Removal of Nickel and Cadmium from Aqueous Solution using Carbonaceous Magnesium Oxide: Thermodynamic and Kinetic study

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Abstract

Generation and entrance of toxic materials to aqueous environment causes many problems to human health. In the current study, the removal efficiency of Cd (II) and Ni(II) from aqueous solution was investigated by carbonaceous magnesium oxide. Three types of C-MgO adsorbents were synthesized via pyrolysis of prepared magnesium complex Mg(acac)₂ at three temperatures. Fabricated C-MgO adsorbents were characterized by XRD, SEM, and BET. XRD results revealed that the synthesized adsorbents consist of only magnesium oxide and carbon phase without any impurities. SEM technique used to characterizes the surface morphology of C-MgO samples. N₂ adsorption-desorption isotherm used to calculate the BET surface area of prepared samples. The SEM results had a good agreement with BET measurement which improved that the high temperature increase the particles size and reduce the surface area. The adsorption studies showed that the carbonaceous magnesium oxides have good removal efficiency for Cd (II) and Ni(II) removal from aqueous solution and kinetically follow the pseudo-second order model.

Key words: Adsorption, Nanoparticles, Isotherm, Efficiency, Langmuir

1. Introduction

Metal ions removal, such as Cd, Pb, Ni, Hg, Cu, Co, Zn and Fe represent one of the important fields for environmental researchers [1-5]. Nickel (Ni) is an example of these heavy metal ions. Many industrial applications resources introduce it in the environment such as production of batteries and paints, mineral processing, manufacturing of sulfate, porcelain enameling and electroplating[6]. Hazardous of Nickel element is well known, it can cause gastrointestinal distress, lungs disorder severely and kidney damage [7]. Similarly, cadmium (Cd) is other example heavy metals, it can be introduce the environment via series of activities, such as metal plating, discharges from mining, plastic batteries, and paper industries [8].

Until now, different methods have been used to reduce water content from the heavy metals, such as membrane filtration, chemical precipitation, ion exchange, evaporation, ion exchange, reverse osmosis and electrodialysis [9–12]. However, among the various available efforts for removing of heavy metal from the aquatic environment is the adsorptive removal. Adsorption represents one of the referred and suitable methods due to its simplicity, a lower energy requirement, and absence the secondary waste products [13-14]. The efficiency of any adsorption process mainly depends on the adsorbents capacity for adsorption. Materials with a large pore volume and high specific surface area are categorized as efficient adsorbents. The adsorbent large pore volume and high surface area facilitate the diffusion of mass and transport metal ions onto the adsorbent, thus enhancing the metal ion removal performance from the wastewater [15-16]. Metal oxides-carbon materials offer an important route for synthesizing new and improved functionalized materials with unique aspects of their components. Such materials have promising applications in catalysis, energy storage (super capacitors and batteries) and as adsorbents.

The inherent electronic conductivity and specific surface area of the most metal oxides will enhanced...
by the addition of carbon to these material.[17–26]. Different carbon forms, such as carbon spheres, activated carbon, carbon nanotubes, carbon fiber and graphene have been utilized to synthesize metal oxide-carbon materials[27–34].

2. Experimental

2.1 materials
Acetylacetone, magnesium powder and toluene were purchased from Sigma Aldrich and used without further purification.

2.2 Synthesis of carbonaceous magnesium oxide
Magnesium acetylacetonate Mg (acac)_2 was prepared via refluxing acetylacetone with magnesium metal. Then, the solvent and slurry were transferred to another flask to remove the solvent by decantation. The resulted complex washed with boiled toluene and evaporated until dryness. To prepare carbonaceous magnesium oxide, about 1 g of as-prepared magnesium complex subjected to pyrolysis at three different temperatures at 500, 600 and 700 °C in quartz tube. The tube firstly evacuated and then filled with nitrogen gas to desired temperature and allowed to cool to room temperature naturally. Finally, the produced composite collected and washed with ethanol several times. The product labeled as C-MgO-500, C-MgO-600 and C-MgO-700 where C refer to Carbonaceous and 500, 600 and 700 represent the pyrolysis temperatures.

2.3 Preparation of Ni^{2+} and Cd^{2+} Stock Solutions
Stock solution (1000 ppm) for Cd^{2+} and Ni^{2+} were prepared by dissolving the cadmium chloride (NiCl_2) and nickel chloride (CdCl_2) in deionized water, respectively.

2.4 Removal experiments
To measure the removal efficiencies, 0.5 g of MgO-500 adsorbent added to Cd^{2+} and Ni^{2+} solutions (150, 250, 350, and 450 ppm) and stirred at 250 rpm for 2 h at 25 K. Then, solutions were filtrated and the concentrations of Cd^{2+} and Ni^{2+} measured by atomic absorption spectrooscope (Varian AA240) to calculated the removal percentages.

2.5 kinetic experiments
Kinetic experiments were performed by adding 0.5 g of MgO-500 adsorbent to Cd^{2+} and Ni^{2+} solutions (25 mL, 150 ppm) and stirred at 250 rpm at 25 K for different time intervals (25, 50, 75, 100, 125, 150, 175, 200 and 225 min). After filtration, the concentration of to Cd^{2+} and Ni^{2+} in solutions were measured by atomic absorption spectrooscope.

2.6 Characterization
The phase and pattern of prepared samples characterized by XRD(X-ray diffractometer, Panalytical, Model MPD) using CuKα radiation. SEM images carried out by (MIRA3, TESCAN-RMRC) (TM - 1000 ,Hitachi tabletop, Japan). The surface area of synthesized samples characterized by Nitrogen gas isotherm (adsorption-desorption) at 77K (Nova 2000, quantachrome, USA).

3. Results and discussion
The obtained XRD patterns of magnesium complex pyrolysis are shown in figure 1. From figure 1, it can be seen that the XRD pattern of all samples display two characteristic peaks at 2theta 25.1 and 44.2 assigned to the carbon (100) and (101) planes respectively [35].

Fig.1 XRD patterns of C-MgO-500, C-MgO-600 and C-MgO-700
Also, the peaks belonged to the crystalline cubic structure of MgO appeared at 2 theta values 36.9, 42.8, 62.2 and 78.4 related to the (111), (200), (220) and (222) MgO planes respectively.
REMOVAL OF NICKEL AND CADMIUM FROM AQUEOUS SOLUTION.....

Fig. 2 SEM images of (A) of C-MgO-500 (B) C-MgO-600 and (C) C-MgO-700

Figure 2(a-c) illustrate the SEM surface morphology micrographs related to the C-MgO composite. It can be seen that the surface of synthesized composites showed a small, ordered and spherical structure for all samples with about (15-25 nm) particle size. Also, there is an increase in the particles size at high pyrolysis temperatures due to gradual growth and aggregation of particles at high temperatures.

Figure 3: N2 adsorption isotherms of C-MgO-500, C-MgO-600 and C-MgO-700

Figures 3 show the N2 adsorption-desorption isotherms of prepared carbonaceous magnesium oxides at 77 K. The isotherms of the composites display typical IV type behavior according to (IUPAC classification) and the lower N2 uptakes recorded at low pressure values.

The BET surface area of prepared samples were (329, 225 and 139 m² g⁻¹) for C-MgO-500, C-MgO-600 and C-MgO-700 respectively. However, it is obvious that rising the pyrolysis temperature significantly reduce the BET surface area in good agreement with SEM results which improved that the high temperature increase the particles size.

4. Adsorption studies
4.1 Batch Experiments

All the adsorption studies of Cd²⁺ and Ni²⁺ ions carried out by (C-MgO-500) which has the larger surface area therefore expected to showing better adsorption behavior. Technique of Batch equilibrium is used to evaluate the adsorption performance of C-MgO-500 adsorption toward Cd²⁺ and Ni²⁺. Also, this method used to determine the effect of all control parameters. The removal efficiency and adsorption capacity were calculated using the following equations:

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

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

Where:
- \( R\% \) is the removal efficiency,
- \( q_e \) is the adsorption capacity (mg/g),
- \( C_0 \) is the initial ions concentration (mg/L),
- \( C_e \) is the equilibrium ions concentrations (mg/L),
- \( V \) is the solution volume (L), and
- \( m \) is the weight of adsorbent (g).

4.2 Adsorption efficiency of Ni²⁺ and Cd²⁺ ions

The calculated removal efficiency of Cd²⁺ and Ni²⁺ ions from aqueous solution by C-MgO-500 are listed in table 1. As can be observed, the highest removal efficiencies recorded were 81.47% and 96.83% at 150 ppm Cd²⁺ and Ni²⁺ initial concentration, respectively. Also, there are gradually decreases in the removal efficiency as the concentration Cd²⁺ and Ni²⁺ increases attributed to the saturation of C-MgO-500 sites by the ions at high concentrations.

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>RE% of Cd²⁺</th>
<th>RE% of Ni²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>96.83</td>
<td>81.47</td>
</tr>
<tr>
<td>250</td>
<td>95.92</td>
<td>80.29</td>
</tr>
<tr>
<td>350</td>
<td>94.33</td>
<td>73.64</td>
</tr>
<tr>
<td>450</td>
<td>92.84</td>
<td>53.45</td>
</tr>
</tbody>
</table>

4.3 Langmuir Adsorption Isotherm

Langmuir monolayer isotherm can be calculated by plotting the calculated equilibrium concentrations
and adsorption capacities according to the following equation:

\[ C_e = \left( \frac{1}{q_m} \right) \ast C_e + \left( \frac{1}{q_m K_L} \right) \]

Where, \( C_e \) (mg L\(^{-1}\)) is the concentration of adsorbate at equilibrium, \( q_e \) (mg g\(^{-1}\)) is the adsorbent adsorption capacity at equilibrium, \( q_m \) (mg g\(^{-1}\)) is the adsorbent highest adsorption capacity and \( K_L \) represent Langmuir constant.

The calculated Langmuir constants and Langmuir isotherms for Cd\(^{2+}\) and Ni\(^{2+}\) ions listed in table 2 and showed in figures (4-5).

Table 2 calculated Langmuir constants

<table>
<thead>
<tr>
<th>ion</th>
<th>( q_m ) (mg/g)</th>
<th>( K_L ) (L/g)</th>
<th>Regression R(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cadmium</td>
<td>147.058</td>
<td>0.00058</td>
<td>0.96</td>
</tr>
<tr>
<td>nickel</td>
<td>64.935</td>
<td>0.00764</td>
<td>0.98</td>
</tr>
</tbody>
</table>

Fig.4 Langmuir isotherm of Nickel ions

Fig.5 Langmuir isotherm of Cadmium ions

According to the results in table 3, the \( R_L \) values lies between 0.919 and 0.225for both ions therapy the adsorption follow monolayer chemisorption.

Table3. Calculated \( R_L \) values for Nickel and Cadmium ions

<table>
<thead>
<tr>
<th>( C_o ) (mg/L)</th>
<th>( R_L ) Ni(^{2+}) (L/mg)</th>
<th>( R_L ) Cd(^{2+}) (L/mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>0.465</td>
<td>0.919</td>
</tr>
<tr>
<td>250</td>
<td>0.343</td>
<td>0.872</td>
</tr>
<tr>
<td>350</td>
<td>0.272</td>
<td>0.830</td>
</tr>
<tr>
<td>450</td>
<td>0.225</td>
<td>0.792</td>
</tr>
</tbody>
</table>

4.4 Freundlich Isotherm

Multi-layer adsorption can be described by Freundlich isotherm and calculated from the following equation:

\[ \ln q_e = \left( \frac{1}{n} \right) \ln C_o + \ln K_F \]

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

As can be observed from R\(^2\) values in table 3and figures (7-8), the adsorption of Cadmium ion by C-MgO-500 in good agreement with Freundlich isotherm compared with Nickel ion.

Also, the Freundlich positive and gradient constants values for both ions refer to multilayer adsorption of Ni and Cd ions onto the C-MgO-500.

According to the results that obtained from the two adsorption models, the Langmuir model is more suitable for adsorption Nickel ions while Freundlich model favorable for adsorption Cadmium ions. The results also reveal that the adsorption of nickel ions by C-MgO-500 is belonged to chemisorption process while the chemisorption and physisorption processes responsible for the adsorption of Cadmium ions.

Table4. Calculated Freundlich constants

<table>
<thead>
<tr>
<th>ion</th>
<th>( 1/n ) (mg/g)</th>
<th>( K_F ) (L/g)</th>
<th>R(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cadmium</td>
<td>14.15</td>
<td>0.00058</td>
<td>0.99</td>
</tr>
<tr>
<td>nickel</td>
<td>13.32</td>
<td>0.00764</td>
<td>0.80</td>
</tr>
</tbody>
</table>

Fig. 7 Freundlich isotherm of Cadmium ions

Another important parameter is the separation factor \( R_L \), which calculated according to the following equation:

\[ R_L = \frac{1}{(1+K_{LCo})} \]

Where, \( C_o \) (mg/L) is the adsorbate initial concentration and \( K_L \) (L/mg) is the Langmuir constant.

\[ \text{Egypt. J. Chem. 64, No. 8 (2021)} \]
5. Kinetics Studies

Adsorption of Cadmium and Nickel ions by C-MgO-500 is monitored by pseudo-second order kinetic model and the results showed in figure 9 and summarized in table 4. Also, the adsorption capacity variation for both ions with time is plotted and showed in figure 8.

Table 4. Pseudo-second order parameters for adsorption Cd and Ni ions

<table>
<thead>
<tr>
<th>ion</th>
<th>$R^2$</th>
<th>$K$ (g mg$^{-1}$-min$^{-1}$)</th>
<th>$Qe$ (mg g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>0.9807</td>
<td>0.03393</td>
<td>0.773395</td>
</tr>
<tr>
<td>Cd</td>
<td>0.9912</td>
<td>0.0335</td>
<td>0.744491</td>
</tr>
</tbody>
</table>

Fig. 8 Adsortion capacity of of Ni and Cd ions by C-MgO-500

Fig. 9 Pseudo-second order model of Ni and Cd ions

As can be noted from figure 9, the values of $R^2$ suggested that the pseudo-second order model is valid to describe the adsorption of Cd and Ni by C-MgO-500 adsorbent. The adsorption process of both ions can be occurred in two steps, the first including transfer of the soluble ions to the surface of C-MgO-500 sorbent, then diffusion of the adsorbed ions in the sorbents interior pores.

6. Conclusions

Carbonaceous magnesium oxide (C-MgO) has been successfully prepared using pyrolysis of Mg(acac)$_2$ complex at different temperatures. The result of SEM technique reveals that the surface morphology of the C-MgO samples were small, ordered and spherical structure with (15-25 nm) particle size. The obtained XRD patterns of magnesium complex pyrolysis display the characteristic peaks of magnesium oxide and carbon. The results of BET showed the BET surface area of prepared samples were (329, 225 and 139 m$^2$. g$^{-1}$) for C-MgO-500, C-MgO-600 and C-MgO-700 respectively. Adsorption experiments results show the maximum removal efficiency of Cadmium ions by C-MgO adsorbent were 96.83% and 81.47% for Cadmium and Nickel ions respectively. Isotherms model results revealed that the Langmuir model is more suitable for adsorption Nickel ions by C-MgO-500 while Freundlich model favorable for adsorption Cadmium ions. The results also show that the adsorption of nickel ions by C-MgO-500 is belonged to chemisorption process while the chemisorption and physisorption processes responsible for the adsorption of Cadmium ions. The kinetic studies suggested that the pseudo-second order model is valid to describe the adsorption of Cadmium and Nickel ions by C-MgO-500 adsorbent.

7. References


Chemistry, 62(Special Issue (Part 1) Innovation in Chemistry), 177-195.


8. Arabic Abstract

تستورد المواد السامة ودخلها إلى البيئة المائية في حدوث العديد من المشاكل الصحية الإنسانية، في الدراسة الحالية، تم اختيار كفاءة أكسيد المغنيسيوم الكربوني لإزالة أيون الكادميوم (II) وأيون النيكل من المحلول المائي. تم تضمين دراسة تحضير ثلاثة أنواع من المادة المازة (أكسيد المغنيسيوم الكربوني) عند درجات حرارة مختلفة بواسطة التحلل الحراري لمعركة (أكسيد المغنيسيوم الكربوني) المتضمنة إثرًا لسوب (أكسيد السبيروكينات) المحضر. تم فحص المواد المحضرة بواسطة طيف حيوي الأشعة السينية، المجهر الإلكتروني الماسح، وفحص السطع السطحية. أظهرت نتائج الدراسة السيئيني أن المواد المحضرة تتكون فقط من أكسيد المغنيسيوم الكربوني بدون أي شوائب أخرى. جودة الحواف مع قياسات المادة المازة السامة المستخدمة تأثير إزالة أيون الكادميوم II والنيكل II من المحلول المائي وحركية الامتزاز تتبع نموذج الرتبة الثانية الكاذبة.