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Removal of Cadmium Chloride from Contaminated Residual Soil using Carbon Nanotubes (CNTs)

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***Abstract*— Industrial waste inorganic pollutants are normally produced from mineral compounds, such as for example heavy metals, salts, and minerals. These inorganic pollutants can be managed by selecting the appropriate removal techniques. By implementing the removal technique, the number of contaminants may decrease as pollutants reach the soils during certain reaction periods because of chemical reactions and sorption. These reactions depend on both the additive removal material in use, the soil and the environment's chemical characteristics. In soil contamination, reaction rates can be experimentally monitored, and the adsorption mechanism can be measured. The aim of this paper is to experimentally observe the mechanism of heavy metal removal of cadmium chloride in contaminated residual soils using carbon nanotube (CNT) adsorbent. In this research, a series of multi-wall carbon nanotube (MWCNTs) adsorption experiments were used to evaluate the adsorption of residual soil contaminants Cadmium chloride with a concentrations range of 50-200 mg / L. The tests were conducted with different weights of MWCNTs and a concentration of 50 to 200 mg / L of Cadmium Chloride contaminant. The temperature was thoroughly investigated on kinetics and the equilibrium of sorption contaminants in MWCNTs. It shows that MWCNT's can be used to remove heavy metal pollutants, evaluated based on the adsorption mechanism of Langmuir and Freundlich's isotherm models, from the contaminated residual soil as an effective adsorbent. As regards adsorbent models, the balance data in the Freundlich equation are reasonably proven compared to the Langmuir isotherm. As regards adsorbent models, the equilibrium data in the Freundlich equation are reasonably proven compared to the Langmuir isotherm.**

***Keywords*— equilibrium isotherm; carbon nanotubes; adsorption mechanism; contaminated residual soil.**

I. INTRODUCTION

One of the world's biggest problems today is environmental pollution in the soils, air and water, which is serious and irreparable damage to the natural and human society. Industrial, agricultural and domestic waste contributes to pollution of the environment. Inorganic pollutants from industrial wastes are generated usually from mineral compounds for instances of heavy metals, salts as well as minerals. For many years, there are a number of removals and recovery techniques from contaminated soils for inorganic material, like chemical precipitation, extraction of solvents, reverse diffusion, exchange of ions, flotation, evaporation, and adsorption materials used in the field of environmental engineering. From those techniques, the use of adsorption materials is one among the common ways for the removal of contaminant material because of its economical and relatively uncomplex procedure. Over the last few years, different adsorbent materials, i.e. plant phytoremediation processes [1], fly ash [2], dolomite and clay materials for natural adsorbents [3], activated carbon [4] as well as recent manufactured carbon nanotube materials [5], have been utilized to remove contaminants from contaminated soils.

CNTs is a new material of the carbon component group which, because of advantages in many various applications regarding its chemical composition, has attracted substantial attention [6]. CNTs is a quite suitable element in the in the treatment of organic pollutants [7]. Its adsorption characteristic is highly pH-dependent when pH increases, as it is expected for metals onto hydroxyl groups. Mahdavian [8] also reported that the use of carbon-nanotubes is significantly higher dioxin elimination efficiency for absorption of pollution in the environment.

Physical modelling to any scientific evaluation usually supports the proposal of empirical relationships with a higher intensity of multivariate analysis for the exploitation of experimental data [9]. The empirical correlation is typically shown visually as a solid-phase against its residual concentration, representing a significant role in modelling and applied the experimental practice of Surface Assimilation Systems (SASs) [10]. The aim of this study is to experimentally observe the adsorption mechanism by carbon nanotubes (CNTs) of heavy cadmium metal in the residual soil. Consequently, the experimental metadata from the tests is also being correlated with the Langmuir and Freundlich Isotherm equations.

II. Materials and Method

A. Materials

The absorbents used in this study were carbon nanotubes and residual soils. The heavy metal of cadmium was selected as adsorbates of liquid contaminant. The properties of these materials are described as follows:

1) Carbon Nanotubes (CNTs): In this study, CNTs type of Multiwalled Carbon Nanotubes (MWCNTs) of GRAPHISTRENGTH C 100 was used. The MWCNTs is a black powder which was purchased from Arkema (France). The MWCNT has a very high surface area (Table 1) as the thickness of this nanomaterial is between 0.2 to 0.4 nanometres (nm) resulting in extensive total inside and outside surface area [5].

TABLE I
Basic Properties Of The MWCNTs Used In This Study

Properties	Value
Average diameter	10-20 nm
Purity	> 90 %
Average thickness	0.2 - 0.4 nm
Total surface area	1200 m^2/g
Density	50-400 kg/m^3

2) Residual Soil: A local residual sedimentary soil that is extensive within the Malaysian peninsula obtained as the main adsorption medium. Table 2 shows some characteristics of the soils. The pH scale of the soil is acidic. Typical of tropical soil whenever hot and humid climate with severe rain of concerning 2000 mm / year causes abundant carbon dioxide within the atmosphere is transferred as acid soil rendering low in pH to the soil. The soil indicates that the foremost clay mineral within the soil is kaolinite.

Based on Unified Soil Classification System (UCSC) ASTM D-2487, the soil samples were categorized as sandy soil. According to plasticity index (PI) and liquid limit (LL), the soil was also consisting of the clayey fraction with low to medium plasticity (CL).

TABLE II
Residual Soil Properties as Adsorption Medium in This Study

Properties	Value
Natural moisture content	20.7 %
Cation exchange capacity, CEC (meq/100g)	10.9
Plasticity Index (PI)	16.96
pH (20°C)	5.14
Soil classification (plasticity chart)	CL
Clay fraction (<2µm)	26.9 %

3) Cadmium: Cadmium (Cd) in natural and wastewater industries such as Pigments, Mining, Smelting as well as Electroplating is categorised as a heavy metal pollutant [11,12]. Cadmium is also an aquatic organism's highly toxic metal [13]. Adsorbate of Cadmium Chloride (Cl_2Cd) used in this study was supplied from Sigma Aldrich, USA.

B. Methods

This adsorption study was experimentally done with a constant temperature (25 ± 1°C) under continuous stirring. The series of experimental samples have been performed with the adsorbent of MWCNTs and residual soil. Various weights of MWCNTs were agitated in 60 mL of a solution containing a Cadmium contaminant with a concentration of 50 to 200 mg/L. They were then stirred during a certain time in a magnetic stirrer at 430 rpm. The weight of MWCNTs is taken a percentage from 0, 0.25, 0.5, 0.75 to 1 % of dried soil weight. The pH of the solution was also adjusted to the required value with 0.1 N HNO3 and 0.1 N NaOH solutions.

Furthermore, the samples were treated with five different weights of MWCNTs for series of experiments. Therefore, 16 experiments were performed for each concentration of operations, and it was 54 tests totally. The samples were conducted at observed time intervals and filtered using Whatman Paper No.42 (7-9 µm retention particles). The contact time to at equilibrium was set for 15 days. Also, the equilibrium concentration of the solutions was obtained by a UV/VIS spectrometry (Shimadzu Model UV-1601) by evaluating the absorbance changes at a wavelength of maximum absorbance (505 nm). All samples were tested in duplicates.

This adsorption study was conducted under constant stirring with a continuous temperature (25 ± 1°C). The experimental testing series were performed with the MWCNT adsorbent and residual soil. A solution containing Cd contamination of between 50 to 200 mg / L was tangled in 60 ml by numerous MWCNT's weights. They were then moved in a very magnetic stirrer at 430 rpm for a certain time. A proportion of 0, 0.25, 0.5, 0.75% to 1% of dried soil weight shall be used to reduce the MWCNT burden. In addition, with 0.1 N HNO3 and 0.1 N NaOH, the pH of the solution was adjusted to the specified value. Therefore, the samples were treated for a series of experiments with five entirely different weights of MWCNTs. For every concentration of operations, 16 experiments were thus operated, and all 54 tests were carried out. The samples have been performed at known time intervals and filtered with Whatman Paper No.42 (7-9 µm of retention particles size). The time of contact to the balance was 15 days. In regards, by evaluating the absorbing changes at a wavelength of highest absorption range (505 nm), the balance concentration of the solutions was achieved by UV / VIS spectrographic analyses (Shimadzu model UV-1601). All samples have been double tested. The equation was employed to quantify the amount of adsorbed contaminant (q_e):

$$q_e = \frac{V\left(C_0 - C_e\right)}{m} \tag{1}$$

where q_e is a volume per weight of the absorbent solute at equilibrium, V is a volume of solution, m is an activated carbon mass, C_0 and Ce is respectively the initial and equilibrium adsorbate concentration.

C. Isotherm Models

The model of Langmuir takes some assumptions into consideration, that is the maximum adsorption takes place when a saturated monolayer of solute molecules on the adsorbent surface is present, the energy adsorptions are relatively constant and adsorbent molecules do not flow on the surface. The original model of Langmuir isotherm adsorption on activated carbon was developed by Foo & Hamed [14] to identify gas-solid phase adsorption. There are two assumptions of the model, that is, firstly, interaction forces among adsorbed molecules are negligible, and, secondly, that no more sorption occurs if a molecule occupies a site. Through homogenous adsorption without transmigration of the adsorbate in the plane to the surface, the isotherm equation of Langmuir is derived [14]. The isotherm of Langmuir defined in mathematical equation as follows:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

Where, the Langmuir constants, q_m and K_L, represent a maximum solid-phase level of adsorption and an adsorption heat energy constant respectively. A relation between $(1/q_e)$ and $(1/C_e)$ can be traced as follows to the Langmuir isotherm constant:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L C_e} \quad (3)$$

The isotherm model of Freundlich is an empirical relation expressing the adsorption of solutes from a fluid to a solid surface. The mathematical relationship of the amount of contaminants adsorbed by unit mass of adsorbent (q_e) is a Freundlich adsorption isotherm equation and the balance concentration (Ce) as described:

$$q_e = K_f C_e^{1/n} \quad (4)$$

The equation can be rewritten in logarithmic function as follows:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (5)$$

where K_f and n are the Freundlich constants of system qualities indicating respectively the adsorption capacity and the adsorption intensity.

III. Results and Discussion

A. Physical Properties of Adsorbents

Figure 1 and 2 show FESEM micrographs of the loaded contaminant of MWCNTs. The surface texture and porosity of the contaminant are observed both blank and loaded. CNTs were determined by randomly selected areas on solid surfaces before and after contaminant adsorption and analysis was carried out by FESEM. These figures also show that after loading of cadmium contaminants, the surface texture of the blank contaminant changes significantly and shows that it has been reduced to a contaminant on the adsorbing surface.

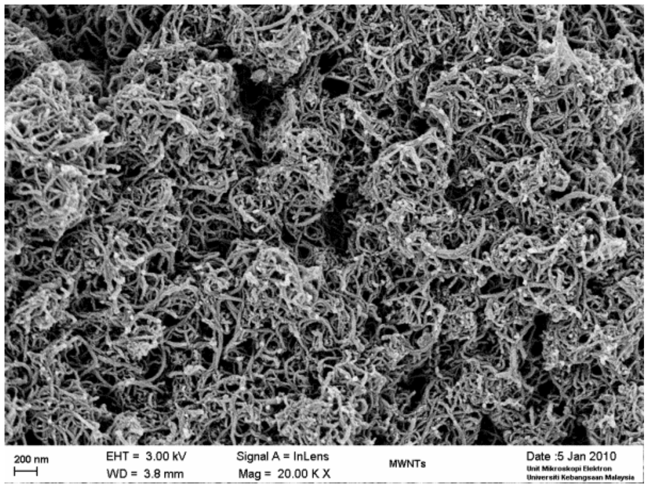

Fig. 1 FESEM micrograph of 0 % MWCNTs of dried soil weight before loaded contaminants at 20.00 K X

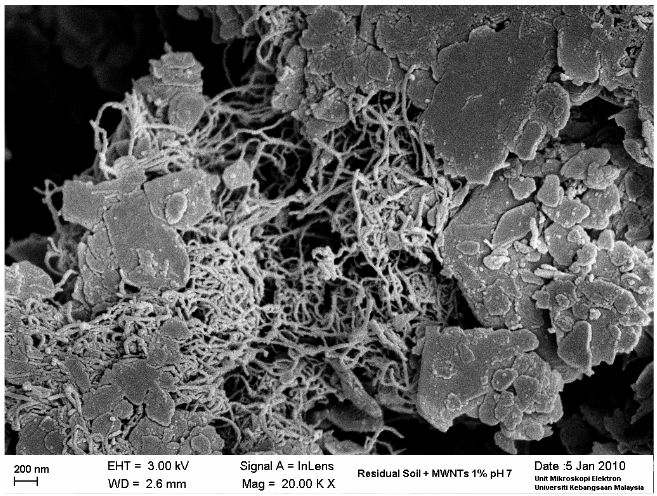

Fig. 2 FESEM micrograph of 1 % MWCNTs of dried soil weight after loaded contaminants at 20.00 K X

B. Batch Study

Experimental tests were performed on the removal of contaminant-coated MWCNTs by batch adsorption. In the design of an adsorption system for removing the contaminant being studied it is essential to evaluate various parameters, equilibrium concentration (q), contact time (t), concentration (C). The adsorption effect of these parameters is shown by the addition of MWNTs. The effect of contact time on cadmium contaminant adsorbent were assessed at a room temperature of 25^{o} C in order to observe the equilibrium time during the absorption process (Fig.3). Contact time for the different concentrations between 50 and 200 mg / L. The contaminant was measured. The percentage of cadmium adsorption was found to increase over time and to achieve balance after approximately two days. Figure 4 displays adsorbed cadmium on the surface of MWCNTs depending on contact time. Results similar to that of Shao et al. [15] are that the balance time after 45 hours (2 days) for the elimination of contaminants using MWCNTs is essentially at first contact time. Figure 4 also shows the increase in the number of Cd removal by adding MWCNTs to the contaminant concentration. At 200 ppm, more than 50% of the cadmium contaminant is discharged.

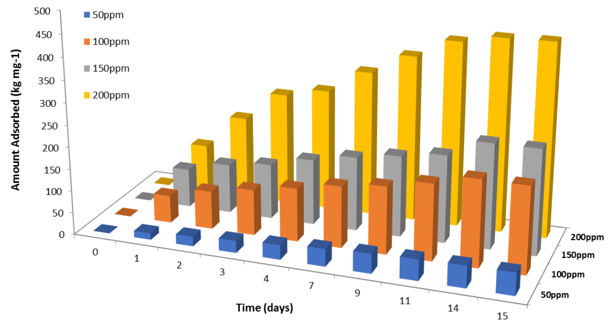

Fig. 3. Effect of contact time adsorbed onto MWCNTs

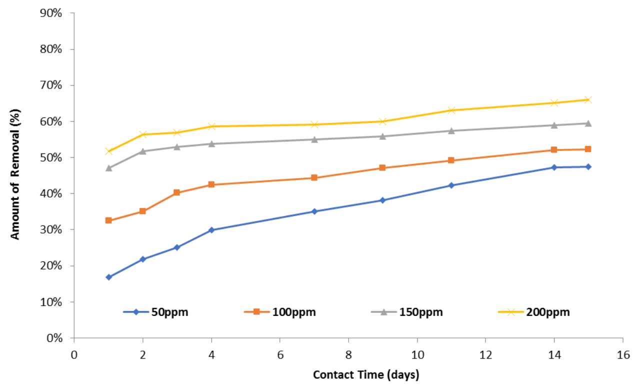

Fig. 4. Amount of Cadmium removal adsorbed onto MWCNTs

Figure 5 shows that cadmium adsorption increased as there was an increase in the MWCNTs. Because adsorption sites were able, the maximum values of adsorptions were obtained at the highest MWCNT level. The highest percentage of adsorption from this study was 75 percent when 1 percent MWCNTs were added. While the percentage of adsorption was observed with only residual soils as absorbents at 40 %. It has demonstrated that the MWCNTs almost double their adsorption capacity. All results show that more than 50% cadmium is 0.25 to 1% MWCNTs of dried soil weight removed from the solution. The high capacity of the MWCNTs adsorption is also indicated.

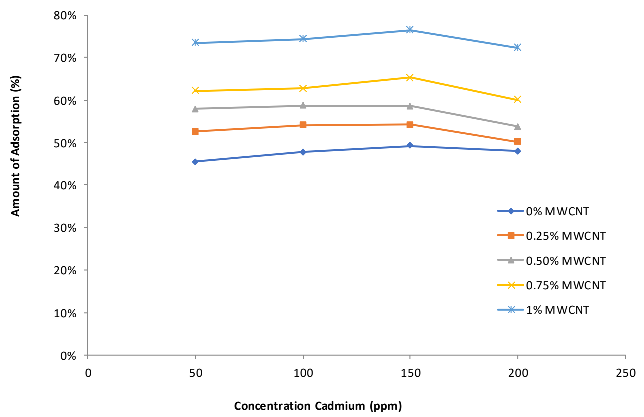

Fig. 5. Adsorption of Cadmium by various amount of MWCNTs

The experimental relationship between the equilibrium concentration (C_e, mg/L) and amount of contaminant adsorbed by MWCNTs or adsorption capacities at equilibrium or adsorbent concentration (mg/kg) were then obtained. The experimental model from this study was compared with adsorption isotherm models, e.g., Freundlich and Langmuir, in order to assess the adsorption of the contaminant by CNTS. These adsorption isotherm models are a quantitative pattern demonstrating the distribution of adsorbed matters between fluid and adsorbent in accordance with a prevailing assumption related mainly to the adsorbent's heterogeneity, coverage type but also interactions chance. The results of these models are presented in the Figure 6 and 7. They also shows the comparison with the experimental model.

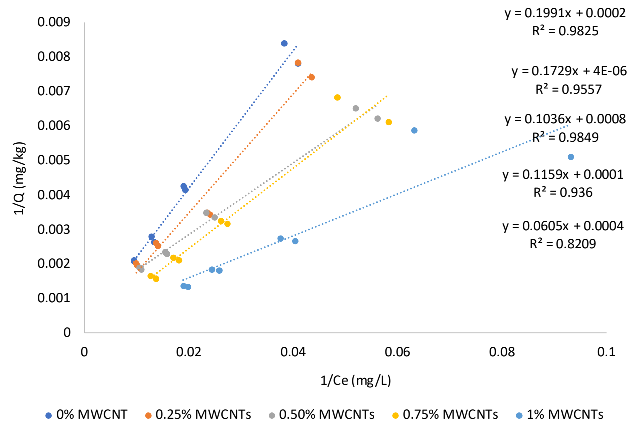

Fig. 6. Linearized Langmuir isotherm model for Cadmium on MWCNTs

The Langmuir and Freundlich models have been examined for their adaptability to the experimental data. From Figure 6, the constant and maximum Langmuir adsorption values were 0,0008628 L/mg and 1,000 mg/kg, respectively at 0,25% MWCNT, and were also found to be 0,001452 L/mg and 5,000 mg/kg at 10% MWCNT. The adsorption energy level of the Langmuir constant is related to the maximum adsorption capacity of MWCNTs, which is related to the quantity of adsorbate adsorbed on the coating of monolayers. Figure 7 shows the linear Freundlich Cadmium isotherm on MWCNT's. The nonlinear equation (Eq.4) becomes a linear form (Eq.5). The logarithmic pattern of *Ce* versus q_e is used to produce an intercept value or a constant of K_f, that is, the capacity of adsorption and the slope of n.

As seen in Figure 7, with an increasing number of MWCNTs, the intercept increases. It shows that the capacity of adsorption increases. K_f is equivalent to the adsorbed amount at a C_e value. The higher slope indicates a more homogeneous surface when an isotherm equation is linearized into a log scale. In this study, Freundlich's slope values were all higher than 1. It shows that isotherm energy is conducive to adsorbent (MWCNTs and residual soil) in the test conditions and that the Cadmium can be removed from the solution with good quality. From this study, it can be concluded that the correlation coefficient produced from Freundlich isotherm model is higher than Langmuir model. It indicates that a good correlation between experimental data and the model which is presented by linearized Freundlich model.

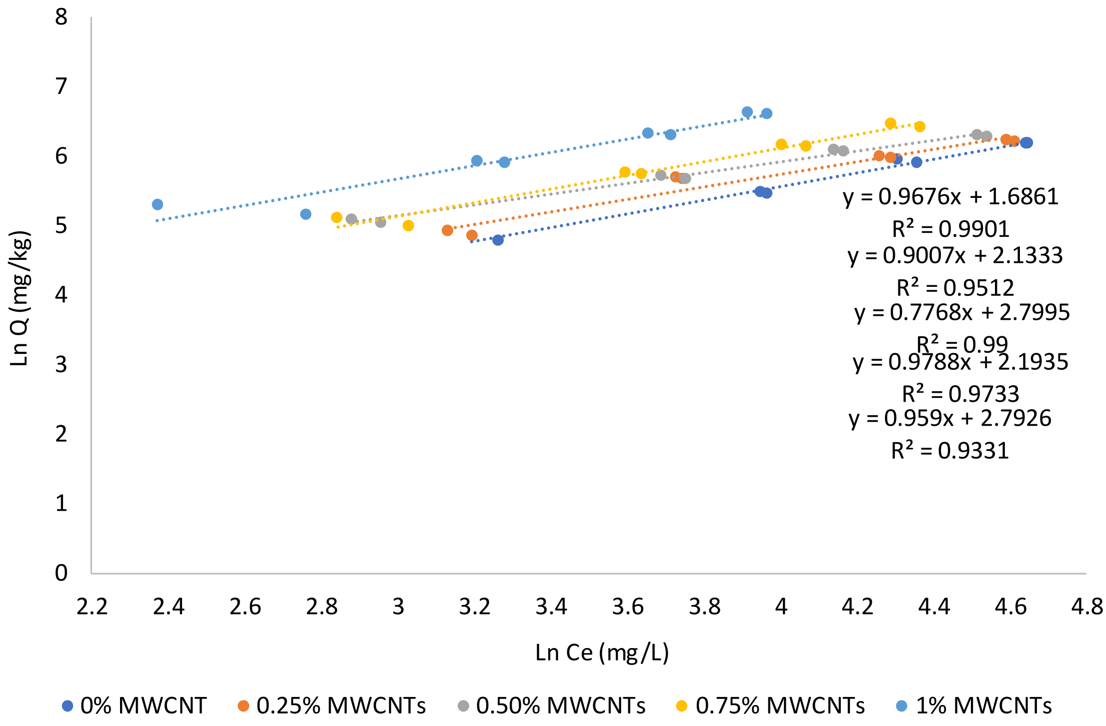

Fig. 7. Linearized Freundlich isotherm model for Cadmium on MWCNTs

IV. Conclusions

Experimental study on adsorption mechanism of the carbon nanotubes (CNTs) on contaminated soil was conducted. From this study, it concludes that the MWCNTs have excellent adsorption capability for removing various organic and inorganic contaminants. This study used MWCNTs in a series of adsorption tests to examine the adsorption of contaminants from residual soil. At different times of contact and contaminant concentration, the adsorption rate has been investigated quantitatively. With increasing time, removal of the adsorption concentration was found to be higher. It has consequently been found that after two days of observation the equilibrium concentration value tends to be relatively constant. MWCNT-adsorbed contaminant also increases due to an increase in the equilibrium of concentration. Regarding adsorbent isotherm models, the equilibrium data for the Freundlich equation in comparison to the Langmuir isotherm are reasonable. The best fit of equation explained the adsorption mechanism on experimental data from this study. Each experimental result has shown that MWCNTs can be applied as an effective adsorbent for contaminated organic and inorganic soils.

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