Adsorption of Ca (II) & Mg (II) ions from Aqueous Solutions by Surface Modified Silica gel

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Abstract

The unmodified silica gel (for chromatography) and modified silica gel by poly acrylamide (PAAM) at optimum conditions were used to remove calcium (Ca²⁺) and magnesium (Mg²⁺) ions from aqueous solutions by the use of batch experiments at pH 10. The unmodified silica gel exhibited low percentage values about 15% and 17% for Ca²⁺ and Mg²⁺ ions removal, respectively comparing with that for modified silica gel 21.68% and 56.3% removal for Ca²⁺ and Mg²⁺ ions, respectively.

Key words: Modified silica gel, Adsorption.

1. Introduction

The objective of this study is to use modified silica gel for remove some metal ions from aqueous solutions. Silica gels have very low organic compound levels the gels were subjected to carbon, nitrogen and sulfur analysis to determine organic content [1-4]. The modification of inorganic supports, such as silica gel, has been often used in the areas of heterogeneous catalysis, ionic chromatography and chemosorption of metals of interest [5-9] and in several industrial applications [10-12], due to its

Scheme 1: Different distribution forms of the silanols groups on the surface of silica gel: free (A), geminals (B) and local (C).

The modification of the silica surface by polyacrylamide (PAAM) was based on in situ polymerization of the acrylamide monomer using ceric ammonium nitrate (CAN) as an initiator. A series of experiments were carried out to obtain a product in a maximum yield of high nitrogen content. Therefore, all influence factors that control and process were studied. Factors that influence and controls the process such as initiator concentration, reaction temperature, reaction time, quantity concentration of sodium sulfite as an activator of the overall process. Through the concentration of sodium sulfite as an activator of the overall process. Through the

previously obtained data, indeed, the surface of silica gel has been modified by acrylamide. Modified silica gel obtained at all optimum conditions are exemplified. An Encap-SiO\textsubscript{2}/PAAM hybrid was obtained by physical adsorption of the obtained PAAM on the surface of the silica network. The organic–inorganic hybrid composites particles with silica core and PAAM shell and therefore the PAAM shell is expected to dominate the surface characteristics of hybrid as shown in (Scheme2). [14].

\[
\begin{align*}
\text{H}_2\text{N} & \quad \xrightarrow{\text{Ce(IV), Na}_2\text{SO}_3} \quad \text{Silica gel} \\
& \quad \xrightarrow{\text{CH}_2=\text{CH}\text{CONH}_2} \\
& \quad \text{Encapsulation} \\
\end{align*}
\]

Scheme2

Hardness water the total concentration of alkaline earth metal ions, such as calcium and magnesium, in water determine the hardness of water. Is usually determined by measuring the total amount of calcium and magnesium present, since the concentrations of these ions far exceed those of other alkaline earth metals. Several methods were used to measure water hardness which caused by the high level of calcium and magnesium. (EDTA chelating agent that can donate electrons /Lewis base thereby forming a complex with metal ions /Lewis acid). The EDTA will complex first with Ca\textsuperscript{2+} and then with Mg\textsuperscript{2+} in the presence of Eriochrome Black T (EBT) as indicator at pH=10 [15-17].

2. Experimental Section

2.1. Materials
Silica gel (for Chromatography) from Northampton, U.K. Modified Silica Gel Eriochrome Black T. Magnesium Sulphate from farmitalia carloerea S.P.A and MERCK Darmstadt F.R. GERMANY.

2.2. Batch Techniques
Silica gel was modified by polymerization using acrylamide in the presence of (CAN). [14].

The batch adsorption experiments of Ca (II) and Mg (II) ions between the aqueous phase and the solid adsorbent were performed in closed Erlenmeyer flask inside a shaker water bath flask at fixed temperature (25\textdegree C). An appropriate amount of adsorbent placed in a 100mL Erlenmeyer flask containing 25mL of Ca (II) or Mg (II) ion solution at pH =10 (ammonia buffer). The mixture was shaken at 200rpm at (25\textdegree C). The metal ion concentration was
determined by titration with solution of EDTA (0.1 and 0.01M) and (EBT) as indicator. Then the percentage of the metal ion removed calculated.

\[ U\% = \left[ \frac{(C_0 - C_e)}{C_0} \right] 100 \]  

(1)

The adsorption capacity (qe) was determined by the following equation:

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

(2)

3. Results and Discussion

3.1. Removal of Ca\(^{2+}\) and Mg\(^{2+}\) using the Modified Silica gel.

Modified silica gel was exploited to remove calcium (Ca\(^{2+}\)) and magnesium (Mg\(^{2+}\)) ions from aqueous solutions. Since, samples of synthetically Ca\(^{2+}\) or Mg\(^{2+}\) solution at pH=10 (ammonium buffer) were prepared and the removal capacity of the modified silica then estimated. The effect of several factors that control the removal process was studied at room temperature (25\(^{\circ}\)C) using batch equilibrium sorption technique. The concerned factors included are influence of contact time of Ca\(^{2+}\) and Mg\(^{2+}\) on the modified silica, volume of the aqueous phase to mass of modified silica (V/m), and metal ion concentration.

3.1.1. Influence of contact time of Ca\(^{2+}\) and Mg\(^{2+}\) on modified silica gel.

The variation of percent removal of the selected ions as a function of contact time is given in Table 1 and Figures (1&2). It is clear that the removal percentage of both Ca\(^{2+}\) and Mg\(^{2+}\) increases with contact time to reach maximum values, and then decreases after the values. However, the time totally varies with used cations. In case of Ca\(^{2+}\), the maximum removal (21.68%) is attained in 45 minutes while, 15 minutes dipping time, Mg\(^{2+}\) exhibits the larger value of removal (56.3%) than Ca\(^{2+}\).

3.1.2. Influence of an aqueous volume to mass of modified silica gel ratio (V/m) on removal of Ca\(^{2+}\) and Mg\(^{2+}\) ions.

Particularly, in sorption studies, the removal percent of the respective ion is found to be varying with V/m ratio [18, 19]. Hence it is necessary to determine an appropriate V/m value that can result in a high significant removal percent. Here, through the presented data for both Ca\(^{2+}\) and Mg\(^{2+}\) in Table 2 and Figures (3&4), it is clear that the removal percent firstly increases as V/m decreases up to an optimal ratio of V/m equals to 250. The percentage of removal then decreases with further decrease of V/m.

3.2. Adsorption isotherm

Two mathematical models such as Langmuir and Freundlich have been used to study the relation between adsorbate and adsorbent.
Table 1: Variation of the removal percentage of Ca$^{2+}$ and Mg$^{2+}$ at different contact times.

<table>
<thead>
<tr>
<th>Time(min)</th>
<th>Metal ion</th>
<th>$C_0$ mg/ml</th>
<th>$C_e$ mg/ml</th>
<th>$X$ mg/g ($C_0 - C_e$)</th>
<th>Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td></td>
<td>1.9</td>
<td>1.728</td>
<td>0.172</td>
<td>9.05</td>
</tr>
<tr>
<td>15</td>
<td>Ca$^{2+}$</td>
<td>1.9</td>
<td>1.680</td>
<td>0.22</td>
<td>11.58</td>
</tr>
<tr>
<td>30</td>
<td></td>
<td>1.9</td>
<td>1.600</td>
<td>0.300</td>
<td>15.79</td>
</tr>
<tr>
<td>45</td>
<td></td>
<td>1.9</td>
<td>1.488</td>
<td>0.412</td>
<td>21.68</td>
</tr>
<tr>
<td>60</td>
<td></td>
<td>1.9</td>
<td>1.648</td>
<td>0.252</td>
<td>13.26</td>
</tr>
<tr>
<td>120</td>
<td></td>
<td>1.9</td>
<td>1.648</td>
<td>0.252</td>
<td>13.26</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>2</td>
<td>1.440</td>
<td>0.56</td>
<td>28.00</td>
</tr>
<tr>
<td>10</td>
<td>Mg$^{2+}$</td>
<td>2</td>
<td>1.325</td>
<td>0.675</td>
<td>33.75</td>
</tr>
<tr>
<td>15</td>
<td></td>
<td>2</td>
<td>0.874</td>
<td>1.126</td>
<td>56.30</td>
</tr>
<tr>
<td>30</td>
<td></td>
<td>2</td>
<td>1.008</td>
<td>0.992</td>
<td>49.60</td>
</tr>
<tr>
<td>45</td>
<td></td>
<td>2</td>
<td>1.152</td>
<td>0.848</td>
<td>42.40</td>
</tr>
</tbody>
</table>

3.2.1. Langmuir adsorption isotherm [20]

Langmuir adsorption isotherm model is widely used for adsorption studies by forming a monolayer of adsorbate molecules on a homogeneous surface of adsorbent at equilibrium. The linearized form of Langmuir equation as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L a_L} + \frac{a_L}{K_L} C_e$$

Where: $a_L/K_L$ = maximum adsorption capacity ($q_{max}$) and $1/K_L$ = intercept.

The plots of $C_e/q_e$ versus $C_e$ allows to obtained straight line of slop equal $1/q_{max}$ (Table 3 and Figures 5, 6). The calculated $q_{max}$ of Ca$^{2+}$ and Mg$^{2+}$ ions were 232.56 and 59.5 mg/g. The values of R$^2$ in case of Ca$^{2+}$ and Mg$^{2+}$ ions were 0.662 and 0.667, respectively. The low values of R$^2$ in both cases means that, the adsorption of Ca$^{2+}$ and
Mg\(^{2+}\) ions onto modified silica gel was not fitted on Langmuir adsorption isotherm.

**Fig. 1:** Influence of contact time on the removal of Ca\(^{2+}\) ion by the modified silica gel.

**Fig. 2:** Influence of contact time on the removal of Mg\(^{2+}\) ion by the modified silica gel.
### Table 2: Variation of the removal percentage of Ca\(^{2+}\) and Mg\(^{2+}\) ions using different V/m values.

<table>
<thead>
<tr>
<th>V/m</th>
<th>Metal ion</th>
<th>(C_0) mg/ml</th>
<th>(C_e) mg/ml</th>
<th>(X) ((C_0 - C_e))</th>
<th>Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2500</td>
<td>Ca(^{2+})</td>
<td>1.9</td>
<td>1.600</td>
<td>0.3</td>
<td>15.79</td>
</tr>
<tr>
<td>1000</td>
<td>Ca(^{2+})</td>
<td>1.9</td>
<td>1.552</td>
<td>0.348</td>
<td>18.32</td>
</tr>
<tr>
<td>500</td>
<td>Ca(^{2+})</td>
<td>1.9</td>
<td>1.520</td>
<td>0.38</td>
<td>20.00</td>
</tr>
<tr>
<td>250</td>
<td>Ca(^{2+})</td>
<td>1.9</td>
<td>1.488</td>
<td>0.412</td>
<td>21.68</td>
</tr>
<tr>
<td>166.6</td>
<td>Ca(^{2+})</td>
<td>1.9</td>
<td>1.584</td>
<td>0.316</td>
<td>16.63</td>
</tr>
<tr>
<td>125</td>
<td>Ca(^{2+})</td>
<td>1.9</td>
<td>1.584</td>
<td>0.316</td>
<td>16.63</td>
</tr>
<tr>
<td>2500</td>
<td>Mg(^{2+})</td>
<td>2</td>
<td>1.728</td>
<td>0.272</td>
<td>13.6</td>
</tr>
<tr>
<td>1000</td>
<td>Mg(^{2+})</td>
<td>2</td>
<td>1.603</td>
<td>0.397</td>
<td>19.85</td>
</tr>
<tr>
<td>500</td>
<td>Mg(^{2+})</td>
<td>2</td>
<td>1.344</td>
<td>0.656</td>
<td>32.8</td>
</tr>
<tr>
<td>333.33</td>
<td></td>
<td>2</td>
<td>1.104</td>
<td>0.896</td>
<td>44.8</td>
</tr>
<tr>
<td>250</td>
<td>Mg(^{2+})</td>
<td>2</td>
<td>0.874</td>
<td>1.126</td>
<td>56.3</td>
</tr>
<tr>
<td>166.6</td>
<td>Mg(^{2+})</td>
<td>2</td>
<td>1.344</td>
<td>0.656</td>
<td>32.4</td>
</tr>
<tr>
<td>125</td>
<td>Mg(^{2+})</td>
<td>2</td>
<td>1.392</td>
<td>0.608</td>
<td>30.4</td>
</tr>
</tbody>
</table>
**Fig. 3**: Variation of the removal percent of Ca$^{2+}$ ions with different V/m values.

**Fig. 4**: Variation of the removal percent of Mg$^{2+}$ ions with different V/m values.
Table 3: Data for Langmuir adsorption isotherm in case of Ca\(^{2+}\) and Mg\(^{2+}\) ions at Conditions: pH = 10, temperature 25\(^{\circ}\)C.

<table>
<thead>
<tr>
<th>Ce, mg/ml</th>
<th>qe, mg/g</th>
<th>C_e/q_e, g/l</th>
<th>Ce, mg/ml</th>
<th>qe, mg/g</th>
<th>C_e/q_e, g/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.128</td>
<td>15.5</td>
<td>0.008258</td>
<td>0.0816</td>
<td>4.6</td>
<td>0.017739</td>
</tr>
<tr>
<td>0.368</td>
<td>31.5</td>
<td>0.011683</td>
<td>0.154</td>
<td>11.5</td>
<td>0.013391</td>
</tr>
<tr>
<td>0.752</td>
<td>49.5</td>
<td>0.015192</td>
<td>0.293</td>
<td>51.75</td>
<td>0.005662</td>
</tr>
<tr>
<td>1.2</td>
<td>80</td>
<td>0.015</td>
<td>0.48</td>
<td>130</td>
<td>0.003692</td>
</tr>
<tr>
<td>1.488</td>
<td>103</td>
<td>0.014447</td>
<td>0.874</td>
<td>281.5</td>
<td>0.003105</td>
</tr>
</tbody>
</table>

\[ y = 0.0043x + 0.0096 \]
\[ R^2 = 0.6627 \]

Fig 5: Langmuir adsorption plot of Ca\(^{2+}\) ions onto modified silica gel.
Fig 6: Langmuir adsorption plot of Mg\textsuperscript{+2} ions onto modified silica gel.

Table 4: Data for Freundlich adsorption isotherm in case of Ca\textsuperscript{2+} and Mg\textsuperscript{2+} ions.

<table>
<thead>
<tr>
<th></th>
<th>Ca\textsuperscript{2+}</th>
<th></th>
<th>Mg\textsuperscript{2+}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( C_e ), mg/ml</td>
<td>( \log C_e )</td>
<td>( \log q_e )</td>
</tr>
<tr>
<td>0.128</td>
<td>1.190332</td>
<td>-0.89279</td>
<td></td>
</tr>
<tr>
<td>0.368</td>
<td>1.498311</td>
<td>-0.43415</td>
<td></td>
</tr>
<tr>
<td>0.752</td>
<td>1.694605</td>
<td>-0.12378</td>
<td></td>
</tr>
<tr>
<td>1.2</td>
<td>1.90309</td>
<td>0.079181</td>
<td></td>
</tr>
<tr>
<td>1.488</td>
<td>2.012837</td>
<td>0.172603</td>
<td></td>
</tr>
</tbody>
</table>

3.2.2. Freundlich adsorption isotherm [21]

The Freundlich assume that, there are multiple layers of the adsorbate may be formed on the surface of adsorbent. The following equation of Freundlich was also applied in the present work.

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]

Where \( K_F \) and \( n \) are the Freundlich constants.

Plots of \( \log q_e \) versus \( \log C_e \) should be linear. Table 4 and Figures 7 and 8. The values of the slope and intercept expressed to \( 1/n \) and \( \log k_F \), respectively. The obtained values of \( n \) in case of Ca\textsuperscript{2+} and Mg\textsuperscript{2+} ions
were 1.33 and 0.552, respectively. These
values in the range lies between zero and 10,
this means that, the adsorption of Ca\(^{2+}\) and
Mg\(^{2+}\) ions onto modified silica gel were
favorable. The correlation coefficients (R\(^2\))
in case of Ca\(^{2+}\) and Mg\(^{2+}\) ions were 0.9877
and 0.9905, respectively. The high values of
R\(^2\) in both cases means that, the adsorption
of Ca\(^{2+}\) and Mg\(^{2+}\) ions onto modified silica
gel was fitted well on Freundlich adsorption
isotherm.

**Fig 7:** Freundlich adsorption plot of Ca\(^{2+}\) ions onto modified silica gel.

**Fig 8:** Freundlich adsorption plot of Mg\(^{2+}\) ions onto modified silica gel.
4. Conclusion

- Modified silica gel was exploited to remove of Ca\textsuperscript{2+} (21.68\%) and Mg\textsuperscript{2+} (56.3\%) ions from aqueous solutions. Comparing these values with that, the unmodified silica gel which exhibits low percentage values about (15\%) and (17\%) for Ca\textsuperscript{2+} and Mg\textsuperscript{2+} ions removal respectively.

- The adsorption of Ca\textsuperscript{2+} and Mg\textsuperscript{2+} ions onto modified silica gel was fitted well on Freundlich adsorption isotherm.

REFERENCES


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