CHAPTER 3

PREPARATION OF ACTIVATED CARBONS FROM FIVE AGRICULTURAL WASTE PRODUCTS AND STUDIES OF HEAVY METALS REMOVAL

3.1 Introduction

Commercial adsorbents generally are prepared from coal, and peat which are non-renewable and highly cost. There are many adsorbents to carry out the adsorption process but low cost adsorbents are very important for adsorption studies. Agricultural waste has many advantages to remove contaminants from wastewater such as easy operation, good sorption activity, availability and cost effectiveness etc. Agricultural materials are rich in pectin and lignin which are good adsorbents for removing heavy metals. This type of adsorbents need simple alkali or acid treatment for the removal of lignin before application for increasing their efficiency. The main aim of this chapter were to prepare activated carbon from agricultural by-products (rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark) to determine the best adsorbents out of five activated carbon using batch adsorption process on heavy metals removal like lead, nickel, copper, and cadmium from prepared aqueous solution to characterize the best adsorbents using SEM, BET and FTIR analysis.

3.2 Materials and Methods

3.2.1 Reagents

All chemicals were analytical grade obtained from Merck, Germany. Standard solution and stock solution of metals (lead, nickel, copper, and cadmium) were obtained by dissolving metal salts in deionized water. 1.342 g, 4.132 g, 9.333 g, and 2.771 g of lead chloride ($PbCl_2$ >99%), nickel chloride ($NiCl_2.6H_2O$~98%), copper sulphate

($CuSO_4.5H_2O$ >99%) and cadmium nitrate ($Cd(NO_3)_2.4H_2O$~99%), respectively were dissolved separately in 1 L volumetric flask of water to make 1000 mg/L of metal salt solution as 1000 mg/L of stock solution. The working solutions were attained by diluting the stock solutions. From the 1000 mg/L of stock solution, 1 mL, 2 mL, 3 mL, 5 mL, 10 mL and 15 mL of different salt separately mixed with 1000 mL of water to get 1 mg/L, 2 mg/L, 3 mg/L, 5 mg/L, 10 mg/L and 15 mg/L of working solutions. Other chemicals are 0.5M hydrochloric acid (HCl ~70%), 0.5M sulphuric acid (H_2SO_4 >98%), 0.5M nitric acid (HNO_3 ~70%), 1M sodium hydroxide (NaOH), 0.05M sodium nitrate ($NaNO_3$ buffer), (10%) zinc chloride $ZnCl_2$, 1M phosphoric acid (H_3PO_4), and (2%) sodium bicarbonate ($NaHCO_3$).

3.2.2 Preparation of the Adsorbents

The five cost-effective agro adsorbents used for this study were rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark.

Rice husk (RH) adsorbent was collected from Mohammadpur, Magura, Bangladesh. First of all, the sample (100 g) was sun dried for 6 hours. After sun drying, RH was washed with distilled water to remove dust and impurities. The samples were dried in the oven at 110 °C for 12 hours. The rice husk was reduced into smaller particle sizes and sieved at 400-600 µm. The samples were then chemically activated with 0.1 M zinc chloride ($ZnCl_2$) solution soaked (1:2 ratio) for 16 hours then the sample was dried in the oven at 110 °C for 12 hours. Then the sample was kept in the desiccator for further use. The sample of rice husk was placed in the furnace at 700 °C for 60 minutes. It was cooled at normal temperature then put in the desiccator. This sample was washed severally with distilled water. The pyrolysis sample was soaked in 500 mL 0.5 M HCl for 1 hour to remove CaO or minerals for demineralization of the adsorbents. The sample was washed repeatedly with distilled water for removing free acid. The washed sample was dried in an oven at 110 °C for 24 hours. These were then sieved with a sieve of 400-600 µm (Shahmoradi et al., 2015). The activated carbon sample was kept in a polypropylene bottle to avoid moisture. The yield of rice husk (AC) was 16.4%.

Coconut coir was collected infront of Desa Jati, Nilai, Negeri Sembilan, Malaysia. The sample (100 g) was sun dried for 6 hours. After sun drying, coconut coir was washed with 0.5 M sulphuric acid to avoid more water adsorption capacity then the sample was dried in an oven at 110 °C for 12 hours. The coconut coir was reduced into smaller particle sizes. Coconut coir was washed and soaked with (2% w/v) sodium bi-carbonate ($NaHCO_3$) for 18 hours and then filtered and washed with distilled water to remove $NaHCO_3$. Then the sample was dried in the oven at 110 °C for 24 hours and was kept in the desiccator for further use. The sample of coconut coir was placed in the furnace at 700 °C for 60 minutes. It was cooled at normal temperature then put in the desiccator. This sample was washed severally with distilled water. The pyrolysis sample was soaked in 500 mL 0.5 M HCl for 1 hour to remove CaO or minerals. The sample was washed repeatedly with distilled water for removing free acid. The washed sample was dried in an oven at 110 °C for 24 hours. These were then sieved with a sieve of 200-500 μm (Khan & Chaudhuri, 2011). The yield of coconut coir (AC) was 13.6%.

Corn cobs were collected from Giants supermarket in Nilai, Malaysia. The sample (100 g) was sun dried for 6 hours. After sun drying, the sample was washed with distilled water to remove dust and impurities. The sample was dried in an oven at 110 °C for 12 hours. The corn cobs were reduced into smaller particle sizes. These were then sieved with a sieve of 300-600 μm. The sample was then doping using (10% v/v) phosphoric acid (200 mL) for 1 hour. Corn cobs was soaked with phosphoric acid as well as excess acid was dried with oven at 150 °C for 1 hour then carbonized by oven at 280 °C for 6 hours and was washed with distilled water to remove excess acid then chemically activated with 0.1M zinc chloride ($ZnCl_2$) (ratio 1:1) (Okafor et al., 2015) . Corn cobs were placed in a furnace at 800 °C for 60 minutes. It was cooled at normal temperature then put in the desiccator. This sample was washed severally with distilled water. The pyrolysis sample was soaked in 500 mL 0.5 M HCl for 1 hour to remove CaO or minerals. The samples were washed repeatedly with distilled water for removing free acid. The washed sample was dried in an oven at 110 °C for 24 hours. It was crushed and sieved at 300-600 μm. The yield of corn cobs (AC) was 15.91%.

Neem bark was collected from Universiti Sains Islam Malaysia (USIM) campus infront of USIM Alamiyyah. The sample (100 g) was sun dried for 6 hours. After sun

drying, the sample was washed with distilled water to remove dust and impurities. The sample was dried in the oven at 110 °C for 12 hours. The neem bark was reduced into smaller particle sizes. The neem bark was carbonized by oven at 280 °C for 6 hours and cooled in desiccator for 1 hour then chemically activated using zinc chloride (0.1M) and phosphoric acid (10% v/v H_3PO_4) in two separate beaker and both were mixed for producing paste then filtered. Then the sample was dried in the oven at 110 °C for 12 hours. Then the sample was placed in the furnace at 800 °C for 60 minutes. It was cooled at normal temperature for 3 hours then put in the desiccator. This sample was washed severally with distilled water. The pyrolysis sample was soaked in 500 mL 0.5 M HCl for 1 hour to remove CaO or minerals. The sample was washed repeatedly with distilled water for removing free acid. The washed sample was dried in an oven at 110 °C for 24 hours. These were then sieved with a sieve of 400-600 µm (Kenneth et al., 2015). The yield of neem bark (AC) was 19.69%.

Moringa oleifera bark was collected from outside of USIM campus in front of Acacia Avenue. The sample (100 g) was sun dried for 6 hours. After sun drying, the sample was washed with distilled water to remove dust and impurities. The sample was dried in the oven at 110 °C for 12 hours The *Moringa oleifera* bark was reduced into smaller particle sizes. The sample was then chemically activated using the 500 mL 0.1M zinc chloride ($ZnCl_2$) and sulfuric acid (0.5M) with a ratio of 1:5 for 6 hours. Then the sample was dried in the oven at 110 °C for 12 hours. Then the sample was kept in the desiccator for further use (Salmi Abdullah et al., 2017). The sample of *Moringa oleifera* bark was placed in the furnace at 700 °C for 60 minutes and it was cooled at normal temperature then put in the desiccator and this sample was washed severally with distilled water. Then the sample was dried in the oven at 110 °C for 12 hours. The pyrolysis sample was soaked in 500 mL 0.5 M HCl for 1 hour to remove CaO or minerals. The sample was washed repeatedly with distilled water for removing free acid. The washed sample was dried in an oven at 110 °C for 24 hours. These were then sieved with a sieve of 200-400 µm. The activated carbon was kept in a polypropylene bottle. Then activated carbon was used for next process as an adsorbent in the adsorption process. The yield of *Moringa oleifera* (AC) was 14.76%.

Figure 3.1 Raw materials of rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark

3.2.3 Instrument

The analysis of metal ions before and after adsorption were obtained using Atomic Absorption Spectrophotometer (AAS-240 FS AA, Agilent Technologies, USA). Functional groups on surface of adsorbents were determined using Fourier-Transform Infrared Spectroscopy (Perkin Elmer FTIR Model 1600, Perkins Elmer Inc., Greenville, SC, USA). Micro porosity of outer surface of adsorbents and pore size were obtained using Scanning Electron Microscope (SEM-Hithachi SU 6600, Hitachi Scientific Instruments, Tokyo, Japan) and Brunauer-Emmett-Teller (BET: BELSORP-MINI,

Micromeritics Instrument Corp., Chiba, Japan). Water distillatory (2108, GLF, Germany), pH meter (3510, Genway), Shaker (UK), centrifuge, (Mikro 220R, Hettich, UK.) UV/Vis. Spectrophotometer (Cany 50 conc. Varian, Agilent Technologies, USA), analytical balance (CP 2245, Sartorius, USA.), Sieve (B.S.S.410/43, Geologists Syndicate Limited), Oven (Nabertherm B180, Germany), Furnace (Linn Elektro Therm, Germany) are used during the studies.

3.2.4 Batch Studies of Adsorption of Heavy Metals on AC

Stock solutions of 1000 mg Pb/L (using $PbCl_2$), 1000 mg Ni/L (using $NiCl_2$), 1000 mg Cu/L (using $CuSO_4$) and 1000 mg Cd/L (using Cd $(NO_3)_2$) were prepared in deionized water. Adsorption kinetics and equilibrium isotherms were studied from batch techniques. Batch experiments were carried out in 250 mL Erlenmeyer flasks at (25±1) °C and 200 rate per minute. A weighed amount (0.025 g) of adsorbent was added to 100 mL of metal solutions of varying concentrations ranging among 1, 2, 3, 5, 10, and 15 mg/L each time and shaken continuously for 3 hours to attain equilibrium due to shown straight plot after 2 hours not fluctuated. Then after 10, 20, 30, 40, 60, 120, and 180 minutes the samples were withdrawn at different time. The solutions were centrifuged, and the concentrations of metal ions were determined by AAS method. The uptake of metal ions was calculated by the difference in their initial and final concentrations. Effects of pH (2–8), contact time (10–180 min), initial concentration of metal ions (1– 15 mg/L) and adsorbent dose (0.005–0.05 g) on the uptake of metal ions from 100 mL solution of wastewater were studied and the optimum values were used in the experiments. The pH was controlled at 6 for heavy metals solution to get the best adsorption capacity for this experiment. The effect of pH of the solution were adjusted ranging from 2-8 by 0.1N (HCl and NaOH) solutions with sodium nitrate ($NaNO_3$) 0.5 M buffer solution. All metals removal processes from the aqueous solution were conducted using the best parameter at pH (6), initial concentration (5 mg/L), ambient temperature (25± 1 °C) and 0.025 g dosage of activated carbon due to get a good result and graph. According to equation 3.1, the amount of adsorbate adsorbed on the adsorbent at any time, *qt* (mg/g) was calculated and the percent removal of adsorbate was evaluated as expressed in equation 3.2 (Tan et al., 2009).

$$qt = \frac{(Co - Ct)V}{W} \quad (3.1)$$

Where C_0 and C_e (mg/L) were the concentrations of solution at initial and at equilibrium time, respectively. Moreover, V was the volume of the solution (L) as well as W was the mass of activated carbon (g).

$$\% \text{ Removal} = \frac{(Co - Ce)100}{Ce} \quad (3.2)$$

3.2.5 Influence of Initial Concentration

The effects of initial heavy metals concentration were studied on the adsorption capacity and percent removal. Approximately, 100 mL of metals solutions with known initial concentration (1, 2. 3, 5, 10, and 15 mg/L) for copper, cadmium, lead, nickel were prepared in a series of 1000 mL volumetric flasks. The amount of adsorbent that was added into each flask containing the adsorbates was fixed at 0.025 g. The mouth of the flasks were sealed with parafilm. After then the flasks were then placed in an isothermal water bath shaker at constant temperature (25± 1 °C), with rotation speed of 200 rpm, until equilibrium point was reached.

3.2.6 Influence of Contact Time

The effect of contact time on the adsorption of heavy metals onto produced different activated carbon were studied within 10, 20, 30, 40, 60, 80, 120 and 180 minutes. The initial concentrations (5 mg/L) of four metal mixtures (lead. nickel, copper and cadmium) were prepared and then were added with 0.025 g of the activated carbon in flasks. The opening of the flasks was sealed with parafilm and the flasks were then placed in an isothermal water bath shaker with rotation speed of 200 rpm at room temperature (25 ± 1 °C).

3.2.7 Influence of Adsorbent Dosage

The effect of adsorbent dosage was studied on the adsorption capacity using different dose of adsorbent, ranged from 0.0005 g to 0.05 g. The amount of adsorbent that was added into each flask containing the adsorbates was fixed at 0.0005 g, 0.001 g and 0.025 g and 0.05 g respectively. The best adsorbent dose was 0.025 g for all heavy metals removal of 100 mL solution from spiked water. The opening of the flasks were sealed with parafilm and the flasks were then placed in an isothermal water bath shaker at constant temperature (25± 1°C), with rotation speed of 200 rpm, until equilibrium point was reached. In this case, the solution pH was kept original without any pH adjustment.

3.2.8 Influence of pH

The effect of solution pH was studied on the adsorption capacity using different initial pH of the solutions, ranged from 2 to 8. Hydrochloric acid (0.1 M) and sodium hydroxide (0.1 M) was used to adjust the pH of solution. The initial concentration was 5 mg/L for each flask and was added with 0.025 g of adsorbent. The solution temperature was at (25± 1) °C.

3.2.9 Equilibrium studies

The nature of the adsorption isotherms was determined by the equilibrium studies. Adsorption equilibrium also was led to define the adsorption capacity of the adsorbents. For this experiment, the metallic concentration was taken 1, 2, 3, 5, 10, 15 mg/L separately in 100 mL solution with best dosage 0.025 g adsorbent. Each sample flask was agitated at 200 rpm in a shaker. Time was recorded from 10 minutes to 180 minutes. Samples were taken from the shaker at definite time intervals. After filtration then filtrate solution was analysed to determine the final residual concentration by Atomic Adsorption Spectroscopy.

3.2.10 Kinetic Studies

The kinetics of adsorption of heavy metals describes the rate of adsorbate uptake on activated carbon. It controls the equilibrium time. The pseudo-first-order, pseudo-second-order kinetic models were applied to study the kinetics of the adsorption process. The intraparticle diffusion model was further tested to determine the diffusion mechanism of the adsorption system which all model equation (2.10-2.16) were discussed in chapter (2). For the kinetic studies based on adsorption of heavy metals, a fixed mass (0.025 g/100 mL) of activated carbon was taken in a 250 mL flask for 100 mL solution. This experiment was conducted for 2 hours at a shaker agitated at 200 rpm using a flask. After adsorption of metals, solutions (100 mL) were taken out at specific time intervals ranging of 10, 20, 40, 80 and 120 minutes. Then the solution was evaluated for remaining concentration of heavy metals following equation 3.1.

3.2.11 Desorption Studies

The batch desorption process was conducted in a shaker using varieties of solvents. Desorption techniques are a very important factor to check the importance of reuse of the adsorbents. Several solvents were studied for the desorption process such as hydrochloric acid (HCl), sulphuric acid (H_2SO_4), and sodium carbonate (Na_2CO_3) of different concentration which was best concentration (0.1M) of solvents for metal loaded activated carbon of rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark. Hydrochloric acid is the most used solvents to desorb contaminants from adsorbent (Bello et al., 2010). After separating the 5 mg/L metal-loaded adsorbents, 100 mL solvent of hydrochloric acid, sulphuric acid, and sodium carbonate were mixed separately with (0.025 g) metal-loaded adsorbents where HCl was the best desorbent solvent and then the mixture was shaking in the shaker at 200 rpm. After the desorption process then solutions were taken out and evaluated for the release metal concentration. The reusability of activated carbon was investigated through cycled adsorption/ desorption runs using only hydrochloric acid desorbent in heavy metal solutions (Co = 5mg L^{-1}, pH = 6) performed at room temperature with *S/L* = 0.025 g/100 mL. After

completing every adsorption process, the activated carbon was separated from the solution by filtration and washed with distilled water. It was then dispersed in a solvent 0.1 M HCl. It was then washed with distilled water several times and dried.

The desorption efficiency of adsorbents was evaluated from a relationship (3.3) (Liu et al., 2018):

$$\text{Desorption (\%)} = \frac{qd\ x\ 100}{qe} \tag{3.3}$$

When, q_d is the quantity of the metal ions (mg/g) desorbed from the adsorbents. Another side, q_e is the quantity of metal ion (mg/g) adsorbed onto the adsorbents. The value of q_d (mg/g) is evaluated from equation (3.4):

$$q_d = \frac{Cd\ x\ Vd}{W} \tag{3.4}$$

Where, C_d is the concentration of the metal ion (mg/L) remaining in solution after desorption. Furthermore, V_d is the total volume (L) of the solution as well as W is the mass (g) of the metal loaded activated carbon.

3.2.12 The Point of Zero Charge (pHpzc)

The point of zero charge (pHpzc) is an important factor to determine the nature of the adsorbents. The net surface charge of adsorbents in the solution can be determined using pHpzc. This process was maintained by using 0.1N HCl and 0.1N NaOH solutions. The experiments were carried out by using solid to liquid of 1:1000 to measure the pHpzc. For completing this process, 0.1 mg of activated carbon was taken and added with 100 mL distilled water. The pH of the solution was adjusted from 2 to 12 by adding HCl and NaOH solutions due to find out the point of zero charge and shaken with a shaker for 24 hours. Then final pH of the solution was taken out and it was plotted against the initial pH of the solution to determine the point of zero charge of adsorbents (El-Sayed et al., 2014).

3.3 Results and Discussion

For determining the effects of the functional parameters such as (1) initial concentration, (2) equilibrium time, (3) adsorbent dose, (4) pH of the solution on adsorption process, the experiments were conducted. The batch absorption techniques were evaluated due to the uptake of the heavy metals by the activated carbon of rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark.

3.3.1 Influence of Initial Concentration

Figure 3.2 shows the effect of initial concentration on the adsorption capacity of different metals onto the activated carbon at equilibrium, q_e at different initial concentrations (1, 2, 3, 5, 10 and 15 mg/L). The graph was shown a significant increase as initial concentration increased. The equilibrium adsorption capacity of rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark for copper were increased from (3.98, 3.98, 3.98. 1.43, and 3.98 mg/g) to 19.84, 19.95, 13.19, 7.49 and 20.09 mg/g) as the metal's initial concentration were increased from 1 to 5 mg/L while for cadmium were (4.22, 2.57, 4.36, 0.95, 3.4 mg/g) to (11.57, 11.05, 14.16, 8.46, and 11.42 mg/g), respectively. The initial concentration serves as the driving force for higher mass transfer in order to develop the relationship between adsorbate and the adsorbent (Ahmad & Alrozi, 2011). A large number of vacant sites were available during the initial stage of adsorption. The increase of the initial concentration of all metals had increased in the driving force between metal molecules and activated carbon (Ahmad & Alrozi, 2011).

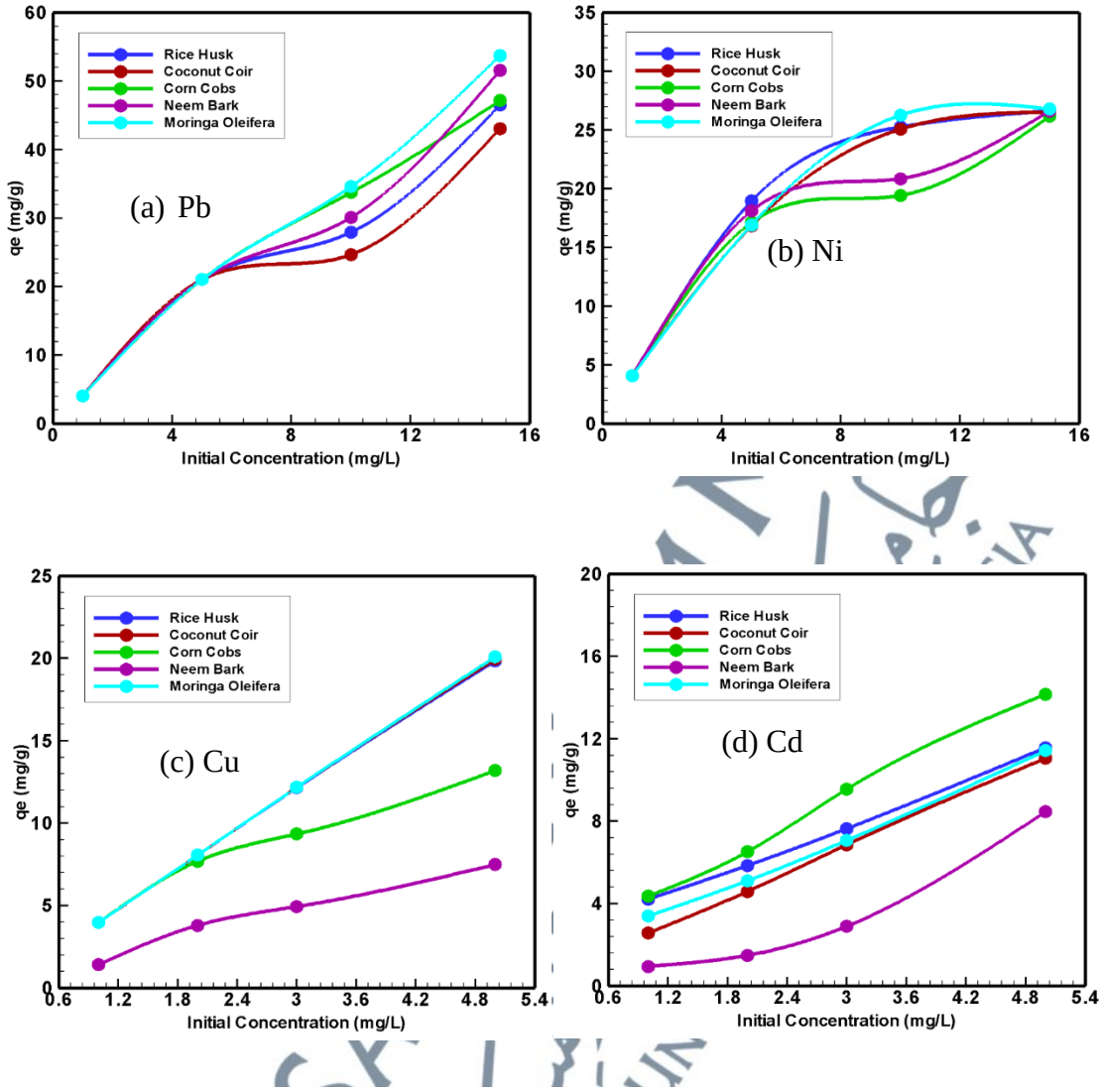

Figure 3.2 Influence of initial concentration on the adsorption capacity of (a) lead, (b) nickel, (c) copper, and (d) cadmium for rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark

The graph was shown that at lower initial concentrations (1 and 5 mg/L), the adsorption capacity of rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark at equilibrium time were 4.08 and 21.05 mg/g for lead, respectively (or 100 % removal for all) while were (4.08, 4.08, 4.08, 4.08, and 4.08 mg/g) and (18.96, 16.82, 17.14, 18.12, and 16.92 mg/g) for nickel. At 10 mg/L and 15 mg/L initial concentration, equilibrium adsorption capacity of rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark for lead were (27.95, 24.68, 33.74, 34.6, and 30.11 mg/g) and (46.51, 43.08, 53.73, 51.57, and 47.16 mg/g), respectively while were (25.26. 25.08, 19.43, 20.86, 26.27 mg/g) and (26.62, 26.52, 26.17, 26.62, and 26.79

mg/g) for nickel, respectively. At this stage, the difference between their pore size and surface area affect significantly the adsorption capacity of five activated carbon. The higher mass transfer for five activated carbon was due to the increased in the driving force which was the initial concentration of heavy metals (Ahmad & Alrozi, 2011).

3.3.2 Influence of Contact Time

The adsorption experiments were necessary to define the contact time required to reach the equilibrium position. Firstly, the percentage of metal uptake was very good but after some time decreased due to not reaching the equilibrium state then again increased steadily with the end time as shown in Figure 3.3(a)-(d). After 60 minutes it reached an equilibrium state where all metals could not be eliminated from the system more for all activated carbon (Azouaou et al., 2010). Dynamic equilibrium state was that point where the amount of adsorbed metal ions in adsorbents and desorbed from the adsorbents were the same. The equilibrium time was considered through the time needed to obtain the equilibrium state. The maximum adsorption capacity was considered by the quantity of metal ion bind at equilibrium time.

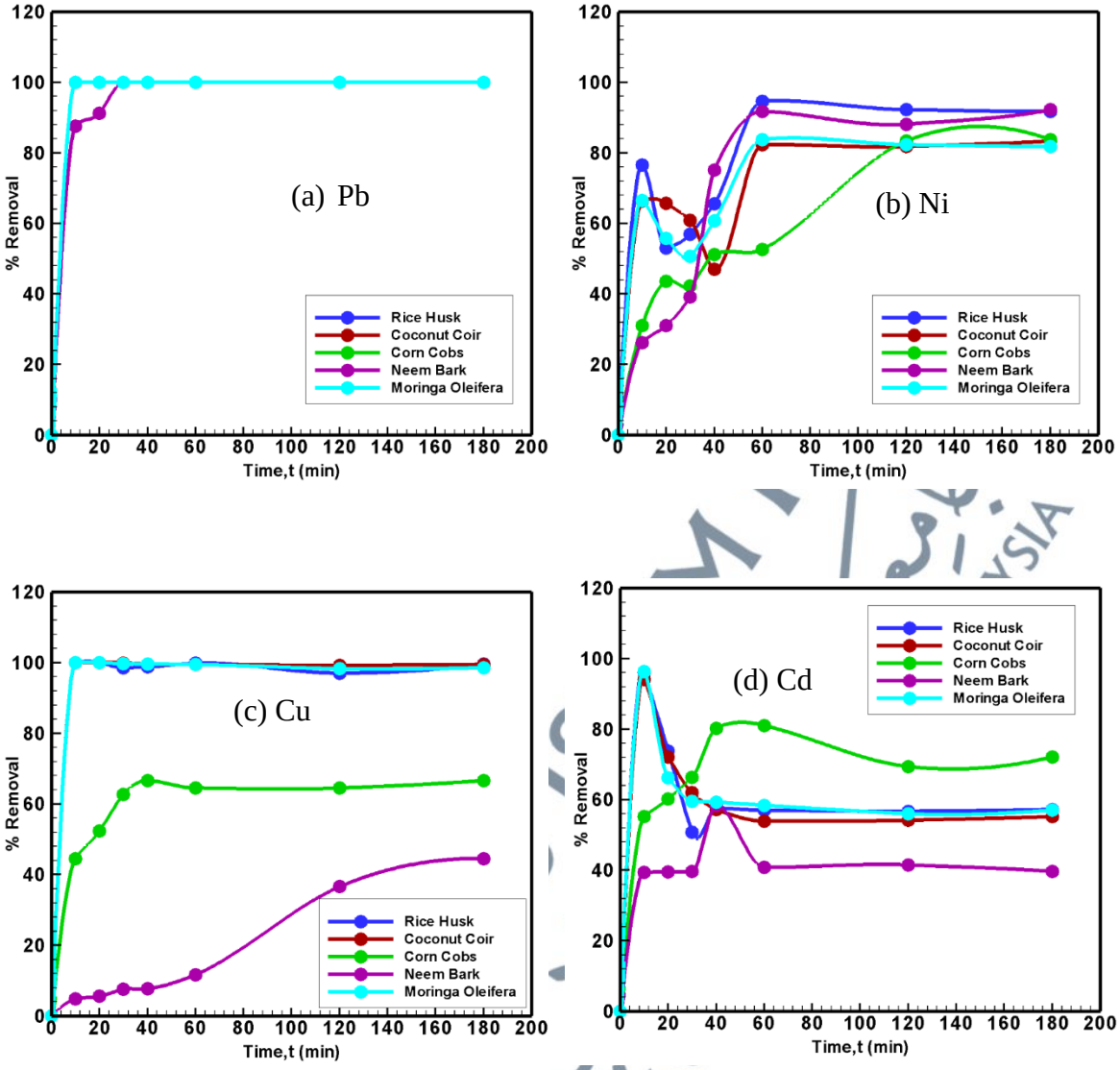

Figure 3.3 Influence of contact time of (a) lead, (b) nickel, (c) copper, and (d) cadmium for rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark

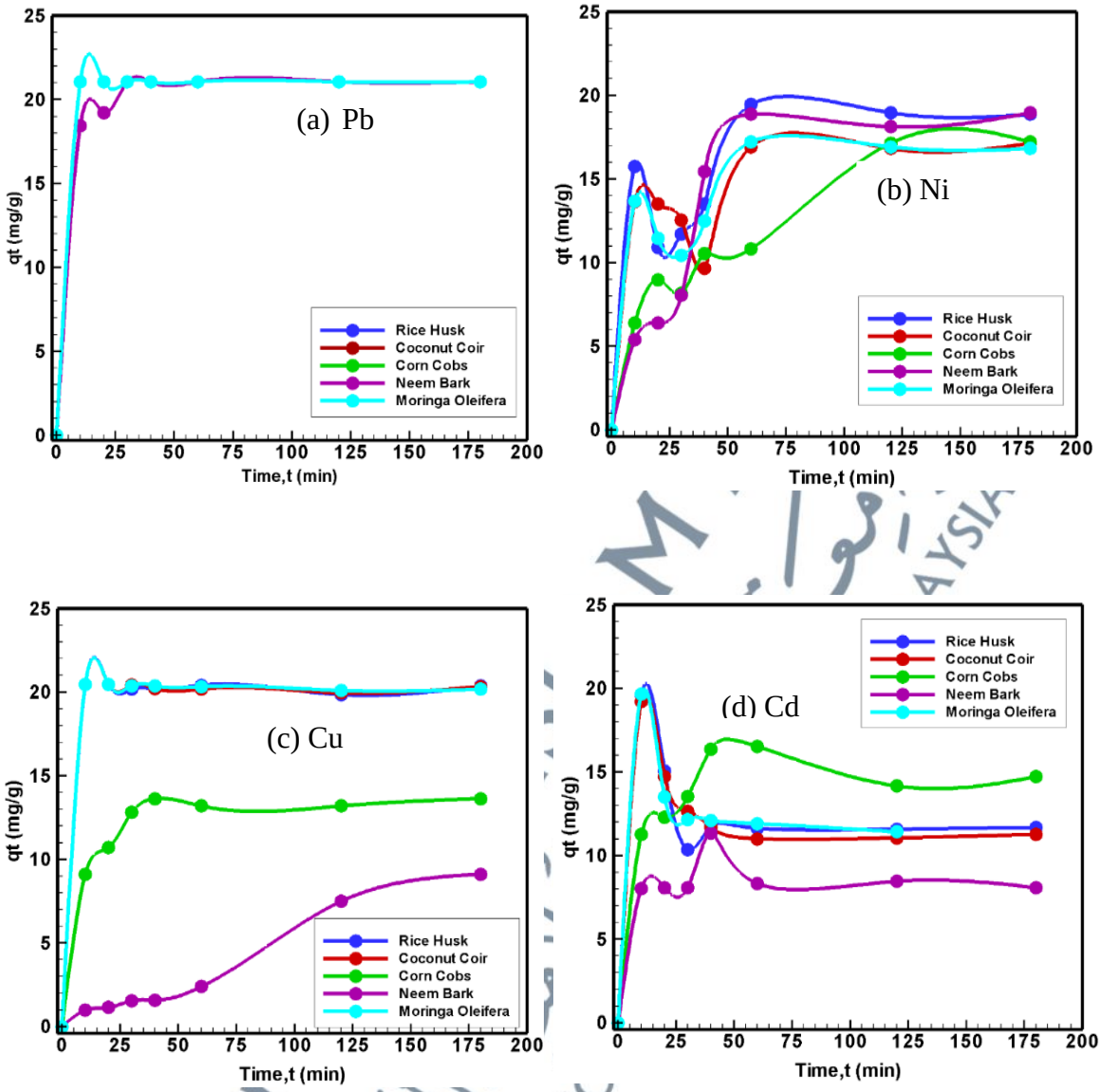

Figure 3.4 Adsorption capacity in 5 mg/L of (a) lead, (b) nickel, (c) copper, and (d) cadmium for rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark

From Figure 3.3, lead was absolutely removed from aqueous solution within 10 minutes to till 180 minutes for rice husk, coconut coir, corn cobs, and *Moringa oleifera* bark but lead was removed 99 % within 10 minutes for neem bark and after sometimes, it was removed 100 %. For this reason, only two graphs were shown in Figure 3.4(a). There is no significant change in the percentage lead removal after 10 minutes for all

adsorbents due to filling up all pore of adsorption sites quickly. From this study observed that the quantity of adsorption of lead (21.05 mg/g) was higher than other metals (nickel, copper, cadmium). This is due to increases of adsorption by ion exchange with increasing ion radius. Here the ion radius of Pb^{2+} is higher than Cu^{2+}, Cd^{2+}, and Ni^{2+}. Moreover, lead can easily form complexes with oxygen functional groups of adsorbents. Even, lead (Pb^{2+}) can be adsorbed by the pie (π) electrons of adsorbent surface (Alfarra et al., 2004 & Badruddoza et al., 2013). The removal percentage of metal ions from aqueous solutions were different due to the nature of the ions in solution, ions with smaller sizes have been known to be heavily hydrated and become larger than the less hydrated with larger sizes. These less hydrated metals can be more attracted to the active adsorption sites of activated carbon rapidly than larger hydrated ions (Jimoh et al., 2011).

However, the adsorptive amount of lead (II) was higher than those of copper (II), cadmium (II), and nickel (II). The adsorption of the metal ion by adsorbents was good within 10 minutes for rice husk, coconut coir, and *Moringa oleifera* bark but after 10 minutes occurred some desorption of nickel and cadmium then uptake metal ion adsorption increases with time up to 1 hour. It can be observed that increased contact time corresponds to increased percentage removal efficiency irrespective of cadmium, and nickel. There was no significant upgrading metals removal after 10 minutes for three adsorbents. Therefore, the optimum contact time was 10 minutes. This indicates that adsorption active sites were saturated due to huge competition among the selected heavy metals such as lead, nickel, copper and cadmium.

Then, further increase in contact time did not significantly remove metals removal due to the occurrence of biphasic kinetics mechanism. The rapid phase which was an instant sorption occurred within 10 minutes due to availability of binding sites of the adsorbents suggesting that external diffusion phase as fast phase. The slower removal of heavy metals from aqueous solution using adsorbents accounted for the internal diffusion at second phase and at contact time of 120 minutes, equilibrium was attained for nickel and cadmium as shown in Figures 3.4(b) and 3.4(d) respectively. At this stage, there was the highest uptake capacity of the heavy metal ions due to saturation of adsorption sites. After passing the equilibrium time, the removal rate became constant.

The biphasic adsorption mechanism involves external and internal diffusion processes of activated carbon (Wu et al., 2010). On the other hand, the removal percentage of copper was good steady from 10 minutes to till equilibrium state for rice husk, coconut coir, and *Moringa oleifera* bark but the removal percentage of cadmium, nickel and copper was increased for corn cobs and neem bark with increasing contact time to till equilibrium state at 120 minutes. It may be described according to ionic/ atomic radii of these metals. The smaller ionic radius of metals would diffuse faster onto the pores of the activated carbon than larger metals (Horsfall et al., 2005).

The order of removal of heavy metals irrespective of this research are as follows: lead > copper > nickel > cadmium. It can also be possible that the heavily hydrated ions blocked the small size ions from reaching the adsorption active sites. For this reason, smaller ionic radii of metals are shown to lower the removal efficiency of ions. Therefore, lead was absolutely removed faster from aqueous solution than others. The adsorption capacities of each activated carbon was different for varieties of metal and did not follow a specific trend. These indicated that the removal proficiency of the metals was agricultural-adsorbent specific. In competitive systems, binding of different metal ions on biomaterials having different functional groups depends on ionic properties such as electronegativity, ionic radius, and redox potential of these metals (Naja et al., 2010). Sulaymon et al. (2011) showed that large ionic radius resulted in greater adsorption efficiency. Atomic radius of lead, cadmium, copper and nickel were 1.75, 1.54, 1.28, and 1.24 A° respectively. Some researchers (Bohli et al., 2013) reported that the adsorption of metals having a large ionic radius was higher than for those with a smaller ionic radius. The best adsorbent for all metals was *Moringa oleifera* bark with the order Pb (II) > Cu (II) > Ni (II) > Cd (II). The structure of the hydrated lead (II) ions is strongly affected by the lone pair electron, giving complexes with low symmetry. The effectiveness of the adsorption process depends also on the size of ions in the aqueous phase; the hydrated radius of Pb (II) (0.401 nm) is higher as compared to the ionic radius of Pb (II) (0.112 nm) (Kadirvelu et al., 2008). Therefore Pb (II) ions have more accessibility to the surface and pores during the adsorption from the solutions. Bohli et al. (2013) noted that the important uptake of lead, even at low pH,

may be related to a higher affinity of the surface functional groups of carbons for this metal ions compared to the affinity towards copper and nickel.

For the first 10 minutes, the q_t for lead, nickel, copper, and cadmium were fast where it was reached (21.05, 13.67, 20.45, and 19.65) mg/g respectively of *Moringa oleifera* bark, (21.05, 15.75, 20.45, and 19.59) mg/g respectively of rice husk, (21.05, 13.64, 20.45, 19.20) mg/g respectively of coconut coir, (21.05, 6.39, 9.11, and 11.26) mg/g respectively of corn cobs and (18.44, 5.48, 0.98, and 8.03) mg/g respectively of neem bark. After 1 hour metal adsorption became almost constant at last time, indicating a slower adsorption process. At equilibrium time, the adsorption plot were more horizontal and the value of q_t were (18.96, 16.82, 16.92) for nickel, (19.84, 19.95, 20.09) for copper, (11.57, 11.05, 11.42) mg/g for cadmium using the activated carbon of rice husk, coconut coir and *Moringa oleifera* bark respectively. On the other hand, the adsorption of the metal ions were increased till 1 hour then it became constant like (17.14, 13.19, 14.16) mg/g using corn cobs and (18.12, 7.49, 8.46) mg/g using neem bark for nickel, copper and cadmium respectively at equilibrium time. But lead (Pb) was absolutely adsorbed like 21.05 mg/g from the initial stage to the end of the experiments using all activated carbon. The metal binding rate of adsorbents were more predominant during the initial stages due to available large number of surface sites. After some time, it decreases and then becomes steady after 120 minutes to the end of the experiment due to the presence of repulsion between the solute molecules of the solid and bulk phases caused some resistant for the remaining surface sites to be filled (Ahmad & Rahman, 2011).

When the metal ion was contacted with the active site of adsorbents then it was involved soon in metal complexation. During the initial stages, the adsorption of pollutants was involved by the functional groups available on the surface of adsorbents. Then the second factor was involved by the occupying of porous structures which was provided from the surface area of activated carbon. It can be indicated that the ratio of the available surface area to the initial number of adsorbate molecules was higher at lower concentration (Rao & Rao, 2006).

3.3.3 Influence of Adsorbent Dose

The dosage of activated carbon was an important factor in the adsorption process to adsorb heavy metals from spiked aqueous solution as shown in Figures 3.5(a)-(d). Increasing the adsorbent dosage, the uptake of heavy metals from an aqueous solution also increased. It was reached an equilibrium position above 0.025 g/100 mL solution. The uptake of metal ions improved in the adsorption process with a growing quantity of adsorbents (Azouaou et al., 2010). It can be occurred due to having more active sites of activated carbon due to adsorption.

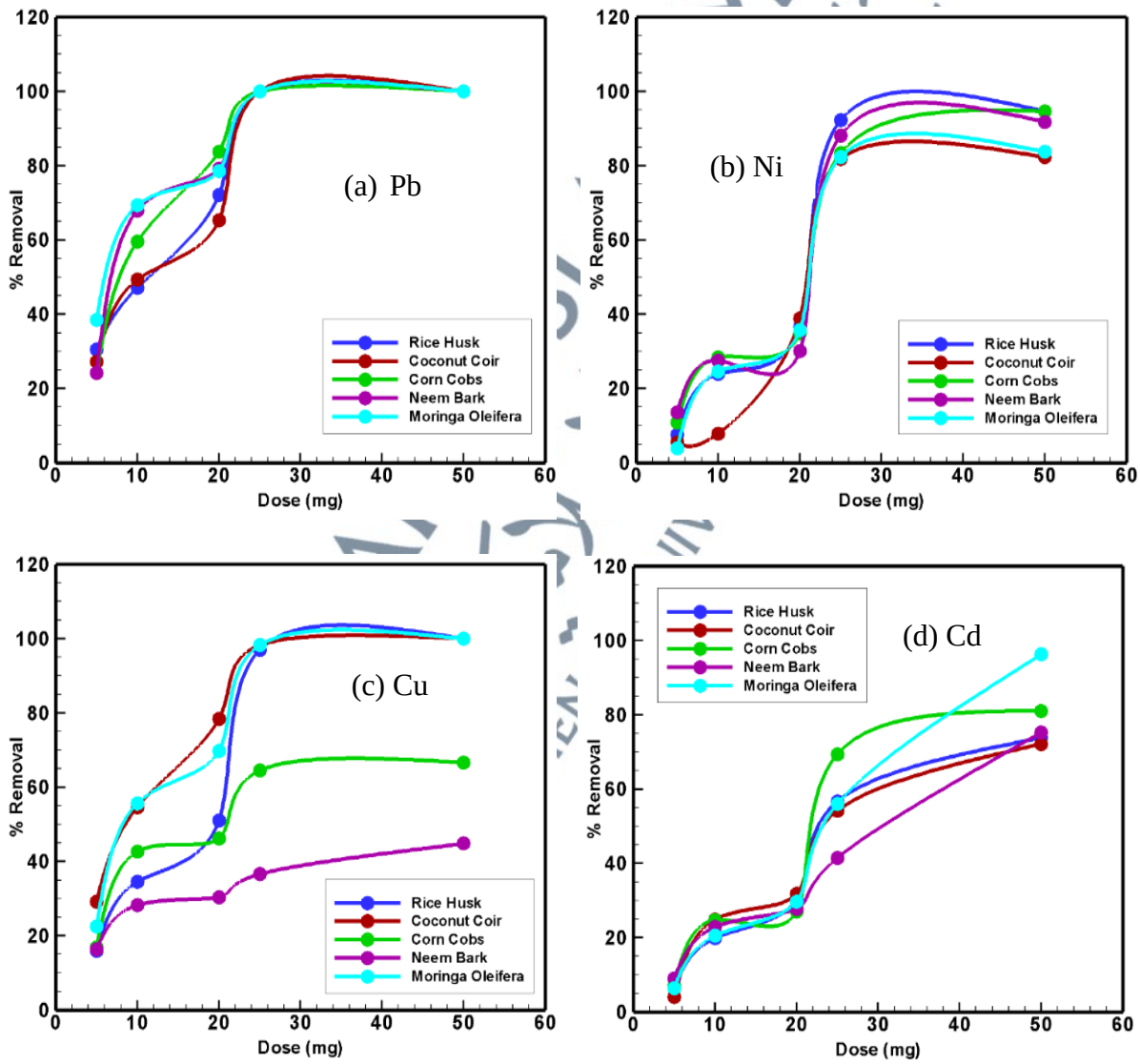

Figure 3.5 Influence of adsorbent dose in 5 mg/L of (a) lead, (b) nickel, (c) copper, and (d) cadmium for rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark

We can be observed that further increasing the dose but metal-binding quantity was not increased significantly. It can be happened due to reaching an equilibrium state of both bound to the activated carbon and unadsorbed contaminant in solution.

3.3.4 Influence of pH

The pH of the solution is a vital factor of the surface chemistry of adsorbent and adsorbate for the adsorption process. The surface chemistry of prepared activated carbon has been considered by determining their point of zero charge pH(pzc). Figure 3.6 shows the plot of the initial pH against the final pH. The intersection of these plots was considered to be the pH(pzc) which followed the y = x function. The pH(pzc) of all activated carbon was found to be around (4.1-5.4) such as rice husk (5.1), coconut coir (4.1), corn cobs (5.0), neem bark (5.3) and *Moringa oleifera* bark (5.4) respectively. If the pH of a solution is changed, the dissociation of the functional group of activated carbon also can be changed. That's why the adsorption capacity of adsorbents may be changed (Nomanbhay & Palanisamy, 2005).

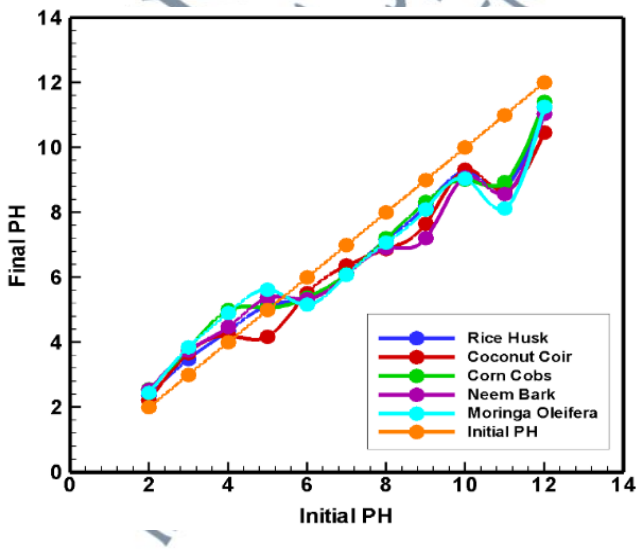

Figure 3.6 The final pH against initial pH plots for rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark

The pH of the solution has two effects: 1) on activated carbon, relied on pH(pzc) value of activated carbon will have a negative or positive charge and 2) on the nature of metal ion in the solution, whether it exist as a cationic (+) or anionic (-) state at a given pH. When the surface charge density is zero, it is called pH(pzc) of the adsorbents. At a pH < pH(pzc), the adsorbent surface will be positively charged and at a pH > pH (pzc), the adsorbent surface will be negatively charged. Adsorption of activated carbon relied on the nature of the metal ions (positive or negative) at different pH values.

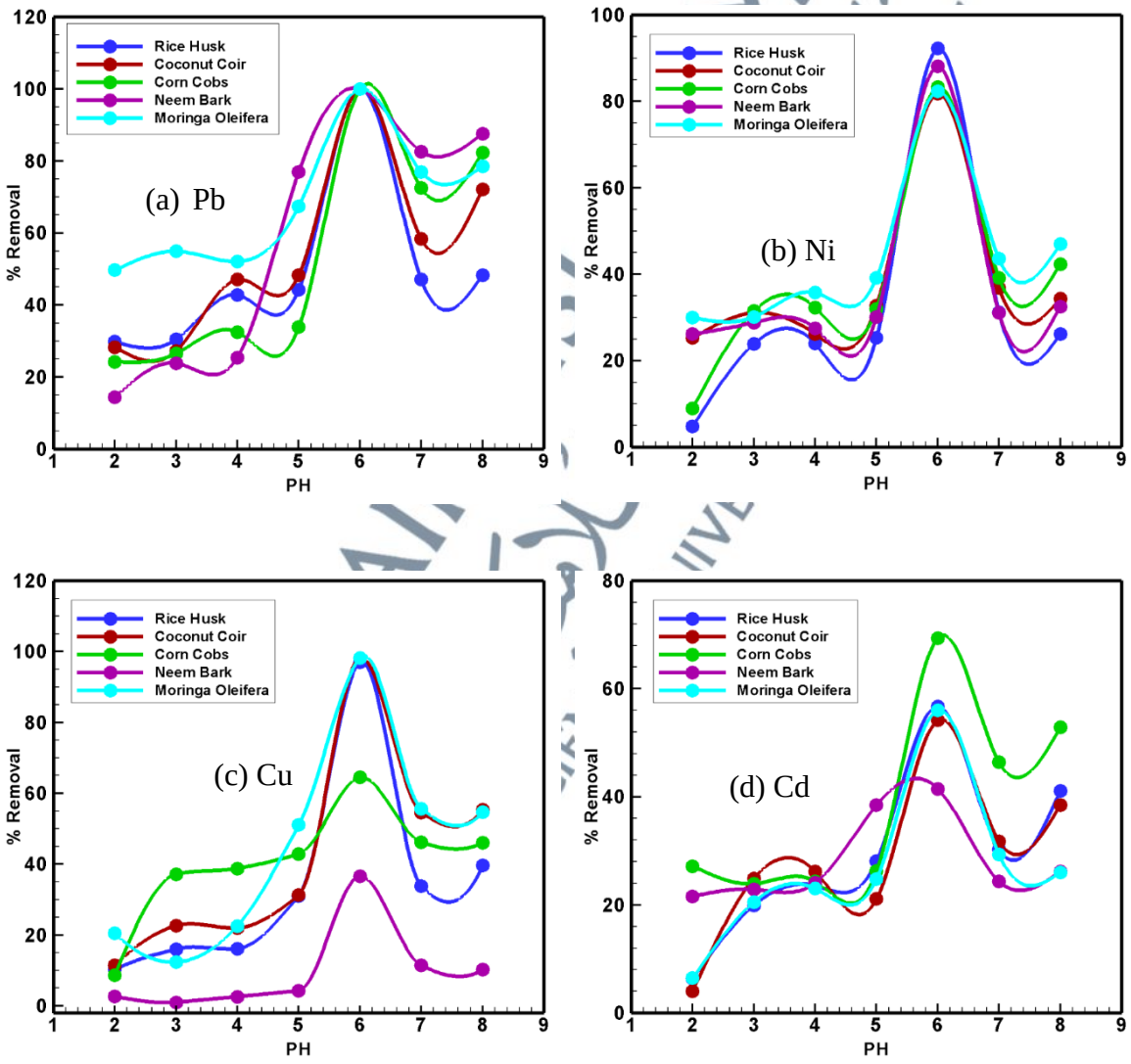

Figure 3.7 Influence of pH plots in 5 mg/L of (a) lead, (b) nickel, (c) copper, and (d) cadmium for rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark

The adsorption percentage of all heavy metals by all activated carbon (rice husk, coconut coir, corn cobs, neem bark, *Moringa oleifera* bark) were increased with increasing pH from 2 to 6 then dropped. The optimum pH value for lead, nickel, copper, and cadmium was at pH 6. At lower pH, the adsorption capacity was unfavourable for all metal solutions by all activated carbon. At low pH value, the adsorbent presented more positively charged surface sites available but a small number of negatively charged sites (Hamdaoui, 2006). At higher pH, heavy metals were formed more positively charged which was more attracted to the negatively charged sites. If any adsorbents contain more positively charged, they cannot be favoured for adsorption due to repulsion (Hamdaoui, 2006). The presence of extra protons (H^+) competed with the cation of the contaminants for the adsorption active sites via electrostatic interactions (Pua et al., 2013). The outer sites on the surface of activated carbon represent active sites for oxygen functional groups which are called chemical adsorptions (chemisorptions). There were some oxygen functional groups in this location, either acidic or basic. Such acidic groups were carboxyl, lactone, hydroxyl and carbonyl and the basic groups were chromene type and pyrone type (Rakić et al., 2015). As discussed in the next chapter, most of the activated carbon had (C-O) oxygen functionalities, which was very polar as it is a hydrogen-bond acceptor (the carboxyl).

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. With the increasing 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 (4.1-5.4). For this reason, to attract metal cations mostly in positive form M^{2+} (Pb^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}) and its simply can adsorb onto adsorbents. The metal (II) uptake on activated carbon may be also described by ion exchange process. The major functional groups of adsorbents were the carboxyl, hydroxyl, methoxy group which can participate in the ion exchange process. The adsorbents were shown below this type of ion-exchange mechanism where H^+ ion from the carboxylic group of activated carbon surface were replaced by metal ions for removal of metal ions from aqueous solution.

$$2\text{-COOH} + M^{2+} = \text{-}((COO\text{-})_2\text{-}M^{2+}) + 2H^+$$

If pH is above 6, the decrease in metal adsorption can be occurred for three factors (Abdel-ghani & El-chaghaby, 2014). First, with increasing the pH value, the negatively charged adsorbent surface also increased. However, at the same time metal was changed from a molecular state to an ionic state. That was significant for the repulsion force between metal ions and the activated carbon. Second, the presence of a repulsion force between the metal ions which were adsorbed by the activated carbon. Third, the negative charges on the activated carbon's surface were repulsive that blocked the disaggregation of metal ions and metal adsorption (Abdel-Ghani & Elchaghaby, 2007). The pH has effects on the surface charge of the adsorbent and adsorbate. So, the pH is a vital controlling factor in this method (Azouaou et al., 2010).

M^{2+} can form several hydrolysis products, which exist under different conditions. In dilute aqueous solutions of pH < 6, lead ions exist as M^{2+} or Pb(OH)+ or both, whereas the formation of M^{2+} hydrolysis products occur at pH > 6.0 which might lead to its polymerisation. Due to this reason all the experiments were carried out at pH 6. The variation in the removal of lead with respect to pH can be elucidated by considering the nature of the physicochemical interaction of the species in solution and the functional groups present on the surface of sorbent. At lower pH (pH <2.0), dissociation of the acidic functional groups like carboxylic acids (pKa value 3.8 to 5) on the surface of adsorbent does not occur. When pH increases (pH > pKa) the surface acidic functional groups deprotonate and negative charge on the adsorbent increases. Hence at lower pH (pH <2), the overall surface charge on activated carbon is less negative compared to surface charge on adsorbents at higher pH, which reduces the attraction of positively charged metal cations towards it. Therefore, an increase of pH from 2.0 to 6.0 increased the biosorption of lead ions. On further increase of pH (pH > 6) biosorption of lead decreased due to the hydrolysis of lead ions as already observed in other biosorbents containing carboxylic acids (Reddy et al., 2010).

This research was conducted at pH ranging from 2 to 8. The maximum elimination effectiveness for lead (II) (100%) and copper (II) (~90%) uptake with five activated carbon were achieved at pH 6, nickel (II) and cadmium (II) also were good removal efficiency. The percentage removal improved quickly and became consistent between 100% and 90%. At pH < 5, the binding effectiveness was found to decline.

At pH > pH(pzc) for adsorbents, the surface of the adsorbents was negatively charged. At a pH > 5, M (II) in solution have cationic species, M^{2+} which was strongly fascinated to the oppositely charged adsorbent. It can be explained that the removal efficacy of all activated carbon was shown to be good. On the other hand, at a pH value lower than their pH(pzc), the adsorbent surface was positively charged. It can be happened electrostatic repulsion between the metal cation (M^{2+}). That's why it can bring lower adsorption. At pH 6, lead can be successfully removed from spiked aqueous solution.

At pH 2, the metal adsorption was lower due to high concentration of H^+ ions. This H^+ ions competed with metal ions for the binding sites, hindering the adsorption of Cd^{2+}, Pb^{2+}, Ni^{2+} and Cu^{2+} ions by activated carbon.

3.3.5 Adsorption Isotherms

An adsorption isotherm was characterized by the surface properties and affinity constant value of the adsorbent. It can be described as the distribution of a solute between the solution and adsorbent surfaces. It must be conducted by some mathematical equation. There are some important models in the Figures 3.8-3.10 like the Langmuir and Freundlich and Dubinin-Radushkevich models. From the model, all constant values with linear regression coefficient (R^2) were shown in Table 3.1. From the values of R^2 in the table, the Freundlich model was fitted very well to the absorption of all data. Langmuir isotherm expressed monolayer of the metal ions were designed on activated carbon. The higher value of b was described as the attraction of activated carbon to adsorb pollutants. The lower values of b were 4.42, 1.68, 0.943, 1.66, and 0.359 of nickel for rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark respectively as shown in Figure 3.8(a).

The value of *b* were 162.87, 159.74, 10.31, 2.37, and 162.07 of copper for rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark respectively which were well fitted for rice husk, coconut coir, and *Moringa oleifera* bark as shown in Figure 3.8(c). The values of *b* were 2.55, 0.109, 3.69, 0.206, and 0.73 of cadmium for rice husk,

coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark respectively as shown in Figure 3.8(b). So, Langmuir isotherm was not well fitted with all data. The q_{max} can be considered as the total number of active sites of adsorbents for binding. But q was considered as the number of active sites which were filled up with pollutants at the final concentration C_f.

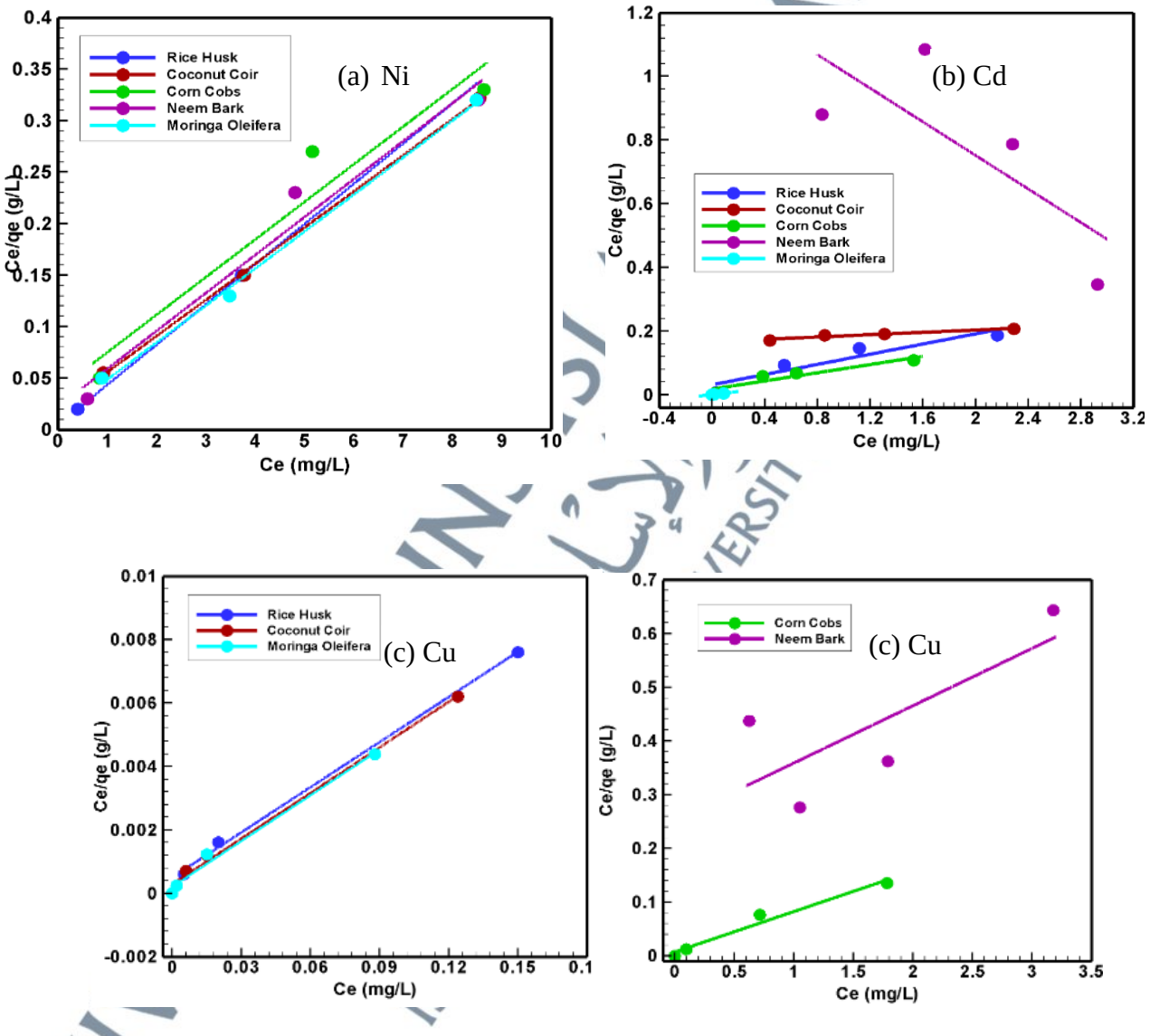

Figure 3.8 Langmuir plot for (a) nickel, (b) cadmium, and (c) copper adsorption of rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark

From the Table 3.1 data, the affinity order of rice husk, coconut coir and neem bark was the same as lead (Pb) > copper (Cu) > nickel (Ni) > cadmium (Cd). On the other hand, the affinity order of corn cobs and *Moringa oleifera* bark was the same as lead > copper > cadmium > nickel.

Note: Five data sets were plotted in one graph for copper, so rice husk, coconut coir and *Moringa oleifera* bark plot are shown in one graph. Corn cobs and neem bark plots were shown in another graph.

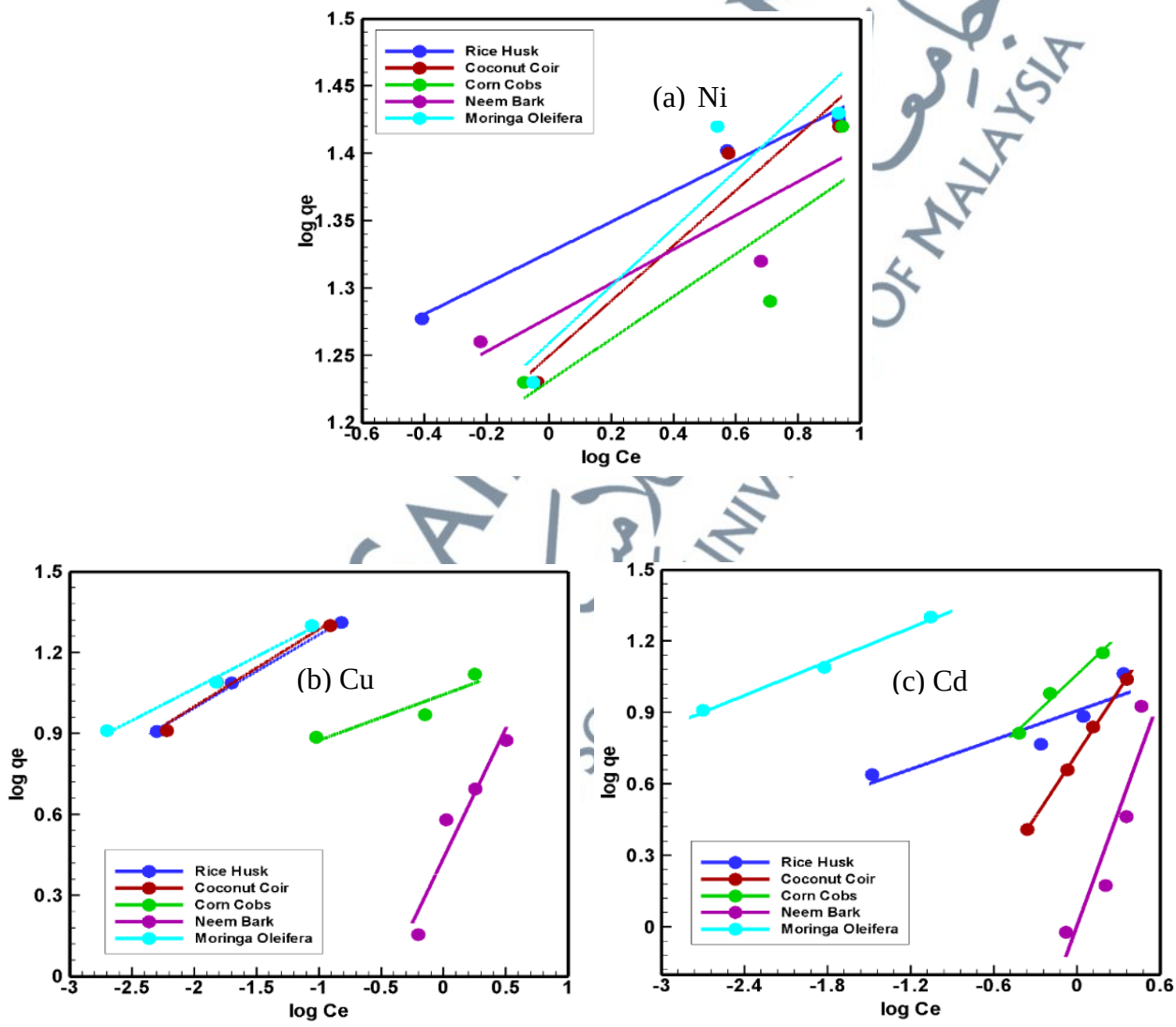

Figure 3.9 Freundlich plot for (a) nickel, (b) copper, and (c) cadmium adsorption of rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark

Note: Lead was removed 100% from aqueous solution using all activated carbon. For this reason, Langmuir and Freundlich isotherm plots can not be plotted for lead.

From the plot of log q against log C_f were obtained the constant K and $1/n$. The Freundlich constants K and $1/n$ were adsorption capacity and adsorption intensity which was summarized in Table 3.1. The Lower value of K was designated the more adsorption (Horsfall et al., 2006). Another constant, with increasing metal ion concentrations, $1/n$ was indicated that adsorption still steady (at $1/n$=1) or decreases. The constant data of all activated carbon were well fitted for Freundlich isotherm like ($1/n < 1$, $K > 1$). The value of $1/n$ and K were (0.114, 0.272, 0.158, 0.126, and 0.214) as well as (21.2, 17.76, 17.01, 18.98, and 18.95) of nickel for rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark respectively as shown in Figure 3.9(a). The value of $1/n$ and K were (0.272, 0.286, 0.17, 0.961, and 0.237) as well as (1.54, 37.35, 11.07, 2.74, and 34.68) of copper for rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark respectively as shown in Figure 3.9(b). The value of $1/n$ and K were (0.204, 0.884, 0.549, 1.602, and 0.524) as well as (8.08, 5.32, 11.47, 1.01, and 6.75) of cadmium for rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark respectively as shown in Figure 3.9(c). Form the value of $1/n$ and K was observed that Freundlich isotherm was well fitted for all metals removal data using five activated carbon.

The Langmuir isotherm constants cannot be described about the chemical or physical properties but it can be identified by the mean adsorption energy (E) which was calculated from the D-R isotherm model (Azouaou et al., 2010). If the adsorption energies (E) is below 8 $kJmol^{-1}$ indicates that the adsorption process is physical forces. On the other hand, The E values (8-16) indicate that the adsorption process follows chemical adsorption. Table 3.1 of adsorption energy values (E) suggested that rice husk (0.264, 0.279, 8.297, and 6.67), coconut coir (0.264, 1.718, 7.813, and 2.71) and *Moringa oleifera* bark (0.264, 1.736, 9.8, and 2.61) respectively indicate a physical adsorption for lead (Pb), nickel (Ni), and cadmium (Cd) metal ions adsorption but copper (Cu) adsorb by chemical adsorption process. On the other hand, corn cobs (0.264, 2,313, 6.024, and 2.134) and neem bark (0.246, 3.03, 1.18, and 0.912) indicate

physical adsorption for all lead and nickel, copper, and cadmium respectively. The Absorption capacity of heavy metals for neem bark was not well without lead due to not having an available active functional group on the surface of activated carbon for binding metals from aqueous solution.

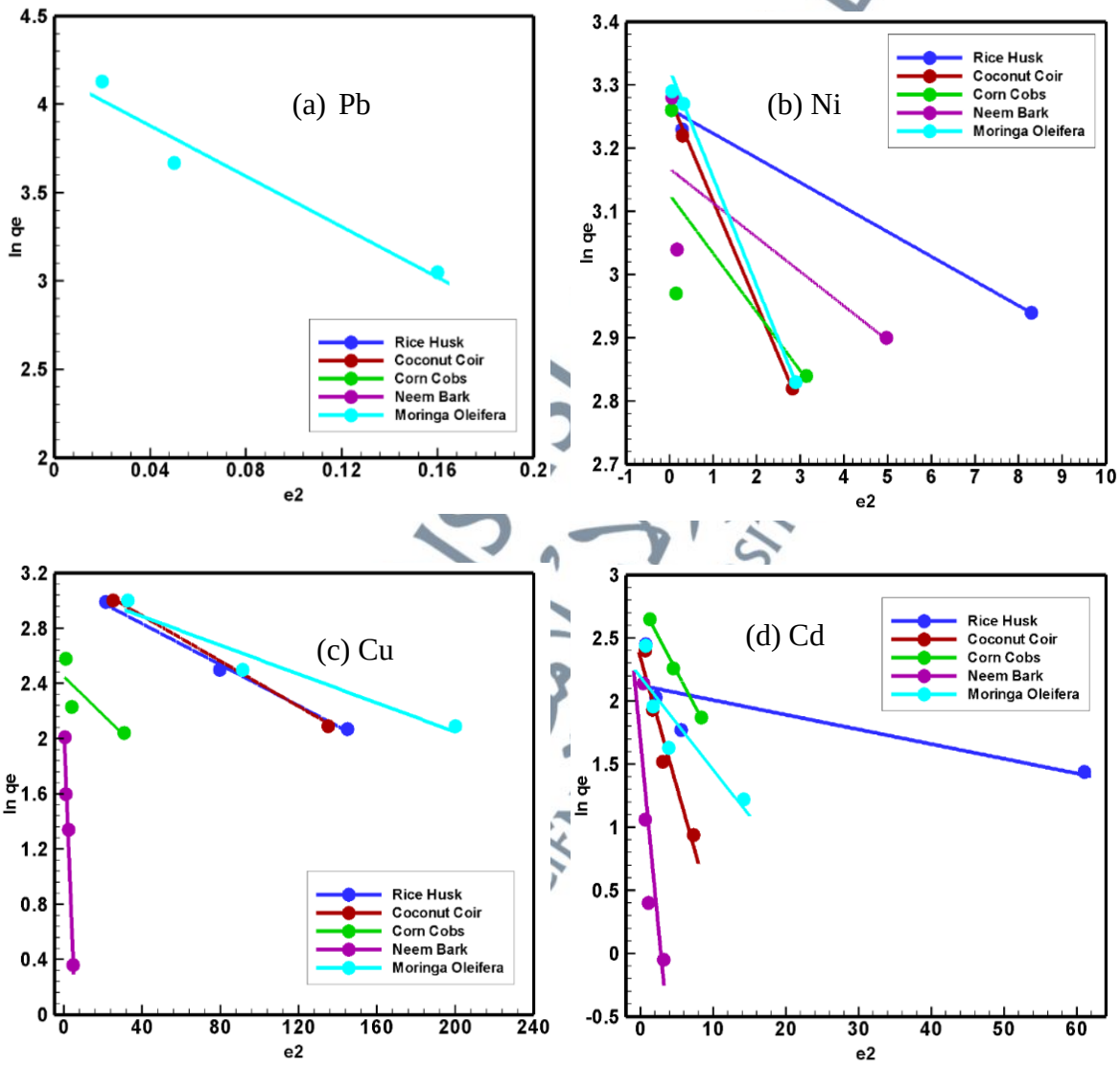

Figure 3.10 D-R plot for (a) lead, (b) nickel, (c) copper, and (d) cadmium uptake of rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark

Table 3.1 Isotherm factors for the uptake of Cu (II), Cd (II), Pb (II) and Ni (II) onto rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark

Activated carbon		Langmuir model			Freundlich model			Dubinin-Radushkevich (D-R) Model		
	Heavy Metals	R^2	q_{max} mg/g	B Lmg^{-1}	R^2	$1/n$	K	R^2	q_{max} mg/g	E $kJmol^{-1}$
Rice husk	Pb	N/A	N/A	N/A	N/A	N/A	N/A	0.94	64.40	0.26
	Ni	0.99	27.17	4.42	0.98	0.11	21.2	0.98	26.05	0.27
	Cu	0.99	20.45	162.87	0.99	0.27	1.54	0.98	22.87	8.20
	Cd	0.89	12.52	2.55	0.82	0.20	8.08	0.63	8.37	6.67
Coconut coir	Pb	N/A	N/A	N/A	N/A	N/A	N/A	0.94	64.40	0.26
	Ni	0.99	28.49	1.68	0.92	0.20	17.76	0.99	26.57	1.74
	Cu	0.99	20.88	159.74	0.96	0.28	37.35	0.99	24.98	7.81
	Cd	0.95	54.95	0.10	0.99	0.88	5.32	0.92	10.43	2.71
Corn cobs	Pb	N/A	N/A	N/A	N/A	N/A	N/A	0.94	64.40	0.26
	Ni	0.93	27.4	0.94	0.75	0.15	17.01	0.57	22.80	2.31
	Cu	0.97	13.3	10.31	0.88	0.17	11.07	0.68	11.56	6.02
	Cd	0.88	15.55	3.69	0.98	0.54	11.47	0.99	16.11	2.13
Neem bark	Pb	N/A	N/A	N/A	N/A	N/A	N/A	0.94	64.40	0.26
	Ni	0.96	27.1	1.66	0.78	0.12	18.98	0.62	23.75	3.03
	Cu	0.58	9.38	2.37	0.91	0.96	2.74	0.98	8.03	1.18
	Cd	0.57	3.79	0.20	0.84	1.60	1.01	0.63	5.47	0.91
***Moringa oleifera* bark**	Pb	N/A	N/A	N/A	N/A	N/A	N/A	0.94	64.40	0.26
	Ni	0.99	27.86	0.35	0.87	0.21	18.15	0.99	27.41	1.73
	Cu	0.98	20.43	162.07	0.99	0.23	34.68	0.94	22.07	9.80
	Cd	0.80	17.01	0.73	0.95	0.52	6.75	0.77	8.94	2.61

3.3.6 Adsorption Kinetics

The adsorption kinetics of heavy metals were determined by some parameters such as first order, second order, intra particle diffusion models and contacting time ranging between 10 to 120 minutes. This study was carried out to experimental data as exposed in Figures 3.11-3.13.

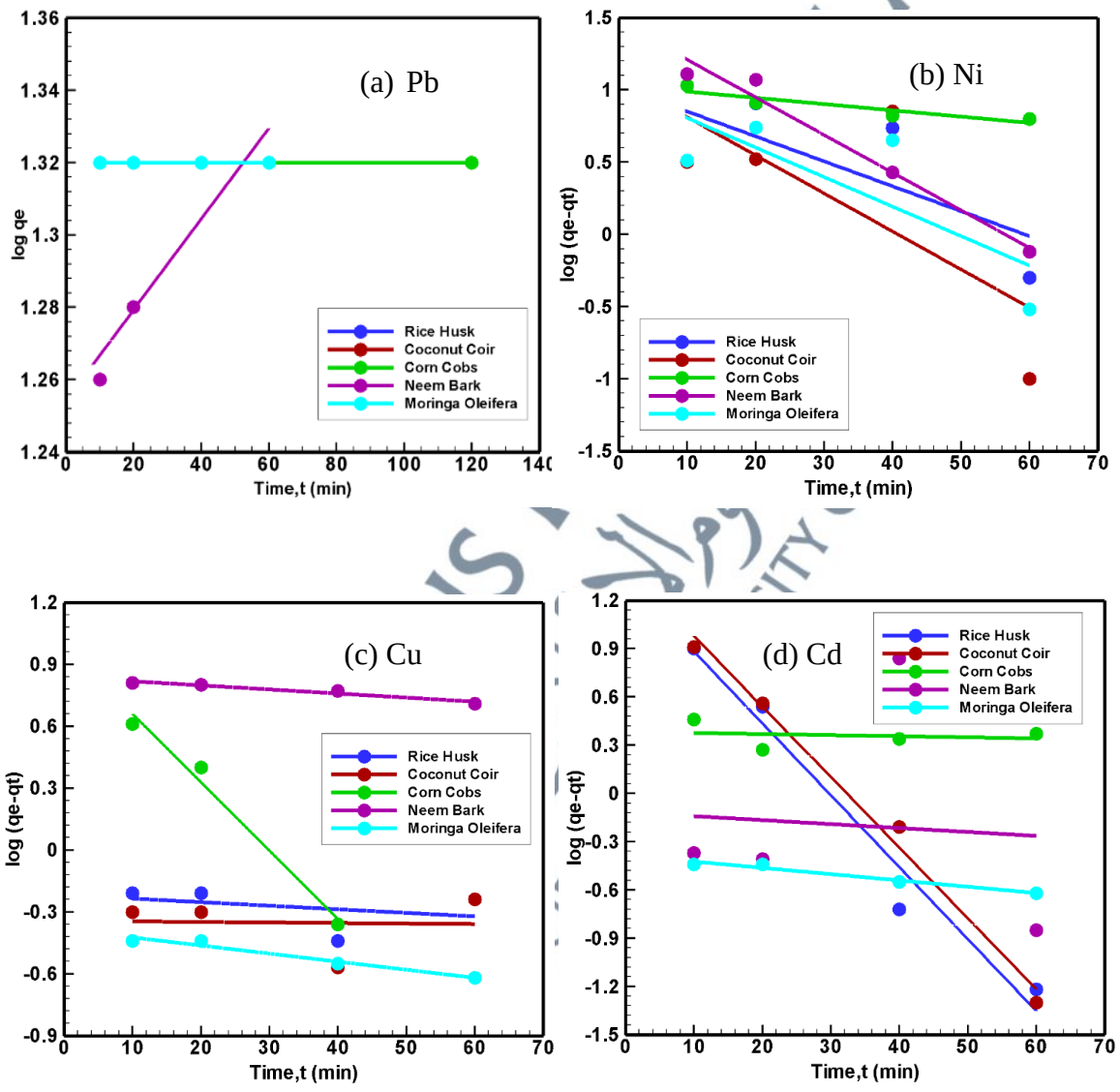

Figure 3.11 First order graph for (a) lead, (b) nickel, (c) copper, and (d) cadmium uptake of rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark

The pseudo first order, pseudo second order and intra particle diffusion constants were compared among the experimental sorption capacities (q_{exp}) and the predicted values (q_{cal}, k_1, k_2, k_d, R^2). These comparable values were shown in Table 3.2.

The pseudo-first-order kinetic graph were shown in Figures 3.11(a)-(d). The values of K_1 and correlation coefficient, R^2 obtained from the plots for lead, nickel, copper, and cadmium adsorption respectively on the adsorbents were given in Table 3.2. The experimental q_e values (21.05 of lead), (18.96, 16.82, 17.14, 18.12, 16.92 of nickel), (19.84, 19.95, 13.19, 7.49, 20.09 of copper), and (11.57, 11.05, 14.16, 8.46, 11.42 of cadmium) for rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark, respectively were not in fitted with the calculated values (N/A of lead for 100% adsorption), (10.54, 11.89, 10.71, 29.54, 4.00 of nickel), (1.64, 3.02, 2.43, 6.88, 2.43 of copper), and (21.25, 26.21, 9.77, 1.31, 8.87 of cadmium) obtained from the linear plots as shown in Figure 3.11(a)-(d). This was shown that the adsorption of heavy metals on all the activated carbon were not in fitted with first-order.

From the Table 3.2, the pseudo second order model was much close between the calculated (q_{cal}) value and experimental (q_{exp}) values for all activated carbon. The experimental q_e values (21.05 of lead), (18.96, 16.82, 17.14, 18.12, 16.92 of nickel), (19.84, 19.95, 13.19, 7.49, 20.09 of copper), and (11.57, 11.05, 14.16, 8.46, 11.42 of cadmium) for rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark, respectively were well in fitted with the calculated values (21.05, 21.05, 21.05, 21.05, 21.05 of lead), (20.88, 18.12, 20.08, 25.25, 18.28 of nickel), (19.80, 19.88, 13.74, 41.49, 20.08 of copper), and (11.12, 10.72, 14.6, 8.31, 11.04 of cadmium) obtained from the linear plots as shown in Figures 3.12 (a)-(d).

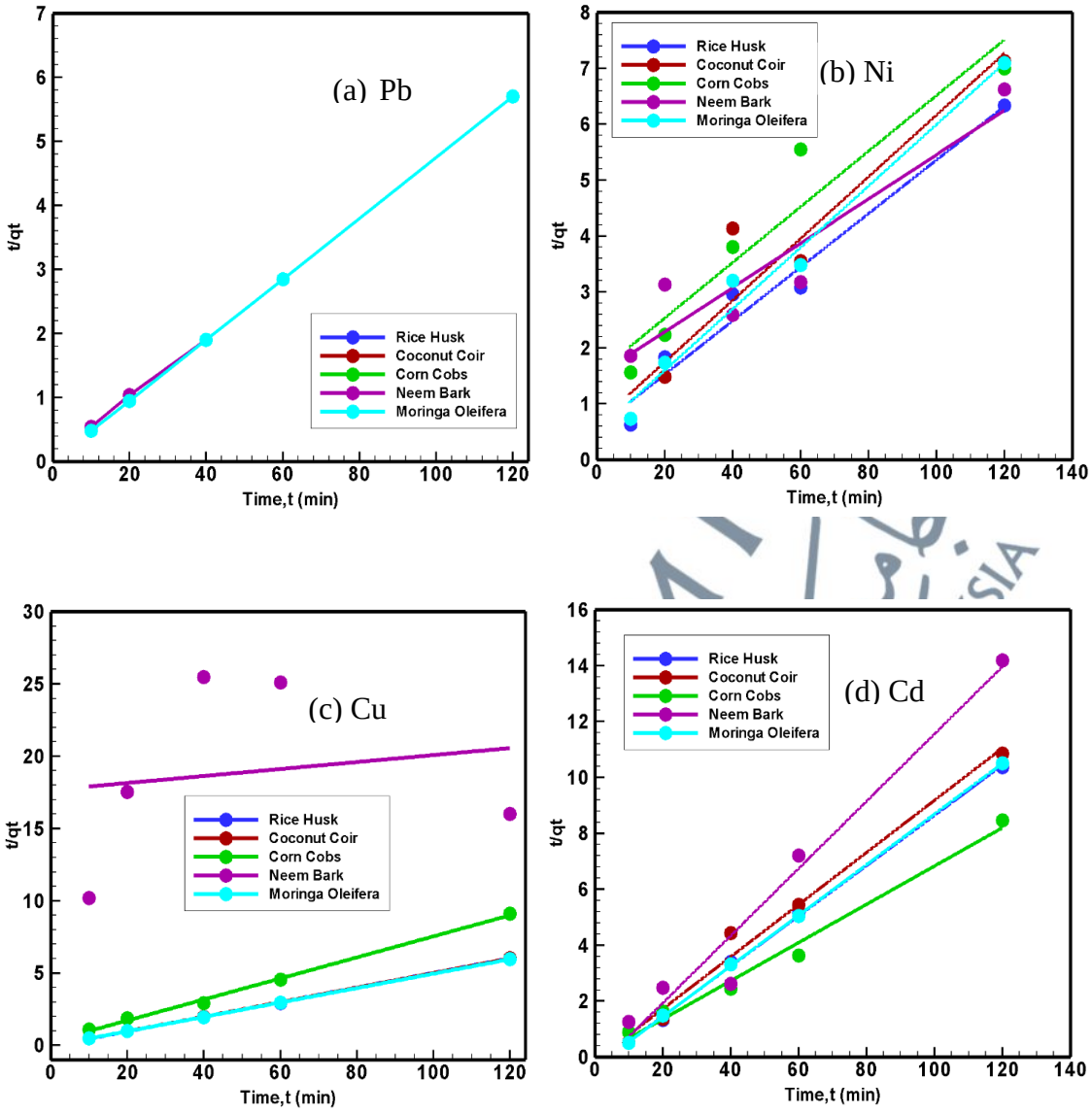

Figure 3.12 Second order graph for (a) lead, (b) nickel, (c) copper, and (d) cadmium uptake of rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark

The second order equation has higher regression coefficient (R^2) values than the first order and intra particle diffusion equation. So, the pseudo second order model was very well fitted for heavy metals (lead, nickel, copper, cadmium) adsorption using all activated carbon. With increasing the contact time, the adsorption of metal also was increased but after reaching the equilibrium state the change was not significant due to the saturation of active sites on the adsorbent. On the other hand, lead was so fast and it was removed absolutely (100%) from spiked aqueous solution after just 10 minutes

to till equilibrium due to lower mass effect and more binding capacity with activated carbon.

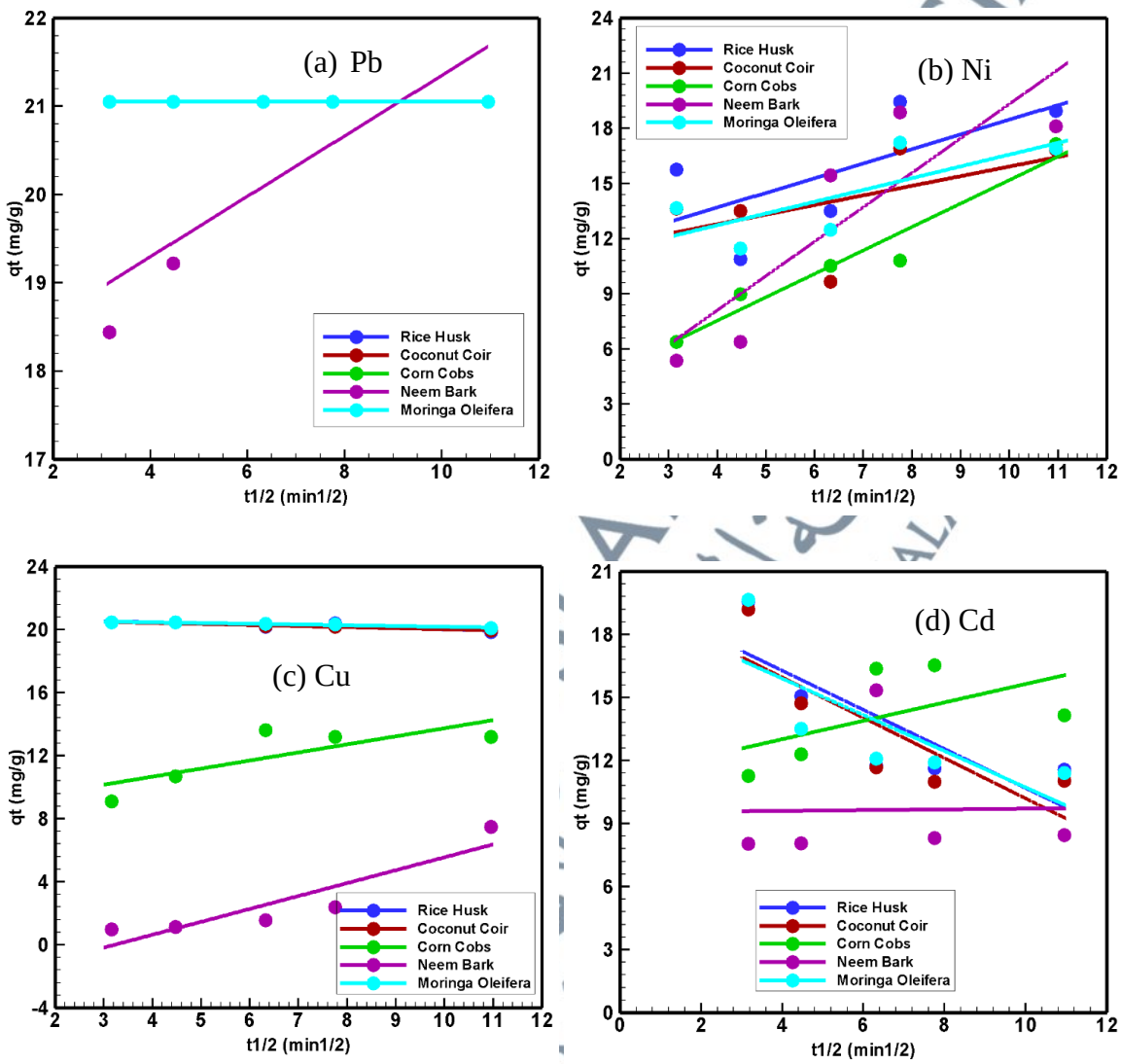

Figure 3.13 Intraparticle diffusion of (a) lead, (b) nickel, (c) copper, and (d) cadmium adsorption for rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark

Figure 3.13(a)-(d) was shown a plot of q_t against $t^{1/2}$ for inter-particle diffusion, derived to give a linear plot with slope k_{id} and intercept C_i. It can be observed from the graph that the linear line for lead, nickel, copper, and cadmium of all activated carbons were not passed through the origin (0). This pointed out that the rate-limiting step was not only the intra-particle diffusion but together with the boundary layer control, which can be operating simultaneously in the sorption process (Kumar et al., 2011).

Table 3.2 Kinetics factors for the uptake of Cu (II), Cd (II), Pb (II) and Ni (II) onto rice husk, coconut coir, corn cobs, neem bark and *Moringa oleifera* bark

Activated Carbon	Heavy Metal	q_{exp} mg/g	First Order			Second Order			Intra –Particle Diffision	
			R^2	q_{qal} mg/g	k_1 min^{-1}	R^2	q_{qal} mg/g	k_2 min^{-1} gmg^{-1}	k_d mgl^{-1} $min^{-1/2}$	R^2
Rice husk	Pb	21.05	N/A	N/A	N/A	1.00	21.05	0.98	N/A	N/A
	Ni	18.96	0.51	10.54	0.04	0.96	20.88	0.004	0.79	0.44
	Cu	19.84	0.12	1.64	0.004	0.99	19.80	0.06	0.07	0.72
	Cd	11.57	0.96	21.25	0.10	0.99	11.12	0.02	0.93	0.65
Coconut coir	Pb	21.05	N/A	N/A	N/A	1.00	21.05	0.98	N/A	N/A
	Ni	16.82	0.49	11.89	0.06	0.91	18.12	0.005	0.52	0.28
	Cu	19.95	0.90	3.02	0.03	1.00	19.88	0.09	0.06	0.96
	Cd	11.05	0.99	26.21	0.10	0.98	10.72	0.06	0.96	0.68
Corn cobs	Pb	21.05	N/A	N/A	N/A	1.00	21.05	0.98	N/A	N/A
	Ni	17.14	0.84	10.71	0.009	0.91	20.08	0.002	1.27	0.94
	Cu	13.19	0.03	2.43	0.002	0.99	13.74	51.20	0.51	0.62
	Cd	14.16	0.98	9.77	0.07	0.98	14.60	0.42	0.43	0.31
Neem bark	Pb	21.05	0.95	17.91	0.003	0.99	21.37	0.03	0.34	0.69
	Ni	18.12	0.97	29.54	0.06	0.88	25.25	0.001	1.87	0.76
	Cu	7.49	0.95	6.88	0.005	0.02	41.49	0.0003	0.81	0.82
	Cd	8.46	0.01	1.31	0.006	0.96	8.31	0.03	0.01	0.003
Moringa Oleifera bark	Pb	21.05	N/A	N/A	N/A	1.00	21.05	0.98	N/A	N/A
	Ni	16.92	0.60	4.00	0.04	0.98	18.18	0.006	0.64	0.55
	Cu	20.09	0.96	2.43	0.009	1.00	20.08	0.11	0.04	0.92
	Cd	11.42	0.86	8.87	0.05	0.99	11.04	0.02	0.86	0.58

3.3.7 Desorption Studies

It can be described as the percent removal of pollutants which was first loaded onto the activated carbon. Regaining metal ions is essential for reuse (Chen et al., 2007). The

studies were conducted by batch desorption technique using HCl, H_2SO_4 and Na_2CO_3 of known concentration of 0.1N as shown in Figure 3.14-3.17. The efficiencies of desorption were compared in Table 3.3. Generally, with increasing cycle numbers, desorption efficiency decreases as given in Table 3.4. In each cycle, new binding sites were decreased which were generated by dilute HCl treatment. For this reason, declining adsorption capability with the increasing cycle number as shown in Figure 3.18-3.21. However, HCl presented the highest desorption efficiency for Pb (II), Cu (II), Ni (II) and Cd (II) for all activated carbon but neem bark desorption efficiency was not good for all metals without Ni (II).

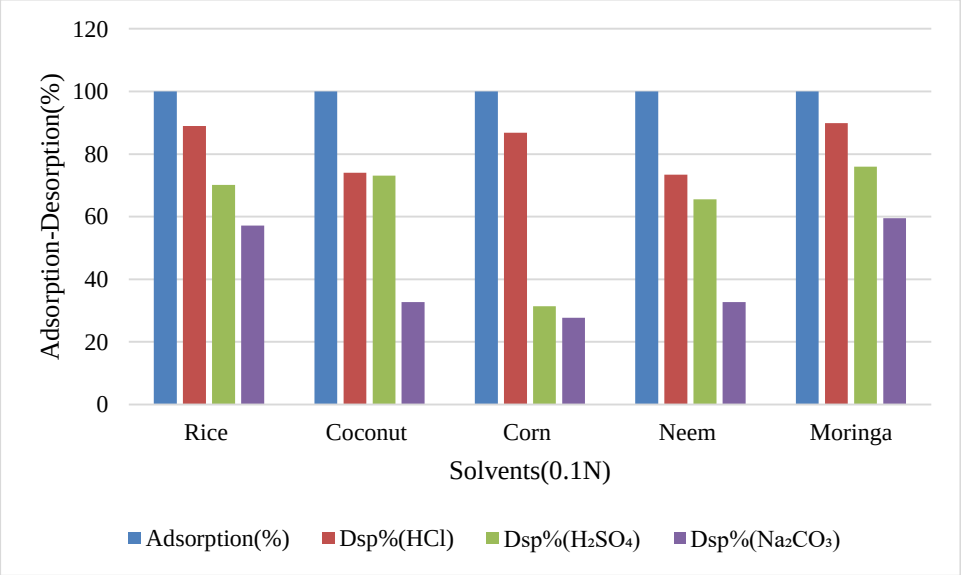

Figure 3.14 Desorption efficiency using 0.1N different solvents for lead of all AC

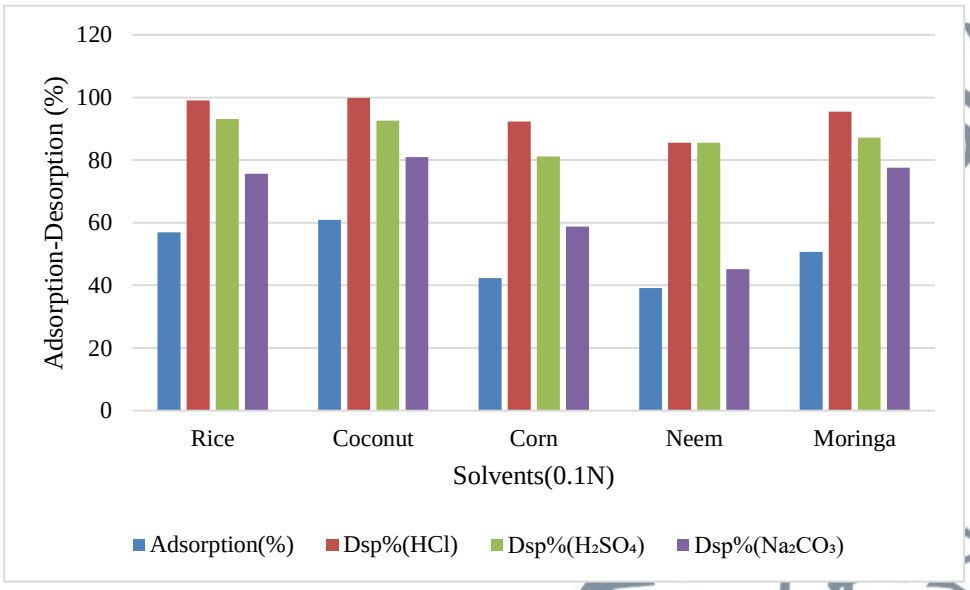

Figure 3.15 Desorption efficiency using 0.1N different solvents for nickel of all AC

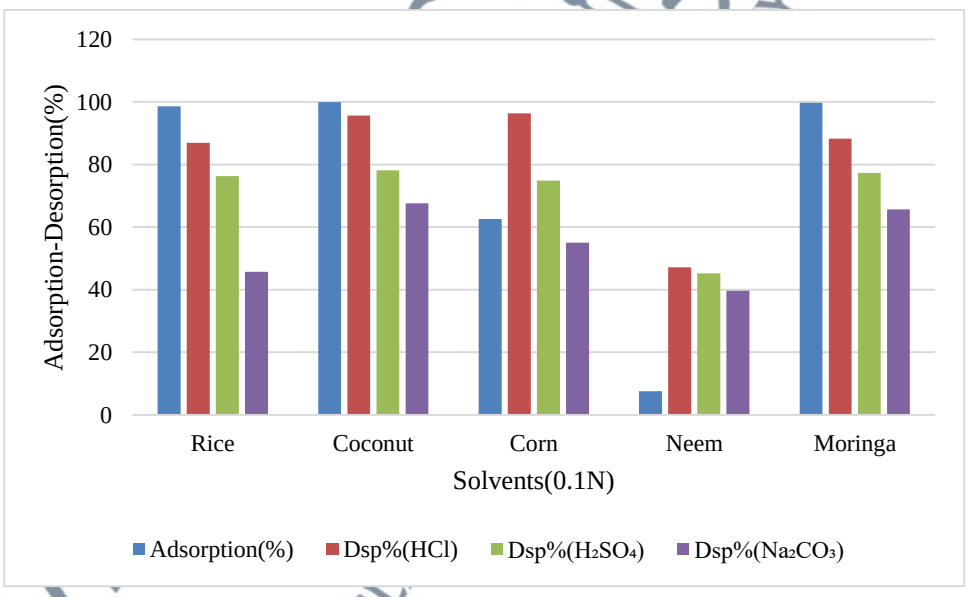

Figure 3.16 Desorption efficiency using 0.1N different solvents for copper of all AC

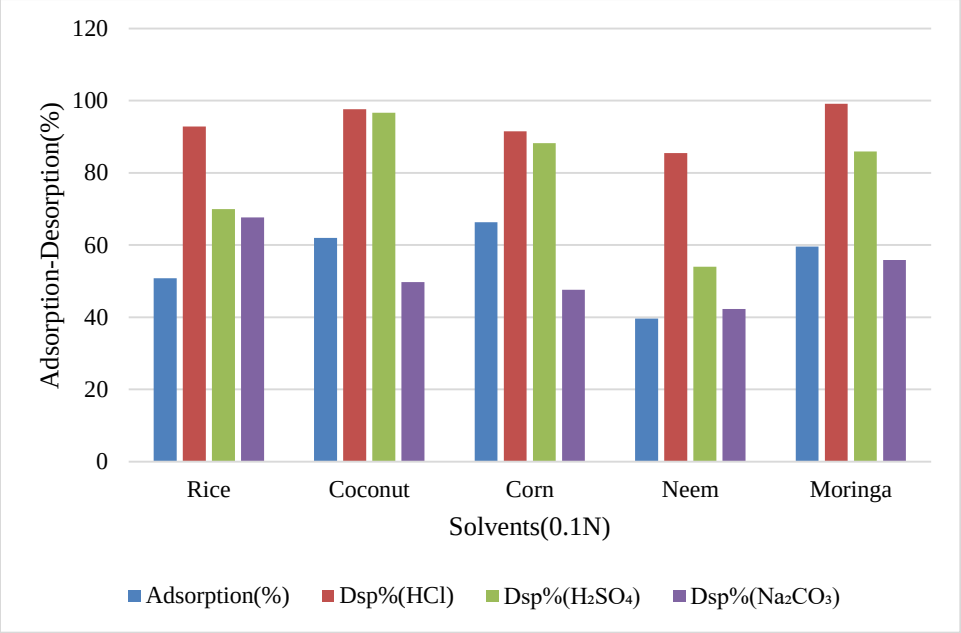

Figure 3.17 Desorption efficiency using 0.1N different solvents for cadmium of all AC

Table 3.3 Adsorption desorption table with different chemical

Activated Carbon	Heavy Metals	Adsorption (%)	Desorption HCl (%)	Desorption H_2SO_4 (%)	Desorption Na_2CO_3 (%)
Rice husk	Pb	100	88.96	70.15	57.17
	Ni	56.94	99.02	93.14	75.61
	Cu	98.6	86.93	76.25	45.72
	Cd	50.8	92.83	69.92	67.68
Coconut coir	Pb	100	74.03	73.06	32.75
	Ni	60.91	99.87	92.57	88.91
	Cu	99.9	95.63	78.09	67.63
	Cd	62	97.65	96.68	49.68
Corn cobs	Pb	100	88.82	31.78	27.71
	Ni	42.34	92.31	81.16	58.72
	Cu	62.6	96.28	74.83	55.04
	Cd	66.34	91.47	88.24	47.63
Neem bark	Pb	100	73.45	65.5	32.75
	Ni	39.17	85.97	85.56	45.19
	Cu	7.54	47.09	45.24	39.68
	Cd	39.6	54.6	53.94	42.27
Moringa oleifera bark	Pb	100	89.92	75.97	59.5
	Ni	50.71	95.44	87.21	77.54
	Cu	99.7	88.26	77.29	65.67
	Cd	59.56	99.13	85.93	55.88

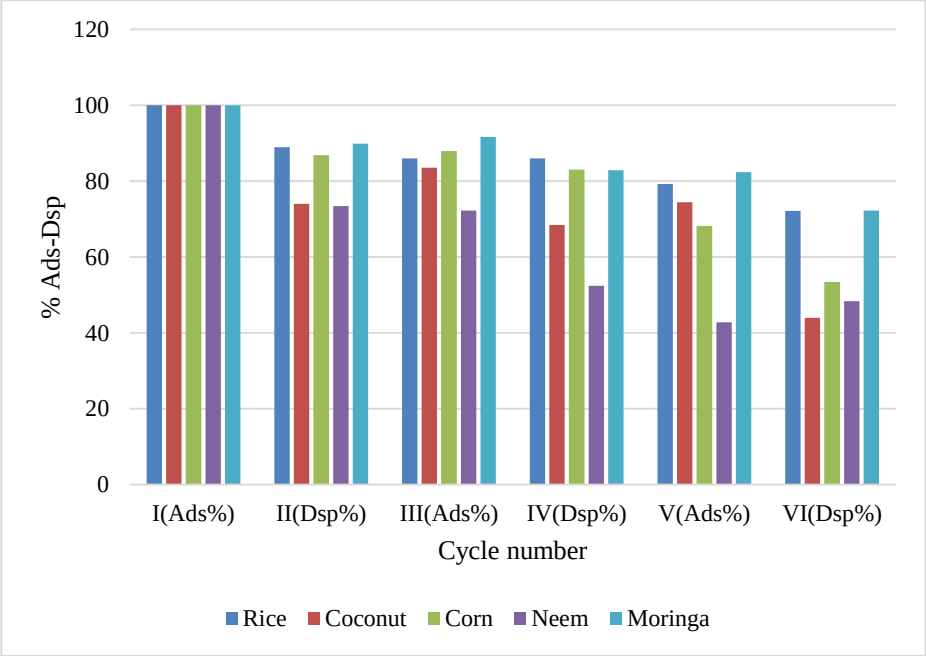

Figure 3.18 Desorption efficacy with 0.1N HCl during several cycles for lead of rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark

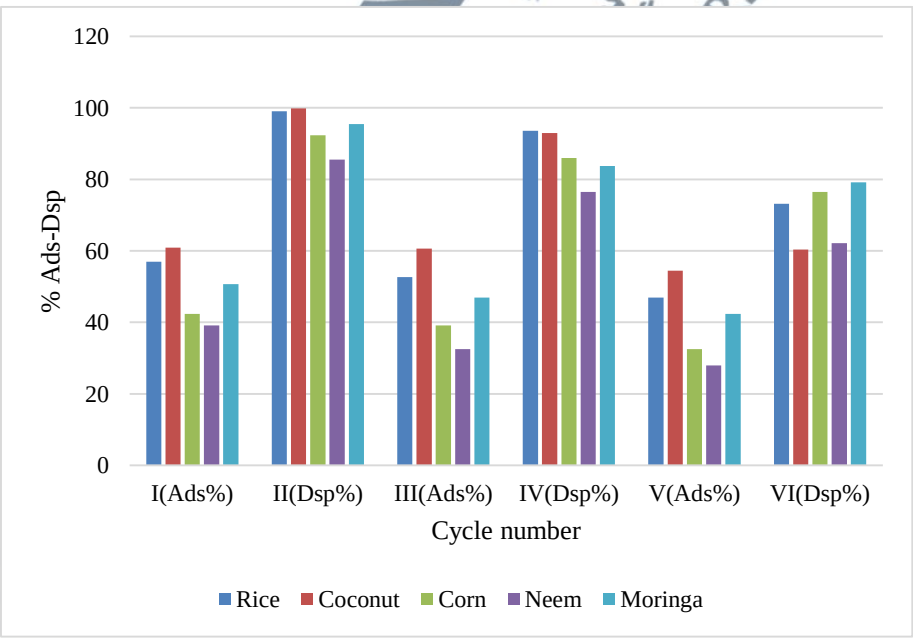

Figure 3.19 Desorption efficacy with 0.1N HCl during several cycles for nickel of rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark

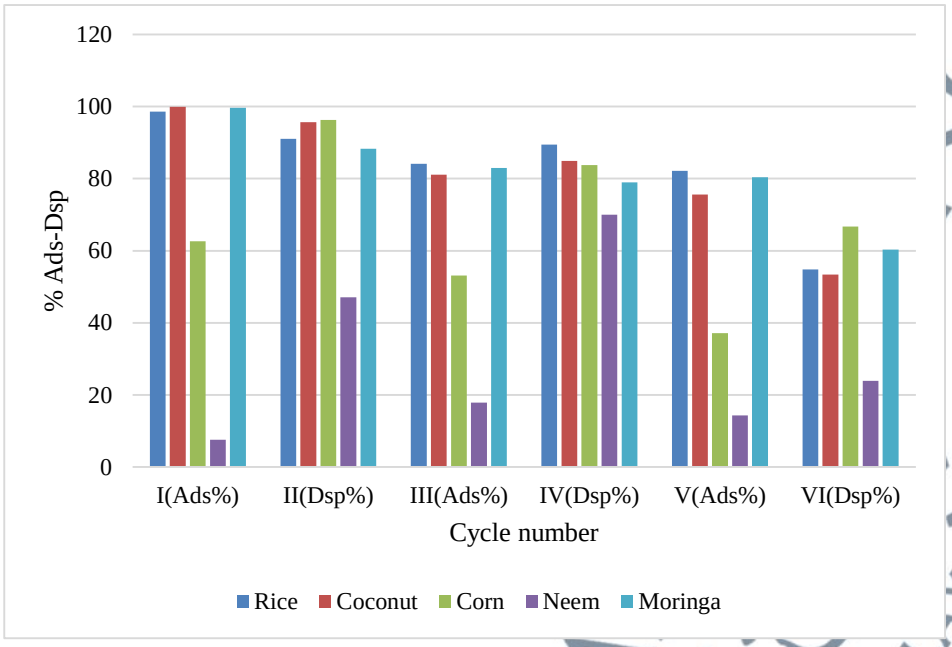

Figure 3.20 Desorption efficacy with 0.1N HCl during several cycles for copper of rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark

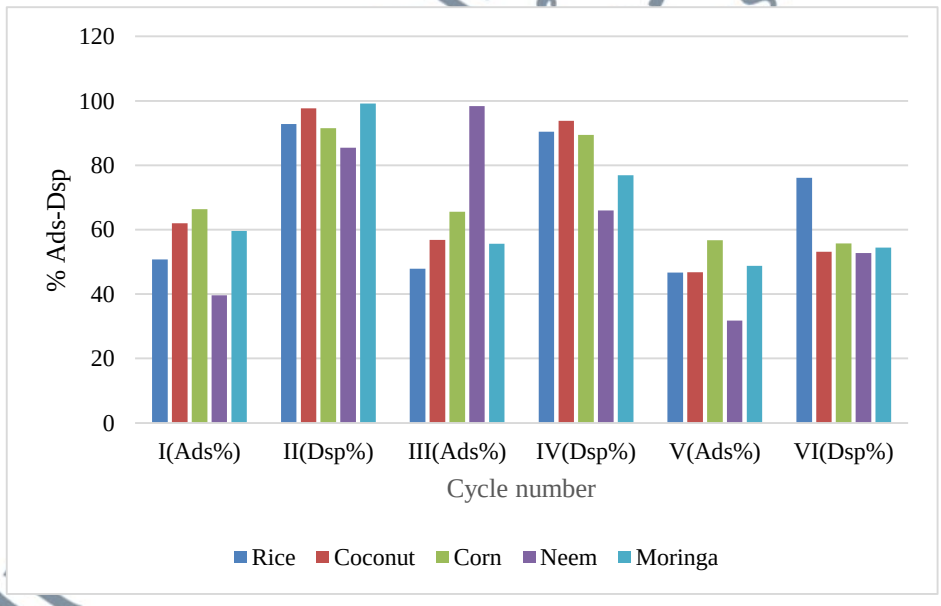

Figure 3.21 Desorption efficacy with 0.1N HCl during several cycles for cadmium of rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark

Table 3.4 Desorption efficacy with 0.1N HCl during several cycles

Cycles		I	II	III	IV	V	VI
Activated Carbon	**Heavy Metals**	**Adsorption(%)**	**Desorption(%)**	**Adsorption(%)**	**Desorption(%)**	**Adsorption(%)**	**Desorption(%)**
Rice husk	Pb	100.00	88.96	86.05	86.03	79.26	72.13
	Ni	56.94	99.02	52.64	93.64	46.96	73.17
	Cu	98.60	91.06	84.08	89.42	82.2	54.84
	Cd	50.80	92.83	47.88	90.43	46.64	76.15
Coconut coir	Pb	100.00	74.03	83.53	68.44	74.41	44.01
	Ni	60.91	99.87	60.67	92.93	54.47	60.37
	Cu	99.90	95.63	81.11	84.95	75.58	53.37
	Cd	62.00	97.65	56.81	93.79	46.82	53.10
Corn cobs	Pb	100.00	88.82	87.98	83.03	68.22	53.41
	Ni	42.34	92.31	39.17	85.97	32.52	76.44
	Cu	62.60	96.28	53.08	83.77	37.16	66.67
	Cd	66.34	91.47	65.57	89.4	56.70	55.73
Neem bark	Pb	100.00	73.45	72.29	50.4	42.83	48.41
	Ni	39.17	85.97	32.52	76.45	27.90	62.14
	Cu	7.54	47.09	17.87	69.98	14.28	23.88
	Cd	39.60	85.45	38.98	65.93	31.74	52.74
Moringa oleifera bark	Pb	100.00	89.92	91.67	82.88	82.36	72.23
	Ni	50.71	95.44	46.96	83.73	42.34	79.15
	Cu	99.70	88.26	82.94	78.93	80.41	60.33
	Cd	59.56	99.13	55.64	76.95	48.82	54.40

3.4 Conclusions

This study suggested that the activated carbons from rice husk, coconut coir, and *Moringa oleifera* bark can be used for the elimination of heavy metals (Cd (II), Pb (II), Ni (II), and Cu (II)) as a low-cost adsorbent from spiked aqueous solution. On the other hand, corn cobs and neem bark were good for lead (Pb) adsorption but remaning metals like nickel, copper and cadmium adsorption were not good. The metals removal were good using best parameters like concentration (5 mg/L), dosage (0.025 g), and pH (6). The adsorption experiments at room temperatures were well designated by the Freundlich isotherm models and second-order kinetic models. Hydrochloric acid (0.1 N) was an effective desorbent for the recovery of metal (Cu (II), Pb (II), Cd (II), and Ni (II)) from adsorbents. Therefore, Rice husk, coconut coir and *Moringa oleifera* bark were the best adsorbents among others for metal adsorption process from spiked aqueous solution and those adsorbents were selected for characterization in the next chapter.