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Silane-Functionalized-Carbon Nanotubes for Cadmium(II) Removal

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Silane-functionalized carbon nanotubes (Si-CNTs) as an adsorbent for cadmium(II) removal was investigated. The method included adsorbent preparation, adsorption study, comparison study, existing model evaluation, and characterization study. The 50 % removal at 2 mg of Si-CNTs was selected as the optimum amount of adsorbent used in order to minimize time and chemical/ materials. The optimum pH and contact time were unadjusted pH 5.61 and 30 minutes, respectively. The removal and uptake of Si-CNT exhibited a double better performance than resin and activated charcoal. For the isotherm study, the Langmuir corresponded to Freundlich with maximum Langmuir uptake at 120 mg/g. Meanwhile, the pseudo-second-order kinetic is a better fit than the pseudo-first-order, thus indicating that chemisorption is the rate-limiting step. Thermodynamic study reveals that cadmium(II) adsorption is a non-spontaneous endothermic in nature and forms an irreversible binding. Such findings suggest ion exchange and complexation mechanisms. The morphology of Si-CNT changed from a rough rope-like surface into dotted patches attached to the surface of Si-CNTs. EDX confirms the attachment of cadmium(II) on the surface of Si-CNTs. Fourier Transform Infrared Spectroscopy analysis reveals functional groups such as hydroxyl, amide, carbonyl and silica oxide. The characterization results support ion exchange and complexation mechanisms. In conclusion, the Si-CNTs are a potential adsorbent for cadmium(II) removal. This study plays a main role in large-scale pilot application studies as well as modelling and digital platform studies.

Keywords: Adsorbent; cadmium(II); comparison; mechanism; silane-functionalised carbon nanotubes

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Cadmium(II) is a common heavy metal found in electroplating, fertilizer, mineral processing and battery production effluent [1-3]. Inadequate effluent treatment and waste management have brought cadmium(II) overloading pollution to the attention of the public, especially in fresh and marine water resources. Cadmium(II) is not often a cumulative poison; but acute and prolonged exposure may be carcinogenic, chronic, and toxic to people and animals [4-6]. In order to tackle the issue and protect the environment, an appropriate treatment approach must be employed.

Adsorption is a frequently used physicochemical technique for removing metals, including cadmium(II). Due to its simplicity and usability, it is one of the most used strategies in the industry. However, coal-based adsorbent, mineral-based zeolite adsorbent, and petro-chemical-based resin exhibit high cost and non-renewable material concerns [7-9]. Therefore, the hunt for potential substitute materials is addressed. The study also incorporates the use of carbon-based materials, specifically carbon nanotubes (CNTs), to improve the effectiveness of small-amount adsorbent loading strategies. This material has a large surface area available for the binding site reactions of hydroxyl, carbonyl, and amine, but it must be modified to increase stability and specificity, thus reducing its toxicity [10-12].

Applications for CNTs include the removal of heavy metals from wastewater, drug delivery in the pharmaceutical industry, aeronautical technology, and biosensing. A recent study discovered that carbon nanotubes (CNTs) have a large surface area for binding heavy metals, yet their toxicity to humans and animals is high [13]. Once the hydroxyl (-OH) group is bonded to the surface of the CNTs, they are considered functionalized-CNTs. Silane-functionalized-CNTs (Si-CNTs) are functionalized CNTs treated with 3-Aminopropyltriethoxysilane (APTES) to increase specificity and the adsorption of heavy metals. Si-functionalized-CNTs exhibit superior dispersion, thermal stability, thermochemical characteristics, fracture resistance, and electrical conductivity compared to unfunctionalized nanotubes [14-15]. The High adsorption performance of Si-functionalized-CNTs

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successfully reduces the heavy metal concentration in wastewater. As a result, the functionalization approach is utilized to resolve the issues. Therefore, Si-CNTs are selected for cadmium(II) removal from wastewater.

This investigation aims to evaluate the potential of carbon nanotubes as adsorbents for the removal of cadmium(II) from an aqueous solution. This research attempts to functionalize CNTs by an acid treatment method and APTES modification. In addition, cadmium(II) adsorption optimization utilizing Si-CNTs and comparison with other resins and activated charcoal are investigated. The isotherms and kinetics studies of adsorption are evaluated. Finally, the characterization of various modified CNTs is examined.

MATERIALS AND METHODS

Preparation of Silane-functionalized-CNTs Adsorbent and Cadmium(II) Solutions

An amount of 75 mg of multi-walled carbon nanotubes was weighed and put in a beaker. Then, a ratio of 3:1 of concentrated sulphuric acid and nitric acid was added to the beaker. The mixture was sonicated and then stirred continuously [16]. Next, the mixture was mixed with 250 mL of distilled water overnight. The mixture was filtered and washed using distilled water until pH 7 was achieved. After that, a 95% (3-Amino propyl) triethoxysilane (APTES) was diluted to 5% APTES with toluene. The functionalized-CNTs were soaked in the 5% APTES solution overnight. Then, the silane-CNTs were washed twice using toluene and dried. The sample was dried and known as silane-functionalized-CNTs (Si-CNTs).

A 1000 mg/L of cadmium (II) stock solution was prepared. A 0.6861 g of analytical grade metal salt of cadmium (II) nitrate hexahydrate ($Cd(NO_3)_2.4H_2O$) was weighed and diluted with ultrapure water. Then, the stock solution was diluted to desired concentrations.

Adsorption Study

An amount of 1 - 8 mg of Si-CNTs was weighed and added with 10 mL of 50 mg/L of cadmium (II) solution. Then, the samples were placed in the incubator shaker (Infors, HT Minitron) for 30 minutes at temperature of 25 ˚C with agitation 125 rpm. After that, the samples were filtered and filtrates were analyzed by using ICP-OES (Perkin Elmer, Optima 8000). The adsorption of Cadmium (II) was calculated based on Equation 1 and 2. A duplicate of samples was prepared and a low standard deviation of 1 was neglected. The procedure was repeated for parameters initial pH at 1 - 6, contact time at 1 - 40 minutes and initial concentration of cadmium (II) at 5 - 50 mg/L.

$$Removal\ (\%) = \frac{(C_o - C_e)}{C_o}\ x\ 100\ \% \qquad \text{Equation 1}$$

$$Uptake\ \left(\frac{mg}{g}\right) = \frac{(C_o - C_e)\,V}{W} \qquad \text{Equation 2}$$

where *Co* is the initial concentration of cadmium(II) in mg/L; *Ce* is the final concentration of cadmium(II) in mg/L; *V* is the volume of solution in L; *W* is the weight of adsorbent in g

Comparison Study

The commercial resin of Amberlite IRN-77, Amberlite IRC-86, Dowex 50WX4 and activated charcoal were compared with silane-functionalized-CNTs. The optimum parameters of Si-CNTs were applied in this comparison study. The results were recorded and compared.

Data Analysis for Existing Mathematical Models

The data from the adsorption batch study of cadmium(II) concentration were fitted to the Langmuir and Freundlich isotherm as shown in Equation 3 and 4. On the other hand, pseudo-first-order kinetic and pseudo-second-order kinetic equations as Equations 5 and 6 were applied for kinetic study. Thermodynamic parameters of Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were calculated based on Equations 7 and 8 for thermodynamic study.

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{b\ q_{max}} \qquad \text{Equation 3}$$

$$\log q_e = \log K_F + \frac{1}{n}\ log C_e \qquad \text{Equation 4}$$

where q_e represents equilibrium cadmium(II) adsorption uptake (mg/g), q_{max} is maximum cadmium(II) adsorption uptake (mg/g), C_e means cadmium(II) concentration at equilibrium (mg/L), b is Langmuir constant, K_F and n are Freundlich constant.

$$\log (q_e - q_t) = \log\ q_e - \frac{t\,k_1}{2.303} \qquad \text{Equation 5}$$

$$\frac{t}{q_t} = \frac{1}{2k_2\ {q_e}^2} + \frac{t}{q_e} \qquad \text{Equation 6}$$

where q_e and q_t are, respectively, the cadmium(II) adsorption uptake at equilibrium and at time (mg/g), t is the time (min), and k_1 and k_2 are, respectively, the constant of pseudo-first-order and pseudo-second-order kinetics.

$$\log K_c = -\frac{\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} \qquad \text{Equation 7}$$

$$\Delta G = \Delta H - T\Delta S \qquad \text{Equation 8}$$

where K_c (L/g) is the distribution coefficient, T is the temperature in Kelvin and R is the gas constant. ΔG is free energy (kJ/mol). ΔH and ΔS were obtained from the slope and intercept of the plots of log K_c versus 1/T.

Characterization Study

Adsorbent samples before and after adsorption of cadmium(II) were analyzed using scanning electron microscopy (SEM/EDX) (Nova Nanosem 40, Oxford X-Max). Approximately 150000x magnification was used for SEM micrographs. Fourier Transform Infrared Spectroscopy (FTIR) (Frontier FTIR Spectrometer, Perkin Elmer) was used to determine the functional groups of samples by averaging 16 scans in the range of 500 to 4000 cm^{-1} at a resolution of 4 cm^{-1}.

RESULTS AND DISCUSSION

Adsorption Study

Figure 1 demonstrates the effect of adsorbent dosage on the percentage removal and uptake of cadmium(II). The percentage removal was in the opposite trend with the uptake of cadmium(II). Two stages of percentage removal were observed with an increase in adsorbent amount. Initially, the percentage removal of cadmium(II) increased rapidly from 26 % to 94 % for 1 to 4 mg Si-CNTs, then saturated at 99 % for 4 to 8 mg Si-CNTs. The presence of the high binding site and surface area of Si-CNTs caused a high percentage of removal. After that, the Si-CNTs reached maximum adsorption and the addition of Si-CNTs in excess did not affect the adsorption removal. For uptake of cadmium(II), it decreased from 130 mg/g – 60 mg/g as the amount of Si-CNTs was increased from 1-8 mg. The ratio of the adsorbate to adsorbent binding site decreased with an increase of adsorbent amount, thus a decrease in uptake trend was observed. This trend is consistent with previously reported work for the removal of cadmium(II) using other nano-size adsorbents such as aluminium oxide impregnated with carbon nanotubes [17], membrane of polyphenylsulfone with multi-walled carbon nanotubes [18] and selenophosphoryl/ multi-walled carbon nanotubes [19].

In this study, the 50 % removal of cadmium(II) at 2 mg of Si-CNTs is chosen for further optimization study because industrial wastewater generally contains a low concentration of cadmium(II) concentration in 10 – 100 mg/L [20-21]. Besides, operating time and chemical or material usage are reduced through this approach.

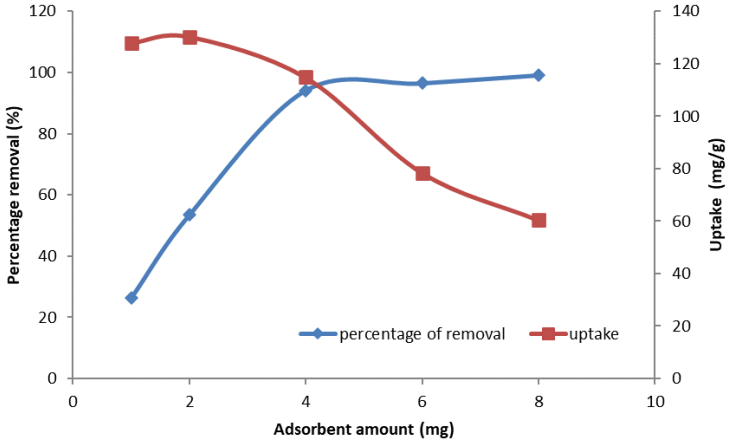


Figure 1. Effect of adsorbent amount on adsorption performance (5.45 initial pH, 30 minutes contact time, 50 mg/L initial cadmium(II) concentration, 25 ºC temperature)

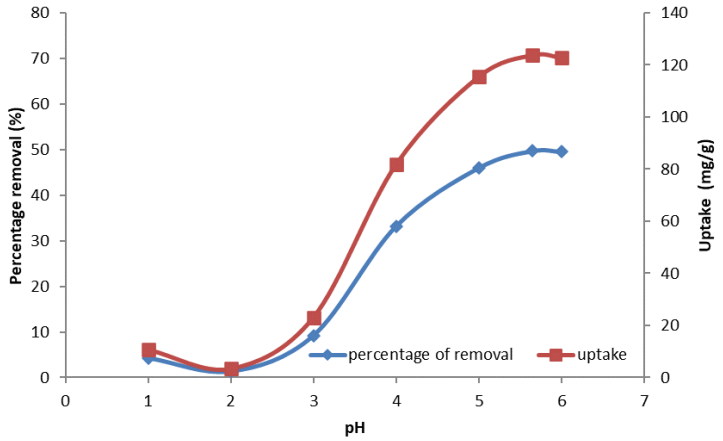


Figure 2. Effect of initial pH on adsorption performance (2 mg adsorbent amount, 30 minutes contact time, 50 mg/L initial cadmium(II) concentration, 25 ºC temperature)

Table 1. Optimum pH condition for various adsorbent for cadmium(II) removal

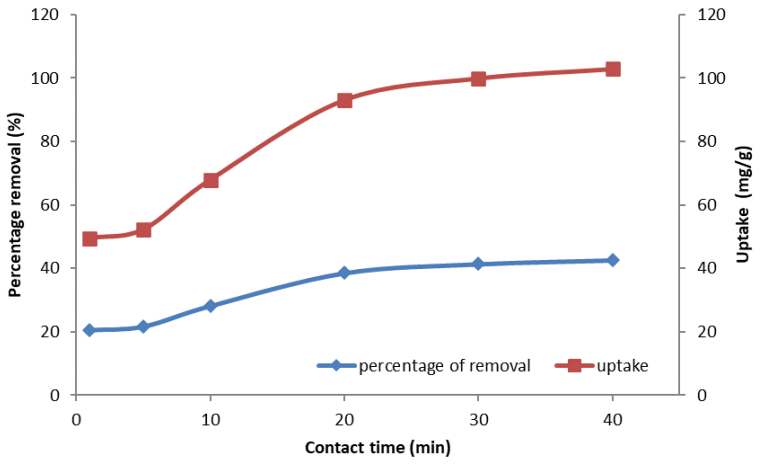
Adsorbent	Range of pH	Optimum pH	References
Multiwalled carbon nanotubes	2-12	7	[25]
Polyhydroxylbutyrate Functionalized Carbon Nanotubes	2-10	5.63-5.65	[26]
Multiwalled carbon nanotubes modified with nanoporous anodic alumina	3-9	6	[27]
Silane functionalized carbon nanotubes		5.65	This study

The influence of different pH on the adsorption of the cadmium(II) was divided into three stages is shown in Figure 2. A slow increase was observed at stage I, a rapid increase at stage II and remain constant at stage III. Initially, the competition occurred between proton and cadmium(II) and the low pH led to the proton dominating the system. At stage (II), there was less proton present in the system and the binding sites of the Si-CNTs were deprotonated and became negatively charged. Therefore, cadmium(II) adsorption increased. The highest removal and saturation of cadmium(II) were observed at stage III as all binding sites were fully occupied. The optimum pH was achieved at unadjusted pH 5.65. At higher pH conditions, cadmium(II) was not observed as the cadmium(II) species was converted to $Cd(OH)_2$ and $Cd(OH)_3^-$, thus the cadmium(II) hydroxide precipitated occurred in the system [22]. Zeta potential study [23-24] also supported that modification of CNT with precursors improves stabilization and renders high colloidal stability in aqueous dispersion and strong electrostatic interaction over a wide pH range. The unadjusted pH 5.65 is chosen for further studies in order to reduce the time and chemicals used during the experiment. Table 1 shows the optimum pH condition using various adsorbents in the cadmium(II) adsorption. The optimum Si-CNTs at pH 5.65 was corresponded to the optimum range 5 to 7 of other modified carbon nanotubes and less chemical usage needed. Therefore, this optimum value for Si-CNTs is reliable.

The time profile for the percentage removal and uptake of cadmium(II) is illustrated in Figure 3(a). Both percentage removal and uptake of cadmium(II) were consistent, where the rapid phase for stage I and plateau phase at stage II. In stage I, the cadmium(II) adsorption increased rapidly because Si-CNTs have vacant binding sites. Then, the vacant binding sites decreased and later achieved saturation condition at stage II where all vacant binding sites were already filled. Since the saturation stage begins at 30 minutes, this contact time is selected for the next parameter. A similar trend was found in the previous research using multiwalled carbon nanotubes modified with cobalt ferrite catalyst on activated carbon [28] and multiwalled carbon nanotubes modified with glutaric dihydrazide [29].

For Inductively Coupled Plasma (ICP) analysis results, an increase in a total concentration of ions such as sodium (Na), potassium (K), calcium (Ca) and magnesium (Mg) was observed (Figure 3(b)). Such trend corresponded with the cadmium(II) removal and uptake [30]. This phenomenon suggests a displacement of alkaline and alkaline earth metal ions with cadmium(II) ions via an ion exchange mechanism. Contact time at 30 min is the selected contact time for kinetics study.

(a)



(b)

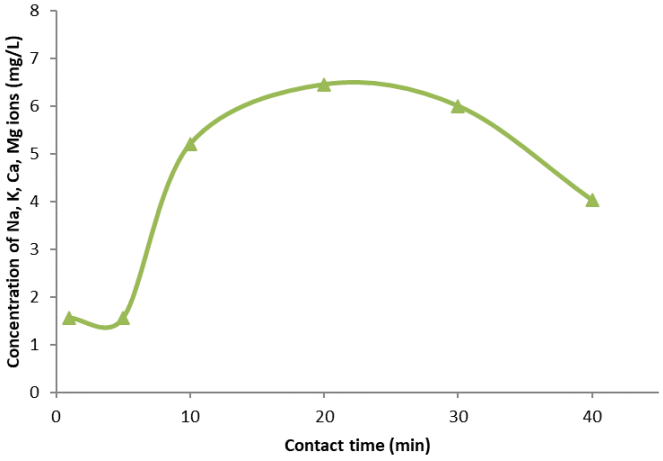


Figure 3. (a) Effect of contact time on adsorption performance (2 mg adsorbent amount, 5.70 initial pH, 30 minutes contact time, 50 mg/L initial cadmium(II) concentration, 25 ºC temperature) (b) ICP analysis on sodium, potassium, calcium and magnesium

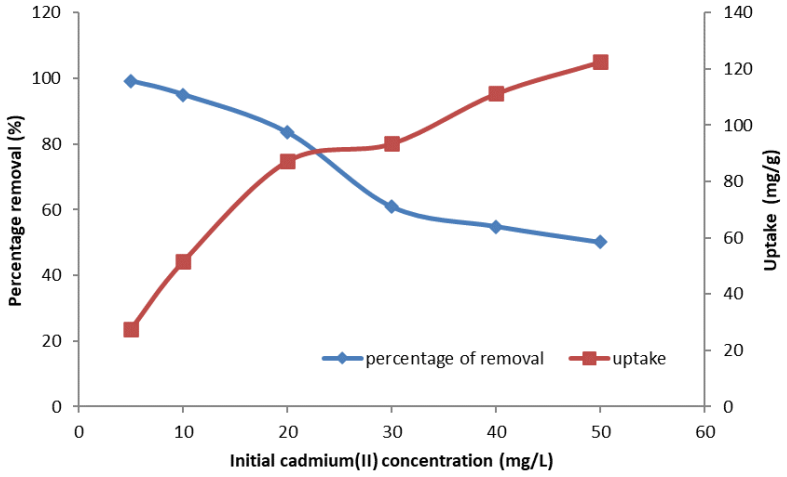


Figure 4. Effect of initial cadmium(II) concentration on adsorption performance (2 mg adsorbent amount, 5.25 – 5.75 initial pH, 30 minutes contact time, 25 ºC temperature)

Figure 4 shows the removal and uptake of cadmium(II) have an inverse trend with an increase of cadmium(II) concentration. Initially, the cadmium(II) removal decreased with an increase of initial cadmium(II) concentration. The ratio of binding sites of Si-CNTs decreased, consequently the removal performance decreased. On the other hand, the uptake of cadmium(II) increased when the initial concentration was increased. An increase in initial concentrations provides a higher driving force and overcame the resistance easily, resulting in an increase in the uptake of cadmium(II). This decreasing trend also found in plumbum and copper reported by Kosa *et al.*, using multiwalled carbon nanotubes modified with 8-hydroxyquinoline [31].

Figure 5 presents the temperature was directly proportional to cadmium(II) removal and uptake. As the temperature increased, the kinetic energy also increased, effective collision increased and binding between cadmium(II) and the surface of Si-CNTs occurred. Thus, the cadmium(II) removal and uptake increased. These indicates the process was endothermic [32]. Similarly, the similar observed trend was recorded by Fard *et al.*, by using ethylenediamine-modified single-walled carbon nanotubes [33].

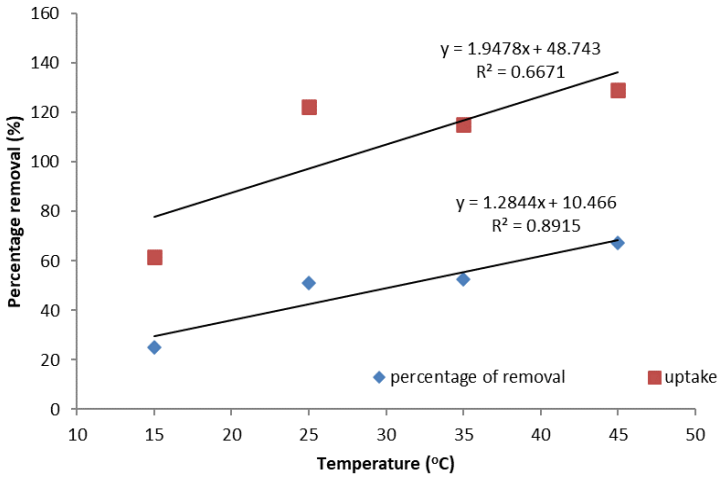


Figure 5. Effect of initial cadmium(II) concentration on adsorption performance (2 mg adsorbent amount, 5.60 initial pH, 30 minutes contact time, 50 mg/L initial cadmium(II) concentration)

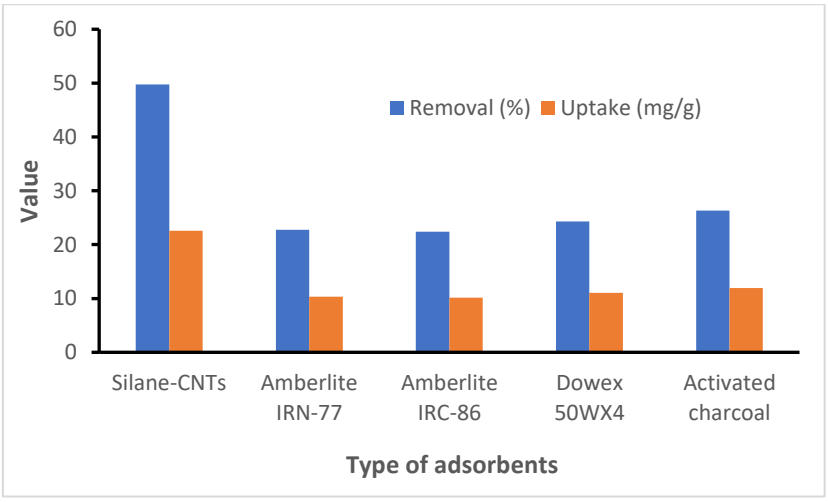


Figure 6. Cadmium(II) adsorption performance for various adsorbents (2mg adsorbent amount, 5.60 initial pH, 30 minutes contact time, 50 mg/L initial cadmium(II) concentration, 25 °C temperature)

Comparison Study

A comparison study of different adsorbents for cadmium(II) removal and uptake is presented in Figure 6. The 50% removal and 23 mg/g cadmium(II) were attained by Si-CNTs. The commercial activated carbon recorded 26% removal and 12 mg/g uptake for cadmium(II). The three petroleum-based resin types named Amberlite RRM- 77, Amberlite IRN- 86 and Dowex 50WX4- 50 were 23%, 22% and 24% cadmium(II) removal and 10 mg/g, 10 mg/g, 11 mg/g cadmium(II) uptake, respectively. The selected materials in this comparison study as these adsorbents are widely applied in industries for wastewater treatment. The size of Si-CNTs is between 2.5 to 20 µm and smaller compared to other resins and activated charcoal (supplementary S1). Thus, this reveals the high surface area of Si-CNTs resulted in cadmium(II) removal and uptake increased. The salinization process modified the carbon nanotubes led to the attachment of amide to Si-CNTs as a functional group and created δ^+ condition. Such circumstances increased the efficiency and effectiveness of the system. On the other hand, the acidic condition of resins and activated charcoal caused the competition between proton and cadmium(II), hence cadmium(II) removal and uptake decreased. Therefore, the size of adsorbents and functional groups are major factors to determine the adsorption efficiency and effectiveness of the cadmium(II). These results also confirmed the relationship of cadmium(II) adsorption with characterization results in the following characterization study section.

Table 2. Comparison of Langmuir and Freundlich isotherm models for cadmium(II) adsorption

Langmuir		Freundlich	
q_{max} (mg/g)	120	K_F	68.17
b (L/mg)	0.86	n	4.36
r^2	0.9823	r^2	0.9837

Table 3. Comparison of the Langmuir maximum uptake for cadmium(II) for adsorbents

Adsorbent	q_{max} (mg/g)	Reference
Multiwalled carbon nanotubes	181.80	[34]
Magnetized and polydopamine surface functionalized single-walled carbon nanotubes	186.48	[35]
Charcoal TiO_2 composite	185.00	[36]
Aloe vera/carboxylated carbon nanotubes nanocomposite	50.25	[37]
Magnetic multi-walled carbon nanotube	28.24	[38]
Silane-CNTs	120.00	This study

Table 4. Comparison of pseudo-first-order kinetic and pseudo-second-order kinetic models for cadmium(II) adsorption

Pseudo-first-order kinetic		Pseudo-second-order kinetic	
q_e (mg/g)	74	q_e (mg/g)	112
K_1	0.04	K_2	0.004
r^2	0.9542	r^2	1.000

q_{exp} (mg/g) = 102

Data analysis for Existing Mathematical Models

Table 2 shows the isotherm of Langmuir and Freundlich parameters. It was found that the correlation coefficient of Langmuir Isotherm was $R^2 = 0.9823$ and Freundlich Isotherm was $R^2 = 0.9837$. Therefore, the silane-CNTs fitted well with both Langmuir and Freundlich Isotherm. The Langmuir Isotherm assumes monolayer adsorption on the surface of silane-CNTs and the Freundlich isotherm refers to the heterogeneous adsorption of cadmium(II). The maximum Langmuir uptake was found at 120 mg/g and the low b value implied low selectivity. High K_F and n values represent a fast reaction in adsorption. Table 3 summarizes the calculated Langmuir maximum uptake for this study is better/ in-range to other adsorbents.

Kinetic study for pseudo-first-order kinetic and pseudo-second-order kinetic is shown in Table 4. A higher regression coefficient for Pseudo-second-order kinetic than pseudo-first-order kinetic, indicates the rate-limiting step is chemisorption compared to physisorption. The calculated uptake for pseudo-second-order kinetic at 112 mg/g more corresponded to experimental uptake at 102 mg/g when compared to pseudo-first-order kinetic uptake at 75 mg/g. This findings confirm the chemisorption is the rate limiting step in adsorption of cadmium(II). Studies by Egbosiuba et al. [39] and Li et al. [40] were in agreement with pseudo-second-order kinetic and supported rate-limiting step of chemisorption rather than mass transport physisorption.

The values for enthalpy change (ΔH), entropy change (ΔS) and free Gibb energy (ΔG) were 58383 kJ/mol, 230 kJ/mol and 7717-14603 kJ/mol, respectively. The positive value of ΔH indicates that the adsorption of cadmium(II) using Si-CNTs adsorbent is an endothermic reaction. Approximate 230 in ΔS meant a high degree of derangement happened at the solid-solution interface thus confirming the non-reversible bonding was formed. The positive ΔG suggests that the adsorption of cadmium(II) is a non-spontaneous reaction.

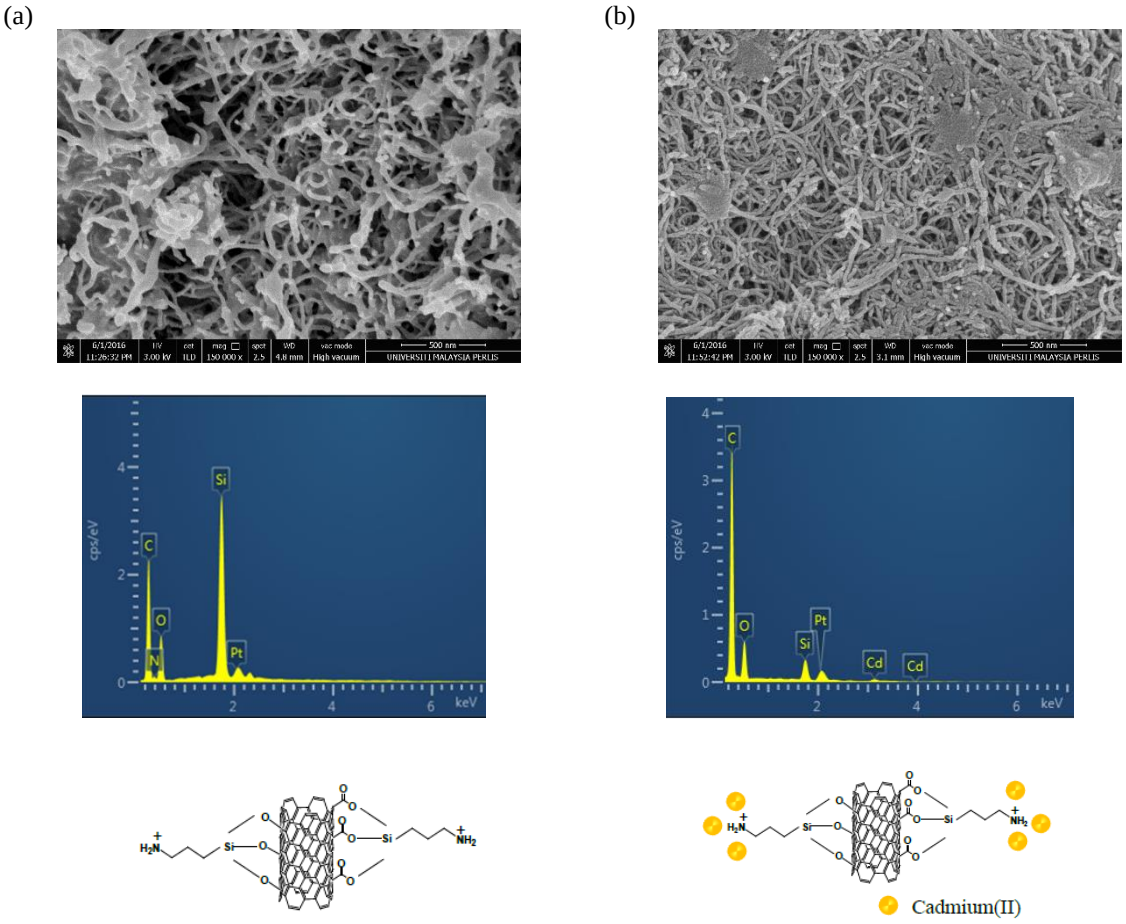


Figure 7. SEM micrographs and EDX spectrum (a) before and (b) after cadmium(II) adsorption using Si-CNTs

Characterization Study

Figure 7 illustrates the characteristics of Si-CNTs under SEM micrograph before and after cadmium (II) adsorption. Si-CNTs showed rope-like and rough surface morphology before the adsorption of cadmium(II) (Figure 7a). After the adsorption, the dotted spot showed the cadmium(II) was adsorbed on the surface of the Si-CNTs (Figure 7b). This reveals that the amine group present on the surface of the Si-CNTs was bonded with the cadmium(II), resulting in the efficient removal of cadmium(II) and uptake by Si-CNTs adsorbent. This result is further verified with EDX analysis of Si-CNTs before and after adsorption. The presence of carbon, oxygen, nitrogen, silicon and platinum was observed for Si-CNTs before cadmium(II) adsorption. The platinum in the spectra was due to it was used for sample coating to become conductive. After cadmium(II) adsorption, an additional peak of cadmium was observed in the samples and indicates the cadmium(II) attached on the surface of the Si-CNTs. At the same time, the nitrogen was absent because the amide groups bind with the cadmium(II). The similar results were also observed in the carbon nanotubes buckypaper membrane [41], carbon nanotubes modified with 5, 7-dinitro-8-quinolinol [42] and amino and thiol modified magnetic multiwalled carbon nanotubes [43].

Figure 8 and Table 5 summarize the shifted peaks with assignation for different types of CNTs samples. Initially, the bare CNTs indicate the broad peaks of hydroxyl group (-OH) at 3446.01cm^{-1} from adsorption of atmospheric water during the FTIR measurements and the presence of C-O stretching of alcohol at 1019.70 cm^{-1} [44]. After acid treatment, the peaks became intense at 3436.57 cm^{-1}. The functionalization of CNTs successfully attached C-O stretching of alcohol at peaks of 1019.70 cm^{-1}, 1037.30 cm^{-1} and 1019.20 cm^{-1} and carbonyl group (C=O) stretching on the surface of CNTs from 1649.03 cm^{-1} to 1643.60 cm^{-1}. The presence of CH_2 originated from the multiwalled carbon nanotubes appeared at 2923.60 cm^{-1}, 2926.58 cm^{-1}, 2920.60 cm^{-1} and 2920.60 cm^{-1} for all types of CNTs samples. After the salinization process, the sharp peak at 671.14 cm^{-1} indicates that the silane group was effectively functionalized onto the surface of acidified CNTs [45]. Since the peaks were reduced to 668.40 cm^{-1}, the silane that bonded with amine groups was used in the process of adsorption. The cadmium(II) was actively bonded to amine groups at 1651.04 cm^{-1} and 1594.70 cm^{-1} respectively and 3435.98 cm^{-1}, 3444.50 cm^{-1} for -OH group. In summary, the bare-CNTs has the carbon in allotropes form. Acid treatment process was introduced to activate the -OH group and C=O group on the surface of the bare CNTs. Further

treatment with 5% APTES added the amine (-NH) group and SiO group. These -NH group absorbed the cadmium(II) and increased efficiency in cadmium(II) removal. The SiO reacted with cadmium(II) to form complexation, thus supports irreversible binding occurred in thermodynamic study.

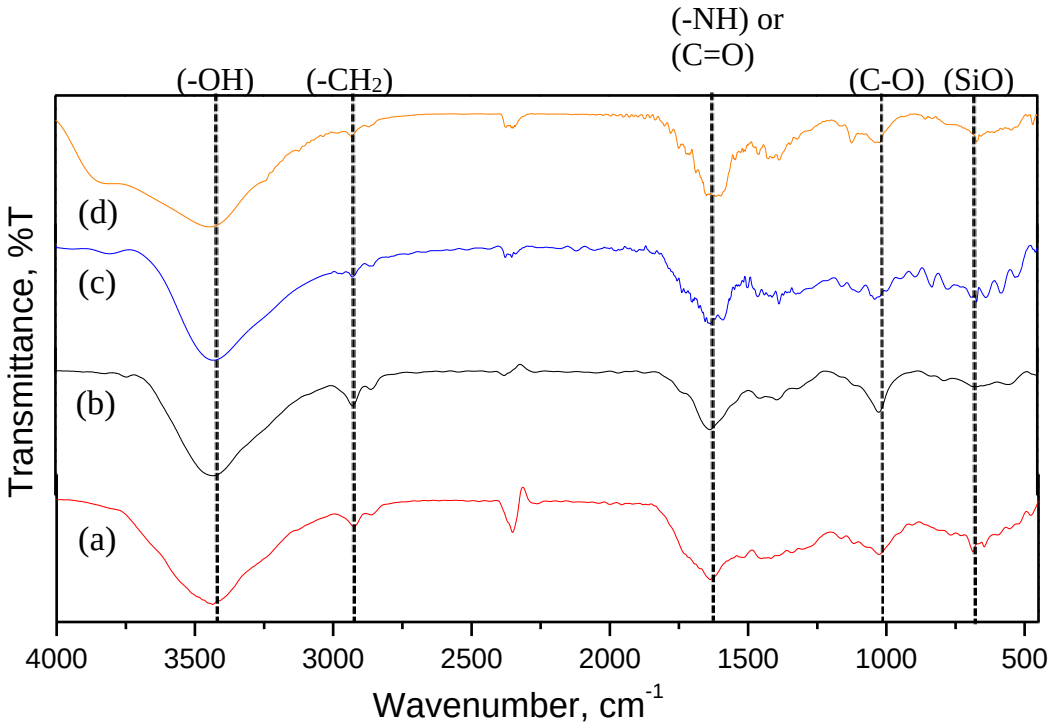


Figure 8. FTIR spectra of a) bare CNTs, b) acidified CNTs, c) Si-CNTs and d) Si-CNTs after cadmium(II) adsorption

Table 5. Shifted peaks from bare CNTs to Si-CNTs after adsorption

Wavenumber of bare-CNTs (cm^{-1})	Wavenumber of acidified CNTs (cm^{-1})	Wavenumber of silane-CNTs (cm^{-1})	Wavenumber of silane-CNTs after adsorption test (cm^{-1})	Assignation	Reference
3446.01	3436.57	3435.98	3444.50	hydroxyl group (-OH)	[46]
2923.60	2926.50	2920.60	2920.60	alkyl group (CH_2)	[47]
1649.03	1643.60	1651.04	1594.70	amide group (-NH) or carbonyl group (C=O)	[48]
1019.70	1019.70	1037.30	1019.20	(C-O) stretching of alcohol	[49]
-	-	671.14	668.40	silica oxide (SiO)	[50]

CONCLUSION

This study investigates the Si-CNTs as an adsorbent for cadmium(II) adsorption. The selected 50% removal at 2 mg Si-CNTs, unadjusted pH 5.61 and 30 minutes contact time were determined as optimum conditions with the aim to save time and materials used. ICP observation on the displacement of cadmium(II) with earth metals and alkaline metals suggests an ion exchange mechanism. In comparison with resins and activated charcoal, the Si-CNTs showed double performance in removal and uptake. The Langmuir isotherm was consistent with Freundlich isotherm with a maximum Langmuir uptake at 120 mg/g. However, the pseudo-second-order kinetic showed an excellent fit compared to the pseudo-first-order kinetic. The thermodynamic study reveals that the reaction is endothermic, non-spontaneous and forms irreversible binding. SEM/ EDX illustrated changes in morphology structure and attachment of cadmium(II) on the adsorbent after the cadmium(II) adsorption. FTIR indicates that hydroxyl, amide, carbonyl and silica oxide play a major role in binding and further support the mechanism of complexation. This study provides basic information for further industrial pilot applications and digital platform modelling studies.

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The authors declare that they have no conflict of interest.

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SUPPLEMENTARY

S1. The size and functional group present on different types of adsorbents

Materials	Size	Functional group
Si-CNTs (this study)	2.5 to 20 µm	Amine group, NH_2 (δ^+ condition)
Amberlite IRN-77	600 to 700 µm	Sulfonic acid (acid condition)
Amberlite IRC-86	580 to 780 µm	Carboxylic acid (acid condition)
Dowex 50WX4	37 to 400 µm	Acid condition
Activated charcoal	149 µm	Acid condition