Sorption Performance of Synthetic Nanocomposite of Mg/Al-Aminobenzoate for Removal of Cobalt Ion from Aqueous Solutions

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ABSTRACT

Nanostructured composite sorbent of Mg/Al-aminobenzoate layered double hydroxide was prepared by coprecipitation method. The particle size of the nanocomposite was found to be 10-20 nm. Sorption performance of the prepared material was studied for removal of cobalt ion from aqueous solution. The percent uptake of cobalt ion was found to be 96.1%. The loading capacity of Mg/Al-aminobenzoate composite for Co\(^{2+}\) ion was studied and found to be 5.2 meq/g. From the kinetic studies, the results illustrated that the mechanism of the sorption process was controlled by pseudo-second order model. The sorption process was chemisorptions since the value of diffusion coefficient is in the order 10\(^{-17}\) m\(^2\)/s, as well as the good fit of Elovich model. The sorption was controlled by intra-particle diffusion mechanism. From isotherm investigations, it was found that Langmuir model fitted the results better than Freundlich model. Stripping process was carried out, the results illustrated that cobalt ion can be completely stripped with 3 M HNO\(_3\). A comparison of the sorption capacity of the prepared material with other sorbents reported in the literature was investigated and indicated that the prepared nanocomposite has much higher sorption capacity than many other sorbents. The whole results indicated that Mg/Al-aminobenzoate nanocomposite is an efficient sorbent and recommended for removal of Co\(^{2+}\) ions in a wide range of concentrations.

Keywords: Nanostructure / Composite / Sorption / Layered Double Hydroxide / Cobalt.

INTRODUCTION

The recent increasing uses of nanostructured materials for metal ions removal studies encouraged us for synthesis of nanocomposite material for application in removal process. Nano sized materials exhibit intrinsic surface reactivity and high surface areas, and can strongly chemisorb many substances. Great attention has recently emerged around the composites in which layered fillers are dispersed at a nanometric level in a polymeric matrix. Such composites possess unusual properties, very different from their microscale counterparts.

Layered double hydroxides (LDHs) are widely known as host-guest materials, anionic clays and hydrotalcite-like compounds. LDHs possess a positively charged hydroxide basal layer due to substitution of trivalent cations for part of the divalent cations in the hydroxide basal layer and are electrically balanced by the intercalation of anions into the interlayer space; the remaining interlayer space is occupied by water molecules. LDHs materials exhibit such favorable characteristics to sorb pollutants as large specific surface areas, porous volumes, good thermal stability, high sorption and regeneration efficiency (1, 2). The structure of LDHs as well as their high anionic exchange capacity makes them suitable for many applications, such as sorption of many inorganic and organic anions as well as potential contaminants in waters (3-6). Also LDHs are used as support in bionanocomposites for medical treatment (7, 8). LDHs could adsorb metal cations from aqueous solution in spite of their positive layer charge (9). These layers attract hydroxide ions around the surfaces of LDH crystals in aqueous solution to induce formation of metal hydroxides. Meanwhile, charge compensating carbonate ion
attached on the surface and edge could also contact with metal cations to form insoluble metal carbonates. There is also another possibility to adsorb metal cations via diarchy, as suggested by Komarneni et al. \(^{(10)}\). These imply that LDHs could be utilized as an adsorbent for metal cations. Therefore, detailed mechanisms of reaction of metal cations in an aqueous solution with LDH are required to exploit these materials in remediation applications.

Organo-LDH composites are prepared by the intercalation of organic substances, e.g. organic carboxylic acid, anionic polymer, cyclodextrin, and organic phosphoric acid, into LDHs \(^{(11)}\). The intercalation of organic substances into LDHs has generally been accomplished by the following methods: anion-exchange, reconstruction, and coprecipitation. In particular, the coprecipitation method has often been used for the direct formation of organo-LDH composites.

There are a number of liquid processes and waste streams at nuclear facilities that require treatment for process chemistry control reasons and/or the removal of radioactive contaminants. Cobalt is one of the most abundant radionuclides in nuclear activities that are routinely or accidentally released. It is considered as hazardous elements for the environment. A number of methods have been developed for the removal of metal ions such as solvent extraction, adsorption, preconcentration, reverse osmosis and ion exchange. In general sorption technique can be a preferred treatment technique.

The current work presents the preparation and characterization of nanometric composite material, Mg-Al-aminobenzoate LDH, as a sorbent for removal of cobalt ion from aqueous solution.

**EXPERIMENTAL**

**Chemicals and reagents**

All chemicals used in this investigation were of analytical grade and used without further purification treatment. Double deionized water was used for preparation of solutions. Cobalt nitrate was purchased from Merck. While Mg(NO\(_3\))\(_2\)·6H\(_2\)O and Al(NO\(_3\))\(_3\)·9H\(_2\)O were purchased from Alpha Chemica. 4-Amino benzoic acid was purchased from Winlab. The pH of solutions was adjusted by the addition of NH\(_2\)OH and/or HNO\(_3\) which purchased from Fluka.

**Preparation of Mg/Al-aminobenzoate LDH**

Mg/Al-aminobenzoate LDH was prepared by coprecipitation method. 250 ml of 10\(^{-4}\) M of NaOH was prepared, and then, weighed amount of 4-amino benzoic acid (10\(^{-4}\)M) was added to the sodium hydroxide solution to give solution number 1. 100 ml of an aqueous solution containing magnesium nitrate and aluminum nitrate in the molar ratio 2:1, respectively, to give solution number 2. Solution number 2 was added drop wise to the vigorously stirred solution number 1 at room temperature and the pH of the solution was maintained at 10.5 by the addition of 1 M of NaOH solution. After the addition of solution number 2, the mixture was reacted at 80 °C for 4 hours. The slurry was then filtered until all the supernatant liquid had been removed. The sample was washed by deionized water and dried at 65 °C. In order to minimize contamination with atmospheric CO\(_2\), the preparation of the LDH–aminobenzoate was under a nitrogen purge. Scheme 1 illustrates a schematic representation of preparation of Mg/Al-aminobenzoate LDH.
Characterization of Mg/Al-aminobenzoate LDH

The following instrumental measurements were carried out at the Central Analytical Laboratory, Faculty of Science, Cairo University.

The transmission electron micrograph image, TEM, for the particle size was recorded on a H800 transmission electron micrograph (Hitachi, Japan) operating at 200 kV.

FTIR spectrum was measured using the disc technique. In this concern, every sample was thoroughly mixed with KBr as a matrix, the mixture was ground and then pressed with a special press to give a disc of standard diameter. The spectra were recorded on BOMEM FTIR, MB-Series.

Shimadzu DTA–TGA system of type DTA-TGA-50, Japan was used for the measurements of the phase changes and weight losses of the sample, respectively, at a heating rate of 10 °C/min in presence of nitrogen gas to avoid thermal oxidation of the powder sample.

Sorption experiments

Batch experiments were performed under kinetic and equilibrium conditions. To determine the pH range at which the maximum uptake of cobalt ions would take place on Mg/Al-aminobenzoate, a series of 50 ml bottles each containing 0.05 g of Mg/Al-aminobenzoate LDH was filled with 10 ml of $10^{-3}$ mol/l metal ion solution. The initial pH was adjusted to values ranging from 3.0 to 8.0 using hydrochloric acid or sodium hydroxide. The pH of the solution was measured using a digital pH meter model HI2211, Hanna, Italy. The bottles were shacked at room temperature overnight to be sure that the equilibrium was attained. The suspension obtained was centrifuged, 6000 rpm, to separate the solid from the liquid phase. The concentrations of cobalt ions in the clear liquid phases obtained were determined using Atomic Absorption Spectrophotometer (Buck scientific model VGP 210). The percent uptake was determined using the following equation:

\[ \% \text{uptake} = \frac{C_0 - C_e}{C_0} \times 100 \]

(1)

Where $C_0$ and $C_e$ are the initial and equilibrium concentrations, mol/l, of metal ion in solution.

Kinetic experiments

Each experiment was carried out in triplicate and the average results are presented in this work. Kinetic studies were investigated at different temperatures (298-328 °K) by taking a series of 50 ml bottles each containing 0.05 g of Mg/Al-aminobenzoate LDH and 10 ml of $10^{-3}$ mol/l metal ion solution. The pH of aqueous solution was adjusted at 6. The bottles were shaken by using shaker water bath at the desired temperature for time range 1–180 minutes. After centrifugation, the clear solution was analyzed for the determination of the amount of not sorbet metal ion present in solution.

Sorption equilibrium experiments

Batch sorption experiments were conducted by introducing 10 ml with known initial concentration of metal ion into glass bottles containing accurately weighed amounts, 0.05g, of the sorbent. The concentration of the metal ions in solution is ranged $10^{-4}$–$10^{-2}$ mol/l. The glass bottles were shaken by using shaker water bath at constant temperature and pH until sorption equilibrium was established. The pH of the mixtures was maintained with 0.1M NaOH and/or 0.1M HNO$_3$ solution. All of the experiments were performed at four different temperatures, 298, 308, 318 and 328 °K. After equilibrium, the sorbent was then removed from liquid phase by centrifugation. The equilibrium concentration of cobalt ions was determined. All the experiments were carried out in duplicate and only mean values are presented. The amount of cobalt sorbet, $q_e$, was determined by the following equation:
\[ q_e = (C_o - C_e) \frac{V}{m} \]  

(2)

Where \( V \) is the volume of metal ion solution, in liter, and \( m \) is the weight, g, of the adsorbent.

**Stripping Investigation**

The stripping investigations were carried out to choose appropriate stripping solutions which can successfully strip cobalt ion. In this concern, 0.1 g of Mg/Al-aminobenzoate nanocomposite loaded by known concentration of Co\(^{2+}\) ion was shaken with 10 ml stripping solutions, HNO\(_3\) and/or NaOH, for 30 min. Different concentrations of the stripping solutions, 0.1M, 0.5M 1M, 2M 3M and 4M were used. The concentration of cobalt ion was determined in the solution after separation in each case.

**RESULTS AND DISCUSSION**

**Characterization of Mg/Al-aminobenzoate LDH**

TEM, TGA-DTA techniques and FT-IR spectroscopy were applied to characterize the synthesized nanocomposite and confirm that aminobenzoate is intercalated into the layers of mg/Al layered double hydroxide. TEM observation reveals that the shape of Mg/Al-Aminobenzoate LDH is nano-sphere with particle size of 10-20 nm, as shown in Fig. 1.

![TEM image of the prepared Mg/Al- Aminobenzoate LDH sorbent](image)

**Fig. (1):** TEM image of the prepared Mg/Al- Aminobenzoate LDH sorbent

Fig. 2 shows the FTIR spectra of Mg/Al-aminobenzoate LDH. A strong absorption band is observed at 1400 cm\(^{-1}\) that is characteristic of carboxylic group, –COO\(^-\) \(^{(12)}\). While the region at 1500–1700 cm\(^{-1}\) is characteristic of C=O vibrations of carboxylic groups \(^{(13)}\). The weak absorption peak of amine N-H stretch is observed at 2900 cm\(^{-1}\) \(^{(11)}\). The characteristic band of aromatic C=C stretching is observed at 1594 cm\(^{-1}\). A broad absorption band between 3700 and 3000 cm\(^{-1}\) is assigned to O–H group stretches of both the hydroxide groups of LDHs and the interlayer water. These peaks demonstrate that amino benzoate was intercalated into the LDHs \(^{(12)}\). In the low frequency region, the absorption peaks of the spectra that correspond to the lattice vibration modes are attributed to M-O at 840 and 650 cm\(^{-1}\) and O-M-O at 430 cm\(^{-1}\) vibration.
As can be seen in Fig. 3, TGA line has two distinct stages of weight losses, the first stage below 350 °C, can be attributed to water release. The second stage exhibited the major weight loss at 500 °C, corresponding to 45 wt% may be due to dehydroxylation of LDHs material, or collapse of the layered structure. DTA pattern of Mg/Al-aminobenzoate LDH presents two endothermic peaks. The intensive one at 398.60 °C, and the other peak at 53.81 °C related to desorption of physisorbed and structural water.

Effect of pH on cobalt sorption

Generally, the sorption of cations on LDHs tends to increase with increasing pH, but in some cases the sorption amounts have no obvious changes due to the pH buffering effect of LDHs (14). In this work, the increase of Co²⁺ ion sorption percent on Mg/Al-aminobenzoate LDH with increasing pH values may be attributed to the surface charge, Fig 4. At low pH values, 3-5, the surface of Mg/Al-aminobenzoate LDH contains a large number of binding sites and may become positively charged due to the protonation reaction on the surfaces. The cations would be repelled by the LDH surface. The electrostatic repulsion occurred between metal ions and the edge groups with positive charge on Mg/Al-aminobenzoate LDH surface results in the low sorption efficiency of Co²⁺. While at high pH values, 6-8, the surface of Mg/Al-aminobenzoate LDH becomes negatively charged due to the deprotonating process and the electrostatic repulsion decreases with raising pH because of the reduction of positive charge density on the sorption edges, which enhances the sorption of the positively charged Co³⁺ ions through electrostatic attraction. The sorption process was not carried out at very low pH values, pH < 3; since the stability of the LDH structures is impaired. Also, it was not processed at high pH values, pH >
8.0; to avoid precipitation of cobalt and it will be difficult to distinguish between cobalt sorption and precipitation. Therefore the optimum pH value for Co sorption is 6.0.

**Speciation modeling**

Prediction of the speciation of cobalt in the aqueous systems as a function of salt concentration and solution pH was performed using the Visual MINTEQ (version 3.0) program. Visual MINTEQ is a chemical equilibrium program that has an extensive thermodynamic database for the calculation of metal speciation, solubility equilibria and sorption \(^\text{[15,16]}\). The speciation was carried out at 10\(^{-3}\) M initial metal ion concentration, ionic strength of 0.01; room temperature and pH range 2-10. From the speciation diagram, Fig. 5, cobalt is present mainly as Co\(^{2+}\) cation within broad pH range from 2.0 to 7.5. The concentration of Co\(^{2+}\) starts to decrease at pH 7.5. Significant amount of other ionic forms (Co\((OH)_{3}^{+}\), Co\((OH)_{3}^{-}\), Co\((OH)^{+}\)) are present in solution between pH 6.5 and 10.0. The precipitation of cobalt started at pH 7.8. It is reasonable to suppose that the dependence of cobalt uptake on pH is closely related to both the surface functional groups on the LDH and the metal speciation in solution.
Mechanism of Sorption Process

Adsorption can be defined as the accumulation of a substance or a material at an interface between the solid surface and the bathing solution. Adsorption can include the removal of solute molecules from the solution and of solvent (continuous phase of a solution, in which the solute is dissolved) from the solid surface, and the attachment of the solute molecule to the surface. Generally, the metal ions may be removed by LDHs via (1) precipitation of metal hydroxides onto the surface of LDHs, (2) adsorption through the bonding with surface hydroxyl groups of LDHs, (3) isomorphic substitution and (4) chelating with the functional ligand in the interlayers. The schematic representation of the sorption mechanisms is shown in Fig. 1. Adsorption, surface precipitation, and polymerization are all examples of sorption\(^{(17)}\).

\[
\text{Capacity} = \frac{\sum \% \text{Uptake}}{100} \times C_o \times \frac{V}{m}
\]  

(3)

Capacity of Mg/Al-aminobenzoate LDH

Loading capacity of Mg/Al-aminobenzoate LDH for Co\(^{2+}\) ion was studied by repeating the sorption steps at room temperature. In this concern, 0.1 g Mg/Al-aminobenzoate with 10 ml volume of the solution containing \(10^{-3}\) mol/l Co\(^{2+}\) was shaken overnight to be sure that the equilibrium was attained. The two phases were separated, Co\(^{2+}\) ion concentration was determined and the same sorbent was used again with fresh Co\(^{2+}\) ion solution. The procedure was repeated several times until the sorbent was saturated with the metal ion, the concentration of the metal ion was determined in each time. The loading capacity of Mg/Al-aminobenzoate was determined, equation (3)\(^{(18)}\), and found to be 5.2 meq/g.

Time-dependent sorption

The time dependence graph of Co\(^{2+}\) ion uptake at different temperatures of 298, 308 and 318\(^{\circ}\)K on Mg/Al-aminobenzoate composite at pH 6.0 is shown in Fig. 6. The quantity of Co\(^{2+}\) ions adsorbed increased with time attaining a maximum value at about 90 min, and thereafter it remained constant. The time required for reaching equilibrium remained practically unaffected by temperature. The values of maximum % uptake are 96.1%, 98.47% and 99.66% at 298, 308 and 318\(^{\circ}\)K, respectively. Therefore the sorption process has endothermic nature, since the quantity adsorbed increase by increasing temperature. The sorption rate initially was fast up to 15–20 min, and then gradually decreased with increase in contact time due to the decrease of active sites of sorbent. The results obtained from the experiments were used to study the rate-limiting step in the sorption process. Moreover, information on the kinetics of metal uptake is required for selecting optimum operational conditions for full-scale metal removal processes. Determination of the kinetic parameters and explanation of the mechanism is often a
complex procedure, as surface effects can be superimposed on chemical effects. Five kinetic models; pseudo-first order, pseudo-second order, intra-particle diffusion, Helfferich, and Elovich equations were used to test experimental data to examine the adsorption kinetics.

Lagerngen suggested a first order equation for the sorption of liquid/solid system based on solid capacity. The Lagerngen rate equation is the most widely used adsorption rate equation for the adsorption from aqueous solution. Lagerngen equation is represented as the following (19):

\[
\log\left(q_e - q_t\right) = \log q_e - \left(\frac{k_1}{2.303}\right) t
\]

(4)

Plot of \(\log (q_e - q_t)\) versus t at different temperatures exhibits straight lines with high correlation coefficients, \(R^2\), and confirms the pseudo-first order rate kinetics for the ongoing adsorption process, Fig. 7. The values of rate constant, \(k_1\), evaluated from Lagerngen plots are found to be 0.0339, 0.0450 and 0.0781 min\(^{-1}\) at 298, 308 and 318 °K, respectively, Table 1. Comparing the values of calculated quantity adsorbed (\(q_{e \text{ Calc}}\), mg/g) and the experimental quantity adsorbed (\(q_{e \text{ Exp}}\), mg/g) is presented in Table 1. It is required that theoretically calculated quantity adsorbed should be in accordance with the experimental quantity adsorbed values. As can be seen from Table 1, although the linear correlation coefficients of the plots are so good, the \(q_{e \text{ Calc}}\) values are not in agreement with \(q_{e \text{ Exp}}\) for all studied sorption processes. Therefore, it could suggest that the sorption of cobalt ion onto Mg/Al-aminobenzoate composite is not a first-order reaction.
Table (1): Parameters of Pseudo-first order and Pseudo-second order models for sorption of Co\(^{2+}\) ion onto Mg/Al-aminobenzoate LDH

<table>
<thead>
<tr>
<th>Temp., °K</th>
<th>(q_{e \text{ Exp}}, \text{ mg/g})</th>
<th>(q_{e \text{ Calc}}, \text{ mg/g})</th>
<th>(K_1, \text{ min}^{-1})</th>
<th>(R^2)</th>
<th>(q_{e \text{ Calc}}, \text{ mg/g})</th>
<th>(K_2, \text{ g/mg})</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>11.34</td>
<td>8.33</td>
<td>0.0339</td>
<td>0.97</td>
<td>11.23</td>
<td>0.0114</td>
<td>0.993</td>
</tr>
<tr>
<td>308</td>
<td>11.62</td>
<td>7.972</td>
<td>0.0450</td>
<td>0.96</td>
<td>12.03</td>
<td>0.0134</td>
<td>0.997</td>
</tr>
<tr>
<td>318</td>
<td>11.76</td>
<td>8.353</td>
<td>0.0781</td>
<td>0.99</td>
<td>12.51</td>
<td>0.0179</td>
<td>0.998</td>
</tr>
</tbody>
</table>

Pseudo-second order model

Pseudo second-order rate model is expressed as \(^{(20)}\):

\[
\frac{t}{q_t} = \frac{1}{K_2q_e^2} + \frac{1}{q_e} t
\]  

Fig. 8 shows a plot of \(t/q_t\) against \(t\) at different temperatures and gives straight lines, from the slope and the intercept one can determine the calculated quantity adsorbed of Co\(^{2+}\), \(q_{e \text{ Calc.}}\), and pseudo-second order rate constant, \(k_2\), respectively. The values of \(q_{e \text{ Calc.}}\) are more close to the experimental value, \(q_{e \text{ Exp.}}\), and high correlation coefficient was obtained \((R^2>0.99)\), as illustrated in Table 1, therefore, the pseudo-second order mechanism is predominant for the sorption process and that the overall rate constant appears to be controlled by the chemisorption process \([19]\).
Intra-particle diffusion

Model of Intra-particle diffusion is of great concern because it plays a significant role in the rate determining step in the adsorption process. It assumes that intra-particle diffusion is the rate-controlling step, which is generally the case for well mixed solutions \((21)\). To reveal the relative contribution of surface and intra-particle diffusion to the entire kinetic sorption process, the experimental data were further fitted with the Morris and Weber model. Film diffusion, pore diffusion and intra-particle transport are the three different steps which have been carried out for the adsorption process. First step, in film diffusion (boundary layer) the adsorbate ion travels towards the external surface of the adsorbent. Second step, in pore diffusion the adsorbate ion travels within the pores of the adsorbent excluding a small amount of adsorption that occurs on the exterior surface. Third step is adsorption of adsorbate ions on the interior surface of the adsorbent. Generally, pore diffusion and intra-particle diffusion were considered to be the rate limiting step for the batch reactor and film diffusion for continuous flow system \((22)\). Morris and Weber model represents the graphical relationship between the amount of metal ion adsorbed, \(q_t\), and \(t^{1/2}\) as illustrated by the following equation \((23, 24)\):

\[
q_t = k_{id} t^{1/2} + C
\]

Where \(k_{id}\) is the intra-particle diffusion rate constant, mg/g.min\(^{1/2}\), and C is the intercept of the plot reflects the boundary layer effect. The larger the intercept the greater is the contribution of the surface sorption in the rate controlling step (the greater the boundary layer effect). As given in Fig. 9, the plot is multi-linear, it is common to segment it into three straight lines and to assume that different adsorption mechanisms control the step represented by each straight line. Slowest of the three steps controls the overall rate during the process. Subsequently, three successive sorption mechanisms are postulated to fit a linear model. The first, steep sloped portion is the external surface adsorption or instantaneous adsorption stage. The second portion is the steady adsorption stage, where intra-particle diffusion is rate-controlled. The third portion is the final equilibrium stage where intra-particle diffusion starts to slowdown due to extremely low adsorbate concentrations in the solution. The high correlation coefficients, \(R^2>0.98\), in the first and the second regions prove that the sorption process is controlled by intra-particle diffusion mechanism and affected by boundary layer. The values of Care 1.65, 2.51 and 4.05 at 298, 308 and 318 °K, respectively. The values of \(k_{id}\) are 1.3, 1.38 and 1.48 mg/g.min\(^{1/2}\) at 298, 308 and 318 °K respectively, this indicated that the rate of diffusion increase by increasing the temperature.
Determination of diffusivity

In order to investigate the contribution of film resistance to the kinetics of cobalt adsorption onto Mg/Al-aminobenzoate LDH, the adsorption kinetic data was further analyzed by Boyd’s film-diffusion model \(^{(25)}\). This model assumes that the bound layer surrounding the adsorbent particle is the main resistance to diffusion. In order to identify the step governing the overall removal rate of the sorption process, the model given by Boyd et al. was applied.

\[
F = 1 - \left( \frac{6}{\pi^2} \right) \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left( -n^2Bt \right)
\]

Where \(F\) is the fraction of solute adsorbed at different times \(t\), \(F = q_t/q_e\), \(n\) is an integer number, 1, 2, 3, . . . , and \(B\) is a mathematical function of \(F\). Reichenberg \(^{(26)}\) evaluated the approximations given below, by applying Fourier transform and then integrated the equation (7).

\[
Bt = - 0.4977 - \ln \left( 1 - F \right)
\]

The linearity test of \(Bt\) versus time plots is employed to distinguish the film and particle diffusion-controlled rates of sorption process. If the plot is a straight line passing through the origin, then the sorption rate is governed by particle diffusion mechanism otherwise it is governed by film diffusion \(^{(27)}\). Fig. 10 illustrates that the plot is linear passing through the origin indicating that the particle diffusion is the controlled rate of sorption process at all studied temperatures. From the slope of the straight line the value of \(B\) can be determined. The effective diffusion coefficient, \(D_{i}\), of the metal ion at different temperatures can be determined using the values of \(B\) as the following equation \(^{(28)}\):

\[
B = \pi^2 \frac{D_{i}}{r^2}
\]

Where \(r^2\) is the radius of the solid particle, \((0.5 \times 15)^2\), assuming the particles are spheres. The calculated values of \(D_{i}\) were found to be \(1.9 \times 10^{-17}\), \(2.4 \times 10^{-17}\) and \(4.3 \times 10^{-17}\) m\(^2\)/s at 298, 308 and 318 °K,
respectively. The magnitude of the diffusion coefficient is dependent upon the nature of the sorption process. For physical adsorption, the value of the effective diffusion coefficient ranges from $10^{-6}$ to $10^{-9}$ m$^2$/s, while for chemisorption, the value ranges from $10^{-9}$ to $10^{-17}$ m$^2$/s \cite{27}. The difference in the values is due to the fact that in physical adsorption the molecules are weakly bound and therefore there is ease of migration, whereas for chemisorption the molecules are strongly bound and mostly localized. Therefore, from this research, the most likely nature of sorption is chemisorptions since the values of $D_i$ were in the order $10^{-17}$ m$^2$/s. According to Arrhenius equation, equation (9), can be validated by plotting of $\ln D_i$ versus $1/T$ which gave a straight line (figure was omitted).

$$\ln D_i = \ln D_0 - \frac{E_a}{RT} \quad (10)$$

Where $D_0$ is a pre-exponential constant analogous to Arrhenius frequency factor. The energy of activation, $E_a$, was calculated from the slope of the straight lines to be 35.6 kJ/mol and the value of $D_0$ was found to be $2.7x10^{-13}$. Values of $E_a$ less than 42 kJ/mol generally indicate diffusion-control processes and higher values represent chemical reaction processes \cite{29}. The relatively small activation energy value suggests that the process has a diffusion control mechanism.

![Bt plot for sorption of Co$^{2+}$ onto nanocomposite Mg/Al-aminobenzoate at different temperatures.](image)

**Fig. (10):** Bt plot for sorption of Co$^{2+}$ onto nanocomposite Mg/Al-aminobenzoate at different temperatures.

**Elovich equation**

In reactions involving chemisorption of adsorbate on a solid surface without desorption of products, adsorption rate decreases with time due to an increased surface coverage. One of the most useful models for describing such activated chemisorption is Elovich equation \cite{30}. It is based on kinetic principle assuming that the adsorption sites increase exponentially with adsorption, which implies a multilayer adsorption. Elovich equation has been applied satisfactorily to systems in which the adsorbing surface is heterogeneous \cite{31}. The Elovich equation can be written as the following \cite{32}:

$$q_t = \frac{1}{\beta} \ln (\alpha \beta) + \frac{1}{\beta} \ln t \quad (11)$$
Where $\alpha$ and $\beta$ are Elovich constants, $\alpha$ is the initial adsorption rate constants (mg/g min) and $\beta$ is constant related to the extent of surface coverage and activation energy for chemisorption (g/mg). A plot of $q_t$ versus $\ln t$ should yield a straight line with a slope of $1/\beta$ and intercept $1/ \beta \ln (\alpha \beta)$ if the kinetic data for the adsorption of cobalt onto Mg/Al-aminobenzoate LDH fits well in the Elovich model. From Fig. 11, it can be seen that the correlation coefficient for the linear plots was higher than 0.98. The values of $\beta$ and $\alpha$ are $0.45$ g/mg and $3.70$ mg/g min, respectively. The good fitment of the Elovich model ensures better chemisorption during the adsorption process.

Sorption isotherm

Sorption isotherm describes the relationship between the amount of adsorbate adsorbed on the adsorbent and the concentration of dissolved adsorbate in the liquid at equilibrium. The effect of the initial cobalt concentration in the aqueous phase on the amount of cobalt adsorbed by Mg/Al-aminobenzoate composite at different temperatures was studied. The quantity adsorbed of Co$^{2+}$ ion at equilibrium, $q_e$, increased with the increase of the equilibrium concentration of the metal ion, $C_e$, which increased by increasing the initial cobalt concentration in the aqueous phase (figure omitted). The possible reason may be that the increase of metal ion concentration leads to increase of number of Co$^{2+}$ ions in solution; therefore the amount of cobalt adsorbed increases. Various theoretical models could be applied to experimental data in order to find a model which adequately describes equilibrium data, such as Langmuir and Freundlich models.

Langmuir isotherm

Langmuir model is probably the best known and most widely applied sorption isotherm. It assumes that the sorption occurs on a structurally homogeneous adsorbent, all the sorption sites are energetically identical and monolayer coverage of the sorption surfaces. Langmuir sorption isotherm is represented as follows \(^{(33, 34)}\):

\[
\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{bQ} \left( \frac{1}{C_e} \right)
\]  

(12)

Fig. (11): Plot of Elovich equation for sorption of Co$^{2+}$ onto nanocomposite Mg/Al-aminobenzoate.
Langmuir constants $Q$ and $b$ are related to the sorption capacity and the energy of sorption, respectively. The linear plot of $1/q_e$ versus $1/C_e$ with high correlation coefficient, $R^2>0.99$, indicates that the sorption obeys to Langmuir model (Fig. 10). The values of $Q$ at different temperatures were determined from the intercept, as can be seen in Table 2, the sorption capacity of Co$^{2+}$ onto Mg/Al-aminobenzoate composite and the energy of sorption increased with temperature showing that the sorption capacity and energy of sorption are enhanced at higher temperatures. This increase in sorption capacity with temperature suggested that the active surfaces available for sorption have increased with temperature. Another reason may be due to the change in pore size and enhanced rate of intra-particle diffusion of solute, as diffusion is an endothermic process $^{(19)}$.

Table (2): Langmuir and Freundlich isotherm parameters for sorption of Co$^{2+}$ ion onto Mg/Al-aminobenzoate nanocomposite

<table>
<thead>
<tr>
<th>Temp., °K</th>
<th>Q, mmol/g</th>
<th>b, L/mol</th>
<th>$R^2$</th>
<th>k, mol/g</th>
<th>$1/n$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>1.12</td>
<td>10.43</td>
<td>0.995</td>
<td>0.14</td>
<td>0.89</td>
<td>0.974</td>
</tr>
<tr>
<td>308</td>
<td>1.28</td>
<td>13.19</td>
<td>0.998</td>
<td>0.23</td>
<td>0.93</td>
<td>0.999</td>
</tr>
<tr>
<td>318</td>
<td>1.87</td>
<td>25.21</td>
<td>0.994</td>
<td>0.47</td>
<td>0.81</td>
<td>0.976</td>
</tr>
<tr>
<td>328</td>
<td>3.32</td>
<td>29.69</td>
<td>0.991</td>
<td>1.22</td>
<td>0.91</td>
<td>0.986</td>
</tr>
</tbody>
</table>

Freundlich isotherm

The empirical model can be applied to non-ideal sorption on heterogeneous surfaces as well as multilayer sorption and is expresses by the following equation $^{(35)}$:

$$\log q_e = \frac{1}{n} \log C_e + \log k \quad (13)$$
n and k are the Freundlich constants. The magnitude of 1/n gives an indication of the adequacy and intensity of the adsorbent/adsorbate system and k is a constant indicative of the relative adsorption capacity of the adsorbent. The linear plot of log q_e versus log C_e as illustrated in Fig. 13 shows that the adsorption obeys to the Freundlich model. The values of 1/n and k are presented in Table 3. The slope of the Freundlich isotherm for all temperatures is less than one, indicating a concentration-dependent sorption for cobalt ion onto Mg/Al-aminobenzoate nanocomposite and favorable adsorption.

Although Freundlich and Langmuir constants, k and Q, have different meanings, they led to the same conclusion about the correlation of the experimental data with the sorption model. The basic difference between k and Q is that Langmuir isotherm assumes sorption free energy independent of both the surface coverage and the formation of monolayer, whereas the solid surface reaches saturation while the Freundlich isotherm does not predict saturation of the solid surface by the sorbate, and therefore, the surface coverage being mathematically unlimited. In conclusion, Q is the monolayer sorption capacity while k is the relative sorption capacity or sorption power \(^{(19)}\). The results show that Mg/Al-aminobenzoate can be fruitfully employed for the removal of Co\(^{2+}\) ion in a wide range of concentrations.

**Determination of thermodynamic parameters**

The dependence of sorption of cobalt ion by Mg/Al-aminobenzoate composite on temperature has been evaluated using Vant Hoff equation as follows:

\[
\Delta G = -RT \ln K_c
\]  
\[
\log K_c = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT}
\]

\(\Delta G\) is the free energy change, kJ/mol, R is the general gas constant (R=8.314 J/mol.K), T is the absolute temperature in Kelvin, and \(K_c\) is the sorption equilibrium constant. \(\Delta H\) is the enthalpy change, kJ/mol, and \(\Delta S\) is entropy change, J/mol.K. The values of \(K_c\) at different studied temperatures were determined from the product of Langmuir equation parameters, Q and b \(^{(18, 20)}\). Plot of log \(K_c\) vs. 1/T for the sorption
of cobalt ion is shown in Fig. 12. The values of ΔH and ΔS were calculated on the basis of the slope and intercept of the plot shown in this figure. The magnitude and sign of the enthalpy change, ΔH, associated with the sorption process will consist of (1) enthalpy change for dehydration, ΔH_d, which can be expected to be positive since energy is required to break the ion–water and water–water bonding of the hydrated metal ion, and (2) enthalpy change for complexing, ΔH_c, which makes ΔH more negative due to the formation of metal complex. The positive ΔH value obtained for the sorption of cobalt ion onto the nanocomposite material indicates that it is endothermic process and the complexation seems to be more significant than dehydration in the sorption system. The values of ΔG, ΔS and ΔH were found to be -5.7 kJ/mol, 220.8 J/mol.K and 60.1 kJ/mol, respectively. The negative value of ΔG indicates that the sorption process is spontaneous; the sorption entropy ΔS is greater than zero, displaying the chelating sorption is a process of entropy increase.

\[
\text{log } K_c = a - b/T
\]

**Fig. (14):** Plot of log K_c vs 1/T for sorption of Co^{2+} ion onto Mg/Al-aminobenzoate.

**Stripping investigation**

In the stripping process, different molarities of HNO_3 and NaOH were used, the results illustrated that, cobalt ion can be stripped from the nanocomposite LDH to be about 100% with 3M HNO_3. HNO_3 is better stripper for cobalt than NaOH (figure omitted). Thus, Mg/Al-aminobenzoate LDH can be regenerated and used for further removal after drying.

**Comparison of sorption capacity of Co^{2+} onto Mg/Al-aminobenzoate LDH with various sorbents**

For comparison, the monolayer maximum capacity values of Co^{2+} ions on the nanocomposite of Mg/Al-aminobenzoate LDH with other adsorbents obtained in the literature are listed in Table 3. It can be seen that the prepared nanocomposite has much higher sorption capacity than many other sorbents. It shows that Mg/Al-aminobenzoate nanocomposite can be considered as a promising material for removal of cobalt ion from aqueous solution.
Table (3): Comparison of sorption capacities of Co²⁺ ion on natural and synthetic sorbents

<table>
<thead>
<tr>
<th>Sorbents</th>
<th>Experimental conditions</th>
<th>Maximum Capacity, mg/g</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene oxide nanosheets</td>
<td>pH=6 and 303 °K</td>
<td>68.2</td>
<td>(36)</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>pH=6 and 303 °K</td>
<td>13.88</td>
<td>(37)</td>
</tr>
<tr>
<td>Natural zeolites</td>
<td>pH=6 and 298 °K</td>
<td>14.38</td>
<td>(38)</td>
</tr>
<tr>
<td>Lemon peel</td>
<td>pH= 6 and 298 °K</td>
<td>25.6</td>
<td>(39)</td>
</tr>
<tr>
<td>Amination graphene oxide</td>
<td>pH=6 and 298 °K</td>
<td>116.35</td>
<td>(40)</td>
</tr>
<tr>
<td>Cation exchange resins IRN77</td>
<td>pH= 5.3 and 298 °K</td>
<td>86.17</td>
<td>(41)</td>
</tr>
<tr>
<td>TSTC[4]AS-s-SA⁺</td>
<td>pH=7 and 298 °K</td>
<td>12.9</td>
<td>(42)</td>
</tr>
<tr>
<td>Fe₃O₄@TSTC[4]AS-s-SA</td>
<td>pH=7 and 298 °K</td>
<td>14.98</td>
<td>(42)</td>
</tr>
<tr>
<td>Hydroxyapatite/chitosan composite</td>
<td>pH=6 and 303 °K</td>
<td>10.63</td>
<td>(43)</td>
</tr>
<tr>
<td>Crab shell</td>
<td>pH=4 and 298 °K</td>
<td>20.47</td>
<td>(44)</td>
</tr>
<tr>
<td>Zn-Al-EDTA LDH</td>
<td>pH=6 and 298 °K</td>
<td>5.3</td>
<td>(45)</td>
</tr>
<tr>
<td>Mg-Al-CO₃LDH</td>
<td>pH=5 and 298 °K</td>
<td>30.6</td>
<td>(46)</td>
</tr>
<tr>
<td>Mg/Al-aminobenzoate LDH</td>
<td>pH=6 and 298 °K</td>
<td>65.9</td>
<td>Present work</td>
</tr>
</tbody>
</table>


CONCLUSION

Nanostructured composite of Mg/Al-aminobenzoate layered double hydroxide was successfully prepared by coprecipitation method. The whole results indicated that Mg/Al-aminobenzoate nanocomposite is an efficient sorbent media and recommended for removal of Co²⁺ ions from aqueous solutions and wastewater. The sorption process obeys Pseudo-second order kinetic model. The sorption process is chemisorptions since the value of diffusion coefficient is in the order 10⁻¹⁷ m²/s, as well as the good fitment of Elovich model. Langmuir isotherm model fitted the results better than Freundlich model. Mg/Al-aminobenzoate nanocomposite can be fruitfully employed for the removal of Co²⁺ ion in a wide range of concentrations.

REFERENCES

(2) A.I. Khan, D. O’Hare, J. Mater. Chem. 12, 3191 (2002).

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