

## Adsorption studies on the treatment of battery wastewater by purified carbon nanotubes (P-CNTs) and polyethylene glycol carbon nanotubes (PEG-CNTs)

W. Abidemi Hamzat, A. Saka Abdulkareem, M. Temitope Bankole, J. Oladejo Tijani, A. Sanni Kovo & O. Kamaldeen Abubakre

To cite this article: W. Abidemi Hamzat, A. Saka Abdulkareem, M. Temitope Bankole, J. Oladejo Tijani, A. Sanni Kovo & O. Kamaldeen Abubakre (2019): Adsorption studies on the treatment of battery wastewater by purified carbon nanotubes (P-CNTs) and polyethylene glycol carbon nanotubes (PEG-CNTs), Journal of Environmental Science and Health, Part A, DOI: [10.1080/10934529.2019.1596701](https://doi.org/10.1080/10934529.2019.1596701)

To link to this article: <https://doi.org/10.1080/10934529.2019.1596701>



Published online: 09 Apr 2019.



Submit your article to this journal [↗](#)



View Crossmark data [↗](#)



## Adsorption studies on the treatment of battery wastewater by purified carbon nanotubes (P-CNTs) and polyethylene glycol carbon nanotubes (PEG-CNTs)

W. Abidemi Hamzat<sup>a,b</sup>, A. Saka Abdulkareem<sup>a,b</sup>, M. Temitope Bankole<sup>a,c</sup>, J. Oladejo Tijani<sup>a,c</sup>, A. Sanni Kovo<sup>a,b</sup>, and O. Kamaldeen Abubakre<sup>a,d</sup>

<sup>a</sup>Nanotechnology Research Group, Centre for Genetic Engineering and Biotechnology (CGEB), Federal University of Technology, Minna, Niger State, Nigeria; <sup>b</sup>Department of Chemical Engineering, Federal University of Technology, Minna, Niger State, Nigeria; <sup>c</sup>Department of Chemistry, Federal University of Technology, Bosso, Minna, Niger State, Nigeria; <sup>d</sup>Department of Mechanical Engineering, Federal University of Technology, Minna, Niger State, Nigeria

### ABSTRACT

Fe–Ni/kaolin catalyst was used for the production of carbon nanotubes (CNTs) via catalytic chemical vapour deposition followed by acid purification treatment and functionalization with polyethylene glycol to give purified carbon nanotubes (P-CNTs) and polyethylene glycol carbon nanotubes (PEG-CNTs), respectively. The as-synthesized CNTs, P-CNTs and PEG-CNTs were characterized by high-resolution transmission electron microscopy (HRTEM), high-resolution scanning electron microscopy (HRSEM), Fourier transform infrared and Brunauer Emmett Teller (BET). The adsorption behaviour P-CNTs and PEG-CNTs to remove specifically Cr and Zn from battery wastewater were examined by the batch adsorption process as a function of different contact time, adsorbent dosage and temperature. The HRSEM/HRTEM/BET analysis confirmed that both nano-adsorbents were tube-like in nature, high porosity and crystalline, with PEG-CNTs possessing high surface area (970.81 m<sup>2</sup>/g) than P-CNTs (781.88 m<sup>2</sup>/g). The optimum contact time and adsorbent dosage to remove Cr and Zn by P-CNTs and PEG-CNTs were 90 and 50 min and 0.3 g, respectively. Under the applied conditions, PEG-CNTs exhibited high adsorption capacity than P-CNTs for the selected heavy metals. The adsorption equilibrium data were better fitted to the Freundlich model while the kinetic data conformed to the pseudo-second-order model. Thermodynamic studies demonstrated the feasibility and endothermic nature of the system. This study demonstrated that both nano-adsorbents purify battery wastewater and with better performance by PEG-CNTs.

### ARTICLE HISTORY

Received 25 August 2018  
Accepted 14 March 2019

### KEYWORDS

Carbon nanotubes;  
polyethylene glycol;  
functionalized carbon  
nanotubes; adsorption

## Introduction

The direct release of untreated industrial wastewater containing heavy metals is a trending source of environmental concern especially to human life and aquatic species due to perceive accumulative and persistence toxicity nature it possess.<sup>[1]</sup> Wastewater originating from a wide range of industries such as metallurgical, electroplating, petrochemical, metal processing, mining, tannery, battery industries contains one or more heavy metal ions such as lead, cadmium, chromium, nickel, arsenic amongst others.<sup>[2,3]</sup> The impact of these potentially toxic metals in the environment is increasing on daily basis due to increasing natural and anthropogenic activities such as flooding, population growth, industrial and technological expansion, energy utilization to mention but a few.<sup>[4,5]</sup> Exposure to heavy metals especially at concentrations well above the limits set by World Health Organization (WHO) and the Environmental protection agency (EPA) has been on the increase in the third-world countries, particularly those with limited water resources.<sup>[6]</sup> The adverse health effects associated with exposure to cadmium, mercury, lead, chromium, arsenic, iron, zinc have

been well established and documented in the literature.<sup>[3]</sup> Heavy metals are toxic, mobile, highly recalcitrant and non-biodegradable and often categorized as chemicals of emerging concern due to the damaging effect on the normal functions of various organs of living cells in the body.<sup>[7]</sup> Thus, remediation of wastewater containing heavy metals prior to discharge is of earnest and great importance.

Different treatment techniques used to remove heavy metals from wastewater include reduction and precipitation,<sup>[2]</sup> coagulation and flocculation, ion exchange,<sup>[8]</sup> membrane technologies,<sup>[9]</sup> electrolysis, ozonisations,<sup>[10]</sup> reverse osmosis, electrochemical separation<sup>[1]</sup> and electro coagulation<sup>[11]</sup> to mention but a few. Despite the satisfactory results obtained via these technologies, there exist some limitations such as large capital or operational costs of chemicals/reagents; generation of toxic sludge, and ineffectiveness removal of heavy metals in the range of 1–100 mg L<sup>-1</sup> from wastewater.<sup>[12]</sup> In view of these limitations, alternative and more effective and economical method are desired and adsorption technology has been identified as a panacea for the removal of heavy metal ions in the range of 1–100 mg

$L^{-1}$  from wastewater.<sup>[4]</sup> Adsorption technology is considered more advantageous compared to other techniques due to its simplicity, relative availability, low cost and effectiveness in the removal of potential toxic element from very dilute complex solutions containing diverse pollutants.<sup>[13]</sup> Other characteristics of adsorption process include: potential for regeneration of the adsorbents, high metal uptake and generation of less toxic sludge.

Several adsorbents have been employed for the sequestration of metal ions from aqueous solutions such as activated carbon,<sup>[12]</sup> alumina,<sup>[14]</sup> peat, modified chitosan,<sup>[11]</sup> sewage sludge ash, peanut hulls, activated carbon clothes,<sup>[15]</sup> sugar beet pulp, biomaterials,<sup>[16]</sup> kaolinite, olive stone,<sup>[17]</sup> alum sludge, bagasse, and resins.<sup>[6]</sup> However, these adsorbents exhibit low adsorption efficiency, weak diffusion limitation; absence of enough active surface sites; and generation of secondary wastes. Therefore, there is need to develop novel, advanced, classical and cost-effective adsorbent for cleaning of industrial wastewater. Multi-walled carbon nanotubes (MWCNTs) have been extensively employed as a novel adsorbent for the removal of various organic and inorganic pollutants wastewater due to its large specific surface area, high aspect ratio and above all exceptional hollow and layered structures.<sup>[4]</sup> Other properties of MWCNTs include high mechanical, thermal, electrical and optoelectronic properties which usually depend on atomic arrangement, the diameter and length of the tubes and morphology.<sup>[18,19]</sup> Despite MWCNTs exceptional properties, agglomeration of the carbonaceous material during and after the synthesis affects and limits its efficiency hence the need to modify the surface of raw CNTs and enhance its adsorption capacity and dispersion rate.<sup>[3]</sup> Chemical modification of MWCNTs by polymers is considered necessary to reduce the rate of agglomeration, increase surface functional groups and surface area of the material.<sup>[20]</sup> Functionalization of MWCNTs for heavy metals removal from wastewater have been independently reported by Mohammed and Robert<sup>[21]</sup> and Bankole et al.<sup>[2]</sup>

In this study, synthesis and characterization of MWCNTs via catalytic chemical vapour deposition (CCVD) followed by purification and functionalization with polyethylene glycol (PEG) were carried out. In addition, the efficiency of purified and PEG functionalized CNTs for adsorption of the chromium and zinc from industrial battery wastewater were investigated. The effects of contact time, dosage of the developed nano-adsorbents and temperature were studied to understand adsorption mechanism of heavy metals removal from battery wastewater by the prepared materials.

## Materials and methods

### Materials

The chemicals used in this study include: iron (II) trioxonitrate (V) nonahydrate, nickel (II) trioxonitrate (V) hexahydrate, dimethylformamide (DMF), PEG, hydrogen tetraoxosulphate (VI) acid and hydrogen trioxonitrate (V) acid. The chemicals were all supplied by Sigma Aldrich, while argon gas, acetylene gas and liquid nitrogen were

supplied by British Oxygen Company, Nigeria. All the chemical and gases were of analytical grade with percentage purity in the range 98–99.99% and used without further purification.

### Preparation of bimetallic catalyst

Fe–Ni/kaolin was prepared by a wet impregnation as described by Bankole et al.<sup>[2]</sup> About 5.05 g of Fe  $(NO_3)_3 \cdot 9H_2O$  and 3.64 g of Ni  $(NO_3)_2 \cdot 6H_2O$  were weighed separately and both dissolved in 50 mL of distilled water to form a mixture. Kaolin (8.0 g) was added into the mixture and stirred on a magnetic stirrer at 300 rpm for 30 min. The resulting slurry was oven dried at 120 °C for 8 h and thereafter cooled to room temperature. The oven dried sample was then pulverized and finally screened through a 150  $\mu m$  sieve and subsequently the final powder was calcined at 500 °C for 14 h.

### Synthesis of carbon nanotubes

Carbon nanotubes (CNTs) were produced by a CCVD method involving decomposition of carbon source (acetylene gas) in a tubular quartz reactor onto the Fe–Ni/kaolin catalyst. A known weight (1.0 g) of Fe–Ni/kaolin catalyst support was heated at 10 °C/min in a CCVD machine under the continuous flow of argon gas at 15 mL/min. As the temperature rose to 750 °C, the argon flow rate was re-adjusted to 100 mL/min and acetylene gas was flown in the reactor at the rate of 200 mL/min. The reaction was monitored for 45 min and thereafter acetylene gas was stopped and the furnace left to cool to room temperature. The ceramic boat containing the carbonaceous material was then removed and the quantity of as-synthesized CNTs was weighed. The percentage yield of CNTs produced was determined using the following equation:

$$\text{CNTs Yield (\%)} = \frac{W_{\text{Product}} - W_{\text{catalyst}}}{W_{\text{catalyst}}} \times 100\% \quad (1)$$

where  $W_{\text{product}}$  is the total mass of the catalyst and final carbon material produced while  $W_{\text{catalyst}}$  represents the initial mass of Fe–Ni/kaolin catalyst.

### Purification and functionalization of CNTs

Acid treatment method described by Wang et al.<sup>[22]</sup> was followed for the purification of the raw CNTs. About 300 mL of  $HNO_3$  and  $H_2SO_4$  mixture (v/v 1:3) was mixed with 5 g of the synthesized CNTs in an ultrasonic bath sonicated at 40 °C for 90 min. This was done to remove residual Fe, Ni, amorphous carbon and support material (kaolin) that remained in as-synthesized CNTs and also to introduce oxygen onto the surface of the CNTs. The CNTs was cooled to room temperature and continuously washed with distilled water and filtered until the pH of 7 was obtained. The wet purified CNTs (P-CNTs) were oven dried at 120 °C for 12 h. The dried P-CNTs were mixed and dispersed with 100 mL of 20% PEG solution and 100 mL of 10% DMF. The mixture

was stirred for 18 h at 25 °C, and then later centrifuged for 10 min. After centrifugation, the black solid residue was washed with distilled water until it reaches the pH of 7. The resultant black solid (polyethylene glycol functionalized carbon nanotubes (PEG-CNTs)) was oven dried at 120 °C for 12 h to get a resultant dried PEG-CNTs crystalline powder.

### Characterization of industrial battery wastewater

The industrial battery wastewater was collected from Fogo Battery (directly from point source) Ilorin, Kwara State, Nigeria. The physicochemical parameters of the wastewater were carried out and the inorganic constituents of the wastewater were determined using the American Public Health Association (APHA) method.<sup>[23]</sup> The pH of the wastewater was determined by pH metre. In the same vein, pH and electrical conductivity were estimated using a multi-parameter analyser C 3010 while dissolved oxygen (DO) metre was used to determine the level of DO. The following chemical parameters: chemical oxygen demand (COD), biochemical oxygen demand (BOD), total dissolved solid (TDS), alkalinity, the total amount of nitrate, nitrite, sulphate, phosphate, ammonium, chloride, cyanide and fluoride were determined by the standard method described by the APHA. All these analyses were performed at Regional Water Quality laboratory, Federal Ministry of Water Resources, Minna, Niger State. The heavy metal analysis was carried out using the Atomic Absorption Spectrophotometer (AAS PG 990 model).

### Batch adsorption experiment

The adsorption efficiencies of P-CNTs and PEG-CNTs for the removal of selected heavy metals (chromium and zinc) from battery wastewater were evaluated at different contact time, dosage of adsorbent and temperature via batch adsorption process. To investigate effect of contact time, 0.1 g of P-CNTs and PEG-CNTs were individually dispersed into 250 mL conical flask containing 50 mL of the battery wastewater. The mixture was corked and stirred on magnetic stirrer at 190 rpm under room temperature at sampling was done at predetermined time interval of 10, 20, 30, 50, 60, 90 and 120 min, respectively. The effect of adsorbent dosage was carried out by adding different amount of nano-adsorbents: 0.1, 0.2, 0.3, 0.4 and 0.5 g to 50 mL of battery wastewater in 250 mL conical flask. The mixture was shaken on a magnetic stirrer for 90 min under constant room temperature and stirring speed. The effects of temperature on the selected heavy metals were performed by adding 0.1 g each of P-CNTs and PEG-CNTs nano-adsorbent to 50 mL of battery wastewater in 250 mL conical flask. The temperature was varied from 303 to 343 K while the stirring speed and the volume of the adsorbate were kept constant. After equilibrium time of 90 min was reached, the sample solutions were filtered through a 0.45 µm membrane filter and the filtrate was analysed for the removal of selected heavy metals using the AAS PG 990 model.

### Data analysis

The amount of metal adsorbed<sup>[24]</sup> by each adsorbent was calculated by using the following equation:

$$Q = \frac{V(C_0 - C_e)}{W} \times 100 \quad (2)$$

where  $C_0$  is the initial concentration of the metal in the battery wastewater before adsorption in  $\text{mg L}^{-1}$ ,  $C_e$  is the concentration of metal ion in the filtrate after adsorption in  $\text{mg L}^{-1}$ ,  $W$  is the weight of the adsorbent (mg),  $V$  is the volume of adsorbate (L) and  $Q$  is the amount of metal ion adsorbed on purified and functionalized CNTs (mg/g) of each adsorbent.

The metal removal efficiency<sup>[25]</sup> ( $E$ ) is given by the following equation:

$$E = \frac{C_0 - C_e}{C_0} \times 100 \quad (3)$$

### Characterization of as-synthesized, purified and functionalized CNTs

As-synthesized, purified and PEG-functionalized MWCNTs were characterized for their surface area/pore volume, microstructures and morphology by the Brunauer Emmett Teller (BET), high-resolution transmission electron microscopy (HRTEM) and high-resolution scanning electron microscopy (HRSEM). While the elemental composition, particle size and functional groups were identified using electron dispersion X-ray spectroscopy (EDS), dynamic light scattering Zetasizer Nano-S series and Fourier transform infrared (FTIR) Perkin Elmer 100 Spectrum Two.

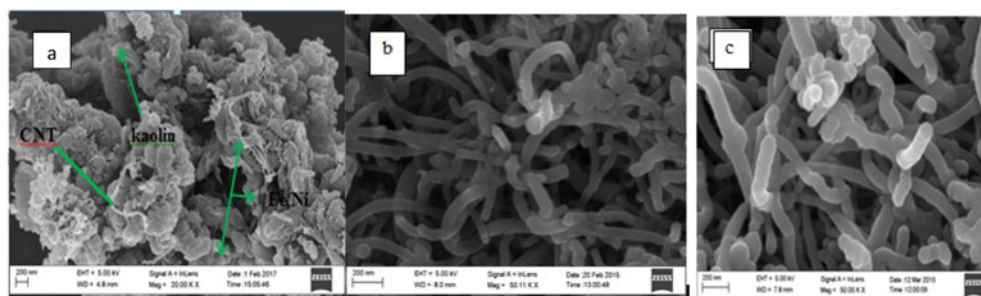
## Results and discussion

### Physicochemical properties of battery wastewater

The untreated and treated battery wastewater was characterized for their physicochemical properties and the result is presented in Table 1. As shown in Table 1, the pH of the wastewater was 1.2, which is highly acidic and on treatment with the nano-adsorbents, the pH increased significantly to 6.30 and 6.45 for P-CNTs and PEG-CNTs, respectively. This may be linked to electrostatic interaction between the heavy metal ions in the wastewater and the functional groups on the surface of the nano-adsorbents resulting to the formation of weak bases. According to WHO, the pH of wastewater should be in the range of 6.5–8.5 and pH of 7 for drinking water.<sup>[7,26]</sup> Hence, the pH of the treated wastewater will pose no threat to the aquatic organisms. The electrical conductivity of battery wastewater prior to treatment was high and above the acceptable limit due to high amount of chlorine (chloride ion)-related raw materials used during the electrochemical process of battery production.<sup>[27]</sup> The maximum discharge limit of conductivity in drinking water is 1000 µS/cm,<sup>[26,28]</sup> however that of the collected battery wastewater was 16,400 µS/cm which is extremely high. After treating with nano-adsorbents, the values of conductivity,

**Table 1.** Physicochemical characteristics of battery wastewater after the adsorption process with nano-adsorbents.

Parameter	Raw	Effect of temperature (°C)		Effect of dosage(g)		NESREA <sup>[26]</sup>	WHO <sup>[28]</sup>
		P-CNTs	PEG-CNTs	P-CNTs	PEG-CNTs		
pH	1.2	6.30	6.45	6.35	6.40	6.5–8.5	5.5–8.5
TDS (mg L <sup>-1</sup> )	10,986	267	230	254	211	–	600
Conductivity (µS/cm)	16,400	399	344	379	315	–	1,000
Dissolved oxygen (mg L <sup>-1</sup> )	3.11	5.12	5.55	5.75	5.85	4.0	5–6
Nitrate (mg L <sup>-1</sup> )	328	3.89	3.57	3.60	2.60	40	50
Ammonium (mg L <sup>-1</sup> )	5.00	0.00	0.00	0.00	0.00	2.0	1.5/0.5
Chloride (mg L <sup>-1</sup> )	2,730	32.2	52.9	55.2	32.2	350	250
Phosphate (mg L <sup>-1</sup> )	1.70	0.05	0.01	0.04	0.00	3.5	0.5
Cyanide (mg L <sup>-1</sup> )	0.50	0.00	0.00	0.00	0.00	0.10	0.05
Fluoride (mg L <sup>-1</sup> )	5.40	0.13	0.11	0.12	0.09	–	1.5/1
Sulphate (mg L <sup>-1</sup> )	112	0.00	0.00	0.00	0.00	500	250/200
COD (mg L <sup>-1</sup> )	680	13.0	10.0	4.75	2.30	30	40.0
BOD <sub>5</sub> (mg L <sup>-1</sup> )	12.0	3.05	2.50	1.15	1.12	6.0	10/5–7
Nitrite (mg L <sup>-1</sup> )	0.24	0.04	0.04	0.03	0.04	0.8	3/0.5
Total bacteria count (cfu/mL)	0	0	0	0	0	–	–
Chromium (mg L <sup>-1</sup> )	0.788	0.068	0.0	0.0	0.0	0.05	0.05
Zinc (mg L <sup>-1</sup> )	3.586	0.119	0.111	0.060	0.045	0.2	2

**Figure 1.** HRSEM images of (a) P-CNTs (b) EDS of P-CNTs (c) PEG-CNTs.

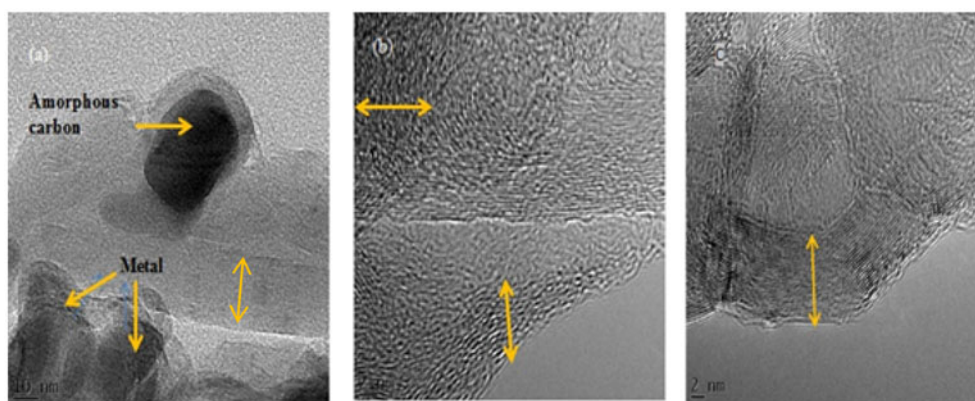
chloride ion and other anions (fluoride, sulphate, nitrite and nitrate) significantly reduced and fall within WHO<sup>[28]</sup> and National Environmental Standards Regulatory and Enforcement Agency (NESREA)<sup>[26]</sup> maximum limit as shown in Table 1. The WHO sets 5–6 mg L<sup>-1</sup> as its discharge standard for DO, NESREA has a minimum discharge limit of 4 mg L<sup>-1</sup>. After treatment, the DO of the wastewater increased from 3.11 mg L<sup>-1</sup> to 5.75 and 5.85 for P-CNTs and PEG-CNTs, respectively, which falls within NESREA<sup>[26]</sup> and WHO<sup>[28]</sup> standards. Furthermore, it can be observed from Table 1 that ammonium, cyanide, COD and BOD<sub>5</sub> were completely reduced upon the interaction with the nano-adsorbents under applied experimental conditions. The results from Table 1 showed that the nano-adsorbents were efficient in the removal of the target contaminants.

### Characterization of the purified and PEG-functionalized CNTs

HRSEM image in Figure 1a revealed the presence of non-uniform aggregated tubes of different diameter embedded with residual kaolin and metallic particles. In the case of HRSEM micrograph displayed in Figure 1b, arrays of long uniform tubes containing less impurity were observed due to the significant reduction of catalytic particles and removal of amorphous carbon deposition by the acids.<sup>[29]</sup> Similarly, the HRSEM micrograph of PEG-CNTs shown in Figure 1c

exhibited additional characteristics of the tube-like structure despite the functionalization by the polymer matrix of PEG; an indication of easy dispersion of PEG on the CNTs. In addition, the functionalization did not affect the side wall of PEG-CNTs, instead additional increment in the diameter and length was observed. It should be mentioned that the functionalization also resulted to rough clustering of polymer matrix on the outer wall of the CNTs surface. It was also noticed that the polymer matrixes expanded at the end of the tube leading to the formation of long diameter tube at the fracture surface. The formation of an open end tube is considered more advantageous during the adsorption process.<sup>[30]</sup>

In the same vein, Figure 2 revealed the HRTEM images of as-synthesized CNTs, P-CNTs and PEG-CNTs. It can be seen that the prepared CNTs is multi-walled in nature due to the presence of multiple layers and concentric tubes. The occurrence of lattice fringes in Figure 2a indicates that the prepared multi-wall CNT is highly crystalline even though small amount of amorphous carbon and other catalytic impurities remained on the outer layer of the CNTs. After the acid purification of as-synthesized CNTs, significant reduction of amorphous carbon and other metal impurities that covered the outer layer of CNTs were observed (see Figure 2b). It is evident from Figure 2b that multiple graphitic walls accompanied by slight defective etching at the outer edges with hollow inner diameter were formed.<sup>[31]</sup>



**Figure 2.** HRTEM images of (a) As-synthesized CNTs (b) P-CNTs (c) PEG-CNTs.

Figure 2c depicts multi-wall CNTs with high degree crystallinity and nested tubules. The small dark spot on the surface depicts polymer embedded on the tubular network of CNTs, this observation is similar to the report of Bankole et al.<sup>[2]</sup> Also, the internal and the external diameter of the CNTs were found to be 21 and 46 nm, respectively. Also in Figure 2c, it was noticed that the polymer dispersed on the wall of CNTs, which suggest the introduction of more functional groups such as  $-OH$ ,  $-COOH$  and  $H-C-H$  on the surface of MWCNTs.<sup>[22]</sup> A tip growth mechanism was observed for the synthesized CNTs, which implied that the Fe-Ni/Kaolin catalyst resided at the tip of the CNT during growth.<sup>[32]</sup> In addition, the functionalization via chemical oxidation of the tip growth CNTs resulted to the attachment of functional groups such as  $-COOH$ ,  $=C-O$  and/or  $-OH$ .<sup>[33]</sup>

The EDS result which revealed the elemental composition present in the nano-adsorbents is presented in Figure 3a–c. In Figure 3a, the percentage composition of C was found to be higher compared to Al, Si and O that originated from kaolin (support) and metal catalyst (Fe and Ni). In Figure 3b and c, it was noticed that the percentage composition of these elements reduced except C and O which increased after the acid purification and polymer functionalization. These two processes have helped in the removal of residual impurities and incorporation of more functional group by PEG.

Figure 4 depicts the particle size (diameter) distribution of both P-CNTs and PEG-CNTs. In Figure 4a, the distribution of diameter size ranges from 21 to 100 nm for P-CNTs, while for Figure 4b, the diameter distribution ranges from 11 to 100 nm. This suggests that the two samples have different diameter distribution and incorporation of PEG onto CNTs, lead to the reduction in size.

Furthermore, the specific surface areas of as-synthesized CNTs, P-CNTs and PEG-CNTs were determined by the BET method under nitrogen multilayer adsorption measurement. It was found that the BET surface area of PEG-CNTs was the highest ( $970.81 \text{ m}^2/\text{g}$ ) followed by P-CNTs ( $781.88 \text{ m}^2/\text{g}$ ) and as-synthesized CNTs ( $583.31 \text{ m}^2/\text{g}$ ). As reported by Peigney et al.<sup>[34]</sup> the experimental measured surface area of multi-wall CNTs generally ranges from 10 to  $500 \text{ m}^2/\text{g}$ , and can increase on purification and functionalization. The chemical treatment of CNTs during the

purification and functionalization allows molecules to have access to both the internal and external surface of the CNTs, thereby enhancing the surface area by 50–380%. Therefore, the high surface area of P-CNTs and PEG-CNTs was attributed to the acid treatment and PEG functionalization of CNTs, respectively.<sup>[35]</sup>

The FTIR spectra of as-synthesized-CNTs, P-CNTs and PEG-CNTs are displayed in Figure 5. The absorption band observed at  $1081 \text{ cm}^{-1}$  for the as-synthesized CNTs (Figure 5a) corresponds to  $-OH$  (hydroxyl group) earlier reported by Muhammad and Abdullahi.<sup>[6]</sup> The frequency band noticed at  $1445 \text{ cm}^{-1}$  for as-synthesized CNT confirmed the presence of  $C=C$  stretching. This is slightly different from the band observed by Muhammad and Abdullahi<sup>[6]</sup> at  $1500 \text{ cm}^{-1}$  probably due to the nature of the precursor and the support used in the synthesis of the catalyst. According to Figure 5a, the peak at  $2148 \text{ cm}^{-1}$  for as-synthesized-CNTs is assigned  $C=C$  bond, while the band at  $3010 \text{ cm}^{-1}$  indicates the presence of  $-OH$ . After the purification (see Figure 5b), the following absorption bands were observed at  $1586$  and  $3114 \text{ cm}^{-1}$ , which correspond to carboxylic functional group ( $-COOH$ ) and hydroxyl group ( $-OH$ ), respectively.<sup>[36]</sup> The peak around  $838$  and  $1069 \text{ cm}^{-1}$  represents out of plane deformation vibrations of the alkyl group and hydroxyl group attached to the CNT surface. After the incorporation of PEG on CNT surface as shown in Figure 5c, a new absorption band was noticed at  $1154 \text{ cm}^{-1}$ , which corresponds to  $-C=O$  of ester group. Also, in Figure 5b, it can be seen that the intensity of the peaks at  $2561$  and  $3138 \text{ cm}^{-1}$  assigned as  $C-H$  stretching vibrations and  $-OH$  increased upon functionalization.<sup>[22]</sup>

## Adsorption parameters

### Effect of contact time

The results of the effect of contact time on the removal efficiency of Cr and Zn from the battery wastewater by the nano-adsorbents are shown in Figure 6a and b. In Figure 6a and b, it was observed that the amount of Cr and Zn ions removed increases with increasing contact time irrespective of the nano-adsorbents up till an optimum time of 20 min for both nano-adsorbent. The fast initial adsorption rate may be due to the higher driving force within the mixture,

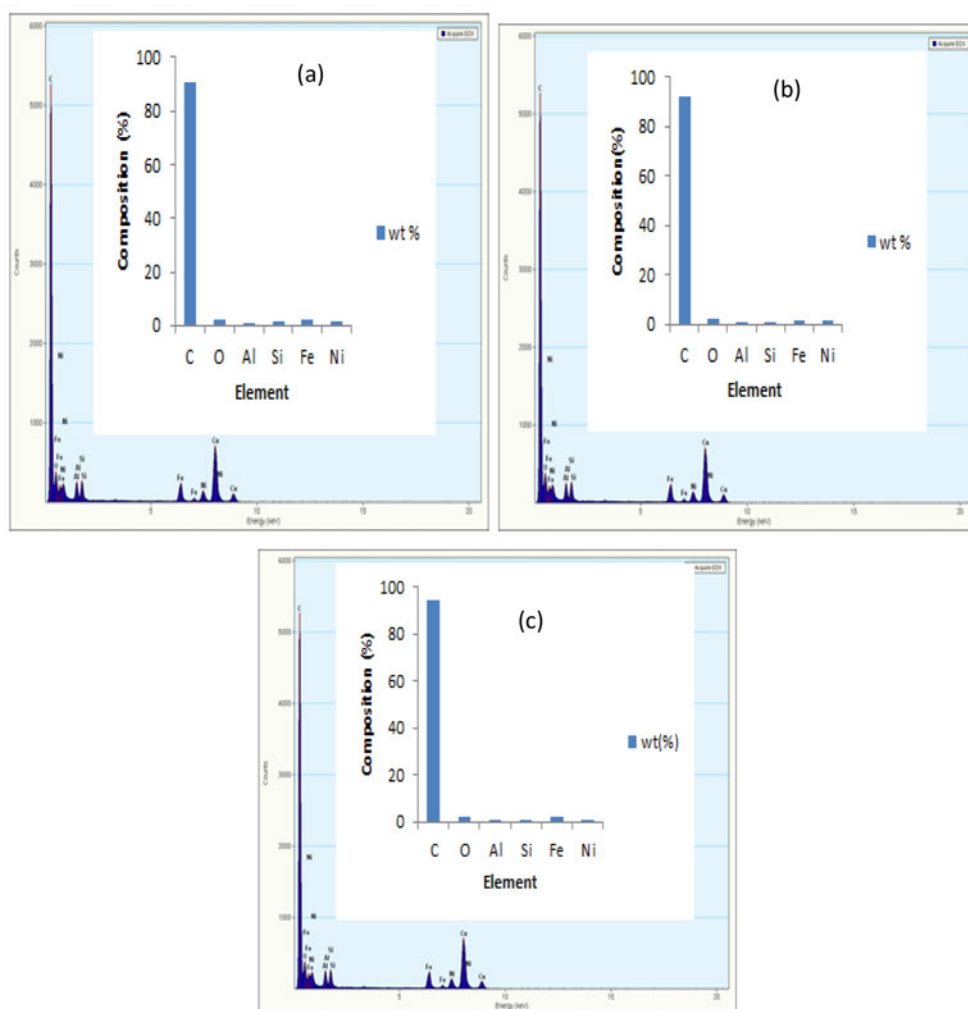


Figure 3. EDS elemental composition of CNTs of (a) As-synthesized CNTs.

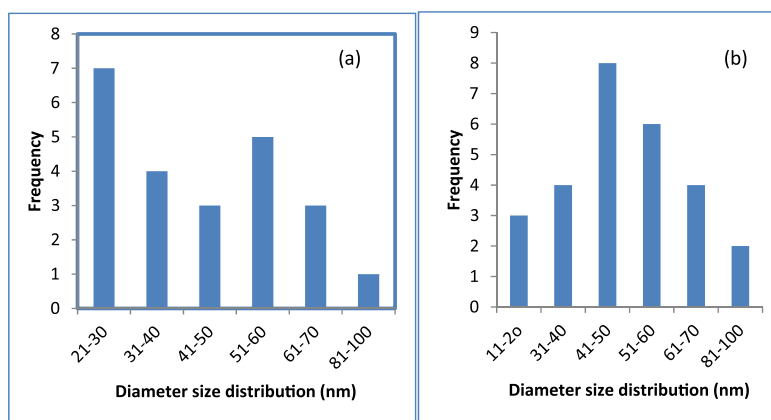
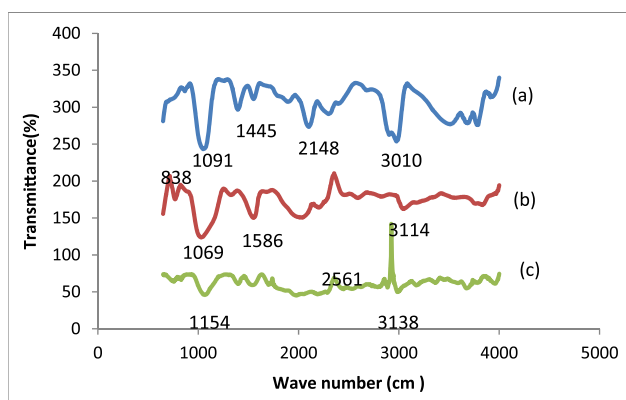


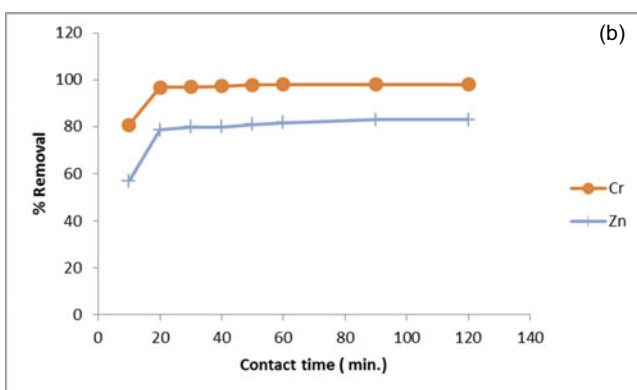
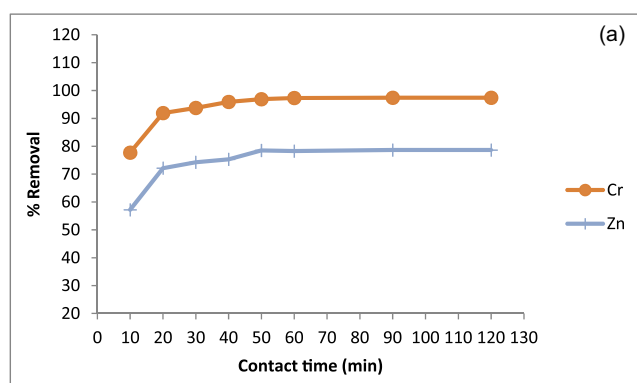
Figure 4. Diameter size distribution of (a) P-CNTs (b) PEG-CNTs.

leading to the fast transfer mechanism between the adsorbed metals and the active site of the adsorbent. It was also observed that for P-CNTs shown in Figure 6a, the optimum contact time was 20 min where Cr and Zn removal efficiency was 91.93% and 72.15%, respectively. While the percentage metal ions removed at equilibrium time of 60 min for P-CNTs were 97.33% (Cr) and 78.26% (Zn). In Figure 6b for PEG-CNTs, the optimum contact time was also 20 min, where the amount of Cr and Zn sequestered was 96.7% and

78.48%, respectively. Unlike P-CNTs, the equilibrium was attained at 90 min with 98.08% removal efficiency for Cr and 82.95% for Zn. It is obvious that at every contact time, the amount of Cr removed was greater than that of Zn. The differences may be ascribed to the fact that Cr with smaller ionic radii (0.62 Å) diffuse faster than Zn with larger ionic radii (0.74 Å). The equilibrium time of 60 and 90 min for both nano-adsorbents was considered as economical route time for wastewater treatment during industrial applications.

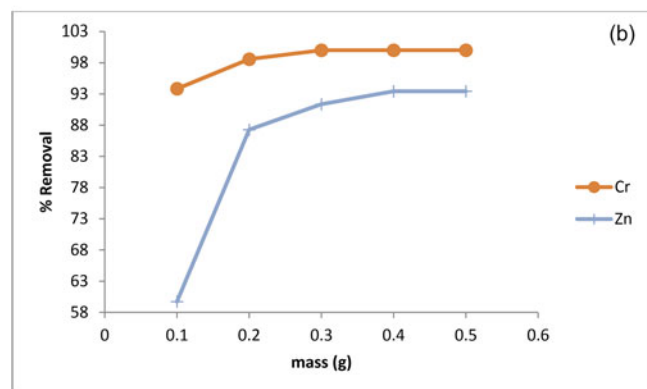
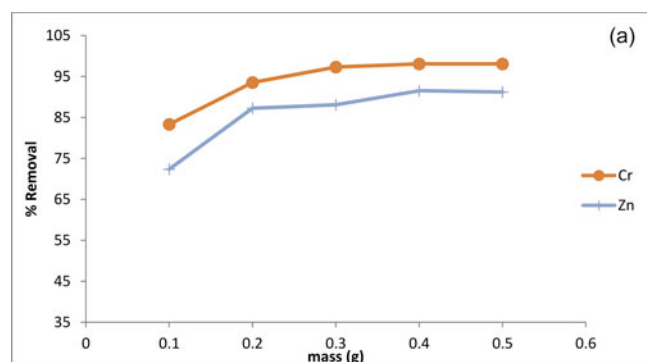


**Figure 5.** FTIR spectra of (a) as-synthesized-CNTs, (b) P-CNTs and (c) PEG-CNTs.



**Figure 6.** Effect of contact time on percentage removal of heavy metals on (a) P-CNT (b) PEG-CNTs [adsorbent dosage (0.1 g), stirring speed (190 rpm) and temperature (25 °C), volume of battery wastewater (50 mL), stirring time (120 min)].

The PEG-CNTs successfully removed more of the metal ions than P-CNTs due to higher surface area and availability of more functional groups and binding sites on the former than the latter. The observed interaction between the nano-adsorbents (P-CNTs and PEG-CNTs) and the heavy metal ions in the industrial battery wastewater is based on the ion-exchange mechanism. The functional groups ( $-\text{COOH}$ ,  $-\text{OH}$ ,  $-\text{C}=\text{O}$ ) attached to the surface of nano-adsorbents shown in Figure 5b and c acted as an electron donor and anchoring sites for pollutants in the wastewater. Again, high dispersion rate of PEG-CNTs (Figure 5b) than that of P-CNTs in the wastewater owing to stronger electrostatic attraction provided by PEG contributed to high adsorption efficiency of PEG-CNTs than P-CNTs.<sup>[22]</sup>



**Figure 7.** Effect of Dosage on percentage removal of heavy metal using (a) P-CNTs (b) PEG-CNTs [stirring speed (190 rpm) and temperature (25 °C), volume battery wastewater (50 mL), stirring time (90 min)].

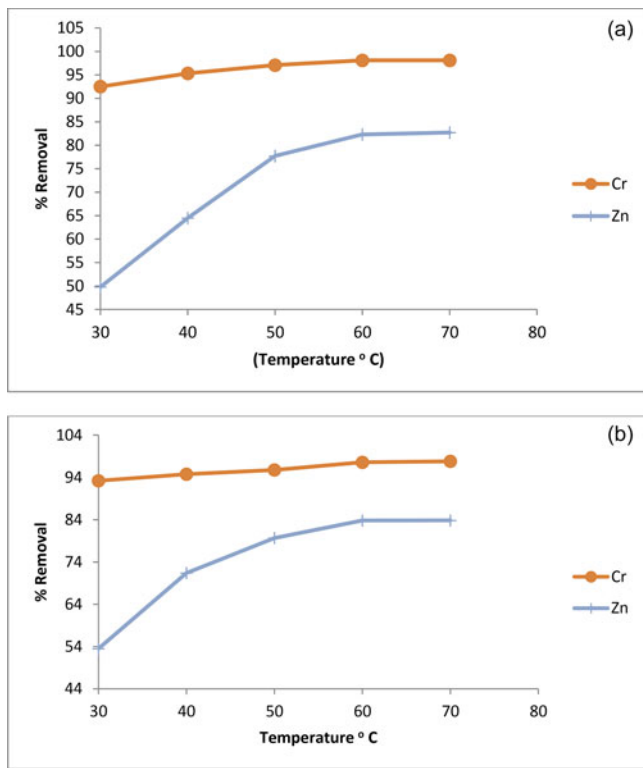
#### Effect of adsorbents dosage

The effects of different mass of nano-adsorbents dosage (0.1–0.5 g) on the selected heavy metals removal from battery wastewater were investigated and the results obtained are shown in Figure 7a and b. It can be seen that the percentage removal increases with increasing amounts of adsorbent (0.4 g for P-CNTs and 0.3 g for PEG-CNTs). It was clear that dosage needed by P-CNTs to reach equilibrium was much higher than PEG-CNTs. The increased in adsorption of metal ions removal by PEG-CNTs may be attributed to high surface area and availability of functional binding active sites. However, a very slow increase in removal beyond optimum dose may be attributed to weak interaction between the sorbate and the sorbent.

#### Effect of temperature

As shown in Figure 8a and b, it was observed that increase in temperature from 303 to 343 K was responsible for the corresponding increase in the removal efficiency and adsorption capacity of the selected heavy metal ions onto P-CNTs and PEG-CNTs. The observed phenomenon may be ascribed to the fact that an increase in temperature caused a swelling effect within the internal and external structure of the nano-adsorbent. This invariably resulted to the corresponding increase in the rate of penetration of the active site of the nano-adsorbents by the metal ions. The optimum temperature for P-CNTs and PEG-CNTs was 333 and 323 K, respectively. Beyond this temperature, there was a slight and minimal increase in the removal efficiency of Cr and Zn.





**Figure 8.** Effects of Temperature on percentage removal of heavy metals on (a) P-CNTs (b) PEG-CNTs [adsorbent dosage (0.4 g), stirring speed (190 rpm), volume of battery wastewater (50 mL) and stirring time (90 min)].

### Adsorption of isotherms

The equilibrium data were analysed using Langmuir and Freundlich isotherm models in order to find out the relationship between the selected heavy metal ions adsorbed on the nano-adsorbents. The Langmuir isotherm model which is fitted for monolayer adsorption on the surface is shown in the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m K} + \frac{C_e}{q_m} \quad (4)$$

where  $C_e$  ( $\text{mg L}^{-1}$ ) was the equilibrium concentration of Cr and Zn in the industrial battery wastewater;  $q_e$  ( $\text{mg/g}$ ) was the amount of adsorbate at equilibrium;  $q_m$  ( $\text{mg/g}$ ) was the maximum adsorption capacity and  $K_L$  ( $\text{L/mg}$ ) was the Langmuir constant related to the affinity binding site. The constants  $q_m$  and  $K_L$  can be determined from the intercept and the slope of the linear plot of  $C_e/q_e$  against  $C_e$ .

The Freundlich isotherm model is expressed in Eq. (5)

$$\log q = \log k_f + \frac{1}{n} \log C_e \quad (5)$$

$K_f$  and  $n$  represent the adsorption capacity and the adsorption driving force, respectively. It has been established that as the  $K_f$  increases, the adsorption capacity increases including adsorption strength ( $n$ ). Generally, for good adsorption, the estimated values of  $n$  ranged between 2–10 with 1–2 for moderate and  $<1$  for poor adsorption.<sup>[2]</sup>

The constants and correlation coefficient ( $R^2$ ) of Langmuir and Freundlich adsorption isotherms are shown in Table 2. It is obvious that adsorption mechanism of the two metals by P-CNTs (see Figure 9) and PEG-CNTs (see Figure 10) fitted well to the Freundlich isotherm model than

**Table 2.** Isotherm parameters for the selected heavy metal removed from battery wastewater adsorption using P-CNTs and PEG-CNTs.

Isotherm parameters	P-CNTs		PEG-CNTs	
	Cr	Zn	Cr	Zn
Langmuir				
$K_L$ (L/mg)	3.3861	1.4303	35.60	3.9158
$Q_o$ (mg/g)	2.1231	4.1494	0.5135	0.4978
$R^2$	0.9229	0.8858	0.2858	0.8744
$R_L$	0.0761	0.5041	0.0079	0.2707
Freundlich				
$K_f$	0.5810	1.8391	0.5114	4.8029
$N$	1.6776	0.8671	3.3979	1.2829
$R^2$	0.9620	0.9429	0.9754	0.9580

Langmuir, which is based on high correlation coefficient ( $>0.9$ ). Conversely, PEG-CNTs possessed high adsorption capacity and removal efficiency for Cr and Zn from the wastewater due to the chemical modification of the nano-adsorbents than P-CNTs. Also, the  $n$ -values of PEG-CNTs for Cr and Zn were higher than that of P-CNTs suggesting stronger electrostatic interaction between PEG-CNTs and the metal ions than with P-CNTs. The high adsorption capacity of PEG-CNTs might probably be due to availability of more functional groups ( $-\text{OH}$  and  $-\text{C}=\text{OH}$ ) on its surface than in P-CNTs alone. In addition, the result shown in Table 2 demonstrates that the adsorption of Cr and Zn onto the nano-adsorbents was multilayer in nature which agreed with the findings of Ibtissem and Malika<sup>[37]</sup> and Padmavathy et al.<sup>[24]</sup>

### Adsorption kinetics

The adsorption kinetics of Cr, and Zn onto P-CNTs and PEG-CNTs were investigated using three models: Lagergren-first-order, pseudo-second-order models and the elovich model. The first-order, second-order kinetic and elovich kinetic models are given in Eqs. (6–8), respectively.

$$\log(q_e - q_t) = \log q_e - \frac{K}{2.303} t \quad (6)$$

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (8)$$

The parameter constants of the three models have been summarized in Table 3.

As can be seen in Table 3, the correlation coefficient ( $R^2$ ) of pseudo-second-order kinetic for adsorption of Cr and Zn was greater than that of pseudo-first-order and the elovich model. This suggests that the pseudo-second-order kinetic model better described adsorption kinetic of Cr and Zn onto P-CNTs. It further implies that the adsorption of Cr and Zn from the battery wastewater is a function of two parameters, namely contact time, adsorbent dosage or temperature. Also, the calculated values of equilibrium adsorption capacity ( $q_{e,cal}$ ) from the pseudo-second-order model were 17.83 and 2.787  $\text{mg/g}$  for Cr and Zn which is closer to the experimental data ( $q_{e,exp} = 17.45, 2.692 \text{ mg/g}$ ),

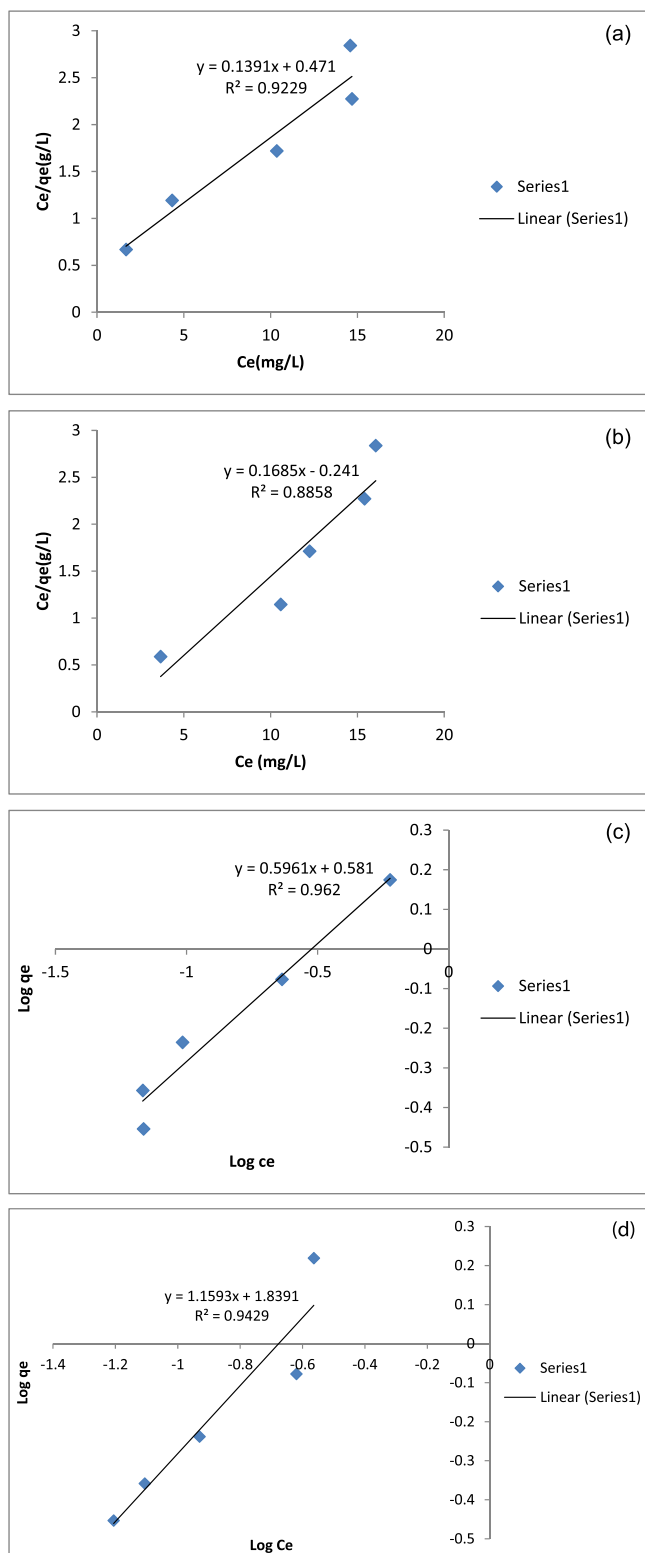


Figure 9. Isotherm plots [(a) Langmuir for Cr, (b) Langmuir for Zn, (c) Freundlich for Cr, (d) Freundlich for Zn] for the selected heavy metal removed from industrial battery wastewater adsorption using P-CNTs.

respectively. The values obtained differed appreciably from that of the pseudo-first-order model.

According to Table 4, it can be noticed that the  $R^2$  value ( $> 0.9$ ) of the pseudo-second-order kinetic model was higher than that of pseudo-first-order kinetic and the

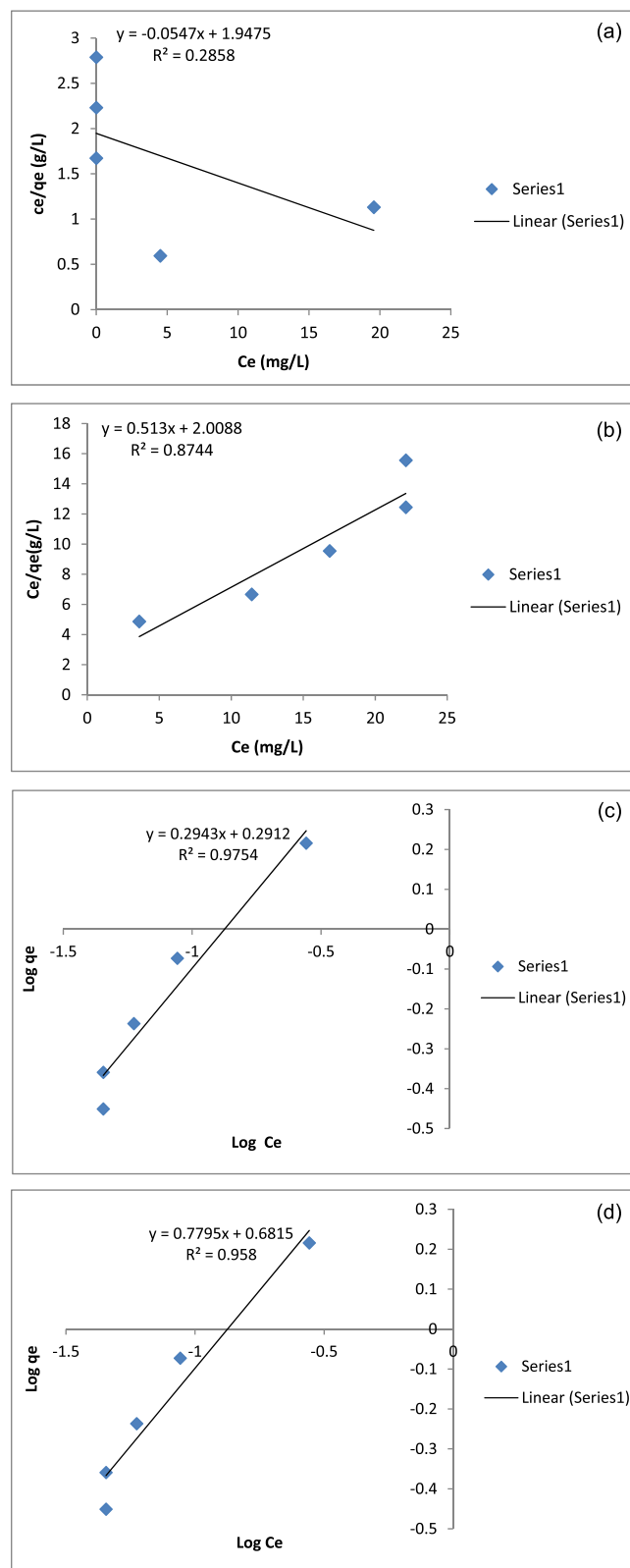


Figure 10. Isotherm plots [(a) Langmuir for Cr, (b) Langmuir for Zn, (c) Freundlich for Cr, (d) Freundlich for Zn] for the selected heavy metal removed from industrial battery wastewater adsorption using PEG-CNTs.

elovich model. Generally, the order of fitness of the kinetic model for the adsorption of Cr and Zn from the battery wastewater by PEG-CNTs occurred in the following order: pseudo-second-order kinetic  $>$  elovich model  $>$  pseudo-first-

**Table 3.** Kinetic parameters for adsorption of selected heavy metals on P-CNTs.

Metal	First-order kinetic model				Second-order kinetic model			Elovich model		
	$q_{e_{exp}}$ (mg/g)	$q_{e_{cal}}$ (mg/g)	$K_1$ (min <sup>-1</sup> )	$R^2$	$q_{e_{cal}}$ (mg/g)	$K_2$ (g/mg.min)	$R^2$	$\beta$	$\alpha$	$R^2$
Cr	17.45	0.0067	0.0023	0.0121	17.83	0.0316	0.9310	1.0043	$7.03 \times 10^5$	0.5707
Zn	2.692	0.0839	0.0265	0.6047	2.787	0.1279	0.9299	3.3047	52.63	0.6654

**Table 4.** Kinetic parameters for adsorption of heavy metals on PEG-CNTs.

Metal	First-order kinetic model				Second-order kinetic model			Elovich model		
	$q_{e_{exp}}$ (mg/g)	$q_{e_{cal}}$ (mg/g)	$K_1$ (min <sup>-1</sup> )	$R^2$	$q_{e_{cal}}$ (mg/g)	$K_2$ (g/mg.min)	$R^2$	$\beta$	$\alpha$	$R^2$
Cr	17.57	0.450	0.0062	0.050	17.79	0.0536	0.9998	0.772	14469.8	0.747
Zn	2.810	0.079	0.0200	0.210	2.937	0.1192	0.9995	3.6711	77.45	0.775

order kinetic. It could be observed that the pseudo-second-order was better suitable to describe the adsorption of Cr and Zn on P-CNTs and PEG-CNTs implying that the rate limiting step was chemisorption in nature (Fig. 11).

### Thermodynamic studies

The effect of temperature on the adsorption potential of the prepared nano-adsorbents was examined by varying the temperature from 303 to 343°K. This was done to predict the possible influence of the thermodynamic parameters, namely: Gibb's free energy ( $\Delta G$ ), entropy ( $\Delta S$ ) and enthalpy change ( $\Delta H$ ) on the adsorption process. The change in free energy ( $\Delta G^0$ ) can be determined by using Eq. (9)

$$\Delta G = -RT \ln K \quad (9)$$

$$K = \frac{q_e}{c_e} \quad (10)$$

The Gibbs free energy was also determined by the following equation:

$$\Delta G = \Delta H - T\Delta S \quad (11)$$

Substituting Eq. (11) into Eq. (9) to obtain Van't Hoff Eq. (12)

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (12)$$

where  $R$  is the universal gas constant (8.314 J/mol K) and  $T$  is the temperature (K). The equilibrium constant was determined using Eq. (10). According to Eqs. (11) and (12), enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) parameters were calculated from the slope of  $\ln K$  versus  $1/T$ . Table 5 shows the thermodynamic parameters for the adsorption of the selected heavy metals from battery wastewater using P-CNTs.

The negative value of  $\Delta G$  which increases as the temperature increases from 303 to 343°K implies spontaneity and feasibility of the adsorption process. Also, the positive value of  $\Delta H$  indicates endothermic nature of the adsorption process. This means that the chemical bonds were broken when heat was absorbed (endothermic) and as a result caused high rate of collision of the heavy metals as the temperature increases within the system. In addition, the positive values of change in entropy ( $\Delta S$ ) implied increase in the degree of randomness and disorderliness

at the adsorbate/adsorbents interface during the adsorption process. The thermodynamic parameters using PEG-CNTs are shown in Table 6 and it was observed that the value  $\Delta H$  obtained was found to be higher than those presented for P-CNTs (see Table 5). The positive values  $\Delta H$  suggest that the adsorption is endothermic, which was supported by the increase in Cr and Zn adsorption onto PEG-CNTs at high temperature. Moreover, the magnitude of  $\Delta G$  which also increased with increasing in temperature illustrated that adsorption occurred at high temperature. The negative value of  $\Delta G$  implied a greater driving force of adsorption resulting into a high adsorption capacity. It is noteworthy to mention that the introduction of more functional group by polyethylene glycol onto PEG-CNTs increased the adsorption capacity for Cr. Also, the enhancement of adsorption capacity of PEG-CNTs at high temperature may also be attributed to increase in surface area as evidenced in BET analysis result. Yul et al.<sup>[38]</sup> reported that  $\Delta G$  value for physisorption and chemisorption processes lies between  $-20$  and  $-80$  kJ/mol. In this study, the values of  $\Delta G$  calculated suggest that the adsorption process was chemisorption and further supported the kinetic data analysis. Furthermore, the positive value of  $\Delta S$  signified affinity of PEG-CNTs for the selected heavy metals and increase in randomness at the solid/liquid interface during the adsorption process.<sup>[39]</sup> Therefore, the results of  $\Delta G$  and  $\Delta H$  imply that the chemisorption process indirectly dominated the adsorption of Cr, and Zn onto PEG-CNTs from industrial battery wastewater (Figure 12).

### Conclusion

In summary, Fe-Ni/kaolin catalyst was prepared via a wet impregnation method and subsequently used for the production of CNTs via the CCVD method. Acid purification of the as-synthesized CNTs by 30% (v/v)  $\text{HNO}_3/\text{H}_2\text{SO}_4$  followed by functionalization of the P-CNTs with PEG, respectively. The purified and PEG-functionalized CNTs were characterized using standard analytical techniques. The HRSEM/HRTEM results indicated that the tubular structures of the CNTs were not destroyed despite the functionalization. The surface area of as-synthesized and P-CNTs was further enhanced after functionalization with PEG. The adsorption efficiency of purified and PEG-CNTs

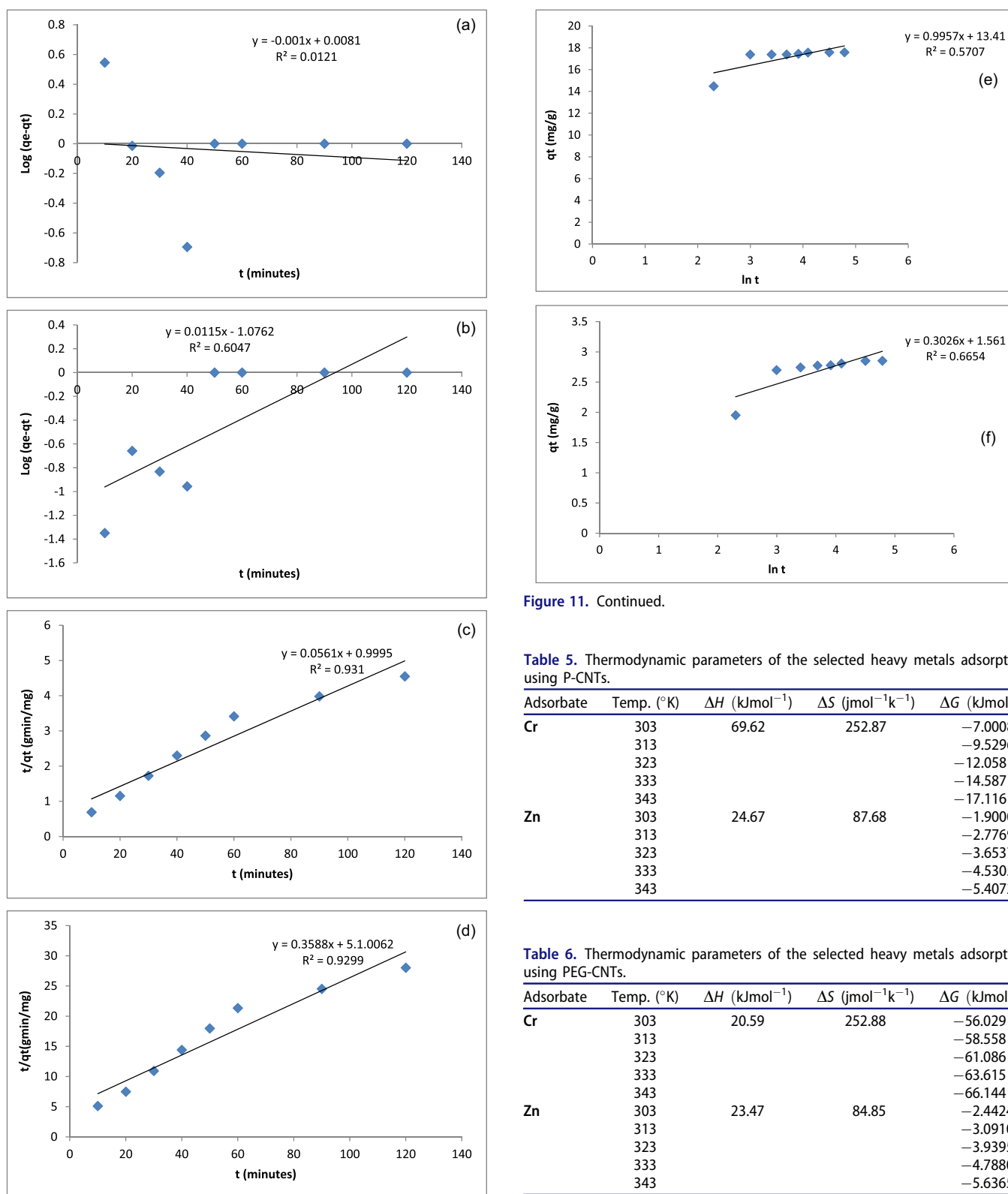


Figure 11. Continued.

**Table 5.** Thermodynamic parameters of the selected heavy metals adsorption using P-CNTs.

Adsorbate	Temp. (°K)	$\Delta H$ (kJmol <sup>-1</sup> )	$\Delta S$ (jmol <sup>-1</sup> k <sup>-1</sup> )	$\Delta G$ (kJmol <sup>-1</sup> )
Cr	303	69.62	252.87	-7.0008
	313			-9.5296
	323			-12.058
	333			-14.587
	343			-17.116
Zn	303	24.67	87.68	-1.9000
	313			-2.7769
	323			-3.6537
	333			-4.5305
	343			-5.4072

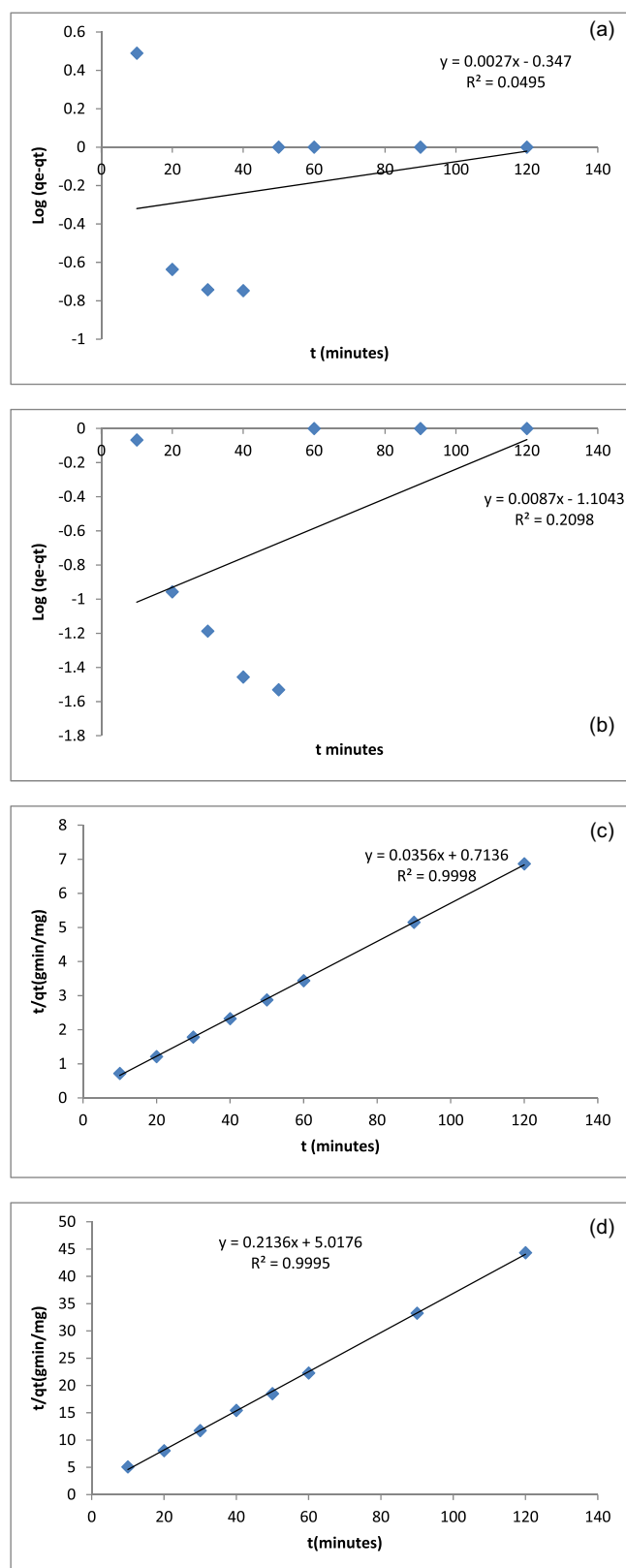
**Table 6.** Thermodynamic parameters of the selected heavy metals adsorption using PEG-CNTs.

Adsorbate	Temp. (°K)	$\Delta H$ (kJmol <sup>-1</sup> )	$\Delta S$ (jmol <sup>-1</sup> k <sup>-1</sup> )	$\Delta G$ (kJmol <sup>-1</sup> )
Cr	303	20.59	252.88	-56.029
	313			-58.558
	323			-61.086
	333			-63.615
	343			-66.144
Zn	303	23.47	84.85	-2.4424
	313			-3.0910
	323			-3.9395
	333			-4.7880
	343			-5.6365

**Figure 11.** Kinetic plots [pseudo-first-order for (a) Cr (b) Zn, pseudo-second-order (c) Cr (d) Zn, elovich (e) Cr and (f) Zn] for adsorption of selected heavy metals on P-CNTs.

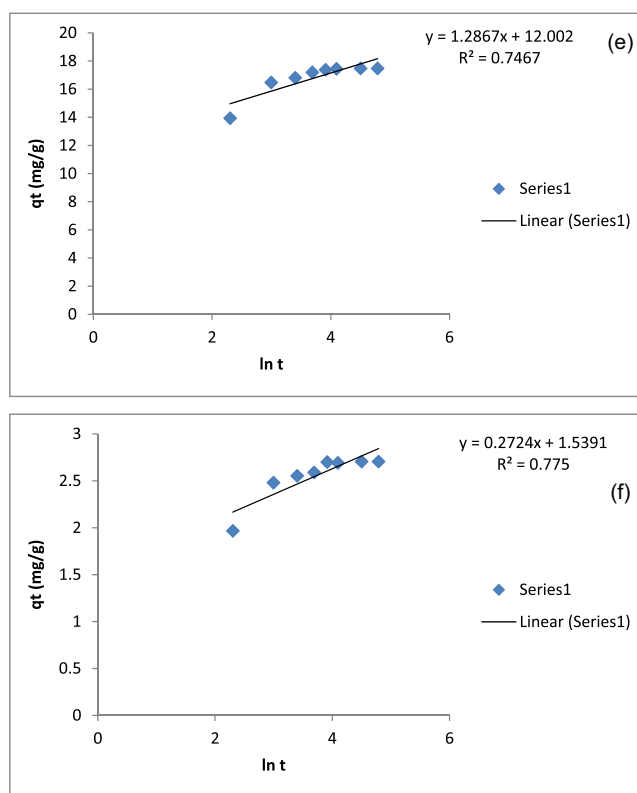
for the removal of Cr and Zn metals from battery wastewater was studied was found to depend on contact time, adsorbent dosage and temperature. The removal efficiency of selected heavy metal was in order of

PEG-CNTs > P-CNTs and the performance of the nano-adsorbents was surface area specific. Also, the adsorption isotherm and kinetic model was best fitted to Freundlich isotherm and pseudo-second-order model, an evidence of multilayer phenomenon. The adsorption process of the selected heavy metal ions from industrial battery wastewater was feasible and spontaneous, random and



**Figure 12.** Kinetic plots [pseudo-first-order for (a) Cr (b) Zn, pseudo-second-order (c) Cr (d) Zn, elovich (e) Cr and (f) Zn] for adsorption of selected heavy metals on PEG-CNTs.

endothermic in nature. This study showed that PEG-functionalized CNTs is a better promising nano-adsorbent compare to its counterpart for the sequestration of heavy metals from industrial battery wastewater.



**Figure 12.** Continued.

## Funding

This work was supported by Tertiary Education Tax fund Nigeria (TETFUND/FUTMINNA/NRF/2014/01) and Centre of Genetic Engineering and Biotechnology, Federal University of Technology, Minna, Nigeria.

## References

- [1] Prachi, P. G.; Deepa, M.; Nair, A. N. B. Nanotechnology in Waste Water Treatment: A Review. *Int. J. ChemTech. Res.* **2014**, *5*, 2303–2308.
- [2] Bankole, M. T.; Abdulkareem, A. S.; Tijani, J. O.; Ochigbo, S. S.; Afolabi, A. S.; Roos, W. D. Chemical Oxygen Demand Removal from Electroplating Wastewater by Purified and Polymer Functionalized Carbon Nanotubes Adsorbents. *Water Res. Ind.* **2017**, *18*, 33–50. DOI: [10.1016/j.wri.2017.07.001](https://doi.org/10.1016/j.wri.2017.07.001).
- [3] Giuseppe, G.; Emanuela, M.; Francesca, P.; Franco, T.; Luigi, T. Product Recovery from Li-Ion Battery Wastes Coming from an Industrial Pre-Treatment Plant: Lab Scale Tests and Process Simulations. *J. Power Sources* **2015**, *206*, 393–401. DOI: [10.1016/j.jpowsour.2012.01.115](https://doi.org/10.1016/j.jpowsour.2012.01.115).
- [4] Fenglian, F.; Qi, W. Removal of Heavy Metal Ions from Wastewaters: A Review. *J. Environ. Manage.* **2010**, *92*, 112–119.
- [5] Obadia, K. B.; Lingling, Z.; Shaldon, L. S.; Hui, J.; Abraham, A. Z.; Zhongwei, Q. Remediation of Water and Wastewater by Using Engineered Nanomaterials: A Review. *J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng.* **2018**, *53*, 537–554.
- [6] Muhammad, H. A.; Abdullahi, A. B. Adsorption of Heavy Metals Using Activated Carbon Produced from Municipal Organic Solid Waste. *Des. Water Treat.* **2016**, *57*, 24519–24531.
- [7] Barakat, M. A. New Trends in Removing Heavy Metals from Industrial Wastewater-Review Article. *Arab. J. Chem.* **2011**, *4*, 361–377. DOI: [10.1016/j.arabjc.2010.07.019](https://doi.org/10.1016/j.arabjc.2010.07.019).
- [8] Xing, Y.; Chen, X.; Wang, D. Electrically Regenerated Ion Exchange for Removal and Recovery of Cr(VI) from Waste

- Water. *Environ. Sci. Technol.* **2007**, *41*, 1439–1443. DOI: [10.1021/es061499l](https://doi.org/10.1021/es061499l).
- [9] Ersahim, M. E.; Ozgun, H.; Derels, R. K.; Ozturk, I. A. Review on Dynamic Membrane Filtration; Materials and Future Perspectives. *Bioresour. Technol.* **2012**, *3*, 60–73.
- [10] Tiwari, D. K. Application of Nanoparticles in Waste Water Treatment. *World Appl. Sci. J.* **2008**, *3*, 417–433.
- [11] Xiangtao, W.; Yifei, G.; Li, Y.; Meihua, H.; Jing, Z.; Xiaoliang, C. Nanomaterials as Sorbents to Remove Heavy Metal Ions in Wastewater Treatment. *J. Environ. Anal. Toxicol.* **2012**, *2*, 1–7.
- [12] Khairia, M. A. Water Purification Using Different Waste Fruit Cortexes for the Removal of Heavy Metals. *J. Taibah Univ. Sci.* **2015**, *10*, 700–708.
- [13] Castrom, M.; Nogueira, V.; Lopes, I.; Vieira, M. N.; Rocha-Santos, T.; Pereira, R. Treatment of a Textile Effluent by Adsorption with Cork Granules and Titanium Dioxide Nanomaterial. *J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng.* **2018**, *53*, 524–536.
- [14] Patra, G.; Das, P.; Chakraborty, S.; Meikap, B. C. Removal of Fluoride from Wastewater Using HCl-Treated Activated Alumina in a Ribbed Hydrocyclone Separator. *J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng.* **2018**, *53*, 601–608.
- [15] Jiaying, L.; Shuyu, C.; Guodong, S.; Jun, H.; Xiaoli, T.; Xiangke, W. Effect of Surfactants on Pb (II) Adsorption from Aqueous Solutions Using Oxidized Multiwall Carbon Nanotubes. *Chem. Eng. J.* **2011**, *166*, 551–558. DOI: [10.1016/j.cej.2010.11.018](https://doi.org/10.1016/j.cej.2010.11.018).
- [16] Jemal, F.; Nurelegne, T.; Helmut, K.; Stijn, W. H. V. Anaerobic Treatment of Blended Sugar Industry and Ethanol Distillery Wastewater through Biphasic High Rate Reactor. *J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng.* **2018**, *53*, 676–685.
- [17] Yujin, L.; Kunyan, S.; Rongzhan, L.; Xin, Z. Removal of Methyl Orange from Aqueous Solution by Calcium Algnite Multiwalled Carbon Nanotubes Composite Fibers. *Energy Proc.* **2012**, *16*, 863–868.
- [18] Mahmoud, A. M.; Ibrahim, F. A.; Shaban, S. A.; Youssef, N. A. Adsorption of Heavy Metal Ion from Aqueous Solution by Nickel Oxide Nano Catalyst Prepared by Different Method. *Egyptian J. Petrol.* **2015**, *24*, 27–33. DOI: [10.1016/j.ejpe.2015.02.003](https://doi.org/10.1016/j.ejpe.2015.02.003).
- [19] Ghazaleh, A.; Payam, A.; Siti, M. T. Methane Decomposition for Carbon Nanotube Production: Optimization of the Reaction Parameters Using Response Surface Methodology. *Chem. Eng. Res. Des.* **2016**, *112*, 163–174.
- [20] Olga, D. K.; Viktor, M. K.; Virender, K. S. Removal of Cu(II) in Water by Polymer Enhanced Ultrafiltration: Influence of Polymer Nature and pH. *J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng.* **2018**, *53*, 33–38.
- [21] Mohamed, A. S.; Robert, B. Synthesis and Characterization of Multi-Walled Carbon Nanotube Modified with Octadecylamine and Polyethylene Glycol. *Arab. J. Chem.* **2012**, *10*, 921–927.
- [22] Wang, W. H.; TangGuang-Ming, Z.; Ji-Lai, G.; Yang, L.; Xi-Yang, W.; Yuan-Yuan, L.; Zhi-Feng, L.; Long, C.; Xiu-Rong, Z.; De-Zhu, T. Simultaneous Adsorption of Atrazine and Cu (II) from Wastewater by Magnetic Multi-Walled Carbon Nanotube. *Chem. Eng. J.* **2012**, *212*, 470–478.
- [23] American Public Health Association (APHA). (2017). Standard Methods for the Examination of Water and Wastewater; APHA, American Water Works Association (AWWA), Water Environment Federation (WEF); ISBN: 9870875532875.
- [24] Padmavathy, K.; Madhub, G.; Haseena, P. A Study on Effects of pH, Adsorbent Dosage, Time, Initial Concentration and Adsorption Isotherm Study for the Removal of Hexavalent Chromium (Cr (VI)) from Wastewater by Magnetite Nanoparticles. *J. Environ. Technol.* **2016**, *24*, 585–594. DOI: [10.1016/j.protcy.2016.05.127](https://doi.org/10.1016/j.protcy.2016.05.127).
- [25] Badreddine, B.; Mohamed, T.; Niamine, A. R. A Kinetic, Equilibrium and Thermodynamic Study of l-Phenylalanine Adsorption Using Activated Carbon Based on Agricultural Waste (Date Stones) Environment. *J. Sci. Technol.* **2016**, *14*, 32–44.
- [26] National Environmental Standards and Regulation (NESREA). Guidelines for Drinking Water, **2011**.
- [27] Joseph, T.; Cim, A.; Ning, A. Treatment of Synthetic and Battery Industry Wastewater by Electrocoagulation. *J. Environ. Manage.* **2014**, *135*, 150–168.
- [28] World Health Organizations (WHO). Guidelines for Drinking Water, 4th ed.; **2011**.
- [29] Hassan, I. O. Development of a Suitable Bimetallic (Fe-Co) Catalyst on Kaolin Support for Carbon Nanotube Synthesis. MSc Thesis, Federal University of Technology, Minna, Niger State, **2016**.
- [30] Kariim, I.; Abdulkareem, A. S.; Abubakre, O. K.; Aliyu, A.; Mohammed, I. A. Hamidu, A. Characterization and Antibacterial Activity of Nickel Ferrite Doped  $\alpha$ -Alumina Nanoparticle. *Eng. Sci. Technol. Int. J.* **2017**, *20*, 563–569.
- [31] Abdulkareem, A. S.; Kariim, I.; Bankole, M. T.; Tijani, J. O.; Olu, S. C. Synthesis and Characterization of Tri-Metallic Fe-Co-Ni Catalyst Supported on CaCO<sub>3</sub> for Multi-Walled Carbon Nanotubes Growth via Chemical Vapor Deposition Technique. *Arab. J. Sci. Eng.* **2017**, *2*, 1–25.
- [32] Banerjee, S.; Naha, S.; Ishwar, K. P. Molecular Simulation of the Carbon Nanotube Growth Mode during Catalytic Synthesis. *Appl. Phys. Lett.* **2008**, *92*, 233121. DOI: [10.1063/1.2945798](https://doi.org/10.1063/1.2945798).
- [33] Rao, G. P.; Lu, C.; Su, F. Sorption of Divalent Metal Ions from Aqueous Solution by Carbon Nanotubes: A Review. *Sep. Pur. Technol.* **2007**, *58*, 224–231. DOI: [10.1016/j.seppur.2006.12.006](https://doi.org/10.1016/j.seppur.2006.12.006).
- [34] Peigney, A.; Laurent, C.; Flahaut, E.; Bacsa, R. R.; Rousset, A. Specific Surface Area of Carbon Nanotubes and Bundles of Carbon Nanotubes. *Carbon* **2001**, *39*, 507–514. DOI: [10.1016/S0008-6223\(00\)00155-X](https://doi.org/10.1016/S0008-6223(00)00155-X).
- [35] Vikas, S.; Akhilesh, S. Nanotechnology: An Emerging Future Trend in Wastewater Treatment with It Innovative Products and Processes. *Int. J. Enh. Res. Sci. Technol. Eng.* **2012**, *1*, 1–8.
- [36] Shirazi, Y.; Tofighy, M. A.; Mohammadi, T.; Pak, A. Effects of Different Carbon Precursors on Synthesis of Multiwall Carbon Nanotubes: Purification and Functionalization. *Appl. Surf. Sci.* **2011**, *257*, 7359–7367. DOI: [10.1016/j.apsusc.2011.03.146](https://doi.org/10.1016/j.apsusc.2011.03.146).
- [37] Ibtissem, G.; Malika, T. Competitive Adsorption of Heavy Metals on Local Land Fill Clay: Review. *Arab. J. Chem.* **2015**, *8*, 25–31.
- [38] Yul, F.; Yanqing, W.; Jie, M.; Chi, Z. Adsorption of Lead on Multi-Walled Carbon Nanotubes with Different Outer Diameters and Oxygen Contents: Kinetics, Isotherms and Thermodynamics. *J. Environ. Sci.* **2013**, *25*, 193–205.
- [39] Chungsyng, L. C. Removal of Nickel (II) from Aqueous Solution by Carbon Nanotubes. *J. Chem. Technol. Biotechnol.* **2016**, *81*, 1932–1940. DOI: [10.1002/jctb.1626](https://doi.org/10.1002/jctb.1626).