

ABSTRACT

This study reports the preparation of nano-adsorbent from Multi-Walled Carbon nanotubes (MWCNTs) for the removal of Fe (II) and Cu (II) ions from pharmaceutical wastewater. Fe-Ni/Kaolin catalyst was prepared by wet impregnation method. The carbon nanotubes (CNTs) was synthesized in horizontal chemical vapour deposition (CVD) reactor using acetylene at 200 mL/min and nitrogen at 100 mL/min. The CVD reactor was operated at a temperature of 750 °C for a period of 45 minutes. After which the as-synthesized CNTs was purified with 100 mL of 30 % HNO₃ acid to give purified CNTs (P-CNTs) and functionalized with 100 mL of 20 % poly ethylene glycol (PEG) to give functionalized CNTs (F-CNTs). The catalyst and CNTs synthesized were characterized to determine its properties to determine its surface area, morphology/elemental composition and the internal morphology via Brunner Emmett Teller (BET), Scanning Electron Microscopy/ Energy Dispersion Spectroscopy (SEM/EDS) and High Resolution Transmission Electron Microscope (HRTEM) respectively. The SEM depicts the formation of long-continuous strand of CNTs formation while the HRTEM shows the hollow nature of the CNTs with multi-walls formation. The results obtained showed that F-CNTs produced has a larger surface area of 970.81 m²/g than P-CNTs. The P-CNTs and F-CNTs were then applied for the removal of Fe (II) and Cu (II) from pharmaceutical wastewater. The effect of contact time, dosage of CNTs, and temperature for P-CNTs and F-CNTs were investigated. The optimum conditions for the adsorption of Fe and Cu ions from pharmaceutical wastewater were 60 minutes, 0.4 g and 60 °C respectively with % removal of 74.37 for Fe and 79.65 for Cu ions. Freundlich models as well as pseudo-second order kinetic best fitted the adsorption of Fe and Cu from the pharmaceutical wastewater. The result revealed P-CNTs and F-CNTs were effective adsorbents for the removal of selected heavy metals from pharmaceutical wastewater.

Keywords: Multi-Walled Carbon nanotube, CCVD, Adsorption, Kinetics, Isotherm

1.0 INTRODUCTION

Water is known to be the most important part of lives and the basic component on earth and it is considered as the most significance resource for development. The consistent access towards pure and reasonably price water is the most reliable goal for civilization, but it remains as the greatest task for 21st century worldwide, (Alizae *et al.*, 2016). The pollution of water by noxious heavy metals is a universal challenge. Contemporary measures, for instance, purifying, metal plating, mining colors, cadmium-nickel-batteries, metal make and release fluid effluents comprising irregular dosage of overwhelming metal particles.

The interest in nanotechnology as a mitigation tool of environmental problems, specifically the nanofiltration, is noticeable for the treatment of drinking water and wastewater (Ali *et al.*, 2014). Based on modern technology, current research focuses objectively on nanoadsorbent, nanoadsorbent base metal, zeolite, polymeric nanoadsorbent and nanoadsorbent mainly based on the Carbon nanotubes (CNTs) (Somborn-Schulz, 2015). Carbon nanostructures such as fullerenes, carbon nanotubes (1-D) and graphene sheets have been extensively studied due to their unique properties such as good electrical/thermal conductivity, excellent corrosion resistance, and enhanced chemical compatibility. Hence, they have found a wide range of applications which include adsorption, polymer composites, electrochemical energy storage and conversion, catalysis, filtration and biotechnology. Adsorption is of great relevance to wastewater treatment and is also very efficient. Of all the adsorbents known in use for adsorption, CNTs have so far, proven to be the widely researched material for adsorption purposes.

In this study, the sourced catalyst was employed for the synthesis of Carbon nanotubes in a CCVD reactor. The purification and functionalization of CNTs were carried out by acid treatment and polyethylene glycol (PEG) addition respectively. The efficiency of purified and functionalized CNTs for the removal of Fe and Cu ions from

pharmaceutical wastewater were investigated in a batch adsorption process. The adsorption isotherms and kinetic studies for the effective removal of Fe and Cu from pharmaceutical wastewater were also fitted. The feasibility of adsorption process was also studied via thermodynamic studies.

2.0 Details Experimental

2.1 Carbon nanotubes Synthesis

The synthesis of the multiwall CNTs was carried out by the decomposition of acetylene (carbon source) on the Ni bimetallic catalyst, with kaolin as support through the CCVD (catalytic chemical vapor deposition) method. The furnace was electronically controlled such that the heating rate, reaction temperature and gas flow rate were accurately maintained. 1.0 g of the bimetallic catalyst was measured and loaded into a quartz boat (120mm*15mm) at room temperature. The tubular quartz containing the catalyst was placed at the center of the furnace where maximum yield occurred. The CCVD machine was then switched on and heated at 10 °C/min while nitrogen gas (carrier gas) was allowed to flow at 20 mL/min after which acetylene gas was introduced at 200 mL/min when furnace has reached reaction temperature of 750 °C. The reaction time was 45 min after which the precursor is stopped and the flowrate of the nitrogen gas was adjusted to as 100 ml/min. The obtained carbon deposit was removed immediately the reactor got cooled. Using chemical oxidation techniques, the carbonaceous as well as the metallic impurities were removed using aqueous HNO₃.

2.2 Functionalization of carbon nanotubes

Functionalization was carried out to prevent nanotube aggregation which can improve interaction between CNTs and solvent matrix. Functional groups are introduced on the CNTs surface, which makes it more dispersed than the impurities such as metal particles. The dried purified CNTs were functionalized with Polyethylene Glycol (PEG) and Dimethyl Formaldehyde (DMF). Every five (5g) of oxidized CNTs was mixed with 100ml of 20 % PEG solution and 100ml of 10 % DMF. The solvent mixture was stirred for 18 hours at 25 °C and then centrifuged at 3000 rpm for 10 minutes. After centrifugation, the black solid obtained was washed with distilled water until the wash water was clear. The remaining black solid was retained after drying in vacuum oven at 120 °C for 12 hours.

2.3 Wastewater Collection

The wastewater used for the adsorption studies was collected follow the immediate discharges from the pharmaceutical company in Ilorin, Kwara State, Nigeria. The collected sample was corked and kept in a fridge for further analysis.

2.4 Adsorption Studies

The effects of contact time, adsorbent dosage and temperature on the percentage removal of Fe and Cu ions were investigated in a batch adsorption process. The concentrations of both ions were determined using AAS technique. The kinetics, isotherm and the thermodynamic of the adsorption process were then studied.

3.0 Result and discussion

The scanning electron micrograph of the produced carbon nanotubes for both the as-synthesized and purified MWCNTs are depicted in Figure 1(a-b).

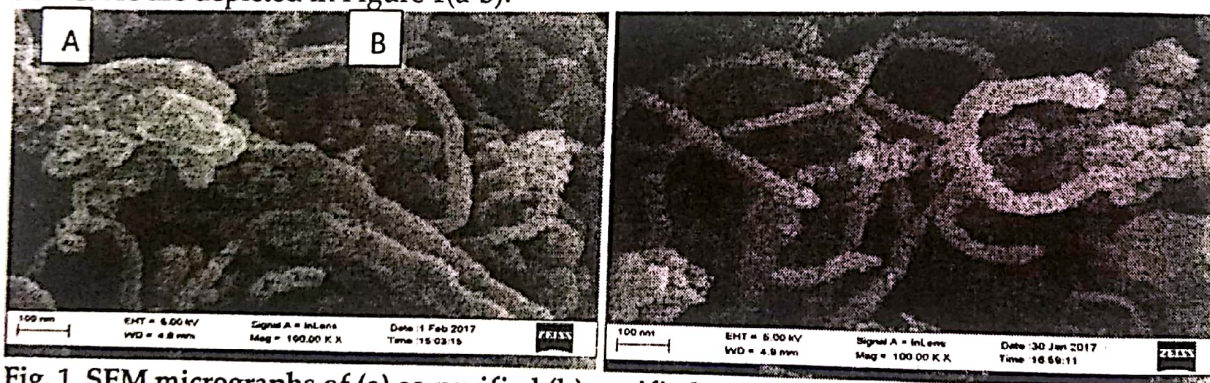


Fig. 1. SEM micrographs of (a) as-purified (b) purified CNTs.

From Fig 1 (b), the purified CNTs are well arranged and not entangled as compared to as-synthesis CNTs, Fig 1a. This is in line with Abdulkareem *et al.* (2016). There are presence of long strand tubes of carbon in both cases although that of as-synthesized carbon nanotubes is compacted (Fig.1a).

The internal morphological make-up of the as-synthesized and purified CNTs were determined via TEM technique and the result is shown in Fig. 2 (a-b).



Fig. 2. TEM micrographs of (a) as-synthesized (b) purified CNTs. The presence of concentric walls were observed in the tubes walls of the as-synthesized carbon nanotubes as indicated with a red mark on Fig. 1a. This indicates that the produced carbon nanotube is multi-walled carbon nanotubes with about 18.02 nm tube diameter. The elemental composition of the purified CNTs and the functionalized CNTs were determined and the results are as depicted in Fig. 3 (a-b). The EDS spectrum revealed that the purified CNT was composed basically of carbon. The elemental analysis revealed that the CNTs are relatively pure containing about 80.92% carbon and low amount of other impurities like Si (2.367%), K (0.07%), Fe (0.82%), Ni (0.76%) and Al (1.91%). Low amounts of Fe and Ni shows that the CNT walls are almost free from the catalyst and the support. (the Fe and the Ni present in the CNTs are direct indication of the nature of the catalyst used during the CNTs synthesis).

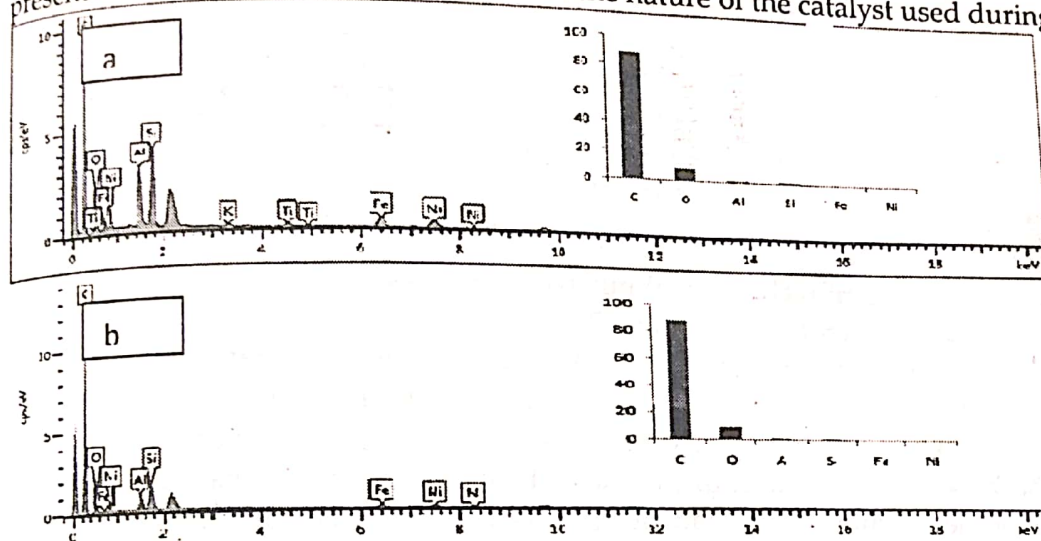


Fig. 3. EDS Spectral of (a) purified and (b) functionalized CNTs. After functionalization; Fig. 3b, the elemental composition of carbon present increased to 88.56%. All other constituents were significantly reduced due to the treatment with PEG.

3.1 Adsorption Results

The effect of varying contact time was investigated between 10 to 120 min for the adsorption of Fe and Cu. The effects of contact time on the percentage adsorption of Fe and Cu are depicted in Fig. 4 (a-b).

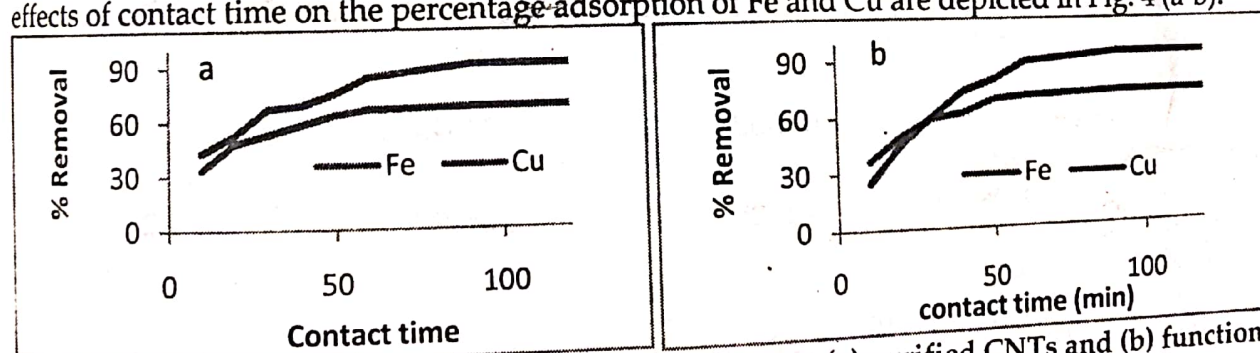


Fig. 4. Effect contact time on the Fe and Cu removal using (a) purified CNTs and (b) functionalized CNTs. The effect of contact time on the removal of Fe and Cu for purified CNT and the functionalized CNT are shown in Figure 4 (a-b). For purified CNT adsorbent, as the contact time is increased, the amount of Fe and Cu adsorbed from wastewater is increased from the various percentage removals of both Fe and Cu. This correlates with the report of Mishra et al, (2016). The higher adsorption rate is a function of concentration gradient between the liquid layer of the adsorbate and the surrounding active sites of adsorbents available for adsorption of metal ions. The effect of adsorbent dosage on the percentage removal was investigated and the result is shown in Figure 5.

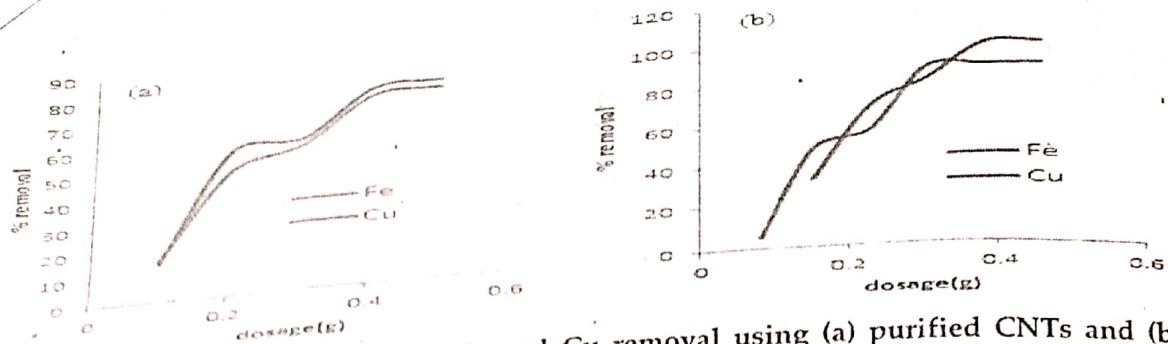


Fig. 5. Effect adsorbent dosage on the Fe and Cu removal using (a) purified CNTs and (b) functionalized CNTs.

From Figure 5 (a-b), there is increase in adsorption capacity of the adsorbents, as more adsorbent provides wider surface area of active sites for adsorption to take place. The cessation in the percentage removal of metals beyond equilibrium is associated with the overlapping of sorption sites due to excess of adsorbent particles (Mishra et al, 2016). It implies that till a certain range of initial metal concentrations, the metal removal is associated with the soil sorption capacity. This is in correlation with the report of (Qiang et al, 2017). The effect of temperature on the percentage removal of Fe and Cu is depicted in Figure 6.

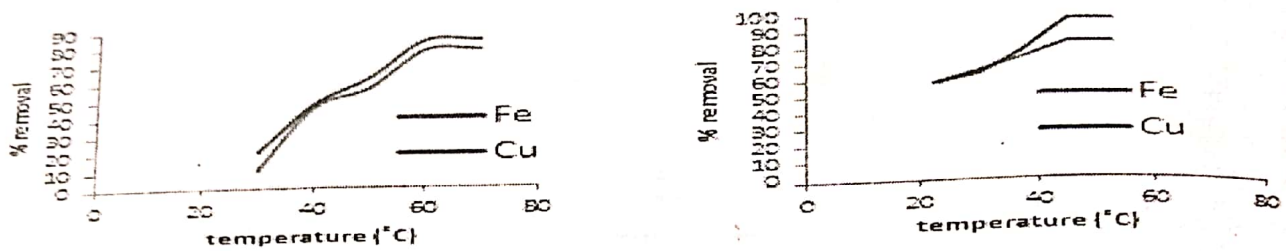


Fig. 6. Effect of temperature on the Fe and Cu removal using (a) purified CNTs and (b) functionalized CNTs.

From Fig 6, it was observed that increase in temperature from 30°C to 70°C resulted in an increase in the percentage removal of both Fe and Cu from the pharmaceutical wastewater, that is, temperature varies directly with % removal of the metals. However, 60°C is the optimum temperature because the most % removal of 74.37 for Fe and 79.65 for Cu are achieved at this temperature. First, increasing the temperature increases the rate of diffusion of the metal ions from the bulk of the solution to the bulk of the adsorbent. Second, the increase of temperature increases the ionization of the function groups (adsorption active sites) which increases their activity towards the adsorption of from the solution (Badawi et al, 2017).

3.2 Adsorption isotherm

Table1: Isotherm parameters for adsorption of heavy metals onto P-CNTs and F-CNTs

Isotherm	P-CNTs		F-CNTs	
	Fe	Cu	Fe	Cu
Langmuir				
$K_L(\text{min}^{-1})$	0.040906	0.80625	0.37043	0.8591
$Q_m(\text{mg/g})$	66.67	1.1325	5.05817	7.2294
R^2	0.730	0.828	0.902	0.5635

The R^2 values of Langmuir isotherms are gotten to be 0.730 and 0.828 for Fe and Cu purified CNTs, and 0.902 and 0.5635 for Fe and Cu functionalized CNT. These values are lower than 0.999 as given in literatures to test the best fit of the isotherm parameter. As such Langmuir is not a best fit for isothermal adsorption. Table 2 depicts the isotherm parameters for the adsorption of Fe and Cu onto P-CNTs and F-CNTs.

Table 2: Isotherm parameters for the adsorption of Fe and Cu onto P-CNTs and F-CNTs.

Isotherm	P-CNTs		F-CNTs	
	Fe	Cu	Fe	Cu
Freundlich				
$N(\text{min}^{-1})$	1.2750	0.6052	1.6405	2.8563
$K_2(\text{mg/g})$	2.7246	1.1612	0.0017	0.6205
R^2	0.8295	0.8615	0.9935	0.9167

Langmuir and Freundlich models were also studied for use in adsorption to determine which model has the best adsorption capacity. The correlation coefficients were calculated by fitting the experimental equilibrium data for the various metal ions system using both Langmuir and Freundlich isotherms, and are presented in Table 1 and Table 2 respectively. These results clearly show that the adsorption of Fe and Cu ions from purified CNTs fits well with the Freundlich model as seen from the high values of R^2 from Freundlich table compared to Langmuir which is much lower.

The other Freundlich constant, n , is a measure of the deviation of the adsorption from linearity. If the value of n is equal to unity, the adsorption is linear. If the value of n is below unity, it implies that the adsorption process is unfavourable, and if the value of n is above unity, adsorption is favorable. The n value of the Freundlich model is 1.275, 1.6405 and 2.8563 which are all in the range of 1 to 10. This is a criteria required for the Freundlich model to fit the adsorption process. The fact that the Freundlich model is a good fit to the experimental adsorption data suggests good and high physical adsorption.

3.3 Adsorption kinetics

Table 3: Table 4.6: Kinetic Parameters for adsorption of selected heavy metal ion on P-CNTs and F-CNTs.

Kinetic Parameters	P-CNTs		F-CNTs	
	Fe	Cu	Fe	Cu
Pseudo first order				
$K_1(\text{min}^{-1})$	0.0279	0.0149	0.0023	0.0111
$q_e(\text{mg/g})$	14.5814	0.1508	0.3399	0.2726
R^2	0.7885	0.2452	0.0029	0.3608
Pseudo second order				
K_2	0.0003	0.0037	0.0003	0.0112
$q_e(\text{mg/g})$	147.059	11.3766	3.9793	93.09
R^2	0.9316	0.9316	0.9536	0.9997

From the Table 3, it could be observed that the results obtained from the analysis did not fit the pseudo-first order rate law, because the coefficient correlation (R^2) values for all the parameters is lower than 0.999. In this pseudo-first order, the rate of adsorption was assumed to be proportional to the difference between the maximum adsorption capacity at equilibrium (q_e) and adsorption at any time (q_t) of the adsorption in a first order at the initial reaction stage.

When the results were subjected to the pseudo-second order rate kinetics it was observed that the correlation coefficient value (R^2) for most of the parameters studied was higher than 0.9, this is an indication that the treatment fit the pseudo-second order rate kinetics. This suggest that the adsorption system is not a first order reaction and that the pseudo-second order model, is based on the assumption that the rate limiting step may be chemical adsorption or chemisorptions involving covalence forces through the sharing of electrons between the CNT adsorbent and the adsorbate.

3.4 Thermodynamics studies

The thermodynamic parameters of the adsorption of Fe and Cu were also investigated and the result is shown in Table 4.

Table 4: Thermodynamic Parameters of heavy metals adsorption on P-CNTs and F-CNTs

Adsorbate	Temp (K)	ΔH (kJmol ⁻¹)	ΔS (J/mol.k)	ΔG (kJmol ⁻¹)	Adsorbents
Fe	303	27.40	109.91	-5.9059	P-CNTs
	313			-7.0050	
	323			-8.1042	
	333			-9.2033	
	343			-10.302	
Cu	303	23.88	82.40	-0.9921	P-CNTs
	313			-1.8161	
	323			-2.6401	
	333			-3.4641	
	343			-4.2882	
Fe	303	37.03	143.09	-6.3264	F-CNTs
	313			-7.7573	
	323			-9.1882	
	333			-10.619	
	343			-12.050	
Cu	303	80.95	269.71	-0.7736	F-CNTs
	313			-3.4700	
	323			-6.1675	
	333			-8.865	
	343			-11.562	

From Table 4, the values of ΔG are all negative. This implies that the adsorption process occurred spontaneously. The values of ΔH , however, were positive. This signifies that the sorption process was endothermic in nature which means that heat was absorbed into the system during adsorption. There is also an increase in the degree of disorderliness of the system as observed from the positive values of ΔS .

4.0 Conclusion

The adsorption capacity of purified and functionalized CNTs for the removal of Fe and Cu from pharmaceutical wastewater was investigated in this study. The synthesized CNTs obtained were purified by acid treatment and functionalized with PEG. TEM revealed the crystalline nature of F-CNTs was more thermally stable than P-CNTs. BET results revealed that F-CNTs had an improved surface area of 970.81 m²/g than P-CNTs. The CNTs adsorbents were employed in the adsorption of selected heavy metals and other contaminants from pharmaceutical wastewater. Optimum adsorption was obtained at adsorbent dose of 0.4 g, 60 °C and equilibrium time for adsorption was achieved within 60 min of contact time. The increase in surface area of the nanoadsorbent contributed to its effectiveness in adsorption process. The kinetic data of Fe and Cu removal were fitted to the pseudo-second order kinetics and Freundlich model described the adsorption isotherm. The thermodynamics studies revealed that ΔG was negative which implies spontaneity of adsorption process. The results of this study also showed that the values of ΔS were positive which implies an increase in the disorderliness of the system. Finally, a decrease in physicochemical properties of pharmaceutical wastewater was observed due to effectiveness of nanoadsorbents.

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