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Adsorptive Removal of Phenol from Aqueous Solution by Using Carbon Nanotubes and Magnetic BioChar

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Abstract

The effectiveness of phenol removal from aqueous solution by different adsorbents was experimentally studied. Results revealed that the pH and adsorbent dosage to be the main factors in this adsorption study. It is found that functionalized carbon nanotubes (CNTs) give the highest removal of 88% followed by 82.3% and 82.2% for magnetic biochar and raw CNTs respectively. Adsorption isotherm studies fit the Langmuir model better than the Freaundlich model and adsorption kinetic follows pseudo-second order.

Keywords

Phenol, Adsorption, Carbon nanotubes, Magnetic biochar

Introduction

Since its first discovery in 18th century, phenol has been widely produced in synthesis of dyes, drugs, plastics, pesticides, pharmaceutical, petrochemical, and chemical industries [1, 2]. Phenol discharged from aforesaid industries cause a carbolic odor to river water and also harmful to organism even at low concentration [3-5]. Adverse effects of phenols to human cardiovascular and urinal-genital have been observed and often expressed by multiple symptoms such as convulsion, coma, cardiac disorder, respiratory failure and collapse [6]. Beside that phenols are corrosive to skin and eyes. Continuous daily skin exposure to phenol has been known to cause acute form of dermatitis [7]. Since phenols have serious effects to environment, they are considered as one of priority pollutant in wastewater. Environmental Protection Agency (EPA) has set a limit of 0.1 mg/L of phenol in wastewater odor threshold at 0.04 ppm. The World Health Organization sets a 0.001 mg/l of phenol in potable water [8-12].

Several techniques have been studied and investigated to remove phenols and its derivatives effectively. Methods such as oxidation, precipitation, solvent extraction, adsorption distillation bio-remediation, reverse osmosis, and gas stripping are widely available. Among all of aforesaid methods, adsorption is found to be the most widely used technique in removing phenols and its derivatives [13-15]. In adsorption methods, it is found that carbon base adsorbents are the most widely used adsorbent to remove organic compound in wastewater. Selection of a good, promising and economically effective adsorbent has been investigated extensively in the past several decades. Magnetic BioChar produced from empty fruit bunch as recent alternative adsorbent has been developed and studied.

In this recent study, the potential of magnetic biochar as a latest alternative adsorbent is investigated experimentally. A comparative study with raw CNTs and functionalized CNTs which have been known by their extraordinary properties and abilities in removing variety of organic and non-organic contaminant is also investigated [2, 16-20].

Materials and Methods

Raw Materials

The magnetic biochar and Multiwall carbon nanotubes (MWCNTs) of 95% purity with an average diameter of 30 to 40 nanometers and 1.5 microns of average length were obtained from my previous work [21, 22]. Phenol in analytical reagent grade was purchased from Merck and used as received.

Pretreatment of Magnetic BioChar

The magnetic biochar was firstly used with distilled water until it is in neutral pH and then it was dried in the oven at 40 °C for 24 hours.

Functionalization of carbon nanotubes

MWCNTs were added to 1 L solution of 0.4 M $KMnO_4$ and 0.4 M HNO_3 with 3:1 volume ratio respectively. The solution and MWCNTs is then sonicated for three hours at 60 °C using sonication equipment. After three hours the functionalized MWCNTs is the filtered and washed with distilled water until it reached neutral pH and dried in the oven at temperature of 60 °C for about 24 hours and crushed to get a powder form of functionalized MWCNTs.

Preparation of stock solution and reagents

Stock solution was prepared by diluting 1 g of phenol into 1 L distilled water. Standard solutions were also prepared for calibration graph preparation. Concentration of 20 mg/l, 40 mg/l and 60 mg/l of phenol standard solution were prepared by further dilution of the stock solution. 0.1 M H_2SO_4 and 0.1 M NaOH were prepared to vary the pH of the solution by diluting 0.25 M H_2SO_4 and 1 M NaOH with distilled water.

Batch Adsorption

A series of experiment were carried out with constant initial concentration. Other factors were varied in order to investigate the optimum condition of each adsorbent to give maximum adsorption capacity. 100 ml Phenol solution with constant initial concentration of 500 mg/l was adjusted to desired pH and mixed with adsorbents at certain dosage and agitated at certain speed according to the given design parameters at room temperature (26 ± 1 °C). The treated aqueous solution is then filtered using whatman filter paper No.42 and the absorbance was measured using Hitachi UV-Vis Spectrophotometer model U-2900 at 210 nm against distilled water and reagent blank. The final concentration was obtained from standard calibration graph. The removal percentage and of phenol (%) adsorption capacity (mg/g) were calculated using the following equations:

$$\%\ \text{Removal of Phenol} = \frac{c_o - c_f}{c_o}\ x\ 100 \qquad (1)$$

$$Adsorption\ Capacity\ \left(q_t\right) = \frac{\left[\left(c_o - c_f\right)V\right]}{M} \qquad (2)$$

Where q_t is adsorption capacity (mg/g) at time t; C_o and C_f are initial and final concentration (mg/l) respectively. M is the adsorbent dosage and V is volume of the solution.

Adsorption isotherm and kinetic study

The adsorption kinetic study and adsorption isotherm was performed by preparing phenol solution with constant initial concentration of 500 mg/l at three different pH (4, 6 and 8) with an adsorbent dosage of 0.5 g and agitated at 350 rpm for 24 h. the samples was withdrawn at different predetermined time intervals. All the samples were filtered and analyzed for residual concentration of phenol.

Results and Discussion

Characterization of adsorbent

The Field Emission Scanning Electron Microscope (FESEM) analysis of raw MWCNTs and functionalized MWCNTs morphology are showed in Figure 1(A, C) and (B, D) respectively. Figure 1A and 1C show the morphology of raw MWCNTs at different magnification of 1000 and 10^6 nm respectively. It could be seen that raw MWCNTs have a structure of long hollow fiber with diameter range from 30-34 nm. While Figure 1B and 1D show the morphology of functionalized MWCNTs surface at 1000 and 10^6 nm magnification respectively. In Figure 1B, it can be seen that after functionalization process the surface of the MWCNTs became rougher compare to raw MWCNTs, the surface

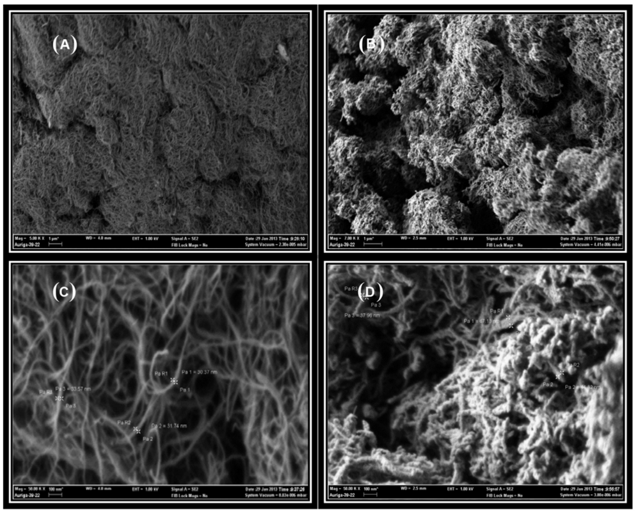

Figure 1: (**A, C**) FESEM images for raw CNTs, (**B, D**) functionalize CNTs.

roughness indicates the effect of attachment of functional group as a result of functionalization treatment. Figure 1D shows that the functionalized MWCNTs have shorter hollow fiber which caused by open ends resulted from functionalization process. These open ends provide more adsorption site for the adsorption process to take place.

The morphology of magnetic biochar resulted from FESEM analysis is showed in Figure 2A and 2B. It can be seen that the structure of the magnetic biochar has irregular porosity. This is resulted from the surface activation by N_2 gas which the diffusion of oxidant agent through carbonaceous matrix involves the removal of impurities and carbon consumption to create porosity. The removal of impurity which involves the removal of exterior surface of the particle at high burn-off has brought to opening and widening of the surface porosity, hence provide the magnetic biochar with large surface area and porous structure.

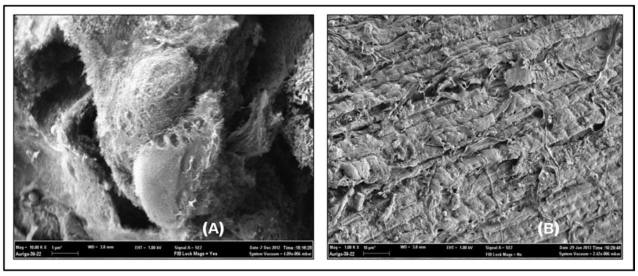

Figure 2: (**A**) and (**B**) FESEM images of Magnetic biochar.

Effect of pH on removal of phenol

Figure 3A and 3B for each experiment. It is clearly shown that for the predicted value is closed to the actual value, indicating that the models developed were successfully bridging all the predetermined physical factors with the removal percentage. The quality of the model developed was evaluated based on the correlation value. The correlation coefficient R^2 of 1, 0.9999 and 0.9947 showed that the predicted and actual removal values are in a good agreement, the closer the R^2 value to unity the closer the predicted value to the actual value. It shows that the variation in removal percentage can be explained by independent variable; pH, adsorbent dosage, agitation speed and contact time.

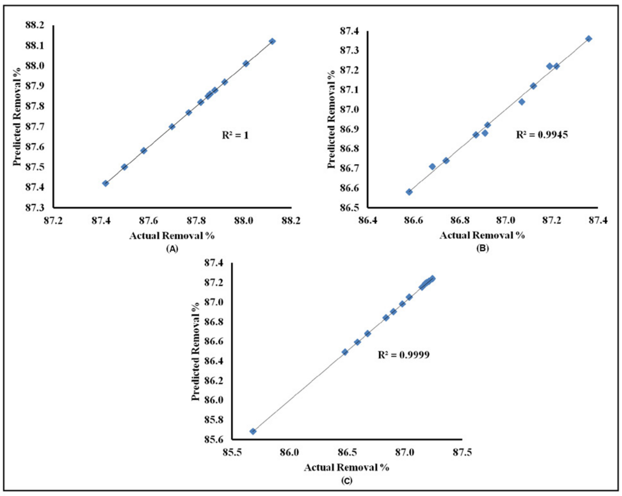

Figure 3: Predicted vs. actual values for each adsorbent (**A**) Functionalized MWCNTs (**B**) Raw-MWCNTs and (**C**) Magnetic biochar.

The effect and interaction of each variable; pH, adsorbent dosage, agitation speed and contact time to the removal percentage of each adsorbent are presented in 2D response surface and contour plot Figure 4(A-C).

From Figure 4(A-C) it can be seen that the surface plot the removal percentage of each adsorbent mainly is an interaction between pH and adsorbent dosage with the agitation speed and contact time. The optimum conditions are obtained at agitation speed of 200 rpm and the equilibrium time is reached by each adsorbent at 75 minutes. It can be seen from Figure 4A and 4B that at optimum condition of 200 rpm and 75 minutes. As the pH increased, the removal percentage decreased. While from Figure 4C it is showed that as the pH increased the removal percentage increased. The effect of pH in phenol removal for each adsorbent is due to the difference in the concentration of $[H^+]$ and $[OH^-]$ in the solution and the surface properties of the adsorbents. Functionalized MWCNTs and raw MWCNTs has active site with negative charged, the low or acidic solution environment can neutralize the negative particles, reduce the hindrance to diffusion of phenol ions and consequently increase the chance of their adsorption. High pH environment will lead to high concentration of $[OH^-]$, which increase the hindrance to the diffusion of phenol ions and thus reduce the chance of their adsorption [18, 23-26]. On the other hand, biochar which has positive active side will give a reverse effect to the low pH environment as high $[H^+]$ will be introduce and increase the hindrance to the diffusion of phenol ions and reduce the adsorption capacity. Increasing in adsorbent dosage will give an increasing of removal percentage as more active sites are provided for the adsorption to take places.

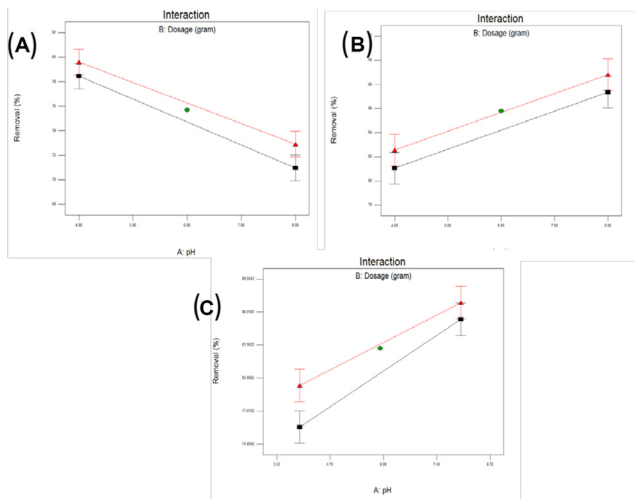

Figure 4: 2D surface plots of effects of physical condition on removal percentage (**A**) Functionalized MWCNTs (**B**) Raw MWCNTs and (**C**) Magnetic biochar.

Adsorption isotherm and kinetic study

Equilibrium studies on the adsorption process are important in order to provide information on the adsorbent capacity or amount required to remove a unit mass of pollutant [26-28]. An adsorption isotherm indicates the surface properties of an adsorbent or to adsorption capacity towards certain pollutant which usually express by certain constant depends on the model being used. The two most common models which have been widely used to describe or to develop the adsorption isotherm model in water and wastewater treatment are Langmuir and Freundlich isotherm models. Freundlich isotherm model is usually used for heterogeneous surface suggesting that the binding sites are not equivalent and or independent. Freundlich isotherm model is expressed as follows:

$$q_e = K_F C_e^{-} \qquad (6)$$

By taking logarithmic on the both side, the linear form of Freaundlich isotherm model is expressed as follows:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \qquad (7)$$

Where q_e is adsorption capacity (mg/g), C_o and C_e are initial and equilibrium concentration (mg/l) respectively. K_F and 1/n are Freundlich adsorption capacity and intensity of adsorption which can be determined from intercept and slope of linear data plot of log q_e versus log C_e.

Langmuir adsorption isotherm model usually indicates monolayer adsorption onto a surface with a finite number of identical sites at various conditions. It is expressed as follows:

$$\frac{c_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e \qquad (8)$$

Where q_e is adsorption capacity at equilibrium (mg/g), C_e is concentration at equilibrium (mg/l), q_m (mg/g) and K_L (mg/l)$^{-1}$ are Langmuir constant which can be determine from slope and intercept of linear plot of C_e/q_e versus C_e. The applicability of isotherm equations is compared by correlation coefficient, R^2 of linear data plot.

The results of adsorption equilibrium of each adsorbent at different pH are graphically presented in Figure 5(A-C).

From Figure 5 above, it can be seen that each adsorbent reaches the equilibrium in the first 2 hours of the contact time. There is not much significant difference until 5 hours of contact time even after 24h of contact time. Both Langmuir and Freundlich isotherm model are applied in this recent study and the resulted model are presented in Figure 6(A-C).

In Langmuir adsorption isotherm model, the value of K_L and q_m for each adsorbent is found from the slope and intercept of the linear plot for each adsorbent. The detail value of each constant for each adsorbent is presented in the following Table 1. It is observed that the adsorption isotherm fit Langmuir adsorption isotherm model very well. It can be proved from correlation index R^2 of 1 for each adsorbent. In Freundlich isotherm model, for each adsorbent shows that the adsorption model is also fitted the model very well. The correlation value R^2 for each adsorbent was obtained to be 0.9999, 0.9998, and 0.9998 for functionalized MWCNTs, raw MWCNTs and Magnetic biochar respectively. The Freundlich constant K_F and n were obtained from intercept and slope of linear plot of Freaundlich isotherm model.

The kinetic study of pseudo first and second order was also investigated in this recent study. The kinetic adsorption data was processed to understand the dynamics of the adsorption process in terms of the rate constant. Adsorption kinetic can be analyzed using several models. The pseudo first order and second order model are used in this study and the both model equation is shown respectively as follows:

$$\ln\left(q_e - q_t\right) = \ln q_e - K_1 t \qquad (9)$$

$$\frac{t}{\ } = \frac{1}{\ } - \frac{1}{\ } t$$

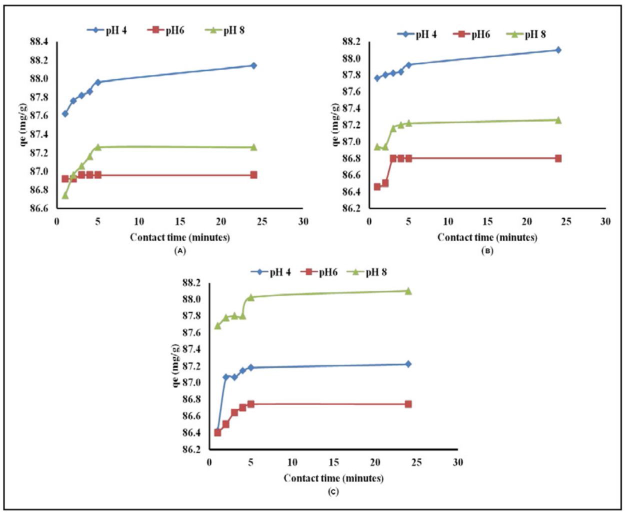

Figure 5: Adsorption capacity of each adsorbent at equilibrium contact time. (**A**) Functionalized MWCNTs (**B**) Raw MWCNTs and (**C**) Magnetic biochar.

(10)

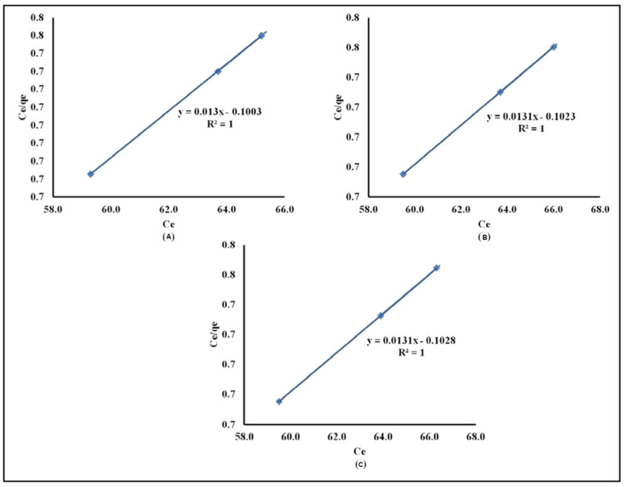

Figure 6: Langmuir Isotherm model for each adsorbent (**A**) Functionalized MWCNTs (**B**) Raw MWCNTs and (**C**) Magnetic biochar.

In these equations, k_1 is the rate constant of the pseudo-first-order adsorption (min^{-1}), k_2 ($gmol^{-1}$ min) is the rate constant of the pseudo second order adsorption, q_e and q_t are the amounts of phenol adsorbed on adsorbent (mol g^{-1}) at equilibrium and at time t, respectively. The plotting of log (q_e– q_t) versus time (t) for pseudo-first order kinetic model did not coverage well and not produced straight line at the studied pH condition. While in pseudo second order adsorption equation was applied by plotting (t/q_t) versus time (t), all of the data converged well into a straight line with a high correlation coefficient R^2.

Table 1: Langmuir and Freundlich isotherm parameter for phenol adsorption by functionalize, raw CNTs and Magnetic biochar.

Adsorbent	Langmuir Isotherm			Freundlich Isotherm		
	q_m (mg/g)	K_L (L/mg)	R^2_1	K_F (L/mg)	n	R^2_2
Functionalized CNTs	76.92	0.1296	1	8.99	7.0572	0.999
Raw MWCNTs	76.34	0.1281	1	9.03	6.9930	0.9998
Magnetic biochar	76.31	0.12754	1	9.01	6.9735	0.9998

Based on these results, it is clear that the equilibrium adsorption from pseudo-second order model is much closer to the experimental data as shown in Table 2. The value of the rate constant (k_2) and the amount of phenol adsorbed (q_e) of each adsorbent were obtained from the slope and intercept.

Table 2: Pseudo second order coefficient for each adsorbent.

Absorbent	q_e			k_2		
	pH 4	pH 6	pH 8	pH 4	pH 6	pH 8
Functionalized MWCNTs	87.72	88.2	87.72	3.25E-02	2.20E-01	2.06E-02
Raw MWCNTs	86.72	87.3	87.96	6.19E-02	6.08E-07	5.55E-07
Magnetic BioChar	85.72	85.1	86.72	8.058E-07	2.95E-02	3.02E-02

The value of k_2 and q_e are increased with decreasing of pH solution and the calculated q_e value shows a consistency with the experimental data which can be proofed by a correlation value R^2 approached unity. These results indicate that the adsorption of phenol from aqueous solution by each adsorbent obeys a pseudo-second order kinetic model.

Conclusion

Comparative study between three adsorbents; Functionalized MWCNTs, MB and RCNTs showed highly competitive adsorbents. The highest removal of phenol was obtained by the highest removal of 88% followed by 82.3% and 82.2% for magnetic biochar and raw CNTs respectively. Adsorption isotherm studies fit the Langmuir model better than the Freaundlich model and adsorption kinetic follows pseudo-second order. Meanwhile for Magnetic biochar, increasing in pH value will give an increasing in removal percentage. Increasing of adsorbent dosage will give an increasing in removal percentage. Magnetic biochar as a new developed low cost adsorbent can be considered as promising adsorbent in removing organic pollutant from aqueous solution. Functionalized MWCNTs showed an effective adsorbent and can be applied in for future work.

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