

## Kinetic and Equilibrium Study of Lead (II) Removal by Functionalized Multiwalled Carbon Nanotubes with Isatin Derivative from Aqueous Solutions

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The carboxylated multiwall carbon nanotubes (MWCNT-COOH) and functionalized with isatin derivative (MWCNT-isatin) have been used as efficient adsorbents for the removal of lead (Pb) from aqueous solutions. The influence of variables including pH, concentration of the lead, amount of adsorbents and contact time was investigated by the batch method. The adsorption of the lead ions from aqueous solution by modified MWCNTs was studied kinetically using different kinetic models. The kinetic data were fitted with pseudo-first-order, pseudo-second-order, and intra-particle diffusion models. The sorption process with MWCNT-COOH and MWCNT-isatin was well described by pseudo-second-order and pseudo-first-order kinetics, respectively which it was agreed well with the experimental data. Also, it involved the particle-diffusion mechanism. The values of regression coefficient of various adsorption isotherm models like Langmuir, Freundlich and Tempkin to obtain the characteristic parameters of each model have been carried out. The Langmuir isotherm was found to best represent the measured sorption data for both adsorbent.

**Key Words :** Carbon nanotubes, Functionalization, Sorption, Equilibrium, Kinetics

### Introduction

Lead is ubiquitous in the environment and is hazardous at high levels. The Long-term presence of lead in drinking water can cause anemia, headache, chills, diarrhea and poisoning leading to the dysfunction of kidneys, reproductive system, liver, brain and central nervous system.<sup>1</sup> Unlike organic compounds, lead is non-biodegradable and, therefore, more stringent requirements for the removal of lead from wastewaters before release into the environment are required.<sup>2</sup>

So far, various technologies have been used for the remove of metal ions, including filtration, chemical precipitation, ion exchange, adsorption and membrane processing. However, among all the methods adsorption as one of the major methods has been extensively employed for the removal of heavy metal ions from solution. The advantage of this technics over other methods is that it is generally easy to handle, can be regenerated by suitable desorption process, is economical and can be used for various situations without large apparatus.<sup>3</sup> Many kinds of adsorbents, such as activated carbon,<sup>4</sup> zeolite<sup>5</sup> and resins<sup>6</sup> have been developed for the removal of heavy metal from water. However, these adsorbents suffer from low adsorption capacities or removal efficiencies of metal ions. Therefore, researchers have carried out investigations on exploiting the use of nanomaterial as adsorbents for purification of water.<sup>7</sup>

The hollow cylindrical structures made of carbon atoms, which carbon nanotubes (CNTs) are introduced, because of high specific surface area and light mass density has attracted great attention as adsorbents.<sup>8</sup> CNTs are mainly divided into two types depending on the layers involved in them: single walled (SWCNTs) and multiwalled carbon nanotubes

(MWCNTs). Multiwalled carbon nanotubes (MWCNTs) are more attractive than single walled carbon nanotubes because of their relatively low production costs and availability in large quantities.

CNTs as superior sorbents are found efficient for removal of various types of contaminants such as metal ions,<sup>9</sup> phenols,<sup>10</sup> dyes,<sup>11</sup> aniline,<sup>12</sup> drugs,<sup>13</sup> and many other chemicals.<sup>14</sup> This superior ability of CNTs to bind pollutants comes from strong interaction with the pollutants as a result of the electrons delocalized on the hexagonal arrays of carbon atoms on the surface of CNTs. On the other hand, less surface functional groups mainly restrict the application of CNTs as adsorbent.<sup>15</sup> Thus, surface functionalization is essentiality. In fact, the functionalization of CNTs can significantly enhance the adsorption capacity after functional groups (such as amino, hydroxyl, amide and carbonyl groups) are introduced on adsorbent surfaces.<sup>15,16</sup>

However, although there are many studies concerning the applicability of using CNTs as adsorbents for various types of pollutants<sup>9-15</sup> and lead ions,<sup>17-23</sup> only a few reports on functionalized CNTs have been presented.<sup>23</sup> Therefore, we decided to improve this work. In this current study, we firstly have investigated the functionalization of MWCNT-COOH with isatin derivative, 3-(2-amino-1-methyl-4-oxo-4,5-dihydro-1H-imidazol-5-yl)-3-hydroxyindolin-2-one (MWCNT-isatin), which was characterized by Fourier transform infrared spectroscopy (FT-IR), Raman, scanning electron microscope (SEM) and thermo gravimetric analysis (TGA). Then, MWCNTs-isatin was used as an efficient adsorbent for the removal of lead ions. Also, the kinetic and equilibrium of the adsorption process was investigated, and experimental data were analyzed to get a sufficient knowledge on the mechanism,

rate, and isotherm of the adsorption process. In other words, the aim of this paper was to compare MWCNT-COOH and MWCNT-isatin as adsorbent for removal of lead ions from aqueous solution.

## Experimental

**Materials and Characterizations.** All reagents and solvents (thionyl chloride, tetrahydrofuran (THF), dimethylsulfoxide (DMSO), creatinine and isatin) from Merck Chemical Inc. and MWCNTs-COOH (95% purity, OD: 10-20 nm, Length: 0.5-2  $\mu\text{m}$ , Neutrino Co., Ltd) were purchased and used as received. 3-(2-amino-1-methyl-4-oxo-4,5-dihydro-1*H*-imidazol-5-yl)-3-hydroxyindolin-2-one are prepared from the reaction creatinine with isatin.<sup>24</sup> FT-IR spectrum was recorded using KBr tablets on a Thermo Nicolet Nexus 870 FTIR spectrometer. Raman spectra recorded on Almega Thermo Nicolet Dispersive Raman Spectrometer (532 nm of an Nd: YLF laser). FE-SEM was used to study the morphology of the MWCNTs. FE-SEM measurement was carried out on the Hitachi S4160 (Cold Field Emission) Electron Microscope. The samples investigated by thermogravimetric analysis (NETZSCH TG 209 F1 Iris) in the  $\text{N}_2$  (10  $^\circ\text{C}/\text{min}$ ). Analytical reagent-grade chemicals were used as well as deionized water from a Milli-Q system (Millipore). The concentration of metals was performed by atomic absorption spectrometry using a Thermo Electron Corporation M series.

**Preparation of MWCNT-isatin:** 250 mg of the MWCNT-COOH were suspended in 30 mL  $\text{SOCl}_2$  and 1 mL DMF. The mixture was then stirred at 70  $^\circ\text{C}$  for 48 h under reflux. Subsequently, the residual  $\text{SOCl}_2$  was removed by reduced pressure distillation to yield the acylchloride-functionalized MWCNT (MWCNT-COCl). 200 mg of MWCNT-COCl were mixed with 400 mg of isatin derivative in 40 mL DMSO and the reaction mixture was stirred at 100  $^\circ\text{C}$  for 96 h. Then, the mixture was cooled to room temperature, filtered and washed thoroughly with DMF, ethyl alcohol and THF. Subsequently, the black solid was dried at room temperature for 8 h under vacuum condition. The procedure for the functionalization of MWCNT-COOH was shown in Figure 1.

**Preparation of Pb(II) Stock Solution:** Analytical grade lead nitrate (Merck, Ion Standard Solution, 1000 mg/L) were employed to prepare stock solutions each containing 100 mg/L of Pb(II). The stock solutions were further diluted with deionized water to the required Pb(II) concentrations in the adsorption experiments.

**Batch Sorption Experiments:** To study the effects of pH on the sorption of lead ions, 30 mg of a given carbon

material was dispersed into 10 mL solutions containing 50 mg/L of lead ion. The initial pH values were adjusted from 1.0 to 7.0 using nitric acid and the suspensions were shaken for 5 h at  $25 \pm 1$   $^\circ\text{C}$ . The amounts of sorbed lead ions were calculated as the difference between the initial and final concentrations when the equilibrium was reached. The results are based on at least three replicate experiments for each pH value.

To estimate the sorption capacity, 30 mg of the appropriate sorbent was mixed with 10 mL of lead ion solution (concentration range 20-100 mg/L). After shaking for 5 h ( $25 \pm 1$   $^\circ\text{C}$ ), the lead concentration in the aqueous solutions was determined by atomic absorption spectrophotometer. The adsorption (%) and sorption capacity  $q$  (mg/g) was obtained as follows:

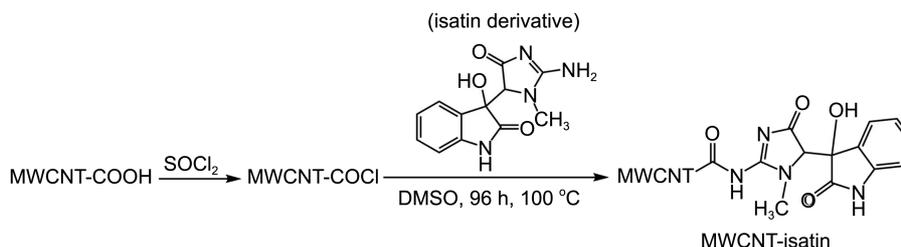
$$\text{Removal\%} = \frac{C_0 - C_e}{C_0} \times 100\% \quad q_e = \frac{(C_0 - C_e) \times V}{m}$$

where  $C_0$  and  $C_e$  are the initial and final concentrations (mg/L) of metal ions in the aqueous solution, respectively,  $V$  (L) is the volume of metal ion solution, and  $m$  (g) is the weight of sorbent. The experiments were performed in duplicate for more precision. The kinetic data were analyzed using three kinetic models to gain an understanding of the sorption process.

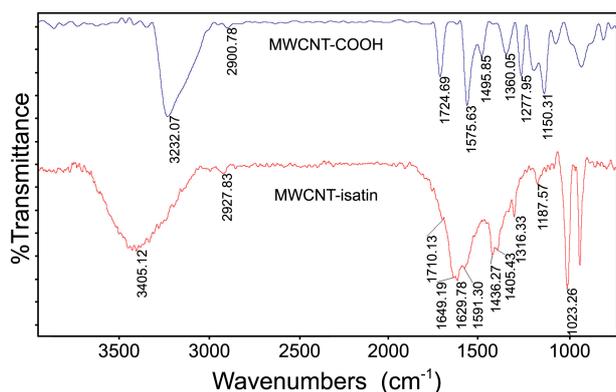
**Kinetic Experiments:** The kinetic experiment was carried out under normal atmospheric conditions at 298 K. Initially, 30 mg of MWCNTs contacted with 10 mL solution containing 50 mg  $\text{L}^{-1}$  lead (II) concentration in glass vials and agitated in isothermal water. Adsorbent and solution were separated at predetermined time intervals, filtered using a 0.45  $\mu\text{m}$  membrane filter and analyzed for residual lead (II) concentrations as described in the previous section.

## Results and Discussion

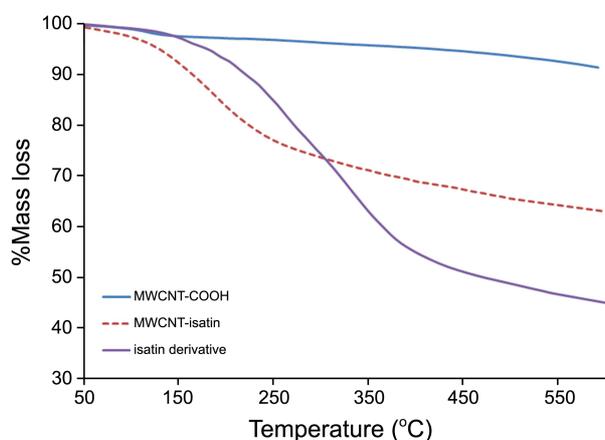
**Characterization of MWCNT-isatin.** The MWCNT-isatin was characterized by FESEM, FTIR, TGA, and Raman spectroscopy. Figure 2 presents the FT-IR spectrum of modified MWCNTs. In MWCNT-COOH, the peak at 1575  $\text{cm}^{-1}$  is assigned to C=C stretching mode of MWCNT-COOH that forms the framework of CNTs sidewall.<sup>25,26</sup> The appearance of absorption peaks at 1724(C=O) and 1150(C-O)  $\text{cm}^{-1}$  in IR spectra of MWCNT-COOH clearly indicates carboxylic groups on the MWCNTs.<sup>25,26</sup> The two bands at around 2800-3000 which seen in two spectra can be related to C-H stretching of MWCNTs defects. In the spectrum of MWCNT-isatin, the new peaks at 1710, 1649, 1629 and



**Figure 1.** Synthesis route of modified MWCNT-COOH.



**Figure 2.** FT-IR spectra (after baseline correction) of modified MWCNTs.

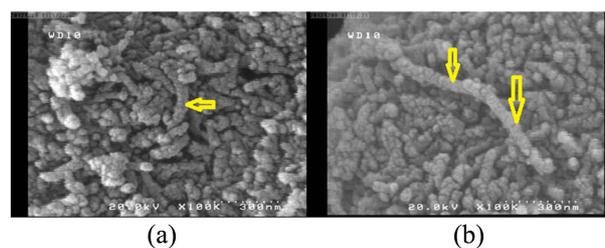


**Figure 3.** TGA curve of modified MWCNTs in the N<sub>2</sub> (10 °C/min).

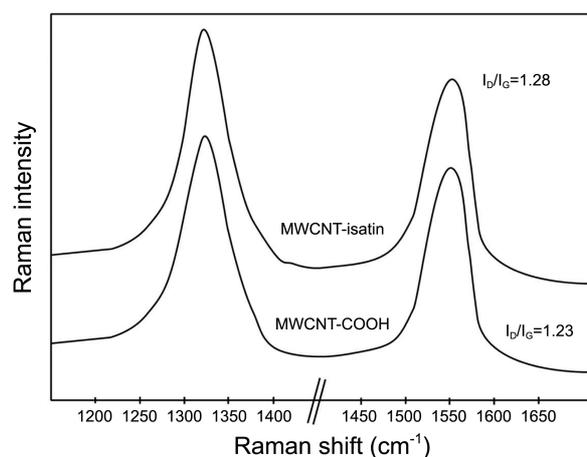
1023 cm<sup>-1</sup> can be assigned to C=O of creatinine, amide groups (C(=O)NH linkage), C=O and C-OH of isatin, respectively, (as compared to 1724 cm<sup>-1</sup> for MWCNTs-COOH) which confirmed the formation of MWCNT-isatin. Also, in spectra of MWCNT-isatin the peaks at around 3100-3500, 1450-1600, 1200-1400 and 1000-1180 cm<sup>-1</sup> correspond to N-H or OH stretching mode, C=C nanotube and aromatic ring modes, C-N and C-O stretching modes, respectively. Thus, FT-IR spectra confirm that MWCNT-COOH has been successfully modified by isatin derivative.

The best evidence for the functionalization of MWCNTs is thermogravimetric analysis (TGA) results that provide quantitative information on the nanotube functionalization. Since MWCNT-COOH are almost thermally stable as shown in Figure 3, the weight loss before MWCNTs decomposition can be used to estimate the quantity of various groups attached to nanotube. According to Figure 3, MWCNT-isatin sample exhibit one major decomposition at around 120-320 °C with a weight loss about 23.41% which were assigned to decomposition of the attached isatin derivative (as compared with TGA curve of isatin derivative). Overall, these results successfully confirm the functionalization of MWCNT-COOH with this compound.

More evidence for the functionalization of MWCNTs was obtained by FE-SEM images. In Figure 4, FE-SEM images



**Figure 4.** The SEM images of (a) MWCNT-COOH and (b) MWCNT-isatin. The yellow arrows in MWCNT-isatin show a slightly increase in thickness on the surface of tubes respect to MWCNT-COOH.



**Figure 5.** The raman spectra of modified MWCNTs. The baseline was corrected for the luminescence background.

of modified MWCNTs are shown. In SEM image of MWCNT-COOH, it seems that the uniform surfaces of nanotubes are relatively smooth. On the other hand, for the MWCNT-Amide a tubular layer of uniform organic compounds (isatin derivative) is clearly present on the MWCNT surface (the rough part) and their diameters are slightly increased as compared to that of MWCNT-COOH. It may be due to covalently bonded isatin derivative on the surface of the MWCNT as compared to that of MWNT-COOH.

The Raman spectra of MWCNT-isatin (Figure 5) showed a slight increase of the D-band at ~1330 cm<sup>-1</sup>, which is attributed to the defects and disorder-induced peaks, relative to the G-band (~1560 cm<sup>-1</sup>), which originates from the in-plane tangential stretching mode of carbon-carbon bonds,<sup>27</sup> ( $I_D/I_G = 1.28$ ) in comparing to MWCNT-COOH ( $I_D/I_G = 1.23$ ). These results (approximately equal 1.23~1.28) indicate which the reactions do not affect on the graphite structure of MWCNT-COOH.<sup>25,26</sup>

**Sorption Kinetics.** Kinetic models are used to examine the rate of the adsorption process and rate-controlling step. There are several kinetic models are being used to simulate the sorption of heavy metals.<sup>22</sup> The modeling of sorption kinetics of lead (II) on MWCNTs was investigated using three models, namely the pseudo-first-order Lagergren model,<sup>29</sup> pseudo-second-order model<sup>30</sup> and Weber-Morris intra-particle diffusion model.<sup>31</sup> Lagergren proposed a method for sorption analysis which is pseudo-first order kinetic equation<sup>29,32</sup> in

**Table 1.** Parameters of pseudo-first-order, pseudo-second-order, and intra-particle diffusion models for lead sorption onto modified MWCNTs. Temperature, 298 K; initial lead concentration, 50 mg L<sup>-1</sup>; mass of MWCNTs, 30 mg; volume of solution, 10 mL; and pH of the sample solution, 7.0

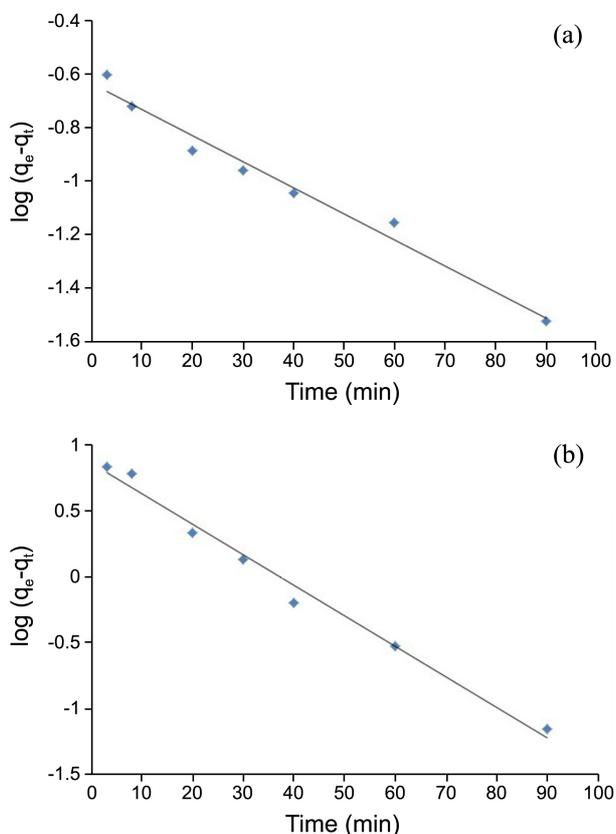
|              | $q_{e,exp}$<br>(mg/g) | Pseudo-first-order model      |                 |                | Pseudo-second-order model                        |                 |                | Intra-particle diffusion model                        |                |
|--------------|-----------------------|-------------------------------|-----------------|----------------|--|-----------------|----------------|---|----------------|
|              |                       | $k_1$<br>(min <sup>-1</sup> ) | $q_e$<br>(mg/g) | R <sup>2</sup> | $K_2$<br>(g mg <sup>-1</sup> min <sup>-1</sup> ) | $q_e$<br>(mg/g) | R <sup>2</sup> | $K_{id}$<br>(mg g <sup>-1</sup> min <sup>-0.5</sup> ) | R <sup>2</sup> |
| MWCNT-COOH   | 16.63                 | 0.0223                        | 0.231           | 0.9766         | 0.3954   | 16.67           | 1.0000         | 0.0252  | 0.9578         |
| MWCNT-isatin | 3.64                  | 0.0532                        | 7.28            | 0.9868         | 0.0124   | 13.91           | 0.9978         | 1.624   | 0.9603         |

the linear form:

$$\log(q_e - q_t) = \log(q_e) - k_1/2.303 t$$

The values of  $\log(q_e - q_t)$  versus  $t$  can be plotted to give a linear relationship which  $k_1$  and  $q_e$  can be determined from its slope and intercept which these values are presented in Table 1 along with corresponding correlation coefficient. If the intercept does not equal  $q_e$  then the reaction is not likely to be a first-order reaction even though this plot has a high correlation coefficient with the experimental data.<sup>33</sup> As shown in Figure 6(a), the plots of MWCNT-COOH were not found linear, indicating that Lagergren's equation is not applicable to lead sorption on MWCNTs. Also, it can be seen from Table 1 that there is no agreement between  $q_{e,exp}$  experimental and  $q_e$  calculated values for the pseudo-first-order model.

The plot of MWCNT-isatin (Figure 6(b)) show which the

**Figure 6.** Linearized pseudo-first-order kinetic model of lead (II) sorption onto MWCNT-COOH (a) and MWCNT-isatin (b).

obtained results ( $R^2$  and  $q_e$ ) are better than MWCNT-COOH data. In Table 1, it indicates that the calculated  $q_e$  value is mainly near to the experimental data. So, the sorption process for MWCNT-COOH is not a pseudo-first order process but it for MWCNT-isatin obeys from this model.

The pseudo-second-order kinetics may be expressed as given in linear form<sup>30</sup>:

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

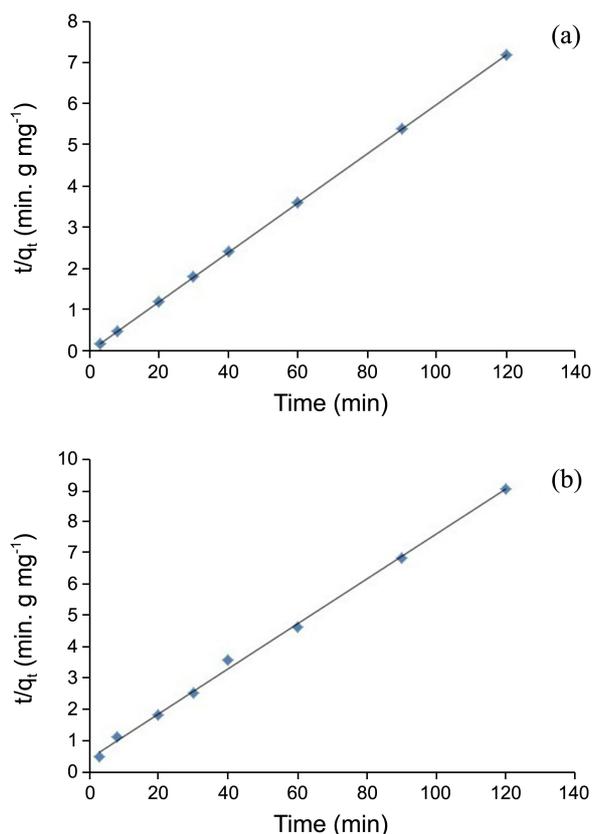
where  $k_2$  (g/(mg min)) is the rate constant of sorption, other terms has already been defined.  $k_2$  and  $q_e$  values can be estimated experimentally from the slope and intercept of plot  $t/q_t$  versus  $t$  as shown in Figure 7(a)-(b) and are presented in Table 1 along with the corresponding regression correlation coefficient ( $R^2$ ).

As it is obvious from Table 1,  $R^2$  values of MWCNT-COOH and MWCNT-isatin for the pseudo-second-order kinetic model is much higher than that for pseudo-first-order kinetic model but only calculated  $q_e$  value of MWCNT-COOH agreed well with the experimental  $q_{e,exp}$  value. These results indicates that the sorption of lead from an aqueous solution onto MWCNT-COOH obeys the pseudo-second-order kinetic model and could be used to determine the equilibrium sorption capacity, rate constants, and percentage of lead removal.

In order to gain better understanding of the various mechanisms and rate controlling steps that affect the kinetics of adsorption, the kinetic data were fitted to Weber–Morris intra-particle diffusion model in order to elucidate the diffusion mechanism.<sup>31,32</sup> This model is expressed as follows:

$$q_t = k_{id} t^{1/2} + C_i$$

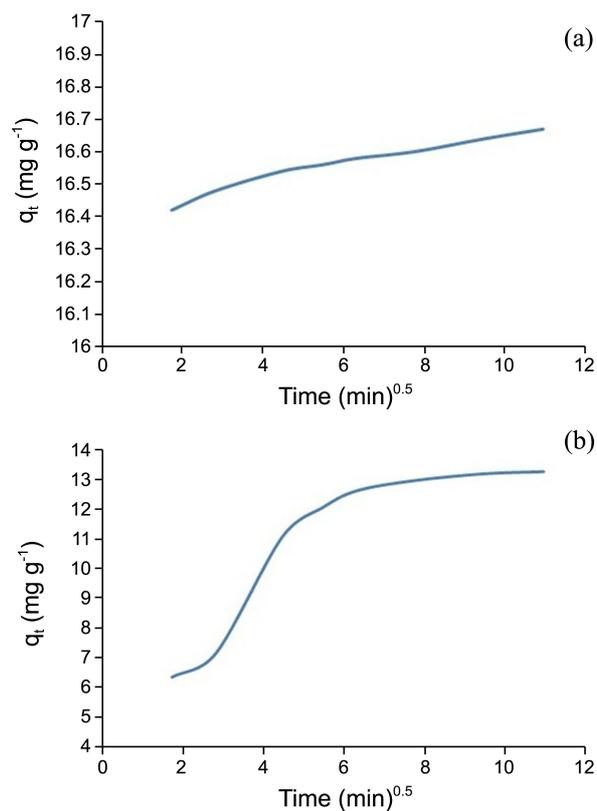
where  $k_{id}$  (mole g<sup>-1</sup> min<sup>1/2</sup>) is the intra-particle diffusion coefficient and  $C_i$  is proportional to the boundary layer thickness. When intra-particle diffusion plays a significant role in controlling the kinetics of the adsorption process, the plots of  $q_t$  versus  $t^{1/2}$  yields a straight line passing through the origin, and  $k_{id}$  can be calculated from the slope and  $C_i$  from the intercept. Figure 8 shows the plot of the amount of Pb(II) sorbed at equilibrium,  $q_t$  versus  $t^{1/2}$  for both MWCNTs. Although the correlation coefficients were approximately good, the deviation of straight line from the origin indicates that intra-particle diffusion is not the rate-limiting step of the sorption mechanism. Also, from plot of MWCNT-isatin it is



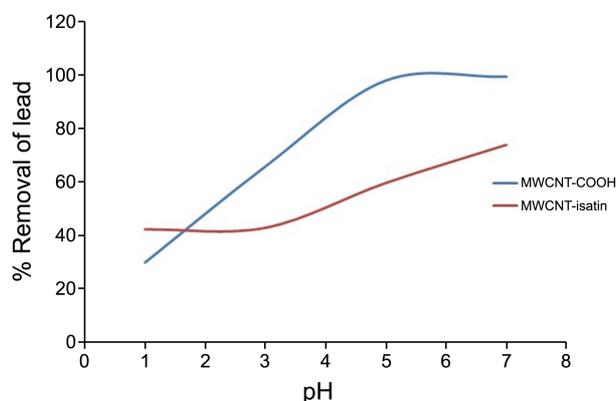
**Figure 7.** Linearized pseudo-second-order kinetic model of lead (II) sorption onto MWCNT-COOH (a) and MWCNT-isatin (b).

clear that intra-particle diffusion of Pb(II) within MWCNT-isatin occurred in two stages as the plot contains two different straight lines. The first stage (initial steep slope) from 0 to 30 min was attributed to the fast diffusion of the Pb(II) ions from the aqueous phase to the outer-surface of the solid MWCNTs. The second stage from 30 to 120 min exhibits a gradual attainment of equilibrium due to the intra-particle diffusion of the lead ions between the MWCNTs aggregates. Therefore, both the external surface sorption and intra-particle diffusion may contribute to the rate-limiting step during the process of Pb(II) uptake by MWCNTs. As shown in Figure 8, the sorption data follow linearity up to 30 min with correlation coefficient,  $R^2$ , of 0.9603.

**Effect of pH.** One of the most important parameters in the sorption behavior is pH effect, as it determines the surface charge of the adsorbent and degree of ionization and speciation of the adsorbents. Although adsorption studies were more significant in the neutral pH because of using in drinking water purification, we in this study have repeated the experiments in the range between 1.0 and 7.0 for the comparison purpose. Also, removal of Pb(II) was not studied in basic medium ( $\text{pH} > 7$ ) due to formation of  $\text{Pb}(\text{OH})_2$  which is insoluble. The effect of pH on Pb(II) sorption by the MWCNT-COOH and MWCNT-isatin is shown in Figure 9. In plot of MWCNT-COOH and MWCNT-isatin, the removal of lead ions increased with increasing pH and then for MWCNT-COOH reached almost a plateau value around pH 6.0. In other words, the removal of Pb(II) with MWCNT-

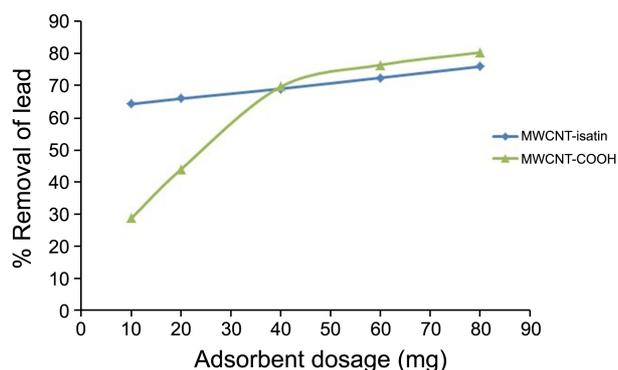


**Figure 8.** Linearized intra-particle diffusion kinetic model of lead (II) sorption onto MWCNT-COOH (a) and MWCNT-isatin (b).

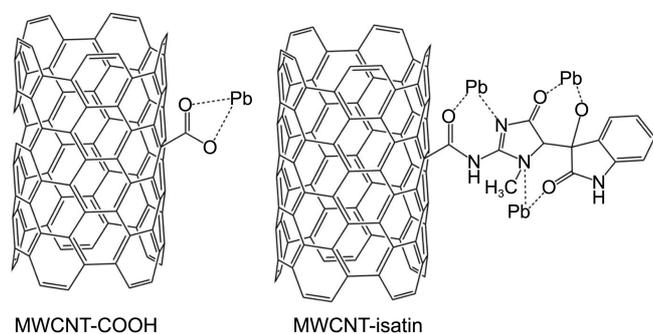


**Figure 9.** Effect of initial pH on lead sorption onto MWCNTs. Temperature 298, K.

COOH and MWCNT-isatin increased gradually from 29.8 to 99.4% and 42.2 to 73.9%, respectively when the pH increased from 1.0 to 7.0. At low pH values, the minimum adsorption observed that it can be related to the higher concentration and mobility of the hydronium ions ( $\text{H}^+$ ) which favored the preferential adsorption of hydrogen ions over lead ions. At higher pH, the surface of the CNTs was more negatively charged, which caused a greater electrostatic attraction of  $\text{Pb}^{2+}$ . Also, as can be seen in Figure 9, the effect of pH on Pb(II) sorption with MWCNT-COOH is more than the MWCNT-isatin. As mentioned above, in MWCNT-COOH with increasing pH, the negative charge density of carboxyl group increased and results in Pb(II) sorption. But,



**Figure 10.** Effect of MWCNT dosage on the adsorption of Pb(II) from aqueous solution (experimental conditions: pH 7; contact time, 5 hours; metal ion concentration, 100 mg/L).

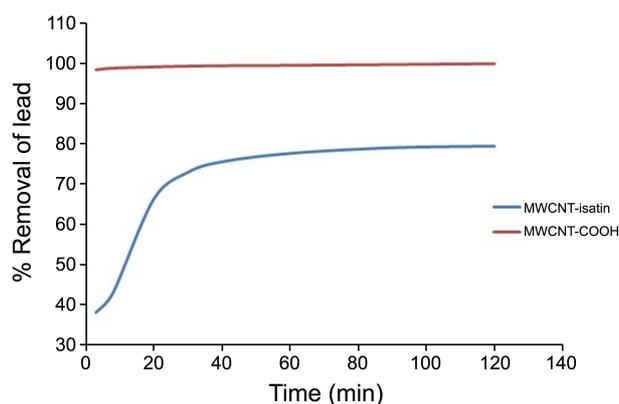


**Figure 11.** Proposed mechanism for sorption of Pb(II). In MWCNT-isatin, there are three possibility for Pb(II) sorption in comparing to one for MWCNT-COOH.

the functional groups of MWCNT-isatin slightly depend on pH values which this topic is observed in plot of MWCNT-isatin. In general, the results indicate that the adsorption was highly pH dependent.

**Effect of CNT Dosage.** The effect of modified MWCNTs dosage on the percentage of lead ions adsorbed from aqueous solution was studied at a lead ion concentration of 100 mg/L (Figure 10). The experimental results revealed that the adsorption capacities of Pb(II) increase with increasing MWCNT dosage and the contact time was kept as 5 h. Specifically, increasing the MWCNTs-COOH mass from 0.01 g to 0.08 g sharply enhanced the percentage adsorption of Pb(II) from 28.7 to 80.38% while for MWCNT-isatin it gradually increased the adsorption of Pb(II) from 64.3 to 76%. This may be attributed to the fact that increasing the adsorbent dose provides a greater surface area or more adsorption sites for the lead ions. Also, the interesting point is that in 0.01 g dosage, the highest Pb(II) sorption is obtained with MWCNT-isatin (64.3 as compared to 28.7 for MWCNT-COOH) which could be attributed to the number of functional groups of presence in MWCNT-isatin (Figure 11).

**Effect of Contact Time.** The effect of contact time on the adsorption of the Pb(II) is one-key factor affecting the removal of any pollutants from the environment via adsorption and the results were shown in Figure 12. It is noted that the adsorption percentage of lead ions increased remarkably at the beginning of the experiment and then reached equilibrium



**Figure 12.** Effect of contact time on the adsorption of Pb(II) from aqueous solution by modified MWCNTs (experimental conditions: pH = 7; MWCNTs mass, 30 mg/10 mL; metal ion concentration, 50 mg/L).

(60 min). The final value for the removal was found to be 99.8% (MWCNT-COOH) and 79.5% (MWCNT-isatin). The contact time for all other studies was kept as 2 h.

**Adsorption Isotherms.** An adsorption isotherm describes the sorption equilibrium of a material at a surface (more general at a surface boundary) at constant temperature. In other words, it indicates how the adsorbate molecules are distributed between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. In this study, three popular equilibrium isotherm models have been used to describe the equilibrium nature of adsorption, namely Langmuir isotherm model,<sup>34,35</sup> Freundlich isotherm model<sup>36</sup> and Tempkin<sup>37</sup> isotherm model.

Langmuir sorption model<sup>34,35</sup> is based on the assumption that the maximum sorption capacity corresponds to complete monolayer coverage of the molecules on the adsorbent surface, with no interaction between sorbed molecules. The Langmuir isotherm model assumes uniform energies of adsorption onto the surface without transmigration of adsorbate in the plane of the surface. Therefore, the Langmuir isotherm model was chosen for the estimation of the maximum adsorption capacity corresponding to complete monolayer coverage on the sorbent surface. The Langmuir equation for homogenous surface can be written as follows:

$$q_e = \frac{bq_m C_e}{1 + bC_e}$$

where  $q_e$  ( $\text{mg g}^{-1}$ ) and  $C_e$  ( $\text{mg L}^{-1}$ ) are the amount of sorbed lead per unit mass of adsorbent and lead concentration at equilibrium, respectively.  $q_m$  ( $\text{mg g}^{-1}$ ) is the maximum amount of the lead per unit mass of adsorbent to form a complete monolayer on the surface.  $b$  is the adsorption equilibrium constant ( $\text{L mg}^{-1}$ ) that is related to the apparent energy of sorption. The Langmuir isotherm parameters can be obtained from its linearized form and is presented in Table 2:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{1}{q_m} C_e$$

A plot of  $C_e/q_e$  versus  $C_e$  should indicate a straight line of

**Table 2.** Determined isotherm model constants for the adsorption of lead on MWCNT-COOH and MWCNT-isatin

| Adsorbent    | $C_0$ (mg/L) | Freundlich                          |      |        | Langmuir model |            |        |        | Tempkin model |        |        |
|--------------|--------------|-------------------------------------|------|--------|----------------|------------|--------|--------|---------------|--------|--------|
|              |              | $K_f$ (mg/g)<br>(mg/L) <sup>n</sup> | $n$  | $R^2$  | $q_m$ (mg/g)   | $b$ (L/mg) | $R_L$  | $R^2$  | $K_1$ (L/g)   | $K_2$  | $R^2$  |
| MWCNT-COOH   | 20           | 23.19                               | 6.49 | 0.9594 | 31.35          | 7.97       | 0.0062 | 0.9972 | 3.2901        | 1486.3 | 0.9747 |
|              | 40           |                                     |      |        |                |            | 0.0031 |        |               |        |        |
|              | 50           |                                     |      |        |                |            | 0.0025 |        |               |        |        |
|              | 60           |                                     |      |        |                |            | 0.0021 |        |               |        |        |
|              | 70           |                                     |      |        |                |            | 0.0018 |        |               |        |        |
|              | 100          |                                     |      |        |                |            | 0.0013 |        |               |        |        |
| MWCNT-isatin | 12           | 1.34                                | 4.23 | 0.6803 | 3.49           | 0.485      | 0.147  | 0.9722 | 0.6021        | 5.70   | 0.6272 |
|              | 40           |                                     |      |        |                |            | 0.049  |        |               |        |        |
|              | 50           |                                     |      |        |                |            | 0.040  |        |               |        |        |
|              | 60           |                                     |      |        |                |            | 0.033  |        |               |        |        |
|              | 70           |                                     |      |        |                |            | 0.029  |        |               |        |        |
|              | 100          |                                     |      |        |                |            | 0.020  |        |               |        |        |

slope  $1/q_m$  and an intercept of  $1/(bq_m)$ . The experimental data of Langmuir isotherm model indicates the homogeneous nature of modified-MWCNTs surface. The values of regression coefficient for both MWCNTs indicate that there is strong positive evidence that the adsorption of lead ions on MWCNTs follows the Langmuir isotherm. The results also demonstrate that adsorption is a monolayer process, and adsorption of all species requires equal activation energy.

The fact that the Langmuir isotherm fits the experimental data very well may be due to the homogeneous distribution of active sites on the MWCNTs surface, since the Langmuir equation assumes that the surface is homogeneous. Also, the closeness of experimental and theoretical adsorption capacity ( $q_e$ ) for MWCNT-isatin (3.64~3.49) indicate the suitability of this model for the evaluation and prediction of experimental data (Tables 1-2).

The essential characteristics of Langmuir isotherm can be expressed in terms of dimensionless equilibrium parameter or separation factor,  $R_L$ , as follows<sup>38</sup>:

$$R_L = \frac{1}{1 + bC_0}$$

where  $b$  is the Langmuir constant and  $C_0$  is the initial concentration of adsorbate in solution. The values of  $R_L$  indicate the type of isotherm to be irreversible ( $R_L = 0$ ), favorable ( $0 < R_L < 1$ ), linear ( $R_L = 1$ ) or unfavorable ( $R_L > 1$ ). The values of  $R_L$  for both adsorbents are listed in Table 2. The values of  $R_L$  in this work were found to be around 0.0013-0.0062 for MWCNT-COOH and 0.020-0.147 for MWCNT-isatin, indicating a favorable behavior toward lead adsorption.

The Freundlich isotherm model<sup>35,36</sup> is an empirical equation and used to describe heterogeneous surfaces. The Freundlich equation is:

$$q_e = K_F C_e^{1/n}$$

where  $K_F$  is an empirical constant related to the sorption capacity of the adsorbent ( $L \text{ mg}^{-1}$ )( $L \text{ g}^{-1}$ )<sup>1/n</sup> and constant  $n$  is an empirical parameter related to the intensity of sorption

and varies with surface heterogeneity and affinity. The linearized form of the Freundlich equation is

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e$$

The value of  $n$  gives an indication of the favorability of the sorption. By fitting the experimental data to the Freundlich equation, the value of  $k_f$  and  $n$  can be calculated by plotting  $\ln q_e$  versus  $\ln C_e$  and the results are represented in Table 2. The low correlation coefficients of MWCNT-COOH (0.95) and MWCNT-isatin (0.68) of this model show that this model is not suitable for the interpretation of experimental data. This implies that the Freundlich model could not represent the data reasonably well for both adsorbent. The Freundlich isotherm describes reversible adsorption and is not restricted to the formation of monolayer. This means that the assumption of multilayer adsorption is not in agreement with the experiment in the studied concentration range.

Tempkin<sup>37</sup> suggested that, because of the existence of adsorbent-adsorbate interactions, the heat of adsorption should decrease linearly with the surface coverage. The Tempkin isotherm equation assumes that the adsorption is characterized by a uniform distribution of the binding energies, up to some maximum binding energy. The corresponding adsorption isotherm can thus be adjusted by the following equation:

$$q_e = k_1 \ln(k_2) + k_1 \ln(C_e)$$

where  $k_1$  is related to the heat of adsorption ( $L/g$ ) and  $K_2$  is the dimensionless Tempkin isotherm constant. Tempkin parameters ( $k_1$  and  $k_2$ ) can be determined from the linear plots of  $q_e$  and  $\ln(C_e)$ . The values of Tempkin constant together with the regression coefficients are presented in Table 2 for the adsorption of lead ions on MWCNTs-COOH and MWCNTs-isatin. The low regression coefficients of MWCNTs-COOH and MWCNTs-isatin show the inapplicability of this model for interpreting Pb(II) adsorption onto modified MWCNTs.

In generally, analysis of  $R^2$  values from Table 2 shows that the Langmuir equation is found to best represent the equi-

librium data for adsorption of Pb(II) ions on both adsorbents.

### Conclusion

MWCNT-COOH and MWCNT-isatin was shown to be effective in removing lead from aqueous solution. Also, it determined which MWCNT-isatin has higher sorption capacity respect to MWCNT-COOH in low dosage. The equilibrium between lead (II) and MWCNTs was approximately achieved in 60 min with removal of 99.8% (MWCNT-COOH) and 79.5% (MWCNT-isatin) of lead. The sorption kinetics was found to follow pseudo-second-order model for MWCNT-COOH and pseudo-first-order model for MWCNT-isatin. The Langmuir model exhibited a better fit to the sorption data than Freundlich and Tempkin. The values of the dimensionless separation factor calculated from the Langmuir constants confirmed favorable sorption of Pb(II) on both MWCNTs.

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