REMOVAL OF Cd(II) FROM WATER BY USING GRAPHENE OXIDE–MnFe₂O₄ MAGNETIC NANOHYBRIDS

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ABSTRACT

In this work, graphene oxide–manganese ferrite (GO–MnFe₂O₄) magnetic nanohybrids were synthesized by co–precipitation technique. The adsorption properties of GO–MnFe₂O₄ for efficient removal of Cd(II) from contaminated water were investigated. The nanohybrids were characterized by using X–ray diffraction, Fourier transform infrared spectroscopy, Brunauer–Emmett–Teller specific surface area (BET), transmission electron microscopy, and vibrating sample magnetometry (VSM). VSM result showed the high saturation magnetization values Mₛ = 27.1 emu/g, the BET specific surface area was 84.236 m²/g. Adsorption experiments were carried out to evaluate the adsorption capacity of the GO–MnFe₂O₄ magnetic nanohybrids and compared with MnFe₂O₄ nanoparticles and GO nanosheets. The equilibrium time for adsorption of Cd(II) onto the nanohybrids was 240 minutes. Experimental adsorption data were well–fitted to the Langmuir isotherm and the pseudo–second–order kinetic equation. The experimental results showed that adsorption of Cd(II) using GO–MnFe₂O₄ magnetic nanohybrids was better than MnFe₂O₄ and GO with a maximum adsorption capacity of 121.951 mg/g at pH 8. Reusability, ease of magnetic separation, high removal capacity, and fast kinetics lead the GO–MnFe₂O₄ nanohybrids to be promising adsorbents for removal heavy metals from contaminated water.

Keywords: cadmium removal, adsorption, magnetic nanohybrids, graphene oxide, manganese ferrite.

1. INTRODUCTION

The strong development of industrialization and urbanization has made emissions into the environment large amounts of heavy metals. Thus, using contaminated water can have serious health effects. Among all heavy metals such as As, Pb, Ni, Cu, Hg, Cd…, cadmium is considered one of the most toxic heavy metal with acceptable levels one–tenth those of most of the other toxic metals [1, 2]. The maximum permissible value for worker according to German law is 15 μg/L. For comparison: Non–smokers show an average cadmium blood concentration of
0.5 μg/L [3]. Severe risks of cadmium on human health such as vomiting, diarrhea, shortness of breath, lung edema, destruction of mucous membranes, kidney damage, “itäi–itäi” disease... [4, 5]. Therefore, it is necessary to remove Cd(II) from contaminated water.

To remove the heavy metals from contaminated water, many studies show that the magnetic nanohybrids of iron oxide–based materials (Fe₃O₄) or ferrite materials (MFe₂O₄, M = Ni, Mn, Zn, Co...) were effective adsorbents [6, 7]. One of them, the manganese ferrite MnFe₂O₄ were used as adsorbent with many advantages such as high magnetic permeability, low magnetic losses, more the active functional groups on the surface [8]. However, magnetic nanohybrids MnFe₂O₄ showed some disadvantages such as instability and agglomeration.

Another adsorbent is graphene oxide (GO) can be used. GO has a large number of oxygenated functionalities and high surface area. Therefore, GO can be a good adsorbent for many ion heavy metals, but after the treatment is still challenging about recovering and agglomeration.

To overcome the disadvantages of both GO and magnetic nanohybrids MnFe₂O₄, GO–MnFe₂O₄ magnetic nanohybrids adsorbent was synthesized and investigated their usage for removal of Cd(II) from contaminated water. GO–MnFe₂O₄ synthesized by co–precipitation technique was characterized using X–ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Brunauer–Emmett–Teller specific surface area (BET), transmission electron microscopy (TEM), and vibrating sample magnetometer (VSM). Adsorption experiments were carried out to evaluate the adsorption capacity of the GO–MnFe₂O₄ magnetic nanohybrids and compared with MnFe₂O₄ nanoparticles and GO nanosheets.

2. MATERIALS AND METHODS

2.1. Materials

Graphite (particle size < 20 μm) was purchased from Sigma Aldrich, Germany. Sulfuric acid (98 wt%), hydrogen peroxide (30 wt%), sodium nitrate (99 wt%), malachite green (99 wt%), potassium iodide (99 wt%), ascorbic acid (99 wt%), PVA (molecular weight 80,000, degree > 98 %), ferric chloride hexahydrate (99 wt%), manganese chloride (99 wt%), sodium hydroxide (99 wt%), and cadmium nitrate (99 wt%) were purchased from Xilong Chemical, China. Ethanol (96 vol%) and potassium permanganate (99 wt%) were purchased from ViNa Chemsol, Vietnam.

2.2. Synthesis of graphene oxide

GO was synthesized by using modified Hummer’s method [9]. In brief, 2.5 g of graphite powder and 1.25 g of sodium nitrate were mixed together. After that, the mixture was added 150 mL of sulfuric acid under constant stirring and the temperature less than 5 °C. After 15 minutes, 7.5 g of KMnO₄ was added gradually to the above solution while keeping the temperature less than 20 ºC to prevent overheating and explosion. The mixture was sonicated at 35 °C for 2 h. The second oxidation was carried out by adding slowly 7.5 g of KMnO₄ and then the mixture was sonicated at 35 °C for 4 h. The resulting solution was diluted by adding 500 mL of water under vigorous stirring. To ensure the completion of the reaction with KMnO₄, 30% H₂O₂ (10 mL) was added. The resulting mixture was washed with H₂O and ethanol respectively, then dried. GO sheets were obtained.
2.3. Synthesized of MnFe₂O₄ nanoparticles

The MnFe₂O₄ nanoparticles were synthesized by a co–precipitation method [10]. Briefly, 2.7 g FeCl₃·6H₂O and 0.99 g MnCl₂·4H₂O were dissolved in 500 mL of deionized water. The mixture was stirred in ambient atmosphere for 30 min so that the molar ratio of Mn:Fe in the solution was 1:2. The solution was then constantly stirred and heated to 80 °C. Then, 2 M NaOH solution was slowly added to the mixture to raise pH of the solution to 10.5. The color of the solution changed immediately from orange to dark brown. The reaction was continued for 1 hours. The precipitated particles were collected by a magnet and washed 5 times with deionized water before being dried at 80 °C for 1 h. The MnFe₂O₄ nanoparticles were obtained.

2.4. Synthesis of GO–MnFe₂O₄ nanohybrids

GO–MnFe₂O₄ nanohybrids were synthesized by a modified co–precipitation method [11]. Brief, 0.5 g GO was added to 400 mL of water and dispersed by ultrasonication for 30 min. In turn, 2.7 g FeCl₃·6H₂O and 0.99 g MnCl₂·4H₂O were added to the colloidal GO solution and stirred for 30 min. The solution was then constantly stirred and heated to 80 °C. Then, 2 M NaOH solution was slowly added to the mixture to raise pH of the solution to 10.5. The reaction was continued for 1 h. The precipitate was collected by a magnet and washed 5 times with deionized water before being dried at 80 °C for 1 h. The GO–MnFe₂O₄ nanohybrids were obtained.

2.5. Characterization

XRD patterns were recorded on an Advanced X8 Bruker machine at wavelength (λ) of 0.154 nm at a step of 0.02° (2θ) at room temperature at Institute of Applied Materials Science (IAMS–VAST), Ho Chi Minh city. FTIR spectra were obtained in the wavenumber range from 4000 cm⁻¹ to 500 cm⁻¹ during 64 scans on an Alpha–E spectrometer (Bruker Optik GmbH, Ettlingen, Germany) at Institute of Chemical Technology (ICT–VAST), Ho Chi Minh city. TEM images were taken using a JEM–1400 at accelerating voltage of 100 kV at Institute of Applied Materials Science (IAMS–VAST), Ho Chi Minh city. The specific surface area was measured on an Altamira–AMI 200 machine at The Center for Molecular and Nanoarchitecture (MANAR), Viet Nam National University Ho Chi Minh City (VNUHCM). Magnetization curves of MnFe₂O₄ nanoparticles and GO–MnFe₂O₄ nanohybrids were measured by MicroSense Easy VSM version 9.13 L machine at Advanced Institute for Science and Technology (AIST–HUST), Ha Noi.

2.6. Adsorption studies

Batch adsorption studies experiments were conducted in 250 mL flasks, each containing 20 mL known concentration of Cd(II) in solution. The amount of GO, MnFe₂O₄, and GO–MnFe₂O₄ absorbent materials used for the experiment was fixed at 0.02 g. First, kinetic experiments (time: 0–480 min, pH: 6.5, C₀: 250 ppm). Secondly, effects of pH (pH: 2–8, C₀: 250 ppm, equilibrated time), the solution pH was adjusted by using 1 M NaOH and 1 M HCl. Thirdly, adsorption isotherm (pH: 8, C₀: 10–400 ppm, equilibrated time). Afterward, the adsorbent was magnetically separated from the aqueous solution, and the residual concentrations of metal ions were determined by UV–VIS spectrophotometer (UV–VIS–T70+). The quantity of ions Cd²⁺ adsorbed per unit mass of used adsorbent at equilibrium time were calculated as follows equation:
Removal of Cd(II) from water by using graphene oxide–MnFe$_2$O$_4$ magnetic nanohybrids

\[ q_e = \frac{(C_0 - C_e)V}{m} \]  
(1)

where $C_0$ is the initial concentration (mg/L) of Cd$^{2+}$, $C_e$ is the concentration (mg/L) of Cd$^{2+}$ after the adsorption, $V$ volume of solution (mL) and $m$ is the weight of GO–MnFe$_2$O$_4$ (g).

The adsorption kinetics of Cd$^{2+}$ onto the surface of GO–MnFe$_2$O$_4$ nanohybrids was studied by pseudo first order and second order equations.

The pseudo first order equation can be described as:

\[ \ln(q_e - q_t) = lnq_e - k_1 t \]  
(2)

The pseudo second order equation can be described as:

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e t} \]  
(3)

where $q_e$ and $q_t$ are the amounts of Cd$^{2+}$ adsorbed on the surface of GO–MnFe$_2$O$_4$ nanohybrids at equilibrium and at time $t$ (mg/g), respectively and $k_1$, $k_2$ are the rate constants of the pseudo first order (min$^{-1}$), second order model for adsorption (g.mg$^{-1}$.min$^{-1}$), respectively [12, 13].

In order to evaluate the adsorption capacity of sorbent, the Langmuir and Freundlich models were used.

The Langmuir isotherm model is expressed as follows:

\[ \frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max}k_L} \]  
(4)

where $q_e$ and $q_{max}$ are the amounts of Cd$^{2+}$ (mg/g) absorbed on the adsorbent at the equilibrium and maximum adsorption capacity, $C_e$ is the equilibrium concentration of Cd$^{2+}$ in the aqueous solution (mg/L), and $k_L$ is the Langmuir binding constant (1/mg).

The Freundlich isotherm model is expressed as follows:

\[ \ln q_e = \ln k_f + \frac{1}{n} \ln C_e \]  
(5)

where the $C_e$ is the equilibrium concentration of Cd$^{2+}$(mg/L), $q_e$ is the amount of Cd$^{2+}$ (mg/g) absorbed on the adsorbent at the equilibrium adsorption capacity. The $k_f$ is the Freundlich binding constant (1/mg) and $1/n$ is a constant related to the surface heterogeneity.

3. RESULTS AND DISCUSSION

3.1. Characterization of materials

3.1.1. XRD patterns

XRD patterns of GO, MnFe$_2$O$_4$, and GO–MnFe$_2$O$_4$ were analyzed for the confirmation of the crystal structure. Figure 1a shows the XRD pattern of the GO, the characteristic peak of GO at 9.86° correspond to (002) reflection from graphitic planes. Figure 1b shows the XRD pattern of MnFe$_2$O$_4$ and GO–MnFe$_2$O$_4$. The diffraction intensity of characteristic peak of GO disappeared due to the loading of MnFe$_2$O$_4$ nanoparticles on the surface of GO sheets, thus increasing the distance between the layers in framework. Further, the diffraction peaks of the GO–MnFe$_2$O$_4$ nanohybrids at 12.02°, 16.83°, 26.92°, 35.38°, 36.05°, 39.53°, 52.05°, 56.47°, and 61.56° can be assigned to the crystalline planes of (101), (111), (220), (311), (222), (400), (422), (511), and (440) of MnFe$_2$O$_4$. These peaks were in agreement the cubic spinel ferrite structure of MnFe$_2$O$_4$ [14, 15].
3.1.2. FTIR spectra

FTIR spectra of GO, MnFe₂O₄, and GO–MnFe₂O₄ nanohybrids are showed in Figure 2. Adsorption peaks appearing at 3449, 1722.41, 1628.32, 1383.46, and 1056.19 cm⁻¹ in the FTIR spectra of pure GO are attributed to OH, C=O (carbonyl and carboxylic groups), C=C, C–O (epoxy) and C–O (alkoxy) stretching vibrations, respectively [10]. All these bands almost remained in the FTIR spectra of GO–MnFe₂O₄ nanohybrids. The additional peaks at 633.27 cm⁻¹ and 481.23 cm⁻¹ were the characteristic peaks of the spinel structure. The high frequency bond (633.27 cm⁻¹) and low frequency bond (481.23 cm⁻¹) are in accordance with the vibration of Fe–O or Mn–O in octahedral and tetrahedral sites, respectively [16].

3.1.3. TEM images

The morphology of GO, MnFe₂O₄, and GO–MnFe₂O₄ nanohybrids were observed as shown in Figure 3. The TEM image of GO sheets in Figure 3a shows transparent sheets and wrinkles indicates that it is thin 2–dimensional sheets. However, on the thin sheets still remain the black areas, it is the agglomeration of the thin GO sheets. Figure 3b shows a TEM image of MnFe₂O₄ nanoparticles. This image indicates the agglomeration of the MnFe₂O₄ nanoparticles. Figure 3c, d show the images of GO–MnFe₂O₄ nanohybrids under different magnifications. These images confirmed the homogenous distribution of MnFe₂O₄ nanoparticles on the surface of the GO.
sheets and reduce agglomeration both of MnFe₂O₄ nanoparticles and GO sheets. There is no independent MnFe₂O₄ nanoparticles outside the GO sheets were observed, which indicates good interactions between MnFe₂O₄ nanoparticles and GO sheets. The average particles size of MnFe₂O₄ nanoparticles obtained is about 10–15 nm.

![Figure 3. TEM images of (a) GO, (b) MnFe₂O₄, and (c, d) GO–MnFe₂O₄ under different magnifications.](image)

### 3.1.4. BET specific areas

**Table 1.** BET specific surface area of MnFe₂O₄/GO and other materials.

<table>
<thead>
<tr>
<th>Materials</th>
<th>BET specific surface area (m²/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnFe₂O₄/GO</td>
<td>84.236</td>
<td>Present work</td>
</tr>
<tr>
<td>MnFe₂O₄</td>
<td>37.8</td>
<td>[16]</td>
</tr>
<tr>
<td>Rice Straw/Fe₃O₄</td>
<td>54.76</td>
<td>[17]</td>
</tr>
<tr>
<td>MnO₂/Fe₃O₄/GO</td>
<td>60.1</td>
<td>[17]</td>
</tr>
<tr>
<td>Fe₃O₄/GO</td>
<td>119.5</td>
<td>[17]</td>
</tr>
<tr>
<td>CoFe₂O₄/Ge</td>
<td>126.36</td>
<td>[18]</td>
</tr>
<tr>
<td>NiFe₂O₄/Ge</td>
<td>57.11</td>
<td>[18]</td>
</tr>
</tbody>
</table>

The BET specific surface area of GO–MnFe₂O₄ nanohybrids was obtained as up to 84.236 m²/g. This result in medium level in comparison with the other materials, which were showed in Table 1. The specific surface area of MnFe₂O₄/GO much higher than MnFe₂O₄ nanoparticles in
comparison with previous publications [16]. This result can be explained as follows: when MnFe$_2$O$_4$ nanoparticles were anchored on the surface of GO sheets, the aggregation of MnFe$_2$O$_4$ nanoparticles was decreased while the specific surface area was increased.

3.1.5. Magnetization by VSM

Figure 4 shows that the GO–MnFe$_2$O$_4$ nanohybrids samples exhibited soft magnetic material behavior with small coercive force (H$_c$ = 0.41 Oe). Figure 4 also shows the saturation magnetization values (M$_s$) of GO–MnFe$_2$O$_4$ was of 27.1 emu/g. With this value, the nanoparticles GO–MnFe$_2$O$_4$ can be easily removed after the completion of the adsorption of process and recycled by applying external magnetic field (see Figure 5).

![Figure 4](image_url)

*Figure 4. Magnetic hysteresis loops of GO–MnFe$_2$O$_4$.*

![Figure 5](image_url)

*Figure 5. Images of the magnetic properties of GO–MnFe$_2$O$_4$.*

### Table 2. The saturation magnetization M$_s$ (emu/g) of materials.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Saturation magnetization M$_s$ (emu/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnFe$_2$O$_4$/GO</td>
<td>27.1</td>
<td>Present work</td>
</tr>
<tr>
<td>MnFe$_2$O$_4$ nanoparticles</td>
<td>53</td>
<td>[19]</td>
</tr>
<tr>
<td>Fe$_3$O$_4$/GO</td>
<td>32.7</td>
<td>[20]</td>
</tr>
<tr>
<td>CoFe$_2$O$_4$/Ge</td>
<td>32.79</td>
<td>[18]</td>
</tr>
<tr>
<td>NiFe$_2$O$_4$/Ge</td>
<td>24.28</td>
<td>[18]</td>
</tr>
</tbody>
</table>
Table 2 shows that the saturation magnetization, $M_s$ (emu/g), of obtained MnFe$_2$O$_4$/GO nanocomposite is medium compared to GO and Ge. Additionally, the $M_s$ of the MnFe$_2$O$_4$/GO is much lower than that of MnFe$_2$O$_4$. This is due to the presence of GO which led to the reduce in saturation magnetization of MnFe$_2$O$_4$/GO [21].

3.2. Adsorption Test

3.2.1. Effect of contact time on adsorption capacity and adsorption kinetics

As shown in Figure 6, most of the Cd$^{2+}$ removal took place within first 60 mins and the equilibrium adsorption time was 240 mins.

![Figure 6. Effect of contact time on adsorption capacity.](image)

The correlation coefficient ($R^2$) for the pseudo second order model had high value, $R^2 = 0.99995$. This indicates that the adsorption process of Cd$^{2+}$ onto surface of GO–MnFe$_2$O$_4$ nanohybrids well fit with the pseudo second order model (see Figure 7).

![Figure 7. Pseudo second order kinetics.](image)
3.2.2. Effect of pH on adsorption capacity

pH is one of the most important controlling parameters in adsorption of Cd on surface of GO–MnFe$_2$O$_4$ process. Precipitation of cadmium starts at pH 8.2 [19]. Thus, in this study the effect of pH was examined from 3 to 8. The results were showed in Figure 8, the adsorption capacity of GO–MnFe$_2$O$_4$ increased with increasing pH of solution. On the surface of GO–MnFe$_2$O$_4$ have a lot of –OH groups of GO and MnFe$_2$O$_4$ (Mn–OH and Fe–OH were formed when dispersed MnFe$_2$O$_4$ nanoparticles in water [22]), add to that –COOH groups of GO. At low pH with a large number of H$^+$ ions, –OH and –COOH groups become positively charged – OH$^{2-}$ and –COOHH$^{2+}$. Therefore, Cd$^{2+}$ ions had to compete with H$^+$ ions for adsorption sites on the surface and the adsorption capacity reduced. When the pH was increased, –OH and –COOH groups are ionized to –O$^-$ and –COO$^-$, leading to the competition between Cd$^{2+}$ ions and H$^+$ ions was decreased. Therefore, the adsorption capacity was enhanced. Thus, pH 8 is the optimum pH condition for adsorption of Cd$^{2+}$ on the surface of GO–MnFe$_2$O$_4$.

The mechanisms of adsorption were showed the following reactions:

On the surface of MnFe$_2$O$_4$ nanoparticles (M is Mn or Fe) [10]:

$$\text{M – OH + Cd}^{2+} \rightleftharpoons \text{M – OCd}^+ + \text{H}^+$$ (6)

$$2\text{M – OH + Cd}^{2+} \rightleftharpoons (\text{M – O})_2\text{Cd} + 2\text{H}^+$$ (7)

$$\text{M – OH + Cd}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{M – OCdOH} + 2\text{H}^+$$ (8)

On the surface of GO [11]:

$$\text{GO – COOH + Cd}^{2+} \rightleftharpoons \text{GO – COOCd}^+ + \text{H}^+$$ (9)

$$2\text{GO – COOH + Cd}^{2+} \rightleftharpoons (\text{GO – COO})_2\text{Cd} + 2\text{H}^+$$ (10)

$$\text{GO – COOH + Cd}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{GO – COOCdOH} + 2\text{H}^+$$ (11)

$$\text{GO – OH + Cd}^{2+} \rightleftharpoons \text{GO – OCd}^+ + \text{H}^+$$ (12)

$$2\text{GO – OH + Cd}^{2+} \rightleftharpoons (\text{GO – O})_2\text{Cd} + 2\text{H}^+$$ (13)

$$\text{GO – OH + Cd}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{GO – OCdOH} + 2\text{H}^+$$ (14)

![Figure 8. Effect of pH on adsorption capacity.](117)
3.2.3. Effect of initial concentration of Cd$^{2+}$

Figure 9 indicates the adsorption capacity was increased with increasing initial concentration of Cd$^{2+}$. At low concentration (0–150 mg/L), the adsorption capacity was rapidly increased and at higher concentration (> 150 mg/L), the adsorption capacity was slightly increased and tend to reach equilibrium.

![Figure 9](image1.png)

*Figure 9. Effect of initial concentration of Cd$^{2+}$ on adsorption capacity.*

As shown in Table 3 and Figure 10, the higher correlation coefficient was obtained from Langmuir plot ($R^2 = 0.9881$) compared to Freundlich plot ($R^2 = 0.9436$). Therefore, the adsorption of Cd$^{2+}$ on GO–MnFe$_2$O$_4$ well fit with Langmuir isotherm model more than Freundlich isotherm model.

*Table 3. Adsorption constants and correlation coefficient ($R^2$) with Langmuir and Freundlich isotherm models.*

<table>
<thead>
<tr>
<th></th>
<th><strong>Langmuir</strong></th>
<th></th>
<th><strong>Freundlich</strong></th>
<th></th>
</tr>
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<tbody>
<tr>
<td></td>
<td>$k_l$ (l/mg)</td>
<td>$q_m$ (mg/g)</td>
<td>$R^2$</td>
<td>$N$</td>
</tr>
<tr>
<td>$k_l$ (l/mg)</td>
<td>0.0172</td>
<td>121.951</td>
<td>0.9881</td>
<td>1.689</td>
</tr>
</tbody>
</table>

![Figure 10](image2.png)

*Figure 10. (a) Langmuir isotherm and (b) Freundlich isotherm of adsorption of Cd$^{2+}$ on GO–MnFe$_2$O$_4$.***
The maximum adsorption capacity, \( q_m \) (mg/g), of obtained MnFe\(_2\)O\(_4\)/GO nanocomposite is about 121.951. This result is compared with some other materials presented in the Table 4.

Figure 11 indicated the adsorption of Cd\(^{2+}\) on GO and MnFe\(_2\)O\(_4\) also well fit with Langmuir isotherm \((R^2 = 0.9935\) and \(0.9881,\) respectively). But the maximum adsorption capacity of GO and MnFe\(_2\)O\(_4\) \((107.527\) mg/g and \(34.364\) mg/g, respectively) are less than GO–MnFe\(_2\)O\(_4\) \((121.951\) mg/g). The results are explained, when MnFe\(_2\)O\(_4\) nanoparticles were anchored on the surface of GO sheets, resulting in decreased aggregation of both of MnFe\(_2\)O\(_4\) nanoparticles and GO sheets and increased adsorption sites.

Table 4. Maximum adsorption capacity \( q_m \) (mg/g) of MnFe\(_2\)O\(_4\)/GO and other materials.

<table>
<thead>
<tr>
<th>Materials</th>
<th>( q_m ) (mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnFe(_2)O(_4)/GO</td>
<td>121.951</td>
<td>Present work</td>
</tr>
<tr>
<td>Graphene oxide</td>
<td>106.3</td>
<td>[23]</td>
</tr>
<tr>
<td>CoFe(_2)O(_4)/Ge</td>
<td>105.26</td>
<td>[18]</td>
</tr>
<tr>
<td>NiFe(_2)O(_4)/Ge</td>
<td>74.62</td>
<td>[18]</td>
</tr>
<tr>
<td>Graphene</td>
<td>188.679</td>
<td>[24]</td>
</tr>
<tr>
<td>Silicate MCM-41, mesoporous</td>
<td>100</td>
<td>[25]</td>
</tr>
<tr>
<td>SWCNT</td>
<td>24.07</td>
<td>[26]</td>
</tr>
<tr>
<td>SWCNT-COOH</td>
<td>55.89</td>
<td>[26]</td>
</tr>
</tbody>
</table>

![Figure 11. Langmuir isotherm of adsorption of Cd\(^{2+}\) on (a) GO and (b) MnFe\(_2\)O\(_4\).](image)

4. CONCLUSIONS

In this work, the GO–MnFe\(_2\)O\(_4\) magnetic nanohybrids were successfully synthesized by co-precipitation method. XRD patterns showed the crystal structure of GO–MnFe\(_2\)O\(_4\) was formed. FTIR spectra indicated the existence of oxygen–containing functional groups in this materials. VSM result showed the high saturation magnetization values \(M_s = 27.1\) emu/g. The BET specific surface area of GO–MnFe\(_2\)O\(_4\) nanohybrids was obtained as 84.236 m\(^2\)/g. TEM images confirmed the homogenous distribution of MnFe\(_2\)O\(_4\) nanoparticles on the surface of the GO sheets, reducing of agglomeration both of MnFe\(_2\)O\(_4\) nanoparticles and GO sheets and the interactions between MnFe\(_2\)O\(_4\) nanoparticles and GO sheets were very strong.
Experimental adsorption data were fitted well to the Langmuir isotherm and the pseudo–second–order kinetic equation. Adsorption of Cd(II) on nanohybrids was better than MnFe₂O₄ and GO with a maximum adsorption capacity of 121.951 mg/g at pH 8.

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