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MWCNTs-Fe₃O₄ Nanocomposite for Hg(II) High Adsorption Efficiency

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Abstract
Magnetic carbon nanotubes composite (MWCNTs-Fe₃O₄) was successfully prepared and characterized using different techniques. MWCNTs-Fe₃O₄ displays entangled network of oxidized MWCNTs attached with Fe₃O₄ clusters with specific surface area of 92 m² g⁻¹. The adsorption performance of as prepared composite was investigated for Hg(II) removal. Several experimental factors affecting Hg(II) adsorption process by MWCNTs-Fe₃O₄ were studied including, adsorbent dosage, contact time, pH and metal ion concentration. A high adsorption capacity of 238.78 mg g⁻¹ was obtained according to Langmuir model. In addition, pseudo-second-order and the Langmuir isotherm model were used to fit the adsorption kinetic and equilibrium data, respectively. The results recommend the successful application of MWCNTs-Fe₃O₄ for Hg(II) removal via batch adsorption technique.

Keywords: Carbon nanotubes, Nanocomposite, Water treatment, Adsorption, Hg(II) removal, Pollutants.

1. Introduction

A serious environmental problem of increasing interest is the heavy metals contamination of aqueous media and industrial effluents because of the toxic nature and accumulation of these metal ions in the food chain, and the subsequent non-biodegradability [1]. Rapid industrialization is the main source for releasing toxic heavy metals to the environment. The major sources of heavy metal ion contaminations are mining industry, battery manufacturing, electroplating, textile industry, petroleum refining, paint manufacture, photographic industries, etc [1, 2]. Due to its
toxicity, long-range transport, persistence and bioaccumulation in the environment, mercury (Hg) is considered as one of the most important environmental contaminants that have caused global concerns [3]. Thus, the removal of such toxic materials from wastewater is becoming a crucial issue. Many physical, biological and chemical techniques have been developed to control this issue [4-8]. Due to its high efficiency and economic consideration, adsorption process was proved to be the most efficient technique [9-11]. In addition, adsorption technique has no harmful effect and doesn’t produce harmful substances [12-15]. Adsorbents materials such as zeolites, polymers, biomaterials, have been tested and examined for possible application of toxic heavy metal ions adsorption [16-19]. Nowadays, developing of effective adsorbents is of increasing global interest for the water treatment application since the adsorption efficiency is mostly depending on the adsorbent properties [16, 17, 20-22]. Therefore, development of more efficient adsorbents has gained the attention of quite a large number of researchers. New nanomaterials-based adsorbents have been proposed as novel adsorbents for the removal of heavy metal ions from wastewater with better adsorption performance [10, 23-25].

Carbon nanotubes (CNTs) have pulled in significant interdisciplinary interest on account of their one of exclusive chemical and physical properties; however, the known hydrophobicity of CNTs could restrict some of their applications [26, 27]. Accordingly, treatments of CNTs with specific functional groups or nanoparticles could have the potential to overcome these drawbacks and widen the applications of CNTs [28-30]. Magnetic metal oxide nanoparticles have been reported as efficient, highly effective and economic adsorbents. Moreover, they are easy to separate under a magnetic field for recovering [31-34]. Metal oxide/non-metal nanocomposites show good enhancement of adsorption efficiency of methylene blue because of their high surface
area and lower particles size [10]. Therefore, nanocomposites of metal oxide and CNTs would be very effective in adsorption process as it possesses unique morphological properties.

This paper discusses the preparation and characterization of a novel nanocomposite adsorbent for the adsorption of Hg(II). The idea is to overcome the known hydrophobicity of multi-walled carbon nanotubes (MWCNTs) through surface treatment of MWCNTs with magnetic Fe₃O₄ nanoparticles. Several experimental parameters such as adsorbent dosage, pH, contact time, metal ion concentration etc, and their effect on the adsorption efficiency will be studied. The objectives of this paper are: (i) to study the efficiency of MWCNTs-Fe₃O₄ as an adsorbent for the adsorption of Hg(II), (ii) to find out the best-fit isotherm model (Langmuir and Freundlich), and (iii) to determine the kinetic parameters that affecting and controlling the adsorption process.

2. Experimental

2.1 Materials

MWCNTs were obtained from NanoAmor Nanostructured & Amorphous Materials, Inc, USA. Chemical vapor deposition (CVD) method was used to prepare MWCNTs with the specification of purity of 95%, outer diameters of 50 nm, length in the range from 500 to 2000 nm and specific surface area of 40 m² g⁻¹. In addition, HgCl₂ aqueous solutions with different concentrations were prepared and used as sources for Hg(II). All other reagents and chemicals were provided by Merck Inc, USA.
2.2 Samples Preparation

MWCNTs-Fe$_3$O$_4$ nanocomposite was prepared as reported in our previous work [35]. Briefly, the bare MWCNTs was treated with HNO$_3$ and then exposed to microwave radiation to be functionalized with carboxylic groups as a result of oxidation reaction occurred. Fe$_3$O$_4$ nanoparticles were prepared by chemical co-precipitation method [36, 37]. The obtained magnetic nanoparticles were mixed with the treated MWCNTs in 40 mL solution of deionized water/ethanol (1:1). The mixture was ultrasonicated for 1 h and stirred for 96 h. A filter membrane of 200 nm was used to separate the solution from the residue, followed by vacuum drying at 50 °C for 16 h. MWCNTs-Fe$_3$O$_4$ preparation stages are shown in Scheme 1.

Scheme 1. A schematic diagram for the synthesis of MWCNTs-Fe$_3$O$_4$.

2.3 Materials Characterization

The synthesized MWCNTs-Fe$_3$O$_4$ nanocomposite was examined by Fourier-transform infrared spectroscopy (FTIR), X-ray powder diffraction (XRD) analysis, transmittance electron microscopy (TEM), scanning electron microscopy (SEM), Thermogravimetric analysis (TGA) and vibrating sample magnetometer (VSM). The instrumentation detailed were given elsewhere [35]. The surface area of the synthesized MWCNTs-Fe$_3$O$_4$ nanocomposite materials was measured using N$_2$ adsorption-desorption techniques.
2.4 Adsorption Experiments

A stock solution of Hg(II) (1000 mg L\(^{-1}\)) was prepared by dissolving HgCl\(_2\) in deionized water. To determine the optimum Hg(II) adsorption parameters, the adsorption experiments were conducted in 100 mL stopper conical flask and shaken using a temperature controlled shaker. The effect of different dosages (2-16 mg) was evaluated at 20 mg L\(^{-1}\) initial concentration (C\(_o\)), 2 h contact time, natural pH, and at 25 °C. The effect of contact time (1-120 min) was also studied at 20 mg L\(^{-1}\), 10 mg, natural pH, 25 °C. The effect of pH from 1-8 was investigated at 20 mg L\(^{-1}\), 10 mg, 1 h, 25 °C. Adsorption equilibrium studies in the single system were performed at 10 - 50 mg L\(^{-1}\) initial concentrations. The adsorbent was separated from the solution at the end of the adsorption process using a magnetic separator. The optimum Hg(II) concentration was determined by atomic adsorption spectrophotometer (GBC-932, AAS, Australia). The adsorption capacity (Q\(_e\), mg g\(^{-1}\)) was calculated according to Eq. 1 [11, 15]:

\[
Q_e = \frac{(C_o - C_e)V}{m}
\]

(1)

where C\(_o\) & C\(_e\) are the initial and equilibrium Hg(II) concentrations (mg L\(^{-1}\)) respectively. V is the volume of adsorption solution (L), and m is the mass of adsorbent (g).
3. Results and Discussion

3.1 Characterization of Adsorbent

3.1.1 Structural Characteristics

FTIR spectra showed the band at 1580 cm\(^{-1}\) indicating the presence of cylinder-like carbon structure. The stretching mode of C=O vibration of the carboxyl group (COOH) is clear from the modified MWCNTs spectrum. The same finding was also observed at 1713 cm\(^{-1}\) for MWCNTs-COOH, and at 1724 cm\(^{-1}\) for MWCNTs-Fe\(_3\)O\(_4\). This band has been reduced significantly in case of MWCNTs-Fe\(_3\)O\(_4\) compared to MWCNTs-COOH. This reduction can be attributed to the formation of a linkage between Fe\(_3\)O\(_4\) particles and MWCNTs, through a reaction between COOH groups and the magnetite particles. The broad band near 585 cm\(^{-1}\) confirms the presence of iron oxide (primary magnetite) in MWCNTs-Fe\(_3\)O\(_4\) [35, 38]. The phase and crystalline structure of cubic Fe\(_3\)O\(_4\) and MWCNTs were confirmed by XRD measurement as shown by their characteristics peaks. The main Fe\(_3\)O\(_4\) peaks are broad, indicating the small crystallite size of Fe\(_3\)O\(_4\) nanoparticles [39]. According to the Scherrer formula [40], the mean size of Fe\(_3\)O\(_4\) crystallites was measured to be 10 nm for MWCNTs-Fe\(_3\)O\(_4\).

3.1.2 Morphological Characteristics

SEM, TEM and BET surface area have been used to investigate the morphology of the prepared nanocomposite materials. Fig. 1 shows the SEM images of the prepared materials. According to Fig. 1a and b, MWCNTs-COOH shows an entangled network of oxidized MWCNTs. However, Fig. 1c and d, MWCNTs-Fe\(_3\)O\(_4\) displays entangled network of oxidized
MWCNTs attached with Fe₃O₄ clusters. There is a little increment in the tube diameters due to attached Fe₃O₄ nanoparticles on the outer surface.

![SEM micrographs](image)

**Fig. 1** SEM micrographs (a), (b) for MWCNTs-COOH, (c) and (d) for MWCNTs-Fe₃O₄ at different magnifications.

Further morphological studies were conducted on the prepared materials using TEM (Fig. 2). Fig. 2a shows spherical Fe₃O₄ nanoparticles (5-10 nm) which is very close to XRD calculations. In addition, Fig. 2b shows uniform tube structure of MWCNTs. On the other hand, Fig. 2c depicts an entangled network of acidified MWCNTs attached with clusters of Fe₃O₄ nanoparticles. The Fe₃O₄ nanoparticles aggregates are composed of sub-units of about 10 nm.
[41], suggesting that large particles may be formed via precipitation followed by aggregation process. The MWCNTs surface is covered with COOH in which Fe₃O₄ nanoparticles are uniformly distributed without aggregation. Carboxylic acid attached to the surface of MWCNTs was stable during the loading iron oxides, because of the simple and easy reaction between carboxylic acid and metal ions due to the presence of a huge number of coordinating functional groups [42]. Fe₃O₄ nanoparticles deposit on the defect sites of MWCNTs by spontaneous redox of between Fe³⁺ and the defect sites [43]. The specific surface area of the MWCNTs-Fe₃O₄ nanocomposite was found to be 92 m² g⁻¹. This high surface area is preferable for the adsorption process, where it provides more active centers for the reaction.
Fig. 2 TEM images of (a) Fe₃O₄, (b) MWCNTs-COOH and (c) MWCNTs-Fe₃O₄ nanocomposite.

3.2 Adsorption Studies

The presence of a satisfactory amount of adsorbent is essential to determine the number of free adsorption sites at a specific concentration. The experiments were conducted at 25 °C (MWCNTs-Fe₃O₄ dose of 2-16 mg, Hg(II) solution volume and concentration were 25 mL 20 mg L⁻¹, respectively). The adsorption of ions increased rapidly with increasing the adsorbent dose (Fig. 3a), due to the enhancement of the active sites with MWCNTs-Fe₃O₄. It seems that the adsorption of Hg(II) reached the equilibrium state at 10 mg. Therefore, 10 mg was selected as the optimum adsorbent dosage in this study.

Equilibrium time is an important parameter that should be carefully determined in the design of economical wastewater treatment systems [44]. The effect of contact time on the adsorption process was studied. We conducted the experiments using 10 mg of MWCNTs-Fe₃O₄ at natural pH and 25 °C. From the results shown in Fig. 3b, the functionalized magnetic MWCNTs-Fe₃O₄ adsorbent exhibit a gradual increase in Hg(II) adsorption capacity with increasing the reaction contact time. The metal adsorption capacity value was found to reach saturation conditions after 60 min by reaching the maximum adsorption of Hg(II). These findings attribute to the binding processes of Hg(II) to the MWCNTs-Fe₃O₄ surface via two different steps [45].

The three linear stages as in Fig. 3b illustrate the adsorption process mechanism. The mechanism seems to has three stages: (i) film diffusion stage in which the mass is transferred of
the adsorbent through the water film to the adsorbent surface. (ii) pore diffusion of the adsorbate occurs, and (iii) equilibrium stage in which occupation of a surface site on the adsorbent by physisorption or chemisorption occurs [46]. The adsorption rate of each stage could be correlated to its slope. The first stage can be seen to be the fastest, involving external diffusion to the surface of the adsorbent. It is related to a gradual increase in the metal capacity with the increase of the contact time from 1 to 60 min because of the occupation of the functional groups of the absorbents by the target metal ion. The second stage involving pore diffusion is a relatively slower process of gradual adsorption. Due to the decrease in the number of Hg ions in the solution as well as active sites on the adsorbent surface. It is directly related to the equilibrium and saturation conditions which require more than 60 min. Accordingly, 60 min. contact time was selected as the optimum contact time in this study. The third and final stage which shows the attainment of equilibrium is the slowest.

The solution pH is a crucial parameter that affects directly the degree of ionization, the solubility of metal ion, and the adsorbents properties [47]. Fig. 3c shows the extent of Hg(II) adsorption versus pH. The efficiency of Hg(II) adsorption increases with the solution pH at the low pH. The optimum removal efficiency was accomplished at pH 2, then it decreases with increasing the pH values. The adsorption process is linked with the equilibrium because of the difference in the thermodynamic equilibrium for each adsorbate-adsorbent interaction.

When Fe$_3$O$_4$ nanoparticles are present on MWCNTs surface, the adsorption efficiency increases as confirmed by previous studies [48]. Several mechanisms have been proposed to explain the role of MWCNTs-Fe$_3$O$_4$ for the adsorption of Hg(II). These mechanisms include complex formation, electrostatic attraction, physical adsorption, and chemical interaction between
Hg(II) ions with the functional groups of MWCNTs-Fe$_3$O$_4$. However, complex formation and electrostatic attraction between Hg(II) ions and the functional groups of MWCNTs-Fe$_3$O$_4$ are the most acceptable mechanisms.

The initial ion concentration is another remarkable parameter that affects the adsorption mechanism. In this paper, we studied the effect of different Hg(II) initial concentration (from 10 to 50 mg L$^{-1}$), on the adsorption capacity using MWCNTs-Fe$_3$O$_4$. According to Fig. 3d, the adsorption of Hg(II) was gradually increased from 249 to 266 mg g$^{-1}$ at the surface of MWCNTs-Fe$_3$O$_4$. This confirms that MWCNTs-Fe$_3$O$_4$ surface has an affinity for Hg(II) ions absorbance due to its small particles sizes and high surface area. The maximum adsorption capacity of Hg(II) was 50 mg g$^{-1}$ using MWCNTs-Fe$_3$O$_4$ adsorbent.
Fig. 3 Effect of (a) adsorbent dosage (20 mg L\(^{-1}\), natural pH, 2 h, 25 \(^{\circ}\)C), (b) contact time (20 mg L\(^{-1}\), 10 mg, natural pH, 25 \(^{\circ}\)C) (c) pH (20 mg L\(^{-1}\), 10 mg, 60 min., 25 \(^{\circ}\)C) and (d) initial concentration (10 mg, 60 min, pH 2 and 25 \(^{\circ}\)C). The solid lines are the linear fits.

3.3 Adsorption Isotherms

Adsorption isotherms were used to describe the interactive behavior between the adsorbates and adsorbents. To estimate the maximum adsorption capacity \(Q_{\text{max}}\) (mg g\(^{-1}\)), the equilibrium data were fitted using Langmuir and Freundlich models [49, 50]. The mathematical forms of these models are given by Eqs. 2 and 3, respectively.
\[
\frac{C_e}{Q_e} = \frac{1}{Q_{max}} K_L + \frac{C_e}{Q_{max}}
\]

(2)

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

(3)

where \( Q_e \) is the adsorbate equilibrium amount in solid phases (mg g\(^{-1}\)), \( K_L \) is Langmuir constant (L mg\(^{-1}\)); \( K_F \) (mg g\(^{-1}\))(L mg\(^{-1}\))\(^{1/n} \) and \( n \) are Freundlich constants due to adsorption capacity and adsorption intensity, respectively. \( Q_{max} \) and \( K_L \) can be calculated from the linear plot of \(1/Q_e\) versus \(1/C_e\) as shown in Fig. 4a. \( K_F \) and \(1/n\) values can be calculated from the intercept and slope of the linear \(\log Q_e \) versus \(\log C_e \) plot as shown in Fig. 4b. The type of isotherm can be determined according to the value of \(1/n\). Irreversible isotherm can be determined at \((1/n = 0)\). Favorable isotherm can be determined at \((0 < 1/n < 1)\). Unfavorable isotherm can be determined at \((1/n > 1)\) [49].

The linear form of Temkin model was utilized to depict adsorbate-adsorbent connection. The model is represented as Eq. (4) [10, 51]:

\[
Q_e = \frac{RT}{2.303 B_T} \log K_T + \frac{RT}{2.303 B_T} \log C_e
\]

(4)

where, \( R \) is the gas constant (8.314 J mol\(^{-1}\) K) and \( T \) (K) is the absolute temperature, \( B_T \) and \( K_T \) are Temkin constants. In addition, Harkin-Jura model represented by Eq. (5) [10, 52] was also applied to fit the experimental data.
\[
\frac{1}{Q_c^2} = \frac{B_{HJ}}{A_{HJ}} - \frac{1}{A_{HJ}} \log C_e
\]

(5)

where \(A_{HJ}\) and \(B_{HJ}\) are Harkins-Jura constants. The results of Temkin and Harkin-Jura models are shown in Fig. 4c and d, respectively.

Langmuir isotherm fits better with experimental data which indicates that the adsorbents surfaces are formed from heterogeneous adsorption patches [13] besides less homogeneous patches [53]. Based on the obtained results, the MWCNTs-Fe₃O₄ surface has better adsorption efficiency for Hg(II) ions. The favorability of the Hg(II) ions adsorption was evaluated using a dimensionless parameter (R_L) as given by Eq. (6):

\[
R_L = \frac{1}{1 + K_L Q_{max}}
\]

(6)

Based on the values of R_L the adsorption process can be irreversible (R_L = 0), favorable (0 < R_L < 1), linear (R_L = 1), or unfavorable (R_L > 1) [54, 55]. The calculated R_L values for the adsorption of Hg(II) ion using MWCNTs-Fe₃O₄ surface is 0.01, therefore, the Hg(II) adsorption onto adsorbent is favorable. The adsorption capacity of MWCNTs-Fe₃O₄ was 238.78 mg g⁻¹, as calculated by Langmuir equation. Table 1 lists all the isotherm models parameters obtained from the above four models. In addition, Table 2 shows a comparison of the adsorption capacity of the MWCNTs-Fe₃O₄ adsorbent with some recent mercury adsorbents based on iron and carbon nanotubes. MWCNTs-Fe₃O₄ has better adsorption capacity for Hg(II) than other adsorbents. These high findings are a result of surface functional groups, high surface area, and high porosity corresponded to the superb adsorption capacity and improved adsorption kinetics. This result
suggests the potential of MWCNTs-Fe$_3$O$_4$ be utilized as a successful adsorbent for the removal of Hg(II) ions in waste/water treatment applications.

**Fig. 4** Adsorption isotherms for Hg(II) on MWCNTs-Fe$_3$O$_4$ nanocomposite (a) Freundlich, (b) Langmuir, (c) Temkin and (d) Harkin-Jura. The solid lines are the linear fits.
Table 1  Fitting parameters of Hg(II) adsorption experimental data to Langmuir, Freundlich, Temkin and Harkin-Jura equations.

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameters</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$ Q_{\text{max}} = 238.78 \text{ mg g}^{-1} $</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$ K_L = 2.81 \text{ L mg}^{-1} $</td>
<td>0.9999</td>
</tr>
<tr>
<td></td>
<td>$ R_L = 0.002 $</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$ 1/n = 0.43 $</td>
<td></td>
</tr>
<tr>
<td>Freundlich</td>
<td>$ K_F = 216.76 \text{ mg g}^{-1} (L \text{ mg}^{-1})^{1/n} $</td>
<td>0.9881</td>
</tr>
<tr>
<td></td>
<td>$ B_T = 89.46 \text{ J mol}^{-1} $</td>
<td></td>
</tr>
<tr>
<td>Temkin</td>
<td>$ K_T = 1.21 \text{ L g}^{-1} $</td>
<td>0.9867</td>
</tr>
<tr>
<td>Harkin-Jura</td>
<td>$ A_{HJ} = 490.58 \text{ mg}^{2} \text{ g}^{-2} \text{ L}^{-1} $</td>
<td>0.9904</td>
</tr>
<tr>
<td></td>
<td>$ B_{HJ} = 0.01 \text{ mg L}^{-1} $</td>
<td></td>
</tr>
</tbody>
</table>
Table 2 Comparison of Hg(II) adsorption capacities using some related nanocomposites adsorbents together with their surface area values.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorption capacity (mg g⁻¹)</th>
<th>Surface area (m² g⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoFe₂O₄ coated with polystyrene</td>
<td>84.30</td>
<td>0.71</td>
<td>[56]</td>
</tr>
<tr>
<td>Fe₃O₄@SiO₂-SH nanocomposite</td>
<td>133.30</td>
<td>-----</td>
<td>[57]</td>
</tr>
<tr>
<td>Polyrhodanine-coated γ-Fe₂O₃</td>
<td>179.00</td>
<td>94.65</td>
<td>[58]</td>
</tr>
<tr>
<td>Magnetic FeS nanoparticles</td>
<td>132.00</td>
<td>21.30</td>
<td>[59]</td>
</tr>
<tr>
<td>Nanoporous carbon impregnated with surfactants</td>
<td>8.10</td>
<td>1193.90</td>
<td>[60]</td>
</tr>
<tr>
<td></td>
<td>8.90</td>
<td>1198.40</td>
<td></td>
</tr>
<tr>
<td>SWCNTs-SH</td>
<td>131.00</td>
<td>-----</td>
<td>[61]</td>
</tr>
<tr>
<td>SWCNTs</td>
<td>40.16</td>
<td>-----</td>
<td></td>
</tr>
<tr>
<td>MWCNTs</td>
<td>0.70 - 3.83</td>
<td>-----</td>
<td>[62]</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>100.00</td>
<td>-----</td>
<td>[63]</td>
</tr>
<tr>
<td>MWCNTs-Amidoamine</td>
<td>101.35</td>
<td>150.00</td>
<td>[46]</td>
</tr>
</tbody>
</table>
MWCNTs with amino and thiol groups 84.66 110.00 [64]

MWCNTs-Fe$_3$O$_4$ 238.78 92.00 This work

3.4 Adsorption Kinetics

To study the rate of the adsorption process different kinetic models were applied such as pseudo-first-order, pseudo-second-order, intraparticle diffusion and simple Elovich to interpret the experimental data [11, 21, 65, 66]. A linear form of pseudo-first-order model could be given as:

$$\log(Q_e - Q_t) = \log Q_e - \frac{K_1}{2.303} t$$

(7)

where, $Q_e$ and $Q_t$ are the amounts of ion adsorbed (mg g$^{-1}$) at equilibrium and time $t$, respectively. $K_1$ is the equilibrium rate constant (min$^{-1}$). The linear fit between the log ($Q_e$-$Q_t$) and $t$ is shown in Fig. 5a.

Eq. (8) represents the linear form of pseudo-second-order model [67, 68]:

$$\frac{t}{Q_t} = \frac{1}{K_2Q_e^2} + \frac{1}{Q_e} t$$

(8)

where $K_2$ is pseudo-second-order equilibrium constant (g mg$^{-1}$ min$^{-1}$). The linear fit between the $t/Q_t$ and $t$ can be seen in Fig. 5b.

The possible effect due to the intraparticle diffusion resistance on the adsorption was explored using the following model [69]:

$$Q_t = K_Dt^{1/2} + D$$

(9)

where, $K_D$ is the intraparticle diffusion rate constant and $D$ is the intercept which is related to the
thickness of the boundary layer. According to this model, when intraparticle diffusion is involved in the adsorption process, the plot should be linear and the intraparticle diffusion is the rate determining step if the line pass through the origin [20]. The relation between \( Q_t \) and square root of \( t \) is shown in Fig. 5c.

The simple Elovich model is expressed by Eq. (10) [10, 70]:

\[
Q_t = K_E + \frac{\beta}{2.303} \log t
\]

(10)

where \( K_E \) represents the rate of chemisorption at zero coverage (mg g\(^{-1}\) min\(^{-1}\)) and \( \beta \) is related to the extent of surface coverage and activation energy for chemisorption (g mg\(^{-1}\)). When \( Q_t \) is plotted against \( \log t \), a linear relation is obtained as shown in Fig. 5d.

Table 3 shows the kinetic parameters obtained from the experimental data fitting using the above-mentioned equations. According to Table 3, the perfect fitting and the high value of correlation coefficients (>0.999), confirms that the adsorption process follows, with good correlation, the pseudo-second-order model. This suggests that chemisorption is the rate-determining step for Hg(II) ion onto MWCNTs-Fe\(_3\)O\(_4\), where valency forces are involved because of the electrons sharing or exchange between Fe\(_3\)O\(_4\) nanoparticles and Hg(II) ions [71].
Fig. 5 Kinetic plots: (a) pseudo-first-order, (b) pseudo-second-order, (c) intraparticle diffusion and (d) simple Elovich models for Hg(II) adsorption on MWCNTs-Fe₃O₄ nanocomposite. The solid lines are the linear fits.
Table 3 The kinetic parameters of Hg(II) adsorption by MWCNTs-Fe₃O₄.

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameters</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first-order</td>
<td>Qₑ = 61.901 mg g⁻¹</td>
<td>0.9745</td>
</tr>
<tr>
<td></td>
<td>K₁ = 0.030 min⁻¹</td>
<td></td>
</tr>
<tr>
<td>Pseudo-second-order</td>
<td>Qₑ = 270.270 mg g⁻¹</td>
<td>0.9990</td>
</tr>
<tr>
<td></td>
<td>K₂ = 0.002 g mg⁻¹ min⁻¹</td>
<td></td>
</tr>
<tr>
<td>Intraparticle diffusion</td>
<td>Kᵰ = 7.328 mg⁻¹ min⁻¹/²</td>
<td>0.9982</td>
</tr>
<tr>
<td></td>
<td>D = 203.730 mg g⁻¹</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Kₑ = 2.278 mg⁻¹ min⁻¹</td>
<td></td>
</tr>
<tr>
<td>Simple Elovich</td>
<td>β = 0.175 g mg⁻¹</td>
<td>0.9804</td>
</tr>
</tbody>
</table>

4. Conclusions

Magnetic carbon nanotubes composite (MWCNTs-Fe₃O₄) was synthesized and efficiently used for the adsorption of Hg(II) ions from aqueous solutions. The adsorption capacity depends on the adsorbent dosage, contact time, pH and initial metal ion concentration. The calculated adsorption parameters and the equilibrium data were best fitted by Langmuir model giving a maximum adsorption capacity of 238.78 mg g⁻¹. The adsorption process was studied kinetically and the results were analyzed by pseudo-first-order, pseudo-second-order, intraparticle diffusion and simple Elovich models. Pseudo-second-order was found to be the best correlation model...
based on the values of the correlation coefficient ($R^2$). This result suggests that MWCNTs-Fe$_3$O$_4$ prepared in this study could be a promising adsorbent for the removal of Hg(II) ions in waste/water treatment and environmental management applications, in terms of high efficiency and feasibility.

Acknowledgements

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References


Highlights

- MWCNTs-Fe$_3$O$_4$ nanocomposite was successfully prepared and characterized.
- MWCNTs-Fe$_3$O$_4$ showed suburb adsorption performance toward Hg(II).
- MWCNTs-Fe$_3$O$_4$ showed high Hg(II) adsorption capacity of 238.78 mg g$^{-1}$.
- The results recommend the successful application of MWCNTs-Fe$_3$O$_4$ for Hg(II) removal.

Graphical Abstract