Rapid removal of noxious nickel (II) using novel γ-alumina nanoparticles and multiwalled carbon nanotubes: Kinetic and isotherm studies

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A B S T R A C T
Novel γ-alumina nanoparticles and MWCNTs were synthesized for the rapid removal of the noxious nickel (II) from the solvent phase. Hence this study investigated the ability of nano-sized particle in Ni (II) adsorption. The influential parameters including contact time (min), adsorbent dosage (g/L), pH and the initial concentration of Ni (II) were investigated and optimized using the batch adsorption study. The adsorption equilibrium and kinetic data were well fitted and found to be in good agreement with Langmuir and pseudo-second order kinetic model respectively and the maximum Ni (II) percentage removal using MWCNTs and novel γ-alumina nanoparticle was 87.65% and 99.41%, respectively under optimum conditions. The maximum removal of Ni (II) was observed at pH = 10. Upon experimentation, it was observed on increasing the adsorbent dosage and initial concentration the amount of Ni (II) removal efficiency also increased. Finally, it can be concluded that the synthesized nanoparticles can be applied as the best adsorbent to remove the Ni (II) from aqueous solution.

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1. Introduction

In recent decades, the water pollution has become one of the major environmental threats due to the release of the toxic and hazardous chemical from various activities [1–3]. The heavy metals are one of the most commonly used materials which are used in various industries, when these metal ions are discharged in the effluent of industries they possess several environmental and detrimental effects on human health as well as prevailing flora and fauna [4–5]. Nickel (Ni) belongs to heavy metal groups and has various industrial applications such as mineral processing, electroplating, production of paints and batteries, manufacturing of sulfate and porcelain enameling [6,7]. Despite the extensive use of Ni, this has been known to be a toxic and hazardous element which can cause severe health problems to lungs, kidneys, gastrointestinal distress such as nausea, vomiting, diarrhea, pulmonary fibrosis, renal edema, and skin dermatitis [8,9]. Thus, the heavy metals, especially Ni, must be rapidly removed and adsorbed from the industrial effluents. The previous studies reported that there are numerous techniques for heavy metal removal from effluents but among all the adsorption process were found to be most effective and extensively used method for this purpose [9,10]. The successful use of this method is due to the unique characteristics including simplicity, low-cost and flexibility of adsorption process [11,12]. Although many adsorbents such as activated carbon, activated alumina and red mud have been found to be potential adsorbent [13]. But the low adsorption capacity and slow kinetics are some of major problems of these common adsorbents and it indicates the necessity of developing more low cost efficient adsorbents [14–17].

Currently, the nano-sized materials are widely used as adsorbents for the rapid removal and fast adsorption of heavy metal, due to its wonderful characteristics such as high capacity, simple operation, and rapid adsorption process give the high potential to this material. Hence it is used as an effective adsorbent for heavy metal removal [18–20].

The aim of the present study was to compare the ability of MWCNTs and γ-alumina nanoparticle in Ni (II) ions adsorption from the solvent phase. The impact of various factors such as the contact time, adsorbent dosage, pH and initial concentration of Ni (II) ions were studied to
determine the optimum condition. Finally, the adsorption isotherm and kinetic studies of Ni (II) ions onto the developed adsorbent were well investigated and evaluated.

2. Material and methods

All the chemicals used in the present study were of analytical grade and were provided by Merck Co, Germany. The specific surface area of the MWCNTs and γ-alumina nanoparticle was determined using the BET surface analyzer (Gemini 2357, Micrometrics Instrument Corporation, USA). The scanning electron microscopy (SEM) was carried out by a Philips XL30 to study the surface morphological and topological properties of both adsorbents.

The stock nickel solution of 1000 mg/L was prepared by dissolving 4.06 g of nickel salt (NiCl₂·6H₂O) in distilled water. The different concentration of Ni (II) ions solutions was prepared by dilution of stock solution with the distilled water. In this work, the influence of contact time (10, 15, 30, 45, 60, 90 and 120 min), pH (4, 7, 8, 9 and 10), Ni (II) ions concentration (15, 25, 50, 60 and 75 mg/L) and adsorbent dosage (5, 10, 20 and 30 mg/L) on Ni (II) adsorption efficiency was well evaluated and investigated. In order to regulate pH of the solution 0.01 N NaOH ions and 0.01 NH₂SO₄ were used. All batch experiments were conducted in 250 mL Erlenmeyer flasks at 30 °C. The experiments were carried out using 100 ml solution with a certain concentration of Ni (II) ions and known amount of the adsorbent in a 250 mL Erlenmeyer flask. The flasks were agitated 2 h at 180 rpm for pre-determined contact times using a mechanical shaker at room temperature. Control experiments were conducted without absorbent to provide correction for metal ion adsorption on the walls of the container. The measurement of residues Ni (II) ions in samples was implemented by the atomic absorption spectrometer (AAS) Perkin Elmer 3100 according to standard methods [14].

In addition, all experiments were repeated 3 times in order to increase the reliability, accuracy and precision of the study. The adsorption capacity (qe) in the equilibrium (mg/g) and the removal efficiency E (%) were calculated by following equations:

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

\[
E = \left(1 - \frac{C_e}{C_0}\right) \times 100 \quad (2)
\]

where \(C_0\) (mg/L) and \(C_e\) (mg/L) are initial and equilibrium concentrations of heavy metals, respectively, \(V\) (L) is the volume of aqueous solution, and \(W\) (g) is the adsorbent mass in the solution [21,22].

3. Results and discussion

3.1. Characterization of adsorbents

Fig. 1(a–d) depicts the microstructure (under BET and SEM) of γ-alumina nanoparticle and MWCNTs respectively. The SEM images show the surface topological and morphological property of both the synthesized adsorbents. Fig. 1a and b reveals the porous morphology with large number of unoccupied active sites of the synthesized γ-alumina and Fig. 1c and d shows the SEM of MWCNTs, which reveals the tubular structure of the synthesized MWCNTs. Also, the internal diameter and diameter of γ-alumina nanoparticles were found to be 2–3 nm and 10–20 nm, respectively. In addition, the specific surface area of MWCNTs and γ-alumina nanoparticle was determined to be was 370 and 412 m²/g, respectively. It can be expected that the used γ-alumina nanoparticle can show relatively better adsorption ability than MWCNTs due to a higher specific surface area [23,24].

![Fig. 1. Morphological BET and SEM images of γ-alumina nanoparticles (a and b) and MWCNTs (c and d).](image-url)
3.2. Effect of adsorbent dosage

To investigate the effect of adsorbent dosage, the amount of each adsorbent was varied in the range of 0.05–0.3 g/L. The adsorbent dosage is considered as one of the most effective parameter in the adsorption process. Fig. 2 shows that higher Ni (II) ions removal efficiency is obtained at higher dosages of both adsorbents but the adsorption capacity is decreased by increasing the adsorbent dosage. The maximum removal of Ni (II) ions using MWCNTs and γ-Al2O3 nanoparticle was 98.2% and 89.7%, respectively. This is due to the fact, on increasing the adsorbent dosage the adsorption surface site also increases and as a result of this the adsorption efficiency increases at higher adsorbent dosage but the decrease in the value of the adsorption capacity (qe) can be explained on the basis of the free active sites available on the surface of the adsorbents [25,26]. Bhat et al. had conducted a study to survey the ability of γ-alumina nanoparticle for lead (II) removal and they observed that the increasing of the adsorbent dosage can enhance the adsorption efficiency [23].

3.3. Effect of contact time and pH

To evaluate the effect of contact time and pH on the adsorbent ability for Ni (II) removal from the solvent phase, the experiments were conducted at different contact time in the range of 10–120 min and at different pH including 4, 7, 8, 9 and 10. The results of these studies are presented in Figs 3 and 4. The contact time and pH have been identified as most effective parameters on adsorption processes. Figs. 3 and 4 shows that the maximum removal of Ni (II) ions was obtained in approximately 30 min and there is no significant increase in the Ni (II) ions efficiency after this time. In fact, the maximum Ni (II) ions adsorption is rapidly obtained in initial minutes of the beginning of study which this is consistent with other studies [27,28].

Figs. 3 and 4 also illustrate that the pH has significant role in Ni (II) removal efficiency and can effectively control the Ni (II) ion adsorption. The Ni (II) ion removal efficiency is increased as the pH of the solution increases. This is due to the fact that the surface charge of nanoparticle becomes more negative at higher pH and the Ni (II) ion has positive surface charge, thus electrostatic attraction is increased between them which it is led to increase of the removal efficiency. These results are agreed with these results of studies [7,28], Yang et al. has been conducted a study to survey the Ni (II) ion adsorption efficiency and has found that the Ni (II) ion removal efficiency developed by increasing of pH. They expressed that this phenomenon can be due to increasing pH concentration probably attributed to the hydrolysis of Ni (II) ion and the surface properties of adsorbent. Also, they mentioned that the high Ni adsorption efficiency at the higher pH can’t be due to the precipitation because of the low precipitation constant which it confirms the results of this study [29].

3.4. Effect of initial concentration of Ni (II)

Adsorption of heavy metal by the various adsorbent is strongly dependent on the initial metal ion concentration. The effect of initial concentration of Ni (II) ion was studied by varying the Ni (II) ion concentrations from 15 to 75 mg/L. Results of this study were presented in Fig. 5. It is clear that the Ni (II) ion removal percentage is decreased with the increase in the initial concentration. The Ni (II) removal efficiency by using of the MWCNTs is increased from 69.82% to 99.41% by increasing of initial concentration of Ni (II) from 15 to 75 mg/L and it is increased from 49.86% to 87.65% by using the γ-alumina nanoparticle. In addition, an increase in the initial concentration of Ni (II) ion increases the amount of Ni (II) adsorbed per unit of adsorbent. The amount of adsorbed Ni (II) per unit of mass of MWCNT and γ-alumina nanoparticle was 74.79 and 104.73 mg/g at Ni (II) ions concentration of 15 mg/L, respectively but these amounts were increased to 675.3 and 745.5 mg/g at the concentration of 75 mg/L. The result is in the agreement with the results of another study [30]. The higher Ni (II) ions adsorption in higher concentration can be due this fact that the increasing of initial concentration of Ni (II) ions develops the driving force which is the need to diminish the resistance to mass transfer of metal ion [31].

3.5. Kinetic studies

For this study, 0.1 g/L of each adsorbent were added 100 mL of Ni solution at the concentration between 15 and 75 mL and then mixed at 25 °C. Then samples were collected and filtered to determine the remaining concentration of Ni (II). The kinetic studies are performed to
determine the rate of the adsorption process. The kinetic models which were used for this purpose are including pseudo-first-kinetic, pseudo-second-kinetic and intraparticle diffusion. The equation of pseudo-first-order kinetic is as follow [32,33]:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t $$

(3)

The equation of pseudo-second-order kinetic is as follow [34]:

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{1}{q_e} t $$

(4)

where \(q_e\) and \(q_t\) are adsorption capacity (mg/g) at the equilibrium time and \(t\) time, respectively.

The \(k_1\) and \(k_2\) are the constant rate of pseudo-first-order (min\(^{-1}\)) and constant rate of pseudo-second-order model (g/mg min), respectively. The adsorption rate constant \(k_1\) for Ni (II) adsorption was calculated from the slope of the linear plot of ln \((q_e - q_t)\) versus time. Kinetic data were plotted as \(t / q_t\) against \(t\) for calculation of \(k_2\).

The intraparticle diffusion is calculated as following [35]:

$$q_t = k_{\text{w}} t^{0.5} $$

(5)

\(k_w\) (mg/g min\(^{1/2}\)) represents intra-particle diffusion rate constant and \(t\) denotes contact time (min).

The variable and constant of each kinetic model were calculated and were presented in Table 1. Also, Fig. 6 shows the pseudo-second-order model diagrams for Ni (II) adsorption by the adsorbents. The correlation coefficient \(R^2\) values of the pseudo-second-order kinetic are higher than pseudo-first-order for both adsorbent. This reveals that the experimental adsorption data can be better described by pseudo-second-order kinetic model. These results are consistent with results of other studies [32,36].

3.6. Isotherm studies

The isotherm studies were conducted to calculate the adsorption capacity of used adsorbents for Ni\(^{2+}\). For this purpose, three commonly used isotherm models i.e. Langmuir and Freundlich, Temkin and BET isotherm.

The equation of Langmuir isotherm model is shown as follows [37, 38]:

$$
\frac{C_e}{q_e} = \frac{1}{q_m \cdot K} + \frac{C_e}{q_m}
$$

(6)

where \(q_e\) is the adsorbed amount of Ni (II) per unit weight of adsorbent at equilibrium (mg/g); \(C_e\) is the equilibrium concentration of the Ni (II) (mg/L); \(q_m\) (mg/g) is the maximum theoretical Ni (II) capacity and \(K\) (L/mg) is Langmuir constant related to the affinity of binding sites. The constants related to Langmuir isotherm model are calculated by the slope and intercept of the plots which is obtained from \(1 / q_e\) versus \(1 / C_e\).

### Table 1

<table>
<thead>
<tr>
<th>(C_0) (mg/L)</th>
<th>(q_e) exp (mg/g)</th>
<th>(k_1)</th>
<th>(q_e)</th>
<th>(R^2)</th>
<th>(k_2)</th>
<th>(q_e)</th>
<th>(R^2)</th>
<th>(K_{\text{int}})</th>
<th>(c)</th>
<th>(R^2)</th>
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<td>(\gamma)-Al(_2)O(_3)</td>
<td>15</td>
<td>12.23</td>
<td>0.0014</td>
<td>4.73</td>
<td>0.999</td>
<td>0.0092</td>
<td>10.4</td>
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<td>0.09</td>
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<td>0.0049</td>
<td>15.17</td>
<td>0.994</td>
<td>0.0016</td>
<td>24.3</td>
<td>0.996</td>
<td>0.14</td>
<td>2.614</td>
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<tr>
<td>50</td>
<td>50.77</td>
<td>0.0076</td>
<td>28.21</td>
<td>0.996</td>
<td>0.0004</td>
<td>50.1</td>
<td>0.995</td>
<td>0.35</td>
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<td>0.812</td>
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<td>40.17</td>
<td>0.997</td>
<td>0.0003</td>
<td>62.5</td>
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<td>75</td>
<td>75.47</td>
<td>0.0124</td>
<td>52.65</td>
<td>0.998</td>
<td>0.0001</td>
<td>71.4</td>
<td>0.998</td>
<td>0.77</td>
<td>5.648</td>
<td>0.852</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>15</td>
<td>8.26</td>
<td>0.0011</td>
<td>3.83</td>
<td>0.784</td>
<td>0.0224</td>
<td>7.40</td>
<td>0.997</td>
<td>0.15</td>
<td>2.062</td>
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<tr>
<td>25</td>
<td>19.34</td>
<td>0.0036</td>
<td>14.21</td>
<td>0.735</td>
<td>0.0301</td>
<td>17.85</td>
<td>0.999</td>
<td>0.34</td>
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<td>43.77</td>
<td>0.0059</td>
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<td>0.0052</td>
<td>43.47</td>
<td>0.998</td>
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<td>0.827</td>
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<tr>
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<td>53.62</td>
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<td>0.0003</td>
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<td>0.997</td>
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<td>5.763</td>
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<td>0.715</td>
<td>0.0002</td>
<td>66.66</td>
<td>0.999</td>
<td>1.12</td>
<td>6.872</td>
<td>0.839</td>
</tr>
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</table>
Another model which is used in this study is Freundlich model. The equation of this model is represented as below [39,40]:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$  \hspace{1cm} (7)

In this equation, $K_f$ is Freundlich constant $n$ is another constant that give information about the heterogeneity degree of the surface sites. The constants of this model are calculated by the slope and intercept of obtained plot from $\log q_e$ versus $\log C_e$.

The Temkin model isotherm model is described as follows [41,42]:

$$q_e = B_1 \ln (K_t) + B_2 \ln (C_e)$$  \hspace{1cm} (8)

In this equation, the $K_t$ and $B$ are the Temkin isotherm constant (L/g) and heat of sorption (J/mol), respectively. The constant of the Temkin model isotherm is obtained by the plots from $q_e$ versus $\ln C_e$.

The BET model of isotherm is another model which can be presented as follows [43]:

$$\frac{C_e}{(C_e - C_0)q} = \left( \frac{1}{q_m - A} \right) + \left( \frac{A-1}{q_m - A} \right)$$  \hspace{1cm} (9)

$A$ shows the binding energy between pollutant and adsorbent.

The isotherms are further beneficial to compare the two adsorbents removal percentage because they are more informative. The slope and the intercept of linear plot obtained from each model were used to determine parameters related to the isotherm models and these parameters are presented in Table 2. As it can be seen, the $R^2$ values of all isotherm models are higher than 0.9 which it shows the applicability of all models to describe the equilibrium data, but the data are relatively better fitted with Langmuir isotherms with the $R^2$ value more than 0.99 for both of adsorbents. This model is based on monolayer adsorption onto specific homogeneous surface sites within the adsorbent. Other studies which are conducted to remove the Ni (II) showed similar results [44–56].

### 4. Conclusion

In this study, the ability of two nano-sized materials, i.e., multi-walled carbon nanotubes (MWCNTs) and Gamma-alumina nanoparticles on Ni (II) ions adsorption efficiency were well studied and the impact of effective parameters i.e. contact time, pH, adsorbent dosage and initial Ni concentration were studied and following results were observed:

- It has been observed that these adsorbent are able to remove the Ni (II) efficiently and the maximum removal efficiency at the optimum condition were found to be 87.65% and 99.41% for (MWCNTs) and Gamma-alumina nanoparticles, respectively. The maximum removal efficiency was obtained at the alkaline pH i.e 10. Also, it was observed that as the pH of the solution increases and the Ni (II) ion removal efficiency also increases. The effect of adsorbent dosage reveals the same trend as followed by the pH of the solution. The adsorption isotherm and kinetic studies showed that Langmuir isotherm and pseudo-second-order kinetic model can better describe the obtained data. Also, since this adsorbent has the large specific surface area, therefore can represent large adsorption capacity than other common and can be used effectively in pollutant removal.

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