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Comparison of Multi-walled Carbon Nanotubes (MWNTs) and Activated Carbon (AC) as Adsorbents in Heavy Metal Adsorption

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Abstract. The present study was undertaken to investigate the ability of granulated charcoal activated carbon (AC) and multi-walled carbon nanotubes (MWNTs) as adsorbents in adsorption process of removing heavy metals from aqueous solutions. The analyses of heavy metal removal are performed on three operational parameters which are agitation time, initial ion concentration and pH. The experiments were carried out at room temperature (25^oC) and metal solutions were agitated on a rotary shaker at constant speed range between 200 to 240 rpm. BET surface area of AC and MWNTs were found to be 898 m^2/g and 213 m^2/g, respectively. Metals adsorptions by both adsorbents were well fitted to Freundlich isotherm. Batch adsorption test showed that metal uptake increases as agitation time increases which are the optimum time are 3 hours and 4 hours by using AC and MWNTs, respectively. Cadmium adsorption by both adsorbents showed the same behaviour where as initial metal ion concentration increases, cadmium adsorption percentage increases. As for nickel, when using AC as adsorbent, as the initial ion concentration increases, the nickel

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adsorption percentage decreases.Adsorption was found to be low at acidic pH and kept on increasing as pH increased.

Keywords: heavy metal adsorption, multi-walled nanotube, activated carbon
PACS: 61.48.De; 81.05.U-

INTRODUCTION

Wastestreams coming from industries which reaches water resources and soil have been identified to contain various contaminants such as heavy metals and dyes. In aquatic systems, the heavy metals are present as dissolved ions and complexes, suspended and colloids ions as well as solid in sediments [1]. This phenomenon is potentially hazard to human and the environment as the metals not degrade into harmless end products and tend to accumulate in living organisms, causing various diseases and disorders. Example of serious impact of metals pollution on livings health is where the excessive intake of copper and lead into the body can affect the gastrointestinal track and nervous system [2]. Besides, effects of cadmium exposure may occur at lower exposure levels than previously anticipated, primarily in the form of kidney damage but possibly also bone effects and fractures [3]. As for nickel, the presence in the body will results in vomiting, chest pain, and shortness of breath [4].

Several methods have been used in wastewater treatment which includes filtration, precipitation, ion exchange and membrane separation. Adsorption is one of the methods for removing heavy metals from contaminated effluents and the most effective among all. Activated carbon (AC) has been widely used as an adsorbent for this purpose [5]. AC could be originated from various raw materials such as apricot stone, rice husk, coconut shell and grape stalk wastes [6-9]. Metal adsorption was found to be optimum at pH range 3 to 8 [2, 6-8, 10].

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Another promising adsorbent for wastewater treatment is carbon nanotubes (CNT) as it has the natural characteristics that influence the metal adsorption such as surface area, pore size distribution and chemical nature of their surface [11]. Metal ionic radius is one of the most influential factors in metal adsorption because if the metal ionic radius is smaller compared to the pore size of adsorbent, the adsorption will easily take place [12]. Unlike AC, CNT has uniform and well-defined structure which can directly relate with well-defined adsorption sites that are available to the adsorbed molecules. There are four mechanisms by which the metal ions are adsorbed onto CNTs such as electrostatic attraction, sorption–precipitation and chemical interaction between the metal ions as well as the surface functional groups of CNTs. [13]

Initially, the use of CNT in environmental protection application is limited due to its high production cost and low yield especially in arc discharge and laser ablation methods of preparation although such techniques produce high quality of CNT crystallinity . However, the recent development of economical large scale synthesis chemical vapor deposition (CVD) technique has increased the applications of CNTs in environmental protection applications [14]. The progress in CNT characterization has revealed the unique adsorption properties of CNTs in which it provides chemically inert surfaces for physical adsorption, large specific surface area, highly porous and hollow structure as well as light mass density. Moreover, the hexagonal arrays of carbon atoms in graphite sheets of CNTs surface have strong interactions with other molecules or atoms [15]. The interaction is due to the strong van der Waals binding energy for molecular adsorbates on well-defined adsorption sites such as interior sites, groove sites, exterior sites and interstitial sites (refer to Figure 1). The interstitial sites appear to be inaccessible to the adsorbate molecule. The internal sites are described as the hollow

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interior of individual nanotubes (provided that the open ends or caps are not blocked) while the interstitial sites are the channels between individual nanotubes in the bundles [16]. As a result, a strong interaction between CNTs and pollutant molecules makes CNTs suitable as adsorbents in removing hazardous pollutants from gas streams and from aqueous solutions.

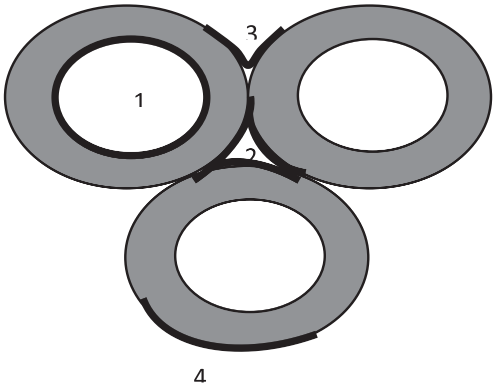

FIGURE 1. Various adsorption sites have been predicted such as (1) internal tube, (2) interstitial channel, (3) external groove site, and (4) external surface [16]

The objective of the research work is to determine the optimum solution pH and metal ion concentration on metal uptake by AC and MWNTs. All of the parameters were varied while the amount of adsorbent was kept constant. The best adsorption isotherm that fit the adsorption behaviour was also been investigated

MATERIALS AND METHODS

AC was purchased from NORIT Company and coded as NORIT GAC1240. It was a granular activated carbon originated from coal which has undergone steam activation while the supplier of MNWTs is Nanostructure & Amorphous Materials Inc. with 95% purity which was produced from CVD method.

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Batch Adsorption Studies

The experiments were carried out at room temperature (25°C). The metal solution were placed in conical flask and agitated on a rotary shaker at constant speed of 200 rpm. The metal concentration was tested using Atomic Absorption Spectrometer. Adsorption percentage was calculated as :

$$\% \, Adsorption = (C_o - C_e / C_o) \times 100 \tag{1}$$

where C_o and C_e are the initial and final concentration of the adsorbate, respectively.

The adsorption capacity, Q_e can be determined from equation below :

$$Q_e = (C_o - C_e) V/m \tag{2}$$

where Q_e is amount metal adsorbed per unit mass of adsorbent (mg/g), C_o is initial metal concentration (mg/L), C_e is final metal concentration (mg/L), V is volume of solution (L) and m is mass of adsorbent (g).

Effect of initial ion concentration

For AC analysis, separated metal solutions with 5 different concentrations of 5, 25, 50, 75 and 100 mg/L were prepared by diluting in respective amount of deionised water using a 1000 ml volumetric flask. Similar method was applied for preparing solution for MWNTs analysis, but concentrations were varied to 5, 10, 15, 20 and 25 mg/L. Metal solutions with constant pH was mixed with adsorbent and agitated for a certain constant period of time.

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Effect of pH

The pH of the metal solutions was varied to five different pH which were 2,4,6,8 and 10 for AC analysis and pH 4, 6,8,10 and 12 for MWNTs analysis. The pH of solution was controlled by addition of 0.1 M NaOH or 0.1 M HCl. The metal solutions with constant initial ion concentration were agitated on shaker for constant agitation time.

RESULTS AND DISCUSSION

For adsorption using CNT that is MWNT, it is believed that the physical adsorption reaches equilibrium faster on external sites (that are grooves and outer surfaces) than that on the internal sites (interstitial channels and internal tube) under the similar temperature condition. This is because the external sites are directly exposed to the adsorbent while at the internal sites, the process can only be taken place if the end of the tubes is not blocked i.e. open pores. As for AC, the adsorption process was readily occurred at all different types of pores that are macropore, mesopore and micropore.

Effect of initial ion concentration

Based on Figure 2(a), by using MWNTs with an average BET specific surface area of 200 m^2/g, cadmium and nickel adsorption capacity increases with the increase in initial metal concentration. This is due to the increase in the driving force of the concentration gradient produced by the increase in the initial cadmium concentration [7]. Figure 2(b) shows that at higher concentration cadmium provide higher adsorption capacity. With a high specific BET surface area of AC at 898 m^2/g, the value of adsorption capacity of 10 mg/g could be reached at initial

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concentration of 25 mg/L. Apparently, the lowest adsorption capacity obtained at a concentration of 5 mg/L for cadmium with an adsorption capacity, Q_e nearly 2 mg/g. Extensions of initial metal concentration could increase the adsorption capacity as it does not reach equilibrium yet.

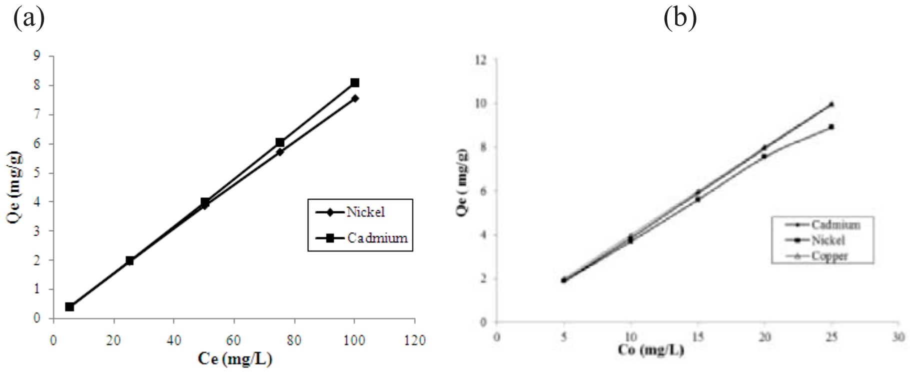

FIGURE 2. Adsorption Capacity of heavy metals using (a) AC and (b) MWNTs

Effect of Ph

Nickel and cadmium adsorption capacity by MWNTs and AC were shown in Figure 3. The agitation time for nickel and cadmium are 120 minutes. The pH of solution is controlled by adding 0.1 M NaOH or 0.1 M H_2SO_4. The research was conducted in the pH range of 2 to 12 as a very high pH value will cause precipitation of metal complexes and should be avoided during sorption experiments where distinguishing between sorption and precipitation metal removal becomes difficult [17]. Adsorption percentages of both metals kept increasing as pH increased. The result explains that the percentage of metal adsorption increase with increasing pH from 2 to 12 and concluded that adsorption by MWNTs and AC was the highest at pH 12 and 10, respectively.

At low pH, solution has high concentration of H^+ ions compared to high pH solution as it is acidic. The presence

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of high H^+ ions in metal solutions created great competition between H^+ ions and metal ions for vacant adsorption sites of adsorbent. The competitive adsorption results in low metal uptake by AC. Optimum pH obtained for cadmium and nickel adsorption by using sawdust and grape stalk wastes were 5 and 5.5, respectively [8,9]. Optimum pH of metals adsorption by MWNTs and AC were higher than achieved by previous researcher which was pH 12 and 10, respectively. Using MWNTs, metal adsorption capacity increased as pH increased from 4 to 12. Optimum pH of metal adsorption by both adsorbents was alkaline and will not corrosive to equipments as if it is applied in industrial applications.

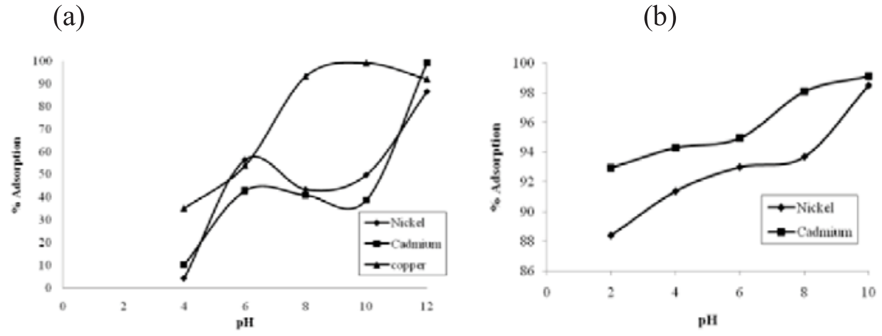

FIGURE 3. Effect of pH on percentage of adsorption using (a) MWNTs and (b) ACs.

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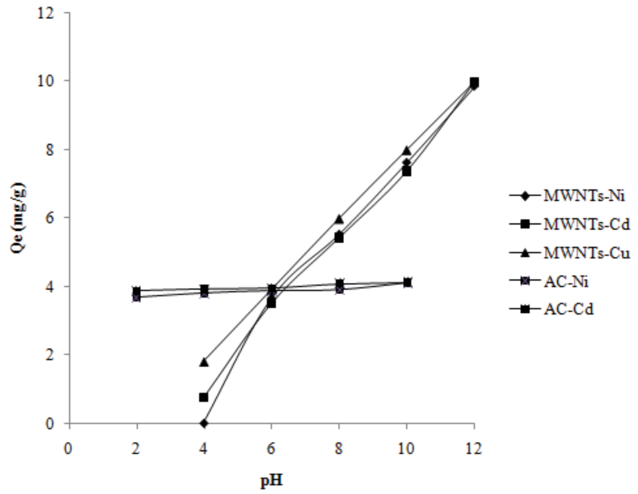

FIGURE 4. Effect of pH on nickel and cadmium adsorption using MWNTs and AC

The order of divalent metal ions towards MWNTs at pH more than 7 is Cu(II)>Cd(II)>Ni(II). Such order agrees with metal-ion electronegativity and of the related metal hydroxide. In additions, a higher pH of the solution, both adsorption and precipitation are involved in the removal of metal ions from the solution [14]. A pH value has greatly affected the adsorption uptake using CNTs as adsorbent as compared with ACs. This can be seen in Figure 4 where as pH increases from 4 to 12, the adsorption uptake increases from 2 to 10 mg/g while using ACs as adsorbent, the adsorption uptake is varied from 3.5 to 4 mg/g only.

Adsorption isotherm

The adsorption isotherm is developed based on the Freundich isotherm equation because it is applicable to highly heterogeneous surfaces [18]. The expression is defined as follows:

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$$Q_e = K_f C_e^{1/n} \qquad (3)$$

where K_f is multilayer sorption capacity, C_e is final concentration of solution after adsorption (mg/L), $1/n$ is Freundlich intensity parameter and Q_e is the amount metal adsorbed per unit mass of adsorbent (mg/g). The constant can be determined by plotting log Q_e versus log C_e following below equation :

$$\log Q_e = \log K_f + (1/n)\log C_e \qquad (4)$$

Figure 5 shows that Freundlich isotherm has R-squared value for nickel and cadmium was 0.995 and 0.980, respectively. The high R-squared value of Freundlich clearly proved that the AC adsorption data is well fitted to Freundlich isotherm and proved that cadmium and nickel adsorptions are multilayer adsorption on the AC surface.

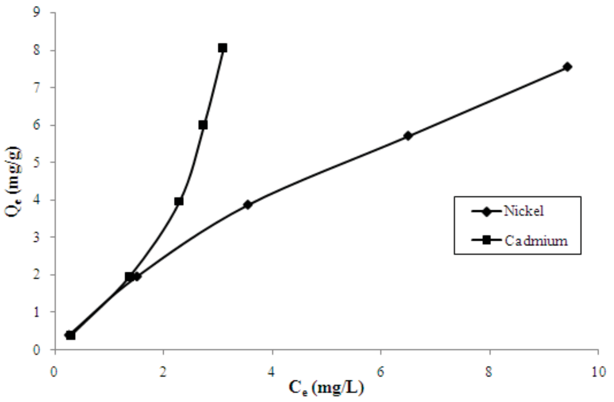

FIGURE 5. Freundlich isotherm for nickel and cadmium adsorption using AC

Among a few available isotherm models, Freundlich adsorption isotherm is used in analyzing the experimental data with regards to metal ions uptake onto MWNTs. Freundlich adsorption isotherm is applicable to highly

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heterogeneous surfaces. The equation is the same as in Equation (4).The value of *n* is observed to determine whether the system is homogeneous or heterogeneous. If *n* value closes to 1, the system is homogeneous while if *n* value approaching zero, the system is heterogeneous. Figure 6(a), (b) and (c) illustrate the Freundlich plot for cadmium, nickel and copper, respectively. Both cadmium and copper have a heterogeneous system while nickel has homogeneous system. A homogeneous solution by the ration of solute to solvent remains the same throughout the solution even if homogenized with multiple sources and stable because the solute will not settle out no matter how long the solution sits [19]. Heterogeneous mixture on the other hand is the substance that is not circulated consistently [20].

The correlation constant for all three metal ions have a value approaching 1. The K_f constant which relate to the adsorption capacity showing that copper has the highest adsorption capacity since the K_f constant is higher than other metal ions. On the other hand, cadmium has the second highest K_f value and followed by nickel. Therefore, the affinity order could be arrange as Cu (II)>Cd (II)>Ni (II).

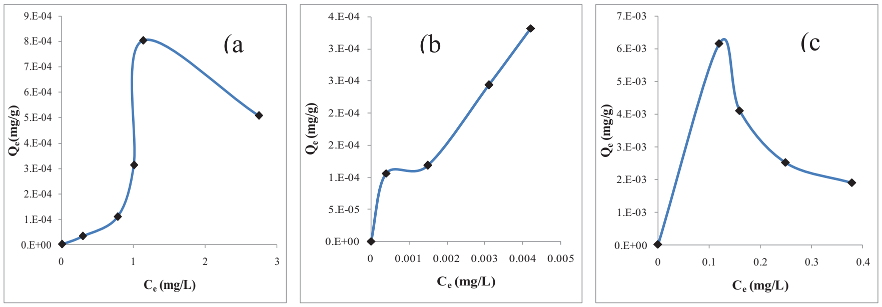

FIGURE 6. Freundlich isotherm for (a) nickel, (b) copper and (c) cadmium adsorption using MWNTs

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CONCLUSION

By using AC as adsorbent, the optimum adsorption of nickel occurred at 120 minutes with 7.8 mg/g of adsorption capacity and 5 ppm metal concentration while the adsorption of cadmium was highest at 120 minutes with 8 mg/g adsorption capacity and 100 ppm metal concentration. For MWNTs, the highest adsorption capacity of cadmium achieved at a period of 4 hours with 9 mg/g adsorption capacity and a concentration of 25 ppm. Meanwhile for nickel and copper, the optimum sorption is at 4 hours and concentration of 20 ppm. Cadmium adsorption by both adsorbents showed the same behaviour where as initial metal ion concentration increases, cadmium adsorption percentage increases. Highest adsorption percentage occurred at 100 ppm for AC and 25 ppm for MWNTs.

Adsorption of metals using AC and MWNTs increase as pH increase because at low pH, solution has high concentration of H^+ ions compared to high pH solution as it is acidic. The presence of high H^+ ions in metal solutions created great competition between H^+ ions and Cd^{2+} ions for vacant adsorption sites of adsorbent. The competitive adsorption resulted in low metal uptake by AC. Using AC, Freundlich isotherm has high R-squared values proving that cadmium and nickel adsorption is multilayer adsorption on the AC surface. Using MWNTs, it can be concluded that both cadmium and copper have a heterogeneous system while nickel has homogeneous system. The correlation constant for all three metal ions have a value approaching 1. Copper has the highest adsorption capacity since the K_f constant is higher than other metal ions. The affinity order could be arranged as Cu (II) > Cd (II) > Ni (II).

Although the BET specific surface area of MWNT is not as high as that of AC, the physical adsorption uptake using that nanomaterial adsorbent is compatible and can be improved if all internal tubes have open ends. Nevertheless,

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both materials can be applied in wastewater treatment depending on the heavy metal ions concentration as well as the pH conditions.

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