيمياء البنتونايت المستخدم. هذا وقد وجد أن أفضل لامتصاز عند المدى 0-4، كما وجد أن معالجة البنتونايت الطبيعي لها الأثر الكبير في إزالة أيونات المعدن. وفي دراسة الامتصاز نجد أن تركيز أيون الفضية المتبقى يصل إلى حالة التوازن في مدة زمنية قصيرة تبلغ 15 دقيقة.

هذه الورقة العلمية تناقش الآثار الثيرموديناميكية للاستراز كطاقة جبس الحرة والانتروبي والانتثالي. تظهر دراسة الامتصاز أيون الفضية على البنتونايت الطبيعي على أنه يتبين معادلة لانجمير

Removal of silver (I) from aqueous solutions by natural bentonite

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كما أن النتائج التي توصلنا عليها توضح بأن عملية الامتزاز تلقائية
وماصلة للحرارة في الظروف العادية.

إضافة إلى ذلك فإنه من الممكن أن يتبع التفاعل الرتبة
الثانية الوعيمة وذلك من أجل وصف عملية الامتزاز. وفي تجربة
إطلاق أيون الفضة الممتاز وجد أن (15%) منه يتم إطلاقه من على
سطح البنتونايت غير المعالج.