Comparative kinetic study of functionalized carbon nanotubes and magnetic biochar for removal of Cd^{2+} ions from wastewater

Manimaran Ruthiraan*, Nabisab Mujawar Mubarak**,***,†, Raj Kogiladas Thines*, Ezzat Chan Abdullah*, Jaya Narayan Sahu****, Natesan Subramanian Jayakumar***, and Poobalan Ganesan*****

*Malaysia - Japan International Institute of Technology (MJIIT), Universiti Teknologi Malaysia, Jalan Semarak, Kuala Lumpur-54100, Malaysia
**Department of Chemical and Petroleum Engineering, Faculty of Engineering, UCSI University, Kuala Lumpur-56000, Malaysia
***Department of Chemical Engineering, Faculty of Engineering, University of Malaya, Kuala Lumpur-50603, Malaysia
****Department of Petroleum and Chemical Engineering, Faculty of Engineering, Institut Teknologi Brunei, Tungku Gadong, P. O. Box 2909, Brunei Darussalam
*****Department of Mechanical Engineering, Faculty of Engineering, University of Malaya, Kuala Lumpur-50603, Malaysia
(*Received 10 June 2014 • accepted 1 September 2014*)

Abstract−We did a comparative study between functionalized multiwall carbon nanotube (FMWCNTs), and magnetic biochar was carried out to determine the most efficient adsorbent to be employed in the Cd^{2+} ion removal. We optimized parameters such as agitation speed, contact time, pH and adsorbent dosage using design expert vrsion 6.08. The statistical analysis reveals that optimized condition for highest removal of Cd^{2+} are at pH 5.0, with dosage 1.0 g, agitation speed and contact time of 100 rpm and 90 minutes, respectively. For the initial concentration of 10 mg/*l*, the removal efficiency of Cd^{2+} using FMWCNTs was 90% and and 82% of magnetic biochar. The maximum Cd^{2+} adsorption capacities of both FMWCNTs and magnetic biochar were calculated: 83.33 mg/g and 62.5 mg/g. The Langmuir and Freundlich constants for FMWCNTs were 0.056 L/mg and 13.613 L/mg, while 0.098 L/mg and 25.204 L/mg for magnetic biochar. The statistical analysis proved that FMWCNTs have better adsorption capacity compared to magnetic biochar and both models obeyed the pseudo-second-order.

Keywords: MWCNT, Cadmium, Heavy Metal, Adsorption, Functionalization, Magnetic Biochar

INTRODUCTION

The effort towards removal of heavy metal ions from water has been a challenging task since the excess amount of heavy metal ions in water causes risk to humans as well as affecting the ecosystem because this substance does not degrade biologically like other organic pollutants [1-5]. The presence of heavy metal ions in water, which indirectly trigger living organisms to consume beyond the threshold limit, leads to accumulation in organisms [6]. The intake of heavy metal in a small quantity for a longer period of time leads to health risk, such as shortage of red blood cells, chromosomal damage, and malfunction of the immune system, cancer, liver damage, urination problems and breathlessness problems [7-10]. Industries such paint industries, electronic industries, battery manufacturing and others are the main consumers of heavy metals [11]. Numerous methods have been employed in treating the industrial waste water: chemical precipitation, evaporation, ion exchange, electrolysis, reverse osmosis [12] and adsorption [13]. Among these, adsorption is widely used due to its high adsorption capability and cost efficiency [4,5,15]. Physical adsorption on carbon-based material such as activated carbon [6-8] allows researchers to further understand on adsorbent - adsorbate pair properties [16], but this material's low adsorption capacity limits its application [5] which seek the interest of researchers to invent more effective material from the carbon family.

Invention of carbon nanotubes (CNTs) [17-19] is one of the fascinating outcomes in the nanoscience research. In 1991 Ijima [20] invented these multilayer hollow tubes made of graphite crystals known as multi-walled carbon nanotubes (MWCNTs) [21] and followed by single-walled carbon nanotubes (SWCNTs). Further researches were carried out by researchers due to their promising properties with extraordinary surface morphology and good chemical [22-25] and mechanical stability [26-28]. Furthermore, the extraordinary characteristics and properties of these hollow graphenes attracts the interest of many to expand the application of CNTs such as for hydrogen storage [29], field emission [30], quantum nanowires [31], chemical sensors [32] and removal of heavy metals, organic compound and inorganic compounds from industrial waste [33]. We employed MWCNTs to adsorb heavy metal from aqueous solution because of the π-π electrostatic interaction and large surface area, which enhances the adsorption capability [13]. In this research study, Cadmium, Cd^{2+} was used to investigate the adsorption capacity by modifying the surface of MWCNTs, and comparative study

†To whom correspondence should be addressed.
E-mail: mubarak.yaseen@gmail.com,
mubarakmujawar@ucsiuniversity.edu.my

was conducted by using magnetic biochar produced from palm oil empty fruit bunch to determine the adsorption capacity both adsorbents. Magnetic biochar is a rich carbon material with high surface, high porosity and better adsorption capacity compared to activated carbon, and the addition of magnetic effect on this adsorbent will be an added advantage of the ease of removing this adsorbent from water. The magnetic biochar used in this research study was prepared from palm oil empty fruit bunch. Malaysia is a tropical country with highest palm oil producer in the world; the biomass produced upon extraction of palm oil can be converted into a useful carbon reached adsorbent besides using this biomass for burning, which will lead to the release of hazardous gasses to environment such as dioxins. Moreover, magnetic biochar is distinguished as a highly efficient and cost effective sorbent for different kinds of pollutant removal [34]. Removal of heavy metals such as Cd^{2+}, Cr^{6+}, and Zn^{2+} is being widely used in electronic industries, paint industries and metal industries leaving a heavy impact on every living being and affecting the entire ecosystem [35-38]. Cadmium in low concentrations causes a health risk, such as muscle pain, fever, headache and sweating. Continuous ingestion of Cd^{2+} leads to chronic diseases such as kidney damage, lung and prostate cancer and ends up being fatal.

The aim of this study was to do a statistical optimization and comparative study on the removal of Cd^{2+} from aquous solution using functionalized multiwall carbon nanotubes (FMWCNTs) and and magnetic biochar. The operating parameters, such as agitation time, dosage and pH, were considered to determine the effect of each parameter in removal of Cd^{2+} using FMWCNTs and magnetic biochar. Also, the thermodynamic parameter, equilibrium, kinetic and isotherm model equation for removal of Cd^{2+} were investigated to determine the optimum condition to obtain the maximum adsorption capacity of both sorbents used in this study.

MATERIAL AND METHOD

1. Raw Materials

MWCNTs involved in this project were synthesized via a method similar to that reported by Mubarak et al. [39]. There was 98% purity with an average diameter of 16 to 23 nanometers and 1.5 microns of average length. The details of fabrication of magnetic biochar from empty fruit bunch were presented in our previous work [40]. Analytical grade potassium permanganate ($KMnO_4$) and nitric acid (HNO_3) were purchased from Merck and used as received to modify the surface of MWCNTs.

2. Functionalization of MWCNTs

The surface modification of MWCNTs was carried out by immersing 9 g of MWCNTs into a flask contain containing 1 : 3 volume ratio of 0.4 M HNO_3 and $KMnO_4$ solution. The water bath sonicator (JAC-2010P) was used for MWCNTs functionalization process. The mixture was sonicated for 3 hours at 40 °C and the fuctionalized multi-walled carbon nanotubes (FMWCNTs) were filtered using a 0.45 mm polytetrafluoroethylene (PTFE) membrane filter. The FMWCNTs were neutralized, initiated by washing with 1.0 M NaOH to remove the residual acid, and repeated washing was carried out with distilled water until the pH reached 7.0. The residue was dried in a vacuum over for 48 hours at 80 °C and characterized by using thermogravimetric analysis (TGA), field emission scanning electron microscopy (FESEM) and Fourier transform infrared (FTIR).

3. Preparation of Magnetic Biochar

The dried empty fruit bunch was crushed and sieved to a particle size of less than 150 μm. Then it underwent an impregnation process for 4 h at room temperature with an impregnation ratio of 0.5-1.15; the crushed biomass was stored in desiccators upon drying at 100 °C. 20 g of the dried biomass was placed inside a quartz tube (35 mm OD, 38 mm ID and 500 mm length) to undergo a pyrolysis process in an HAMiab-C1500 Microwave Muffle System oven. After the reaction ended, the final weight was taken to determine the yield of the product and the magnetic biochar was washed using distilled water until the pH reach neutral.

4. Preparation of Stock Solution

Analytical grade Cd^{2+} standard solution was employed from Merck to prepare stock solutions containing 1,000 mg/L of Cd^{2+} and further diluted with distilled water to the desired concentrations. In this paper, the initial concentration of the solution contains Cd^{2+} ions was 10 mg/L.

5. Batch Adsorption

All batch adsorption experiments were carried out by using 150 ml glass bottle with the addition of 1.0 g of adsorbent in 100 ml of Cd^{2+} solution with initial concentration of 10 mg/L agitated at 50 °C by varying the parameter according to design obtained from the Design of Expert (DOE) as listed in Table 1. Water bath shaker was used for the batch adsorption to maintain the agitating temperature, and 0.4 M of NaOH solution was used to alter the pH of the solution as design using DOE. The adsorption capacity of both FMWCNTs and magnetic biochar was calculated by computing the difference between initial concentration and final concentration of Cd^{2+} ion in the solution and removal percentage was obtained. The adsorption capability of both FMWCNTs and magnetic biochar was computed using equations below:

$$q_t = (C_0 - C_t) \times \frac{V}{m} \quad (1)$$

$$q_e = (C_0 - C_e) \times \frac{V}{m} \quad (2)$$

where q_t and q_e represent the amount of Cd^{2+} adsorbed by both FMWCNTs and magnetic biochar at time t and at equilibrium, respectively (mg/g), C_0 is the initial concentration of the adsorbate (mg/L), C_t is the final concentration of adsorbate after a certain time, t interval, C_e is the equilibrium concentration of Cd^{2+} (mg/L),

Table 1. Optimizing conditions for batch adsorption

No	Parameters	Variations
1	Cd^{2+} stock solution	10.0 mg/L
2	Adsorbent dosage (g) (Functionalized MWCNTs and magnetic biochar)	1.0
3	pH	5.0, 7.0, 9.0
4	Agitation speed (rpm)	30, 60, 90
5	Agitation time (min)	60, 80, 100

V is the initial solution volume (L) and m is the dosage of adsorbent (g).

6. Kinetic Study

Kinetic study was conducted for both FMWCNTs and magnetic biochar by determining the optimizing conditions through batch adsorption experiments. The pH of the solution was varied and the initial concentration of the adsorbate and other parameter was kept constant. The experiment was carried out by collecting Cd^{2+} ion solution every 20 minutes for the first 5 h and the agitation was continued for 24 h before the final concentration was calculated. Atomic adsorption spectrometer was used to measure the concentration of the Cd^{2+} ions solution and the optimum adsorption time was determined.

7. Adsorption Isotherm

The adsorption isotherm study was carried out by varying the initial concentration of the Cd^{2+} ion solution from the range of 10 mg/L-50 mg/L and other parameters were kept constant. The batch adsorption method was used by agitating the solution contains FMWCNTs and magnetic biochar, respectively, for 2 h, and the final concentration was measured with an atomic absorption spectrometer. The isotherm medal of this research was examined using both Langmuir (3) and Freundlich (4) equations as follows:

$$q=\frac{abC_e}{1+bC_e} \tag{3}$$

$$q=K_fC_e^n \tag{4}$$

where C_e is the equilibrium concentration of Cd^{2+} (mg/L), a and b are Langmuir constants and K_f and n are Freundlich constants.

RESULTS AND DISCUSSION

1. Characterization of FMWCNTs and Magnetic Biochar

1-1. Characterization of FMWCNTs

Fig. 1(a) and (b) exhibit the field emission scanning electron microscopy (FESEM) (Zeiss, Auriga) images of functionalized MWCNTs at two different magnification scales (1 μm and 100 nm).

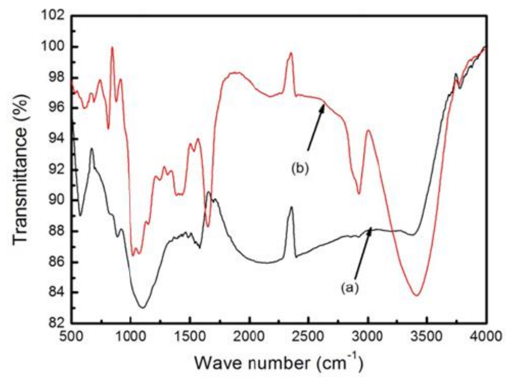

Fig. 2. FTIR spectra (a) raw MWCNTs, (b) functionalized CNTs.

The rough surface formation on the FMWCNTs demonstrates the presence of functional group onto the MWCNTs surface and shorter due to the agglomeration of CNTs upon 3 h of sonication process, which enhances the attachment of functional groups. The FESEM analysis on raw MWCNTs [41,42] gives a smoother surface image compared to functionalized MWCNTs, because no surface modification was done on the surface of raw MWCNTs. In addition, functionalization process will form an open end on CNTs, which allows the functional groups such carbonyl, hydroxyl and carboxylic to bind to the surface of CNTs.

1-2. FTIR Analysis of CNTs

Further analysis of the formation of functional group was done by employing Fourier transform infrared spectroscopy (Bruker, IFS66v/S) which indicated the presence of a functional group acting as an active center for metal caption on MWCNTs upon functionalization process. Fig. 2(a) indicates the surface analysis of raw MWCNTs and (b) shows the analysis outcome of FMWCNTs. The peak exhibits the presence of functional groups [8,9] containing oxygen atoms providing a huge chemical sorption site to enhance the adsorp-

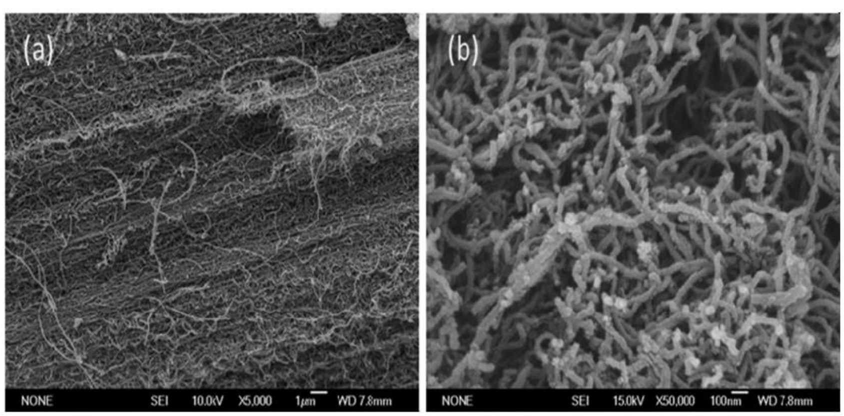

Fig. 1. (a) And (b) FESEM images of FMWCNTs.

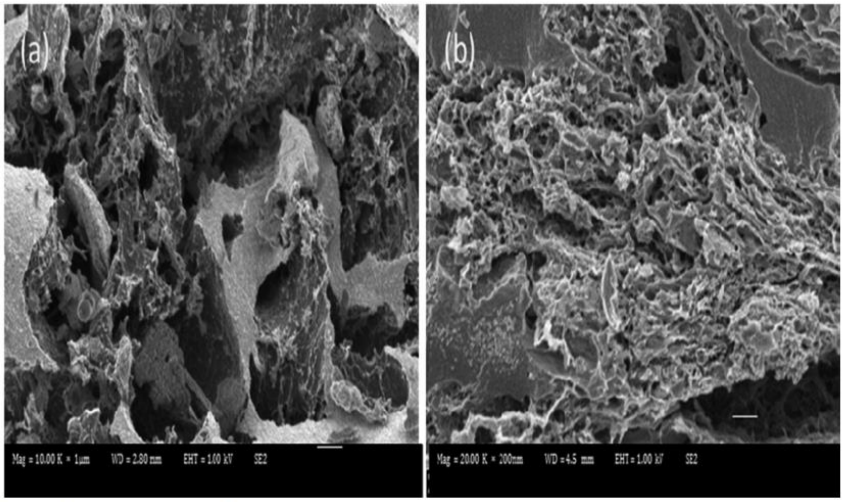

Fig. 3. (a) & (b) FESEM image of magnetic biochar.

tion capacity of the adsorbent [18]. The raw MWCNTs demonstrate an insignificant peak while the FMWCNTs exhibit a number of peaks to determine the type of functional group presence on the functionalized MWCNTs. The peak between 3,500 cm^{-1} and 3,000 cm^{-1} can be attributed to -OH stretch from carboxylic groups (-COOH and -COH), while the peak between 2,000 cm^{-1} and 1,000 cm^{-1} traits the presence of carbonyl, hydroxyl and carboxyl groups [43-48]. Based on the analysis above, it can be confirmed that the functionalization of the FMWCNTs is successful.

1-3. Characterization of Magnetic Biochar

Fig. 3(a) and (b) shows the FESEM (Brand: Zeiss; Model: Auriga) image of magnetic biochar used to observe the surface morphology at different magnification scales (1 µm and 200 µm). Upon undergoing pyrolysis by passing through microwave rays, pores of different size and shape were developed to enhance the adsorption capacity of heavy metal ions. During chemical oxidizing process, N_2 will be passing through on the biochar trigger the diffusion of oxidizing agents to create porosity on the biochar surface as well as to remove impurities on the surface of adsorbent. The effectiveness of N_2 has been clearly seen in this research where the micropores are widely opened and with a shift to meso- and macro-pores while the exterior of the particles are significant at high burn-offs. This shows that N_2 was effective in creating well-developed pores on the surfaces of the precursor, hence leading to magnetic biochar with an excellent surface area and porous structure which portrays

Table 2. Physical properties of FMWCNTs and magnetic biochar

Properties	FMWCNTs	Magnetic biochar
BET surface area (m^2/g)	206.45	890
Pore volume (Cm^3/g)	0.49	0.68
Pore diameter (Å)	96.27	22.81

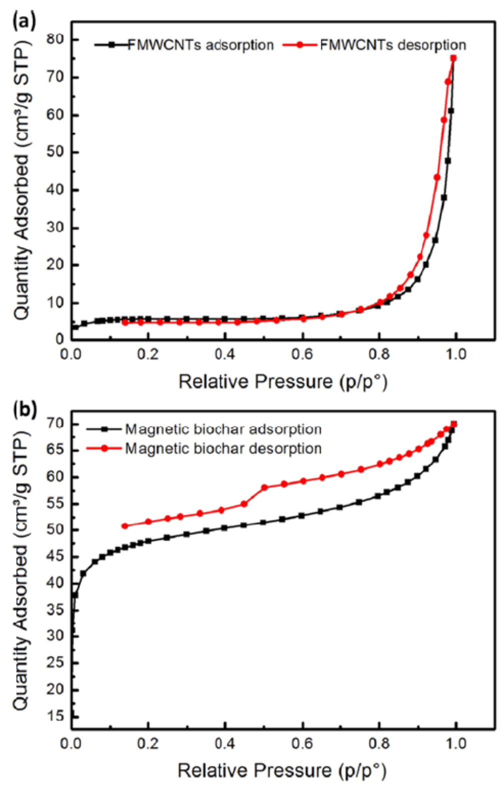

Fig. 4. Nitrogen adsorption isotherm of (a) FMWCTs, (b) magnetic biochar.

Table 3. ANOVA for the removal of Cd^{2+} using functionized CNTs

Source	Sum of squares	DF	Mean square	F value	Prob>F	Status
Model	687.75	6	114.63	36.68	0.0268	Significant
A	105.13	1	105.13	33.64	0.0285	
B	561.13	1	561.13	179.56	0.0055	
C	6.13	1	6.13	1.96	0.2965	
AB	15.13	1	15.13	4.84	0.1588	
AC	0.13	1	0.13	0.040	0.8600	
BC	0.13	1	0.13	0.040	0.8600	
Curvature	25.43	1	25.43	31.45	0.006	Significant
Residual	6.25	2	3.13			
Cor total	694.00	8				

Table 4. ANOVA for the removal of Cd^{2+} using magnetic biochar

Source	Sum of squares	DF	Mean square	F value	Prob>F	Status
Model	3820.00	6	699.92	19.98	0.0484	Significant
A	840.50	1	968.00	27.64	0.0343	
B	2964.50	1	3200.00	91.36	0.0108	
C	2.00	1	2.00	0.057	0.8334	
AB	8.00	1	24.50	0.7	0.4910	
AC	4.50	1	4.50	0.13	0.7543	
BC	0.50	1	0.05	0.014	0.9158	
Curvature	4.67	1	4.67	38.41	0.002	Significant
Residual	58.89	2	35.03			
Cor total	3878.89	8				

as a promising adsorbent in removal of heavy metal ions. The physical properties such as BET surface area, average pore diameter and pore volume of FMWCNTs and magnetic biochar were analysis and the obtained values were summarized in Table 2. The N_2 adsorption isotherm of the FMWCNTs and magnetic biochar was prepared under the optimum as shown in Fig. 4. Accordingly to the International Union of Pure and Applied Chemistry (IUPAC) classification, all isotherms exhibit type I behavior,with a sharp "knee" form at a low relative pressure that tends to turn into an increase linear at higher relative pressures, indicating microporous magnetic biochar. The N_2 adsorption using a FMWCNTs is much higher than compared to magnetic biochar. This can be explained by an increase in the relative pressure of N_2 molecules that are placed in wide pores, resulting in higher adsorption, and indicating the existence of greater amounts of wide micropores and mesopores. The greater amount of N_2 adsorption at low relative pressure ($P/P_0<$ 0.1) indicates the creation of large amount of new micropores. The development of larger micropores and the formation of mesopores is the cause of the increase in N_2 uptake at higher relative pressure. However, for higher relative pressures ($P/P_0>0.2$), the nitrogen adsorption increased gradually, indicating a higher volume of wide micropores and the presence of small mesopores.

2. Statistical Analysis of Adsorption of Cd^{2+} onto FMWCNTs and Magnetic Biochar

The Design Expert software version 8.0 was used to determine the optimizing conditions to conduct batch adsorption experiments for both types of adsorbents. The parameters such as agitation speed, agitation time and pH were optimized, and the best combination was obtained to analyze the heavy metal adsorption capacity using different types of adsorbents. The analysis of variance (ANOVA) and DOE technics were used to identify the optimizing condition.

The analyzed data for both adsorbents obtained in ANOVA are tabulated in Tables 3 and 4. The Fisher F-test value and lower probability (p value) are important details for analyzing the model and determining the best adsorbent with best optimizing conditions for both functionalized MWCNTs and magnetic biochar to identify the best adsorbent for heavy metal removal in aqueous solution. The Fisher F-test values signify the comparison of both sum of square values and mean square values of the residual of a regression model aid to resolve the effectiveness of the model as the value of fisher F-test value increases, the efficiency of model increase. Based on the data, the MWCNTs with 1 : 3 functionalized ratio have the highest Fisher F-test value of 36.68 compared to magnetic biochar with the value of 19.98, and both adsorbents have significant model with the lower probability value (p value) of 0.500 and below, the correlation coefficient (R^2) value and adjusted correlation (Adj R^2) were obtained above 0.95, which are significant values for an effective model. The experimental R^2 values and the predicted R^2 values are very close to each other. The heavy metal removal percentage was calculated by using the developed model equation for both FMWCNTs (5) and magnetic biochar are as below.

Removal percentage of Cd^{2+}:

$$75.33-3.62A+8.38B+0.87C-1.38AB+0.13AC+0.12BC \quad (5)$$

Removal percentage of Cd^{2+}:

$$49.11 - 10.25A + 19.25B + 0.50C - 1.0AB - 0.75AC - 0.25BC \quad (6)$$

The model equations for both adsorbents were developed using coded factorials where A represents pH of the metal solution, B is for agitation time and the C code refers to the agitation speed, while the one factor coefficient refers to a particular factor's effect on the model, and the interaction of two factor coefficient is represented by multiplying the coefficient factors. The positive sign and negative signs in the equation represent synergistic effect and antagonistic effect, respectively.

Three-dimensional diagrams were plotted to observe the relationship between optimizing conditions and the Cd^{2+} heavy metal ions removal percentage. The correlation between agitation time and pH in the removal of Cd^{2+} heavy metal ions shown in Fig. 5(a) and 6(a) indicates that lower pH value at acidic state and longer agitation time present higher removal percentage obtained for both FMWCNTs and magnetic biochar. Also, the higher agitation speed with lower pH at acidic state denotes higher removal percentage compared with pH at alkaline state for both types of adsorbents as shown in Figs. 5(b) and 6 (b). The last analysis was made by comparing the effectiveness of agitation speed and the contact time as shown in Figs. 5(c) and 6 (c). Based on these figures, as the agitation speed and the contact time increase, the removal percentage gives better value for FMWCNTs as well as for magnetic biochar. Thus, analysis clearly showed that at low speed, the adsorption capacity was reduced due to low dispersion of MWCNTs particles.

From the correlation of three parameters used for both adsorbents, the optimum agitation time for the batch adsorption is 90 min and the highest removal percentage recorded for both FMWCNTs and magnetic biochar is 88.71% and 79.61%, respectively. Furthermore, the pH of the solution in acidic condition has the better adsorption capacity compared to in alkaline condition. At a pH of 5.0, the removal percentage reached a maximum of 79.71% for FMWCNTs and 60.61% for magnetic biochar. For the third optimizing condition, the agitation speed was examined and the results indicate that, at speed of 100 rpm, the highest removal percentage was obtained for both FMWCNTs and magnetic biochar of 84.71% and 68.11% respectively. Moreover, based on the result analyzed, the lower agitation speed with longer contact time gives higher Cd^{2+} ions removal percentage, which can be seen in Figs. 5(c) and 6(c) because longer contact time allows the heavy metal ions to disperse and being adsorbed on the surface of the adsorbents through ionic bonding with the functional groups. The maximum adsorption capacity of Cd^{2+} heavy metal ions was higher on FMWCNTs compared to magnetic biochar at various optimizing conditions, and the use of surface chemistry study can be evident in this research work. The physical characteristics, such as specific surface area, average pore diameter and pore volume, of the adsorbents does not fully contribute to attain the maximum adsorption capacity; perhaps the acidity condition of the solution plays a vital role to attain higher Cd^{2+} heavy metal ions removal percentage. This can be clearly

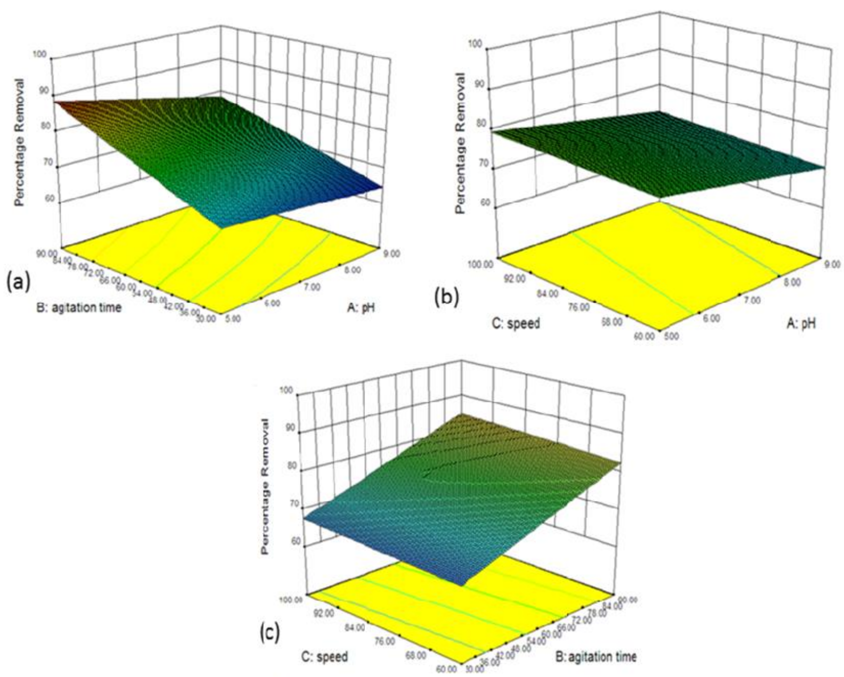

Fig. 5. A 3D interaction plot of the removal of Cd^{2+} using FMWCNT, (a) interaction of FMWCNT agitation time and pH, (b) interaction of agitation speed and pH and (c) interaction of agitation speed and agitation time.

Link to Full-Text Articles:

http://link.springer.com/article/10.1007/s11814-014-0260-7