

# Efficiently Removal of Copper and Cadmium from Wastewater using Activated Carbon Produced from *Moringa oleifera* Bark

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**Abstract**— *Moringa oleifera* is a multipurpose tree. The main aim of this study was to use the *Moringa oleifera* bark with low doses as an adsorbent for the maximum removal of copper (Cu) and cadmium (Cd) from wastewater. There are some vital parameters which influence adsorption process such as contact time, adsorbent dose, initial concentration and pH were investigated. The activated carbon of *Moringa oleifera* bark with surface area of 439.2309m<sup>2</sup>/g and pore volume of 0.189245cm<sup>3</sup>/g was achieved at 700 °C and used (10%) zinc chloride and (0.5M) sulfuric acid as an activating agent to char ratio (5:1). The copper (Cu) was fully eliminated (100%) from aqueous solution within 10 min while cadmium (Cd) also was significantly removed using 0.25gm/L of adsorbents. The Freundlich isotherm, pseudo- second order kinetic equations were well fitted with a correlation coefficient of (0.993 and 1) for copper and (0.953 and 0.999) for cadmium respectively. We observed that at pH 11, adsorbents showed maximum adsorption capacity. Therefore, it can be used as a potential, eco-friendly non-toxic, cost effective application for wastewater treatment. Finally, this works also focused regeneration of adsorbents using solvents for further highest reuse of it.

**Keywords**— *Moringa oleifera* bark; Activated carbon; Adsorption; Heavy metal; Wastewater treatment

## I INTRODUCTION

Pure water has essential mineral elements which are very important for human beings and animals. Every cell of alive body needs pure water to continue normal activities. Pure fresh water does not appear in nature available due to contain huge contaminants in the environment. Many pollutants especially inorganic in nature like heavy metal contaminate water eco-systems and create serious problems. Toxic metal compounds contaminate not only surface water but also ground water. Most of the heavy metal come from industry. Major toxic elements are lead (Pb), copper (Cu), nickel (Ni), cadmium (Cd), chromium (Cr) etc. Wastewater mainly comes from municipal, agricultural and industrial activity [1]. Many

heavy metals are released from paint, ceramics and dyes industries [2]. According to WHO (1997), any change in the physical, chemical and biological properties of water may be dangerous effect on human beings and animals. This is known as 'water pollution'. Pollute water contain various poisonous agents such as heavy metal, colour, dyes, grease, oil and bacteria etc. The presence of these agents in water system may cause various water borne diseases. Human and animal use water for several purposes. But the water purity level is very crucial. For this reason, it can direct effect on health. The traditional wastewater treatment is used aluminium sulphate (alum) and calcium hypochlorite. But it's very costly for developing country. Wastewater is very harmful for human body and environment [3]. Cadmium (Cd) is released from zinc smelting, and paint sludge. Lead is released from lead batteries and ceramics [4]. Metal ions are being importance pollutants due to their toxicity [5]. Toxic heavy metal is very dangerous for non-biodegradability. These all gather in living organism causes appear disease & sicknesses [6]. This poisonousness may influence at nervous systems and other vital organs [7].

There are several conventional methods like physical, biological and chemical methods for eliminating heavy metal from wastewater [8, 9]. Adsorption is one of the vital process for toxic metal removal from wastewater [10]. Most of the water treatment processes are very costly in the global [11, 12]. Adsorption is a physico-chemical phenomenon which can adsorb contaminants from wastewater by surface chemistry of adsorbents. Normally, Commercial activated carbon is used as adsorbent in adsorption process for the wastewater treatment due to high adsorption capacity and environmental friendly [13] but it is very costly process [14]. Therefore, it is essential to find natural alternatives that is cost effective and available. Natural by-products are the essential source for adsorbents. There are some polar

functional groups. Most of the vital groups are hydroxyl, aldehydes, carboxylic, and ketones [2]. These groups can fix heavy metals by providing an electron pair [5]. Several agricultural waste like neem bark, *Moringa Oleifera* bark, rice husk have binding capacity that adsorb pollutant from aqueous solution. Adsorption capacity can be developed using chemically activated adsorbents. Adsorption method is very popular for effectiveness, cheap and available every place [15].

*Moringa oleifera* (MO) is one of these alternatives for wastewater treatment [16, 17]. It has been found useful in nutrition, water purification, and industrial applications. It's also called "Drumstick" or Ben oil tree and is a medium sized medicinal tree. It is available in south Asia, Africa, and South America. Leaves and seeds of MO are very frequently used for water treatment [18]. It has no side effects. It is non-toxic and ecological material [19]. MOCR (*Moringa oleifera* cake residue) don't need further preparation for water purification process [20]. MO seed has excellent coagulant properties to purify contaminated water [21]. It can remove turbidity from wastewater and also has antimicrobial properties [22]. *Moringa oleifera* bark have non-toxic natural organic polymer such as alkaloids, phenols and glycosides which have been employed as an effective adsorbent for purification of wastewater. Many researchers have used *Moringa oleifera* seeds, leaves and fruits for water decontamination. The seeds of *moringa oleifera* contain polyelectrolytes which can bind contaminants. *Moringa oleifera* have the valuable effect as medicine, nutrition, water management and so on [15]. Leaves, fruits, roots of MO are used as vegetables [23] and source of vitamins [24, 25]. Other sides, various parts of MO such as stem, bark, and roots have antimicrobial activities [26, 27]. *Moringa oleifera* leaves have both macro- and micronutrients such as  $\beta$  carotene, protein etc. It's leave possesses hypolipidaemic and antiatherosclerotic activities [28]. *Moringa oleifera* pods have free radicals scavenging abilities [29]. Its act as a natural antioxidant [30] like some other plants which are reported as natural sources of antioxidants [31, 32]. *Moringa oleifera* bark also remove heavy metal like Ni (II) from wastewater [33]. It has maximum adsorption capacity of 30.38 mg/g [34]. *Moringa oleifera* is a low-cost plant and biodegradable sludge. A central carbon atom of glucosinolate is bonded to thioglucose group with a sulfur atom and also bonded to a sulfate group with a nitrogen atom. These functional groups can be used to remove contaminants from wastewater. Finally, the major objective of this experiments was to use activated carbon of the *Moringa oleifera* bark with low doses as an adsorbent to successfully eliminate copper (Cu) and cadmium (Cd) from wastewater.

## II EXPERIMENTAL

### A. Sample collection and preparation

*Moringa oleifera* bark were collected from natural sources near the University Sains Islam Malaysia (USIM) campus, in-front of Akasia Park, Bandar Baru Nilai, Negeri Sembilan, Malaysia and washed with distilled water. The barks were sun dried for 6 hours then it washed with distilled water to remove dirt from its surface and dried in an oven at 110 °C for 13 hours. The *Moringa oleifera* bark were reduced

into smaller particle sizes using mortar & pestle as well as blinder. The samples (100 g) were then chemically activated using 500 ml zinc chloride (10%  $\text{ZnCl}_2$ ) and sulfuric acid (0.5M  $\text{H}_2\text{SO}_4$ ) with ratio of 1:5 for 12 hours. Then the samples were dried in the oven at 110 °C for 12 hrs. It was grinded and sieved at 400 $\mu\text{m}$ . Then the sample was kept in the desiccator for further use. The precursor was placed in the furnace at 700 °C with heating rate of 10 °C/min for 60 min. During the carbonization process, purified nitrogen was flown. It was cooled in normal temperature. This activated carbon samples were washed severally with distilled water. The washed samples were dried in oven at 110 °C for 15 hours. These were then sieved with a sieve of 400 $\mu\text{m}$ . The activated carbon samples were kept in a polypropylene bottle to avoid moisture. These prepared activated carbon of *Moringa oleifera* bark were used for the experiments as the adsorbent in adsorption process.

### B. Instrumentation

Water distillatory (2108, GLF, Germany), pH meter (3510, Genway), analytical balance (CP 2245, Sartorius, USA.), Oven, Furnace, Shaker and Blinder are used during this study. The concentration of before and after adsorption of solution were determined using Atomic absorption spectrophotometer (AAS-240 FS AA, USA). FTIR spectra were determined using (PERKIN ELMER FTIR Model 1600, Greenville, SC, USA) where the spectra were obtained ranging 4000-400 $\text{cm}^{-1}$ . Micro porosity of outer surface of adsorbents and pore size were obtained using Scanning electron microscope (SEM-HITACHI SU 6600, Tokyo, Japan) and Brunauer-Emmett-Teller (BET : BELSORP-MINI, Chiba, Japan).

### C. Chemicals

Almost chemicals were of analytical grading and were directly used without further purification. The chemicals such as  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (>99%),  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (99%), 0.5M HCl (70%), 0.5M  $\text{H}_2\text{SO}_4$  (>98%), 0.5M  $\text{HNO}_3$  (70%), 1N NaOH, 0.05M  $\text{NaNO}_3$  buffer, (10%)  $\text{ZnCl}_2$ , were purchased from Merck, Germany. All chemicals were used as received.

### D. Adsorption Experiments

Stock solution of metal were made by dissolving metal nitrate ( $\text{Cd}(\text{NO}_3)_2$ ) and sulphate salts ( $\text{CuSO}_4$ ) in deionized water. Different concentrations were obtained from the stock solutions. This study was conducted by adding 0.25gm/L activated carbon in solutions. Flask with adsorbents are placed in a shaker at room temperature ( $25 \pm 2$  °C) with 200rpm speed for 2 hours. The pH was controlled at 11 using 0.1N  $\text{NaNO}_3$  buffer solution to get best adsorption capacity for this experiment but to observe the effect of pH of the solution were adjusted ranging from 2-12 by 0.1N (HCl & NaOH) solutions. Then after 10, 20, 30, 60 and 120 minutes the samples were taken and filtered with whatman filter paper. It was analysed using Atomic Adsorption Spectrophotometer (AAS). According to equation (1), the amount of adsorbate adsorbed on the adsorbent at equilibrium,  $q_e$  (mg/g) was calculated and the percent removal of adsorbate was evaluated as expressed in equation (2) [35]:

$$q_e = (C_o - C_e)V/W \dots\dots\dots(1)$$

Where  $C_o$  and  $C_e$  (mg/L) are the concentrations of solution at initial and at equilibrium time, respectively.  $V$  is the volume of the solution (L) and  $W$  is the mass of adsorbent used (g):

$$\% \text{Removal} = (C_o - C_e) \times 100 / C_o \dots\dots\dots(2)$$

Adsorption isotherm and Kinetics equation

The most commonly used adsorption isotherm models are those of Freundlich and Langmuir. In this work, Langmuir Model was tested and given as:

$$q = q_m K_q C / (1 + K_q C) \dots\dots\dots(3)$$

Where  $q_m = q$  for a complete monolayer (g adsorbate/g sorbate),  $K_q = a$  coefficient (kg/m<sup>3</sup> or g/cm<sup>3</sup>). Taking reciprocal and rearranging equation (3) gives:

$$1/q = 1/q_m + 1/K_q q_m C \dots\dots\dots(4)$$

A plot of  $1/q$  versus  $1/C$  gives a straight line of slope  $1/K_q q_m$  and an intercept of  $1/q_m$ . Equation (4) could be expressed in a standard format as given below:

$$C_e/q_e = 1/Q_o + C_e/Q_o \dots\dots\dots(5)$$

Where  $C_e$  is the equilibrium concentration of sorbate (mg/liter or ppm or g/cm<sup>3</sup> or mol/m<sup>3</sup>),  $q_e$  is the amount adsorbed at equilibrium (mgg-1) while  $Q_o$  and  $b$  are the Langmuir constants related to capacity (mgg-1) and energy respectively. A plot of  $C_e/q_e$  Versus  $C_e$  gives a straight line of slope  $1/Q_o$  and intercept of  $1/Q_o b$ . However, a pseudo-first order kinetic model as recommended by [6] is given as:

$$dq_e/dt = K_1(q_e - q_t) \dots\dots\dots(6)$$

Where  $q_e$  and  $q_t$  are adsorption capacity terms at equilibrium and at time  $t$  respectively (mg/g),  $K_1$  is the rate constant. Integrating equation (6) with the boundary conditions gives:

$$\log(q_e - q_t) = \log q_e - K_1 t / 2.303 \dots\dots\dots(7)$$

A plot of  $\log(q_e - q_t)$  versus  $t$  is a linear relationship from where  $K_1$  and  $q_e$  can be determined respectively. In a similar manner the pseudo-second order model is expressed as:

$$dq_e/dt = K_2(q_e - q_t)^2 \dots\dots\dots(8)$$

Where  $K_2$  is the pseudo- second order rate constant of adsorption. After integration:

$$1/q_e - q_t = 1/q_e + K_2 t \dots\dots\dots(9)$$

The linearized form of equation (9) is:

$$t/q_e = 1/K_2 q_e^2 + (1/q_e)t \dots\dots\dots(10)$$

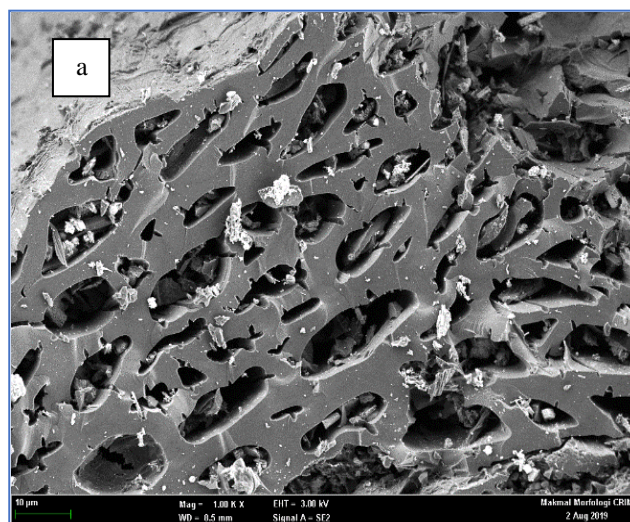
Again, a plot of  $t/q_t$  versus  $t$  will give a linear relationship with  $1/q_e$  and  $1/K_2 q_e^2$  as the slope and intercept respectively.

### III RESULT AND DISCUSSION

#### A.Characterization of Activated carbon

##### 1) Surface Morphology

Figure 1(a) shows the FESEM micrographs of the *Moringa oleifera* bark activated carbon before adsorption under 1000x magnification while (b) is the micrographs of the activated carbon after adsorption under 30000x magnifications. There were presence many hole on its surface. These holes were the available pores, where copper and cadmium molecules were to be captured from wastewater solution. Large and well-developed pore were obtained from prepared activated carbon under optimum condition (at 700 °C temperature, activation time 60 min as well as char: ZnCl<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> impregnation ratio 1:5). It might be occurred due to use chemically activity agent. The adsorb metal molecules got to fill the pores from adsorbent surface to inner pore and at last its bind at the available sites on their surface. Surface area and pore volume development could be happened also during pyrolysis process. This produced well developed pore was the important factor to adsorb the maximum heavy metal from wastewater. Both micrographs presented with the morphological changes of the carbon materials during before and after adsorption processes. Figure 1(b) shows after adsorption most of the pore of activated carbon has been filled-up by heavy metal. After carbonization was performed under inert condition, some irregular holes and pores were developed on the surfaces of the chars. This was due to the sudden burst of the thermal expansion from pyrolysis. Pore development in the char during pyrolysis was important. Since it would develop the surface area and pore volume of the activated carbon after the activation process [36]. The activated carbon formed irregular, large caved-in shaped cavities on its surface. The adsorption of cadmium at the surface of adsorbents might be physiosorption and copper could be occurred chemisorption.





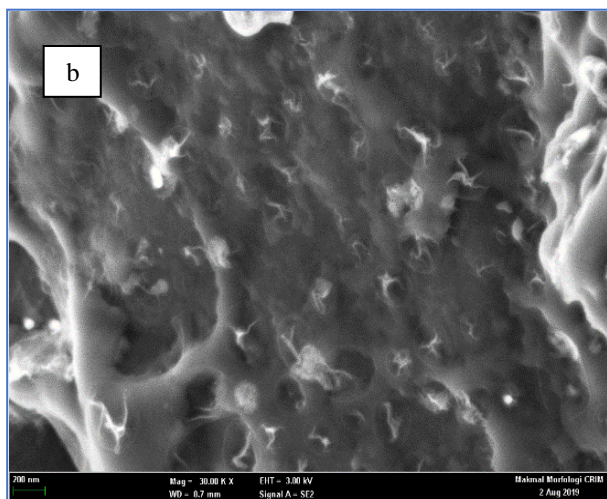


Fig. 1. FESEM micrograph of *Moringa oleifera* bark (Activated carbon); (a) before and (b) after adsorption

## 2) Surface Area and Porosity

In this study, the surface area and porosity of the prepared activated carbon were analysed. The BET surface areas were found to be relatively high. The smallest pore was surface area of 396.9325 m<sup>2</sup>/g and the largest was 435.1738 m<sup>2</sup>/g when pyrolysis was done at 700 °C. The total pore volumes measured as higher for single point and micropore were 0.189245cm<sup>3</sup>/g and 0.153732cm<sup>3</sup>/g respectively. The development of more surface area and pores in activated carbon treated with acid solution is likely to be due to the elimination of impurities on the surface and/or in the pores. The pore size for single pore (diameter) and micropore (width) were analysed as 68.488 Å and 17.234 Å. Activated carbon can consist of mineral matter up to 15 % in the form of ash content, which clogs up in the pores (Aji *et.al.* 2015). According to [37], the minerals are observed as unwanted contaminants such as N, P, Si, Na, K, Zn and Fe. In order to purify the prepared activated carbon and to remove the contaminants, acid solution is usually used during washing part and in further treatment. These inorganic elements could be removed from activated carbon with acid (H<sub>2</sub>SO<sub>4</sub> and ZnCl<sub>2</sub>) treatment in order to reduce the ash content.

## 3) Surface Functional Groups

The FTIR spectra analysis is essential to determine various surface function of *Moringa oleifera* bark (MOB), as shown in Figure 2. The FTIR spectrum of MOB shown broad peaks at 3371 cm<sup>-1</sup> which are attributed to the O-H stretching band of hydroxyl group of phenols and alcohols in lignin and cellulose of MOB before adsorption process [38,39]. The distinct peaks observed in 3183 cm<sup>-1</sup> are detected to the C-H stretching vibrations of aliphatic hydrocarbons [40]. The band at a range of 1615–1430 cm<sup>-1</sup> is attributed to C=C stretching vibrations, and the peak <900 cm<sup>-1</sup> results of C-H (out of plane) confirm the presence of aromatic ring in the adsorbent [41]. The peaks at 1126 cm<sup>-1</sup> may denote the presence of stretching C–O, which includes compounds such as carboxyl groups that provide adsorption sites for the metal ions.

Oxygen functional groups of ketone (C=O) was not detected in the prepared activated carbon. The presence of oxygen (C–O) functional group peak was detected at 1126 cm<sup>-1</sup> on the surface of activated carbon. It was expected to indicate the polarity. After adsorption of heavy metal, peaks were detected with slightly shifting at 3500 cm<sup>-1</sup> (O–H), 1432 cm<sup>-1</sup> (C–O), 1123 cm<sup>-1</sup> (C–O) stretching, peak for 3125 (C–H) stretching due to bind with metal.

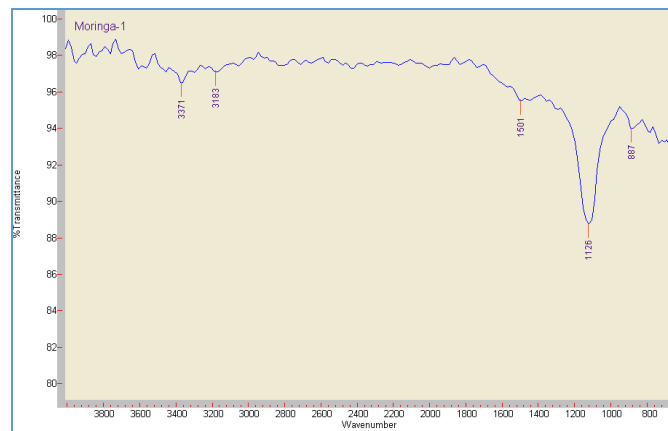


Figure 2. FTIR spectra before metal ion adsorption on *Moringa oleifera*

## B. Equilibrium Studies

The equilibrium curve of copper and cadmium for the *Moringa oleifera* activated carbon was studied and shown in Figure 3. The copper curve shows a concave downward shape due to high affinity between adsorbate and activated carbon. The contaminant metals were cationic form. The adsorption mechanism could be occurred by ion exchange or electrostatic forces due to possess oxygen containing group (COOH) on surface of adsorbents. So, with increasing the oxygen containing group of adsorbents, the quantity of adsorbate also increased. The amount of adsorbate ranged from 3.98 mg/g to 20.45 mg/g within 10 min for ranging initial concentration (1-5) mg/L of copper salt solution were observed where final concentration obtained zero (C<sub>f</sub>=0) and after 120 min the quantity of adsorbate ranged from 3.98mg/g to 20.09mg/g respectively. On contrast, for cadmium salt solution adsorbed amount were obtained from 4.36 mg/g to 19.65 mg/g at 10 min with final concentration as C<sub>f</sub>~0 and at equilibrium state the quantity of adsorbent shown 3.4 mg/g to 11.42 mg/g. Therefore, at 700 °C activation temperature and char: zinc chloride & sulfuric acid with ratio 1:5, the activated carbon showed optimum adsorptive capacity. The results showed a rapid uptake of adsorbate molecules onto the surface of the adsorbent at the first 10 min, and then shown slight desorption and again a slower uptake up to 120 min. The reason for this behavior is that the adsorptive site becomes loaded as molecules adhere to the surface of the carbon structure. The values however greatly depend on the equilibrium concentration of the effluent with the adsorbent.

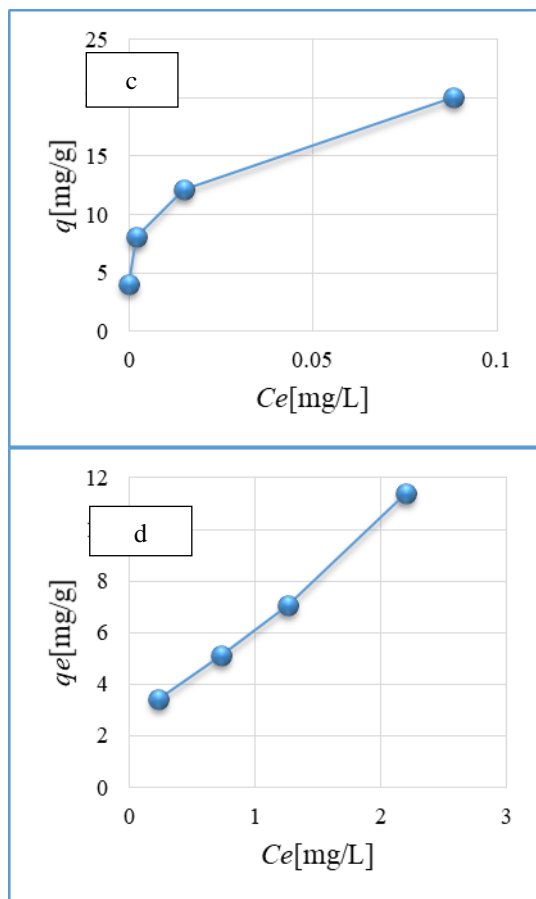


Figure 3. Equilibrium curve for (c)  $\text{Cu}^{2+}$  and (d)  $\text{Cd}^{2+}$  using optimum value obtained

### C. Langmuir and Freundlich isotherms

Langmuir isotherm expressed monolayer of the metal ions are designed on adsorbent. The experimental  $q_{\max}$  for *Moringa oleifera* are found to be 20.43 and 17.01 for Cu and Cd comparable with theoretically calculated  $q_{\max}$  as given in Table 1. The higher value of b is described the affinity of the adsorbent to adsorb metal ions. The value of  $q_{\max}$  can also be considered as the total number of active sites of adsorbents for adsorption. According to the Table 1, the affinity order of *Moringa oleifera* is like  $\text{Cu} > \text{Cd}$ . From the plot of  $\log q$  against  $\log C_e$  were obtained the constant K and  $1/n$ . K is indicated the strength of adsorption. Lower value of K designates the more adsorption [42]. Another constant  $1/n$  is indicated the adsorption intensity. Data would be favourable when n value is ( $1 < n < 10$ ). All data of *Moringa oleifera* are well fitted of Langmuir isotherm and Freundlich isotherm. The mean adsorption energy (E) can describe about adsorption properties. It can be calculated from the D-R isotherm model [43]. If the values of  $E < 8 \text{ kJmol}^{-1}$ , it follows physical adsorption. When the value of E is ranging 8-16, it follows chemical adsorption. From the Table 1 of adsorption energy values suggested that *Moringa oleifera* indicates a physical adsorption for cadmium (Cd,  $E=2.61$ ) metal ions and copper (Cu,  $E=9.8$ ) adsorbed by chemical adsorption process.

The experimental data were well fitted into Freundlich isotherm and represented in Figures 5. For Langmuir isotherm, plot of  $C_e/q_e$  against  $C_e$  shown linear relationship with  $R^2=0.989$  of copper and  $R^2=0.801$  of cadmium. For Freundlich isotherm, plot of  $\log q_e$  against  $\log C_e$  gave also linear relationship with  $R^2=0.993$  of copper and  $R^2=0.953$  of cadmium. The Freundlich plot and the Langmuir plot fitted favourably well with the isotherms because the value of  $R_L$  obtained from slope were 0.0021 for copper and 0.22 for cadmium [favourable when ( $0 < R_L < 1$ )]. For Freundlich isotherm, a value of  $n$  ( $4.22 > 1$ ) for copper and  $1.91 > 1$  for cadmium (favourable when  $1 < n < 10$ ) obtained represents a favourable condition following the works of McKay and Ho (1998).

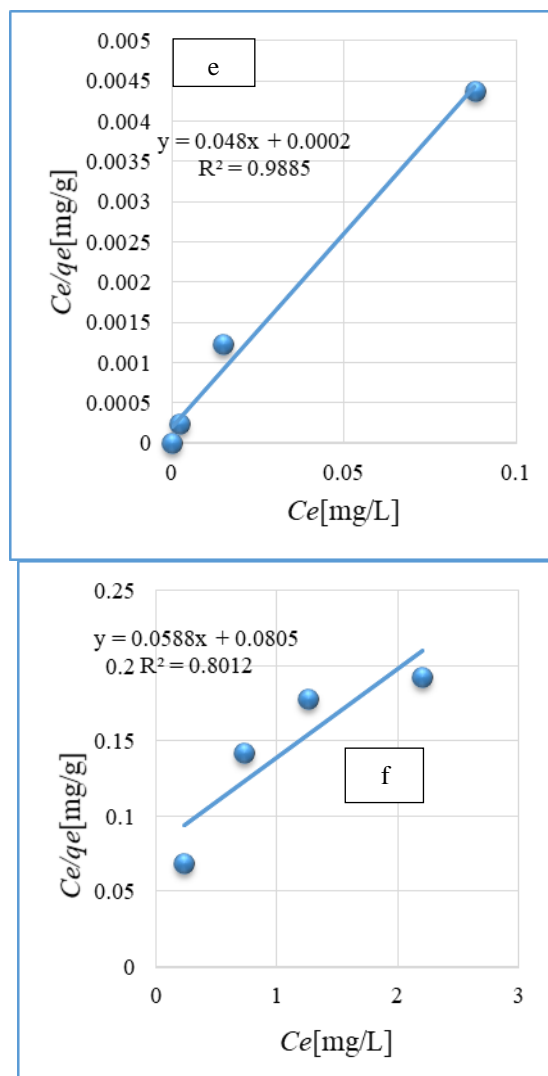


Figure 4. Langmuir plot for activated carbon using optimum value for (e)  $\text{Cu}^{2+}$  and (f)  $\text{Cd}^{2+}$  adsorption

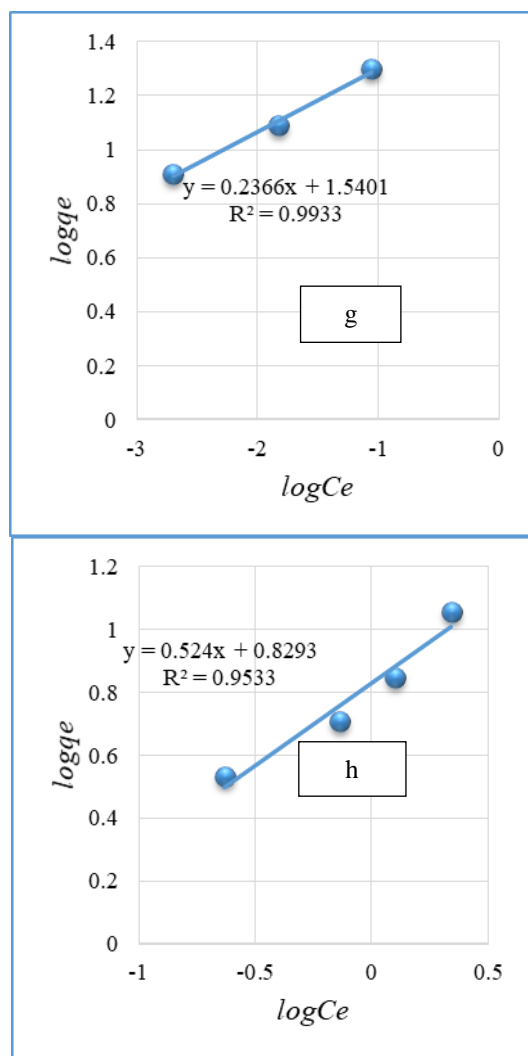


Fig. 5 Freundlich plot for activated carbon using optimum value for (g)  $\text{Cu}^{2+}$  and (h)  $\text{Cd}^{2+}$  adsorption

TABLE 1 Comparison table for Langmuir, Freundlich and Dubinin-raduchkevich of *Moringa oleifera* activated carbon

	Langmuir model			Freundlich model			Dubinin-Radushkevich		
	$R^2$	$q_{max}$	$b$	$R^2$	$1/n$	$K$	$R^2$	$q_{max}$	$E[kJ/mol]$
Heavy Metal		[mg/g]	[Lmg-1]					[mg/g]	
Cu	0.989	20.43	162.07	0.993	0.24	34.7	0.949	22.07	9.80
Cd	0.801	17.01	0.73	0.953	0.52	6.75	0.774	8.94	2.61

#### D. Adsorption kinetic studies

The correlation coefficient, rate constants, calculated metal-uptake and other kinetic constant from the three models studied were shown in Table 2. These calculated kinetic constants indicated pseudo-second-order kinetic with highest correlation coefficient  $R^2$  to fit best. Kinetic does not apply to pseudo-first-order and inter-particle diffusion model. Equally, calculated metal-uptake in pseudo-first-order kinetic is by far less than one obtained from experiment ( $q_e(\text{cal}) < q_e(\text{exp})$ ). Whereas, in pseudo-second-order kinetic, the metal-uptake calculated is closer to that obtained from experiment. This further confirms fitness of kinetic studies with pseudo-second-order.

If the linearity was achieved and the line passes through the origin, it indicates the internal diffusion is the slowest step in the adsorption process. From Figure 6, graph line for copper and cadmium of *Moringa oleifera* were not linearity and did not pass through the origin. It is indicated that the adsorption process was controlled by film diffusion [44]. From the Figures 7 and 8 of this finding, the pseudo-second order well favoured the adsorption process with a regression correlation  $R^2$  of 1 for copper and 0.999 for cadmium while the pseudo first order kinetic coefficient  $R^2$  got 0.963 for copper and 0.864 for cadmium. The correlation coefficient was well fitted for pseudo-second order contrast of first order and inter-particle diffusion. Therefore, the adsorption and kinetics of  $\text{Cu}^{2+}$  ions and  $\text{Cd}^{2+}$  could be well approximated adequately by the second order model.

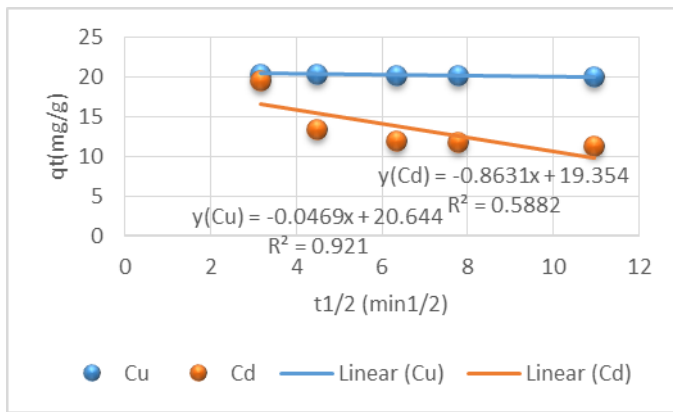


Fig. 6 Inter-particle diffusion for copper and cadmium of *Moringa oleifera*

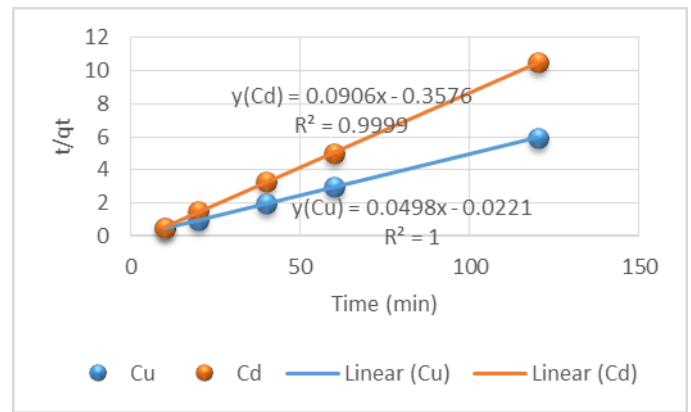


Fig. 8 Pseudo second order kinetic model for  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  adsorption from optimum value obtained

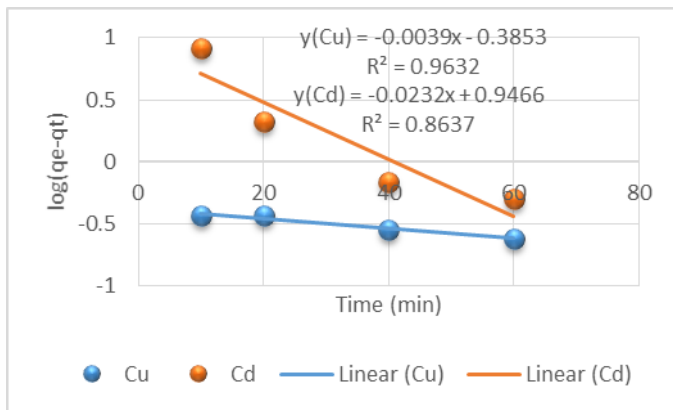


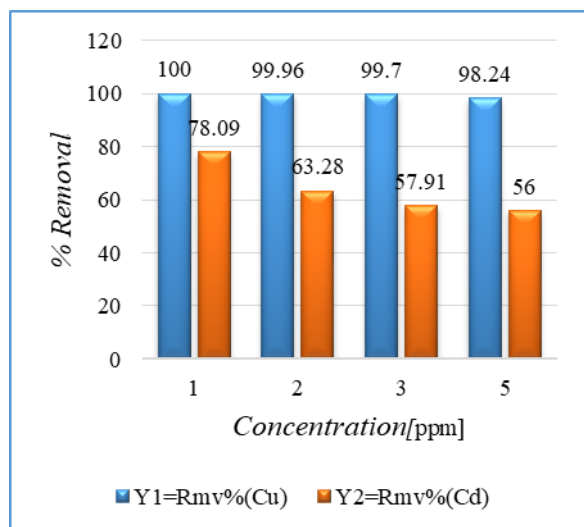
Fig.7 Pseudo first order kinetic adsorption model for  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  from optimum value obtained

TABLE 2 1<sup>st</sup>, 2<sup>nd</sup> order and inter-particle diffusion constant values comparison of *Moringa oleifera* activated carbon

Heavy Metal	$q_{\text{exp}}$ mg/g	Intra -Particle Diffusion							
		First Order			Second Order				
		$R^2$	$q_{\text{sat}}$ mg/g	$k_1$ [ $\text{min}^{-1}$ ]	$R^2$	$q_{\text{sat}}$ mg/g	$K^2$ $\text{min}^{-1}$ [ $\text{gmg}^{-1}$ ]	$K_d$ [ $\text{mg}^{1/2} \text{min}^{-1/2}$ ]	$R^2$
Cu	20.09	0.963	2.43	0.009	1.00	20.08	0.112	0.047	0.929
Cd	11.42	0.864	8.87	0.053	0.999	11.04	0.023	0.863	0.588

### E. Effect of Initial concentration

The effect of initial concentration for the removal of copper and cadmium from wastewater using activated carbon of *Moringa oleifera* shown as Figure 9. The initial concentrations were set at 1,2,3,5 mg/L. It may be described from the graph that with increasing the initial concentration, the removal percentage of copper and cadmium from aqueous solution were decreased but the adsorption capacity of both metals also was increased using all activated carbon. Within 10min for all initial concentration (mg/L), absolutely (100%) percent of copper was removed and the adsorption quantity was 20.45mg/g. but after 120min at equilibrium copper removal percentage was slightly decreased and obtained more than 98% as shown in Table 3. On contrast, the removal percentage of cadmium were 100% for concentration of 1 & 2 mg/L and more than 96% for concentration of 5mg/L in just 10 min. but after equilibrium, the removal percentage of cadmium was decreased and obtained more than 56. This type of pattern suggested that it can be possible due to monolayer formation of pollutant on the adsorbent surface [45].



### F. Effect of Adsorption Time

The adsorption experiments were necessary to define the contact time essential to touch the equilibrium position. The adsorption performance of copper and cadmium were conducted at time intervals 10-120 min as shown in Figure 10. Firstly, the amount of metal uptake was very good from 10 min to equilibrium state for copper but for cadmium after 10 min was decreased then steady with time till equilibrium state. After 120 minute it was reached at equilibrium state where metal cannot be removed from solution more. The quick uptake happened was due to more active sites on *moringa oleifera* bark were open. It permitted rapidly binding pollutant on the adsorbents. Since the active part became used, the adsorption rates fall down. It can be occurred for reducing active part by metal ions. The elimination activity reduced by about 2-40 % with increasing contact time to reach equilibrium position. It caused from

saturation of adsorbent surface with heavy metals followed by adsorption and desorption process after saturation [43].

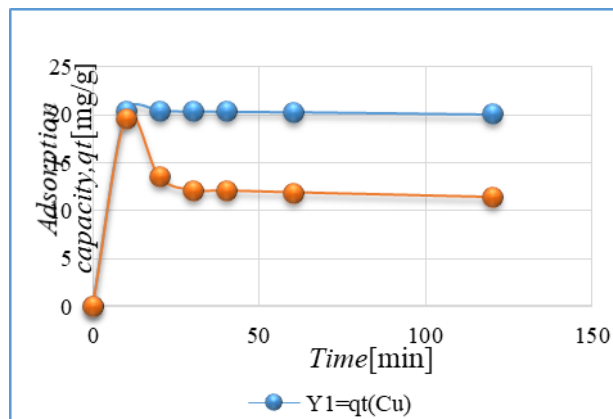


Fig. 10 Effect of time on adsorption capacity of  $\text{Cu}^{2+}$  &  $\text{Cd}^{2+}$

### G. Effect of Adsorbent Dosage

The effect of adsorbent dosage was carried out ranging from 5mg to 50 mg of each activated carbon during removal of heavy metal adsorption from 100ml aqueous solution as shown in Figure 11. This figure shows that with increasing the adsorbent dosage, the removal of metal ion also improved from 20% to 100% for copper and 56% for cadmium. After reaching at 0.025g of adsorbent dosage, the adsorption process also reached equilibrium state. The removal percentage of pollutant improved from aqueous solution with the improving dosage. This can be obtained to have available active part of adsorbents for complexation of heavy metal. Further increasing the adsorbent dose cannot show significant improvement in removal adsorption. This may be occurred due to reach the equilibrium state between binding adsorbate and unabsorbed adsorbate in adsorption process.

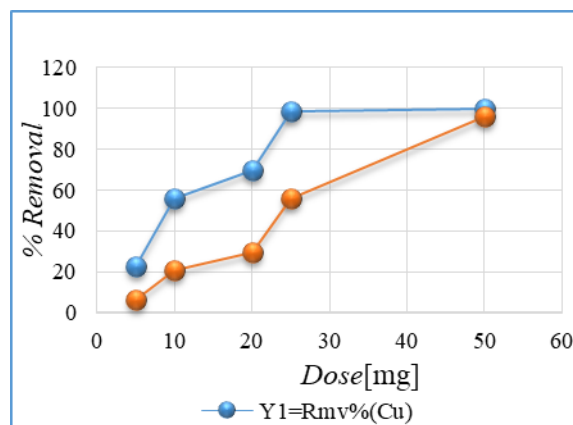


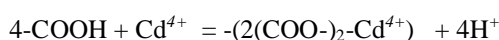
Fig. 11 Effect of dose and on adsorption capacity of  $\text{Cu}^{2+}$  &  $\text{Cd}^{2+}$

### H. Effect of $\text{pH}$

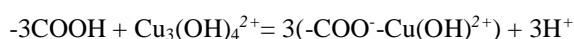
The adsorption performance of activated carbon can affect by pH of solution [46]. This studies removal percentage of both metals were conducted ranging pH 2-12 of solution, as shown in Figure 12. The graph shows that with increasing the pH values, the metal removal percentage also increased and



at pH 11 maximum removal percentage obtained. If the pH value was low, the outer surface of adsorbents was gathered with many positive charges, which provided a greater static repulsion force. If pH increased, the static repulsion forces reduced, and heavy metal adsorption improved. When the pH value less than 8 the dominant species Cd (II) is exist  $Cd^{2+}$ . At the pH range of (9-11), Cd (II) mainly exists in the cationic form of  $Cd_4(OH)_4^{4+}$ . On the other hand, at pH above the 11, Cd (II) is in the form of  $Cd(OH)_2$ . The technique of cadmium (II) in adsorption can be conducted by the electrostatic forces. With the increasing the pH value, the concentration of  $H^+$  ion in solution decreases, the negative surface charge will be an increase on the activated carbon above the pH(pzc) value of (5.4). For this reason, to attract of adsorbing metal cations mainly in the cationic form  $Cd^{4+}$  and they more easily get adsorb onto the adsorbents. The Cd (II) adsorption on activated carbon can be also described by ion exchange mechanism. The main functional groups on the surface of adsorbents are the carboxyl, hydroxyl, methoxyl group which are responsible for ion exchange on to their surface. The mechanism taking place on adsorbents is shown in equation



At lower pH less than 5, Cu (II) mainly exists as  $Cu^{2+}$  but at higher pH range of 7-11 the predominant species of Cu (II) is  $Cu_3(OH)_4^{2+}$ . At around a pH of 6 there is a very small fraction of  $Cu_2(OH)_2^{2+}$  present in the solution. The higher adsorption rate for *Moringa oleifera* activated carbon at a pH 11 can be explained by the mechanism of electrostatic force. At pH > pH (pzc)5.4 for adsorbents, the surface of adsorbent is negatively charged which carry on an electrostatic force between the metal cations  $Cu_3(OH)_4^{2+}$  and active sites of adsorbent. At a lower pH, the adsorbent surface contains positively charge and  $H^+$  ion in the solution inhibit the approach the metal cations and less adsorption occur. On the other hand, the acidic carboxylic group on surface of adsorbents can conduct adsorption of metal ions by ion exchange mechanism which is shown in equation below



At pH 2, the metal adsorption was lower due to present available  $H^+$  ions. This  $H^+$  ions contested with metal ions for the active sites, hampering to adsorb of  $Cu^{2+}$  and  $Cd^{2+}$  ions with activated carbon. Protonated active part was not capable to adsorb metal due to electrostatic repulsion. As the pH increased,  $H^+$  ions decreased. Therefore, huge negatively charged sites were prepared and metal ions uptake increased by electrostatic attraction.

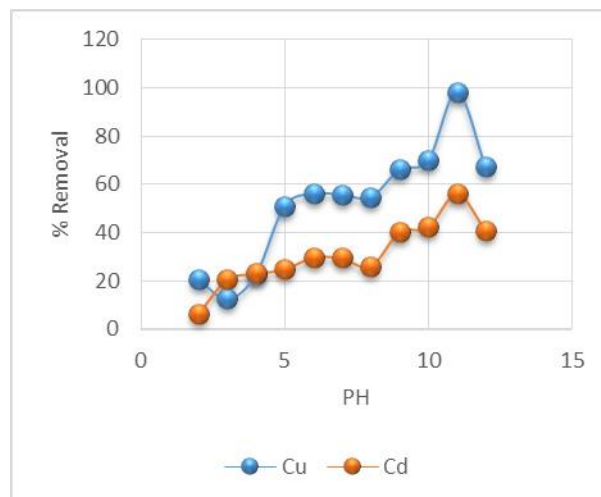


Fig. 12 Effect of pH on adsorption capacity of  $Cu^{2+}$  &  $Cd^{2+}$

### I.Desorption of Heavy Metals

The reusability of *moringa oleifera* was studied by cycling adsorption/desorption process ( $C_0 = 5mg/L$ ,  $pH \approx 11$ ,  $S/L = 0.25 g L^{-1}$  and  $t = 60 min$ ,  $T = 25^\circ C$ ). The studies were conducted by batch desorption technique using HCl,  $H_2SO_4$ , NaOH and  $Na_2CO_3$  of 0.1N with the metal loaded adsorbent, as shown in Figure 13 and Table 4. Hydrochloric acid performed great desorption efficacy for Cu (II) (88.26%) and Cd (II) (99.13%). After every adsorption run, activated carbon of *Moringa oleifera* was separated from the solution by filtration with whatman filter paper and washed with distilled water. It was then dispersed in a solvent (HCl), shaken (200 rpm) for 1 hour and washed with distilled water then dried. Generally, with increasing cycle number, desorption efficiency decreases due to the reduced of adsorption capability as shown in Figure 14 and Table 5. In every cycle, innovative binding sites was decreased which was generated by dilute HCl treatment. Desorption efficiency of *moringa oleifera* was calculated from equation (14):

$$Desorption(\%) = q_d \times 100 / q_e \dots \dots \dots (14)$$

Where,  $q_d$  is the mass of the metal ions (mg/g) desorbed from adsorbents. As well as  $q_e$  is the mass of metal ion (mg/g) adsorbed onto the adsorbents. The mass of metal ion desorbed,  $q_d$  (mg/g) is evaluated from this equation

$$q_d = \frac{C_d \times V_d}{W} \dots \dots \dots (15)$$

Where,  $C_d$  is the concentration of the metal ion (mg/L) left in solution after desorption. The total volume (L) of the solution expressed  $V_d$  and W is the mass (g) of the adsorbent.

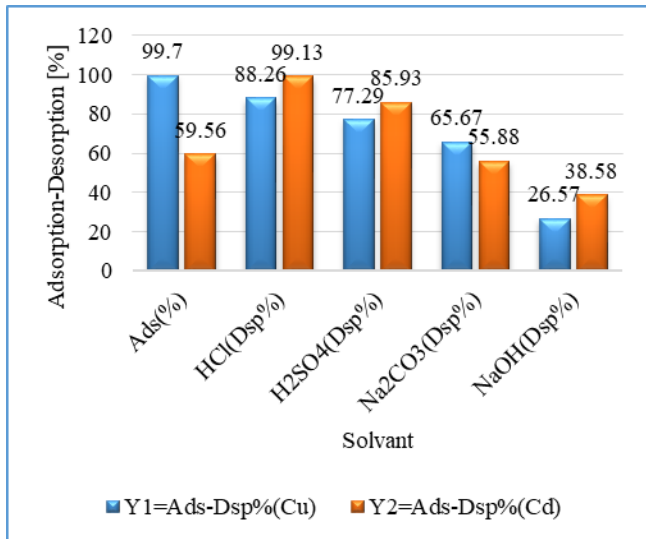


Fig. 13 Adsorption-desorption performance using various solvents of *Moringa oleifera* as adsorbent at  $C_0 = 5 \text{ mg L}^{-1}$ ,  $S/L_{\text{ratio}} = 0.25 \text{ g L}^{-1}$ , and  $T = 25^\circ\text{C}$ .

TABLE 3 Adsorption desorption percentage of *Moringa oleifera* activated carbon with different solvents

Heavy Metal	Adsorption [%]	Desorption HCl [%]	Desorption H <sub>2</sub> SO <sub>4</sub> [%]	Desorption Na <sub>2</sub> CO <sub>3</sub> [%]	Desorption NaOH [%]
Cu	99.7	88.26	77.29	65.67	26.57
Cd	59.56	99.13	85.93	55.88	38.58

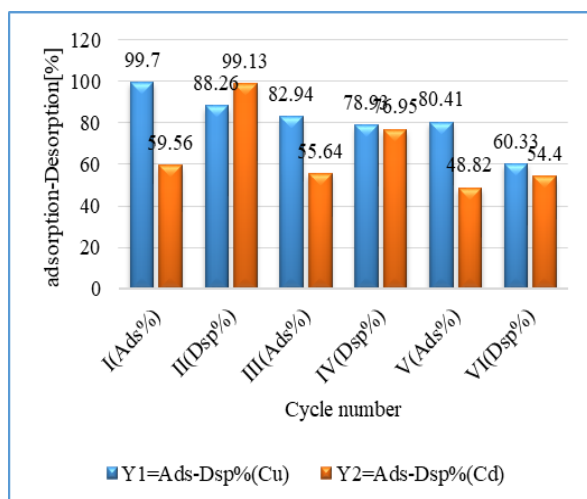


Fig. 14 Adsorption-desorption cycling performance using 0.1N HCl solvents of *Moringa oleifera* as adsorbent at  $C_0 = 5 \text{ mg L}^{-1}$ ,  $S/L_{\text{ratio}} = 0.25 \text{ g L}^{-1}$ , and  $T = 25^\circ\text{C}$ .

TABLE 4 Percentage desorption efficiency of *Moringa oleifera* activated carbon using 0.1N HCl for various cycles

Cycles	I	II	III	IV	V	VI
Heavy Metal	Adsorption	Desorption	Adsorption	Desorption	Adsorption	Desorption
	[%]	[%]	[%]	[%]	[%]	[%]
Cu	99.7	88.26	82.94	78.93	80.41	60.33
Cd	59.56	99.13	55.64	76.95	48.82	54.4

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#### CONCLUSION

The activated carbon from *Moringa oleifera* is an effective adsorbent for eliminating toxic metals from wastewater. The adsorptive capacity of the developed carbon depends on the activation process which has impacts on pore size, pore volume and surface area. The adsorption capacity of 20.09 mg/g for copper and 11.42 mg/g for cadmium were achieved using activated carbon of *Moringa oleifera* bark with an acid concentration of 0.5M H<sub>2</sub>SO<sub>4</sub>. It showed that Cu was 100% removed from solution within 10 min and Cd also removed 96.32% from produced wastewater. From the isotherm plot, it was observed that Freundlich plot well fitted with generated data. A pseudo-second order isotherm with a regression correlation R<sup>2</sup> of 1 for Cu and 0.999 of Cd were well achieved as in contrast to first order model of 0.963(Cu) and 0.864(Cd). Therefore, a pseudo second order kinetic model is preferred to pseudo-first order model for the kinetics of sorption for Cu<sup>2+</sup> and Cd<sup>2+</sup> adsorption. The carbon with higher pore volume and surface area was found to be more effective in removing these heavy metal ions. This plant has various chemical constituents. It also has the biological activities including the depletion of metal concentration. *Moringa oleifera* bark contain the antioxidant properties that are effective to reduce the oxidative stress induced by heavy metal. It was therefore concluded that *Moringa oleifera* bark acts as a well adsorbent for the treatment of wastewater and reuse it. This should be an encouragement for developing countries.

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