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Synthesis, electron microscopy properties and adsorption studies of Zinc (II) ions (Zn^{2+}) onto as-prepared Carbon Nanotubes (CNTs) using Box-Behnken Design (BBD)

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ABSTRACT

The high levels of zinc (II) ions (Zn^{2+}) have long been harmful to the environment and this study explored the feasibility of adsorption of Zn^{2+} on as-prepared carbon nanotubes (CNTs) from simulated aqueous solutions in batch-model process. The as-prepared CNT using chemical vapor deposition (CVD) technique was systematically characterized using electron microscopy techniques. Effects of adsorption parameters were modeled using Box-Behnken design (BBD) of experiment and 99.50% Zn^{2+} ions removal was achieved at adsorbent dosage, 50 mg; pH, 6.0; contact time, 60 min and contact speed, 125 rpm. The Langmuir, Freundlich and Temkim adsorption isotherms were used to verify the as-prepared CNTs adsorption performance. It was found that the adsorption data were well fitted to the Langmuir model. Moreover, the kinetic studies revealed that the adsorption kinetic data follows a pseudo-second-order model. The results indicate high prospect of the as-prepared CNTs for Zn^{2+} ion removal.

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1. Introduction

Heavy metals such as antimony, arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium, and zinc in water have been the main concern for many years because of their toxicity towards the quality of both human health and its environment [1–5]. Although some of these heavy metals are essential in biological system [6], but at high concentration, these metals are toxic and harmful in nature because they do not degrade into harmless end products [7]. For instance, zinc ions above the permissible limits would have detrimental effects on human body, resulting in anemia, kidney failure, nervous system damage, liver damage, internal hemorrhage, respiratory disorders, dermatitis, skin ulceration, chromosome aberrations and cancer [6–9]. However, since the environmental regulations on the discharge of these heavy metals are getting stricter with time, the demand to remove these pollutants from wastewater using sustainable and efficient technologies becomes necessary [10,11]

Over the years, various techniques such as filtration, electrochemical treatment, chemical precipitation, ion exchange mechanisms, sedimentation and adsorption process have been reported for the removal of heavy metals from wastewater [10,12–15] Among this techniques, adsorption is considered as one of the most common methods which is eco-friendly,

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economical, simple to handle, adsorbent regeneration and efficiency in the removal of heavy metals from aqueous solutions [12,16]. In the removal of heavy metals from contaminated aqueous system using the adsorption process, the synthesis of efficient adsorbent is of utmost importance. Conventional credits have been attributed to nano-materials with high adsorption potentials and activity. These nano-materials possess functional group, excellent mechanical properties, high surface area and thermal stability that form complexes with any targeted toxic heavy metals by chelation [10,17].

Carbon nanotubes (CNTs) for heavy metals removal are unique and one-dimensional macro-molecules nano-materials that possess high aspect ratio with tremendous surface area to aid removal via adsorption process [10,17,18]. For instance, the comparisons of CNTs with other adsorbents by many researchers have found that CNTs have a relatively larger surface area, extraordinary surface morphology and good chemical and mechanical properties that provide a good opportunity for the removal of heavy metals [10,17–21]. However, the review of literature shown few studies on the interaction between dependent factors in adsorption of heavy metals with as-prepared CNTs using BBD of experiment. Thus, the optimization of adsorbent dosage, initial pH, contact speed and time by Box-Behnken design (BBD) will be very useful to reduce sludge amount and reach the aim of saving cost during the study of adsorption process.

In this study, adsorption of $Zn^{2\pm}$ on as-prepared CNTs from simulated aqueous solutions in batch-mode process were investigated. The properties of as-prepared CNT were characterized using electron microscopy techniques and the adsorption parameters, including adsorbent dosage, initial pH value, contact time and contact speed were investigated and optimized by Box-Behnken design (BBD) of experiment, while, the interaction between the optimized parameters were validated using MINITAB software V16. Adsorption isotherms model; Freundlich, Langmuir and Temkin isotherms were fitted to the data in the batch system for evaluation. Finally, the kinetic studies were performed to explore and predict the adsorption of $Zn^{2\pm}$ ions onto the as-prepared CNTs.

2. Materials and methods

2.1. Materials

Chemicals used in this study include Zinc (II) trioxonitrate (V) hexahydrate, sodium hydroxide, and trioxonitrate (V) acid were obtained from Sigma Aldrich and they were all of analytical grade with percentage purity in the range of 98–99.99%. Acetylene and Argon gases were purchased from British Oxygen Company/Brin's Oxygen Company (BOC Gases Nigeria Plc, Lagos).

2.2. Methods

2.2.1. Preparation of as-prepared CNTs adsorbent

The as-prepared CNTs adsorbent was synthesized in a CVD reactor. The catalyst used for the synthesis, which was thoroughly characterized in earlier studies [22], had a BET surface area of 3.76 m^2/g, pore volume of 1.9×10^{-3} cm^3/g and pore size of 0.5986 nm, with lattice fringes and particle size of 0.3 nm and 29–31 nm respectively. 0.5 g of the catalyst ($NiFe_2O_4$/kaolinite) was used for the synthesis in a CVD furnace at a heating rate of 10 °C/min in argon (Ar) flow environment (20 mL/min) to create an inert environment, removal of contaminants and prevent oxidation of the catalyst during the experiment. Once the reaction set temperature was attained (650 °C), the Ar flow rate was adjusted to 280 mL/min and C_2H_2 was then introduced at its required flow rate (180 mL/min). The process was allowed to proceed until the reaction time of 30 min was reached after which the flow of C_2H_2 was stopped. Subsequently, the furnace was allowed to cool down to room temperature under a continuous flow of argon (20 mL/min) and the CNTs deposit was weighed.

2.2.2. Characterization of the as-prepared CNTs adsorbent

The morphology of the as-prepared CNTs adsorbent was characterized by high resolution scanning electron microscopy (HRSEM)/ Energy dispersive X-ray spectroscopy (EDX) and high resolution transmission electron microscopy (HRTEM)/ selected area electron dispersion (SAED), Specific surface area/ pore volume by Brunauer-Emmet-Teller (BET) analysis (NOVA 4200e model) and particle size by dynamic light scattering (DLS) technique (Zetasizer Nano-S series).

2.2.3. Preparation of stock solution and the batch adsorption process

Analytical-grade zinc trioxonitrate (V) hexahydrate was used to prepare a stock solutions containing 1000 mgL^{-1} of Zn^{2+}metal ions, which were further diluted with distilled water to attain the desired concentrations. In this study, the initial concentration of $Zn^{2+}$was determined to be 2 mgL^{-1} and the prepared stock solution was used for the batch adsorption experiments.

Batch adsorption experiments were conducted using 250 mL conical flasks by investigating four important factors at three equally spaced levels, coded as −1, 0 and 1. The relationship between the actual and coded values for each factor is presented in Table 1. The actual adsorbent dosage range 25 – 50 mg was treated with the prepared stock solutions. The conical flask was sealed with foil paper and then mounted on a shaker (SHZ-82 by Thermostatic Laboratory, China). The shaker was operated at 30 °C and the chosen range of contact speed 100 - 150 rpm was applied during the sharking with a solution pH that ranged from 4 to 8. The actual contact time 40 - 60 min was considered. Depending on the four factors; the BBD required 26 different combinations of experiments. Regression and statistical significance analysis of the models were

Table 1
Actual and coded values for four factors for Box-Behnken designs (BBD).

Parameters	Coded factor level		
	−1	0	+1
Adsorbent Dosage (mg)	25	37.5	50
Initial pH values	4	6	8
Contact Time (min)	30	45	60
Contact Speed (rpm)	100	125	150

Zn^{2+} ion stock solution = 2 mgL^{-1} vol = 10 mL.

done on the obtained data by MINITAB software V16, which was also used to depict the contour map. The pH value of the stock solution was adjusted using 0.5 M NaOH or 0.5 M HNO_3 solution. The samples were filtered by 0.42 µm pore size filter paper. The atomic adsorption spectrometer (AAS) (PerkinElmer Analyst 400, Perkin-Elmer) was employed to determine the initial and final concentrations of the Zn^{2+} ions in order to calculate the amount of metal ion adsorbed by the as-prepared CNTs adsorbent. Eqs. (1) and (2) were used to calculate the metal ion adsorption capacities onto as-prepared CNTs adsorbent at a certain time designed (t) and also to calculate the adsorption equilibrium of the metal ions respectively.

$$Percentage\ removal\ of\ ficient\ of\ Zn\ ion = \frac{C_o - C_t}{C_o} \times 100 \tag{1}$$

$$q_e = \frac{(C_o - C_e)V}{W} \tag{2}$$

Where, C_o and C_t are the initial and final concentration of Zn^{2+} (mg/L) at time (t). q_e is the equilibrium adsorption capacity of the as-prepared CNTs adsorbent (mg/g), C_e is the equilibrium concentration of Zn^{2+} (mg/L), V is the volume of Zn^{2+} solution (L) and W is the weight of the adsorbent (g).

2.2.4. Adsorption isotherm

The adsorption isotherm study for Zn^{2+} ion was carried out by preparing five different concentrations of 5, 10, 15, 20 and 25 mgL^{-1} of Zn^{2+} ions stock solution. The optimum conditions in Section 2.2.3 (adsorbent dosage, initial pH value and contact speed) were used to conduct this experiment. The AAS was used to measure the final concentration of the solutions. The isotherm data were correlated with the Langmuir, Freundlich and Temkim models in Eqs. (3), (4) and (5) respectively to get the best model [17,23,24].

$$q_e = \frac{Q_o K_L C_e}{1 + K_L C_e} \tag{3}$$

$$q_e = K_f C_e^{\frac{1}{n}} \tag{4}$$

$$q_e = \frac{RT}{b} In(A_T C_e) \tag{5}$$

Where, q_e is the adsorption capacity of the adsorbent at equilibrium in mg/g, C_e is the concentration of metal ion at equilibrium in mg/L, Q_o is the maximum adsorption capacity of the metal monolayer in mg/g, K_L is the Langmuir constant known as bonding energy of adsorption in L/mg, K_f is the Freundlich constant related to the adsorption capacity of the adsorbent, n is the empirical constant depicting the intensity of adsorption which varies with the heterogeneity of the adsorbent, R is the universal gas constant (8.314 J/mol/K), T is temperature at 298 K, A_T and b are Temkim isotherm equilibrium binding constant. Linearizing Eqs. (3), (4) and (5) gives Eqs. (6), (7) and (8) respectively.

$$\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{Q_o K_L} \frac{1}{C_e} \tag{6}$$

$$In\ (q_e) = In\ \left(K_f\right) + \frac{1}{n}\ In(C_e) \tag{7}$$

$$q_e = \frac{RT}{b} In\ (A_T) + \frac{RT}{b}\ In(C_e) \tag{8}$$

$$q_e = \beta\ In\ (A_T) + \beta\ In\ (C_e) \tag{9}$$

$$Where\ \beta = \frac{RT}{b}$$

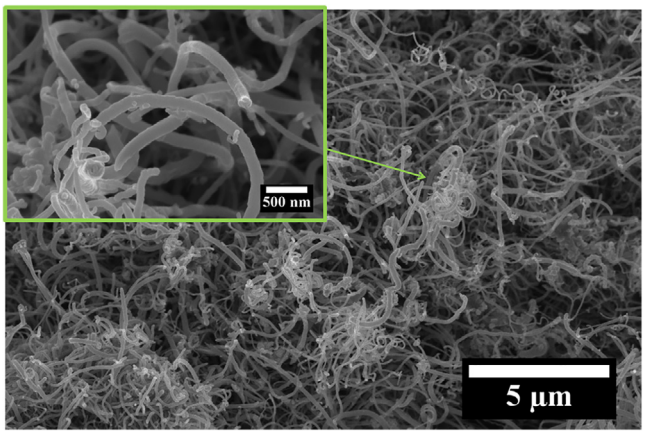

Fig. 1. HRSEM Micrograph of the as-prepared CNTs.

2.2.5. Kinetic study

The kinetics studies were carried out using the optimum parameters (adsorbent dosage, pH value and contact speed) in Section 2.2.3 decided by the batch adsorption process. Four (4) different concentrations of Zn^{2+} ions stock solution of 0.5, 1.0, 1.5 and 2.0 mg/L were used. In order to describe the kinetic process between aqueous and solid phase, the pseudo first order rate was used for surface adsorption of Zn^{2+} ion onto CNTs adsorbent. This model is given by Lagergren as presented in Eq. (10) [25,26].

$$In\ (q_e - q_t) = In\ (q_e) - \frac{K_1}{2.303}\ t \tag{10}$$

The pseudo second order rate equation presented by Ho to describe the kinetic adsorption of divalent metal ion onto the as-prepared CNTs adsorbent is expressed in Eq. (11) [25,26].

$$\frac{t}{q_t} = \frac{1}{K_2 q_e{}^2} + \frac{1}{q_e}\ t \tag{11}$$

Where q_e and q_t are the amount of adsorbed Zn^{2+} ion in mg/g on the MWCNTs adsorbent, at equilibrium and time t, respectively, while K_1 in/min and K_2 in $gmg^{-1}min^{-1}$ are the rate constants of first- and second-order adsorption, respectively

3. Results and discussion

3.1. Characterization of as-prepared CNTs

Presented in Fig. 1 is the HRSEM micrograph of the as-prepared CNTs. The micrograph show a densely populated with branched tubes-like formations having few agglomerated branches and tiny particles on the surfaces. The inserted image in Fig. 1 shows the presence of a uniformly diameter distribution of the as-prepared CNT which are spongy and porous in nature. This observable feature is like those in the literature [27]. A typical of HRTEM images (Fig. 2(a)) shows many rope-like structures with encapsulated metal nanoparticles within the nanotubes. Also inserted in Fig. 2(a) is the SAED pattern (a(ii)) which confirmed a well graphitized CNT formation. It is obvious evidence that the CNTs prepared in this study is multi-walled CNTs (Inserted Figure (b(iv)) in Fig. 2(b)) which consist of many cylindrical graphite layers arranging regularly in the inner wall with a fringe lattice of ~0.34 nm. According to the EDS spectrum in Fig. 2(b), carbon atom (C) shows a prominent peak with Fe, Ni, Al, and Si, in a trace amount as a result of the Fe-Ni/kaolin catalyst used in the synthesis. These trace elements produce the charges on the surface of the as-prepared CNTs and create electrostatic forces of attraction between the as-prepared CNTs adsorbent and Zn^{2+} ion in the stock solution during adsorption process. Furthermore, the BET surface area, pore volume and pore diameter of the as-prepared CNTs were recorded to be 379.25 m^2g^{-1} with 0.1019 cc/g and 31.90 Å respectively. The obtained surface area was found to be higher than the property reported by Kariim et al. [28]. The variation in the surface area might be due to the difference's catalyst support, metal loadings and the calcination temperature. Fig. 3 show a correlation chart between the length, diameter and aspect ratio of the as-prepared CNTs which was developed based on the Z-average diameter (D_h) from the DLS machine. Eq. 12 was used for the estimation of length and aspect ratio based on the Z-average from DLS analysis [10].

$$D_h = \frac{L}{In\left(\frac{L}{d}\right) + 0.32} \tag{12a}$$

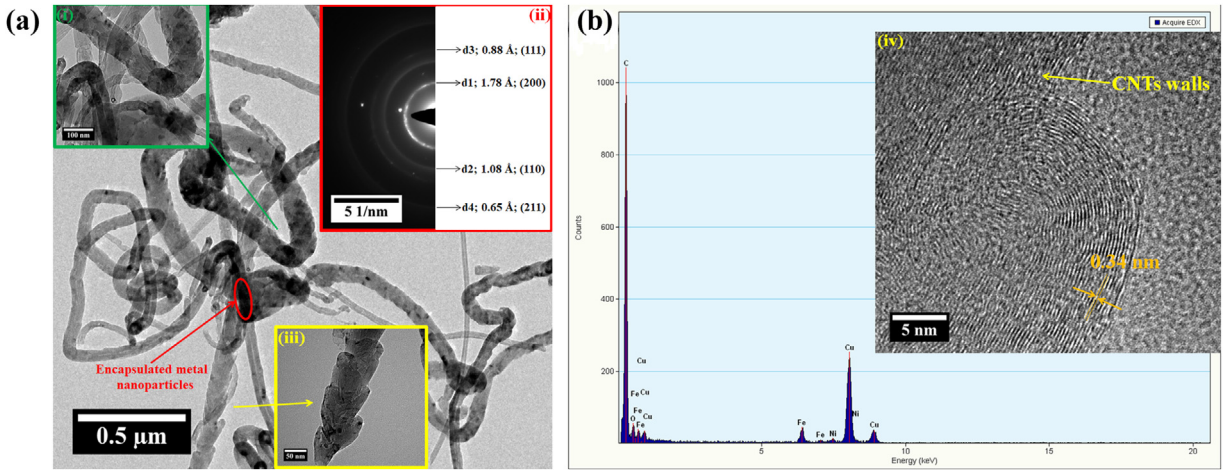

Fig. 2. (a) HRTEM Micrograph (b) EDX spectrum of the as-prepared CNTs.

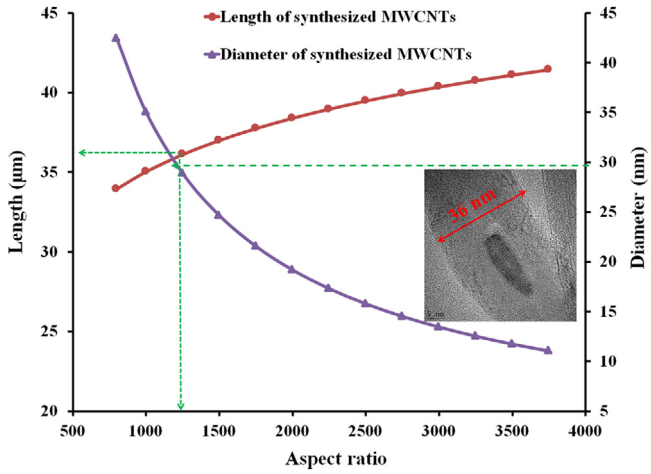

Fig. 3. Correlation chart between the aspect ratio, length and diameter of the as-prepared CNTs.

Where, D_h is the hydrodynamic diameter (Z-average) from the DLS, and "L" and "d" are the length and diameter of the nanotube, respectively. The correlation chart result in Fig. 3 revealed that the as-prepared CNTs has an aspect ratio (L/d) of about 1200 and length of 36 µm which is an important property of a CNTs as a good adsorbent for an adsorption process.

3.2. The effects of adsorbent dosage, initial pH, contact time and contact speed on the percentage removal of Zn^{2+} ion onto as-prepared CNTs on the contour plots

Using BBD, the percentage removal of Zn^{2+}ions on the as-prepared CNTs was optimized and the results of the Zn^{2+} removal responses were presented in Table 2. From the result of the optimization, it was found that the optimal conditions for the maximum percentage removal of Zn^{2+} (99.50%) was attained with at adsorption dosage, 50 mg; pH, 6; contact time, 60 min and contact speed, 125 rpm while the minimum removal of Zn^{2+} ion of 76.53% was attained at experimental condition; adsorbent dosage, 50 mg; pH, 4; contact time, 45 min and 125 rpm contact speed.

Presented in Fig. 4 are the contour view, plotted to study the relationship between optimizing parameters and the percentage removal of Zn^{2+} ion onto as-prepared CNTs. Fig. 4(a), (b) and (c) show the relationship between adsorbent dosage and percentage removal of Zn^{2+}ion. It is obvious that the percentages removal of Zn^{2+}ion increase with increased in the adsorbent dosage from 25 mg to 50 mg. This can be attributed to increases in the availability of the surface area for the adsorption process, in which more of the Zn^{2+} ions were adsorbed onto the surface of the as-prepared CNTs. Also, Fig. 4(a), (d) and (e) show the relationship between pH values and the percentage removal of Zn^{2+}ions. As evident from the Figures, the percentage removal of Zn^{2+} ions were favorable at higher initial pH value because the acidic state increases the competition between the Zn^{2+} and H^+ in regards to the adsorption into the CNT. By increasing the pH value, the competition

Table 2
The results of Zn^{2+} removal responses using BBD of experiment.

Runs	Adsorbent Dosage (mg)	pH values	Contact Time (min)	Contact Speed (rpm)	Percentage removal of Zn^{2+} (%)
1	25.00	4	45	125	76.72
2	50.00	4	45	125	76.53
3	25.00	8	45	125	77.70
4	50.00	8	45	125	89.35
5	37.50	6	30	100	78.20
6	37.50	6	60	100	97.13
7	37.50	6	30	150	97.18
8	37.50	6	60	150	77.60
9	25.00	6	45	100	76.75
10	50.00	6	45	100	97.38
11	25.00	6	45	150	86.55
12	50.00	6	45	150	77.45
13	37.50	4	30	125	77.60
14	37.50	8	30	125	77.95
15	37.50	4	60	125	78.15
16	37.50	8	60	125	99.13
17	25.00	6	30	125	79.10
18	50.00	6	30	125	79.55
19	25.00	6	60	125	77.75
20	50.00	6	60	125	99.50
21	37.50	4	45	100	78.45
22	37.50	8	45	100	77.25
23	37.50	4	45	150	79.70
24	37.50	8	45	150	76.73
25	37.50	6	45	125	97.53
26	37.50	6	45	125	98.90

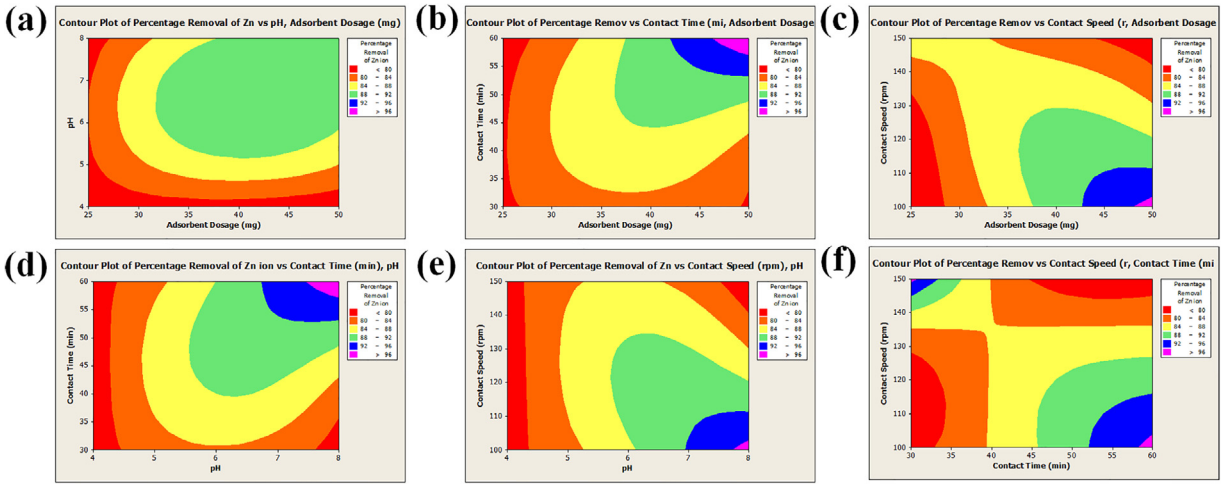

Fig. 4. Contour plot of percentage removal of Zn^{2+} ion onto as-prepared CNTs versus Interaction of (a) adsorbent dosage and pH (b) adsorbent dosage and contact time (c) adsorbent dosage and contact speed (d) pH and contact time (e) pH and contact speed (f) contact time and contact speed.

extinguishes as the OH^- ions increases. This shows that the percentage removal of Zn^{2+}ions perform better in high pH medium than lower medium in the sense that more of the ions were absorbed onto the as-prepared CNTs surface.

Likewise, Fig. 4(b), (d) and (f) show the interaction between the contact time and the percentage removal of Zn^{2+}ions. These figures show that the percentage removal of the Zn^{2+}increases with increased in contact time for the batch adsorption process. The reason for this observation can be attributed to the fact that at longer contact time, the interaction between the Zn^{2+} ions and the adsorbent surfaces increases which favors adsorption process. Furthermore, Fig. 4(c), (e) and (f) show the interaction between contact speed and percentage removal of Zn^{2+} ions. These figures show that, the Zn^{2+} ions adsorption rate increases, with increased in contact speed. This is attributed to the increased in kinetic energy in which more molecules collide with each and enhance increases the adsorption capacity of the Zn^{2+} ions into the as-prepared CNT binding sites.

Table 3
The ANOVA of results of Zn^{2+}ion removal response.

Source	Seq SS	DF	Adj MS	F-value	P-value Prob > *F*	Status
Regression	1878.17	14	134.155	6.35	0.002	Significant
Linear	400.12	4	100.029	4.73	0.018	Significant
A	170.17	1	170.178	8.05	0.016	Significant
B	87.8	1	87.804	4.16	0.066	Inignificant
C	131.21	1	131.209	6.21	0.030	Significant
D	10.93	1	10.925	0.52	0.551	Insignificant
Square	631.21	4	157.860	7.47	0.004	Significant
A^2	29.57	1	255.065	12.16	0.004	Significant
B^2	373.03	1	573.750	27.16	0.000	Significant
C^2	10.24	1	91.600	4.34	0.061	Insignificant
D^2	218.60	1	218.605	10.35	0.008	Significant
Interaction	846.61	6	141.102	6.68	0.004	Significant
AB	35.05	1	35.046	1.66	0.224	Insignificant
AC	113.42	1	113.423	5.37	0.041	Significant
AD	220.97	1	220.968	10.46	0.008	Significant
BC	106.40	1	106.399	5.04	0.046	Significant
BD	0.02	1	0.018	0.00	0.977	Insignificant
CD	370.76	1	370.755	17.55	0.002	Significant
Residual	232.40	11	21.127			–
Lack of fit	231.46	10	23.146	24.66	0.156	Insignificant
Pure Error	0.94	1	0.938			–
Total	2110.56	25				–

A= Adsorbent dosage *B*= Initial pH *C*= Contact Time *D*= Contact speed.

3.3. Statistical analysis of adsorption of Zn^{2+} ion onto as-prepared CNTs

3.3.1. The establishment and test of the regression model

Table 3 presents the results of the standardized residuals of Zn^{2+} ion removal responses from Table 2, and it can be concluded that the responses deviate strongly from normality [29]. The Lack-of-Fit test is used to analyze whether the model fit is appropriate. It is important to note that, if the "Lack-of-Fit F-values" is not significant, it shows that the model fits data well and there is no significant influence from other factors under investigation which therefore implies that the statistical significance of a response functions is check with the F-test [30]. In view of this, it can be deduced that the four factors (i.e. adsorbent dosage, pH, contact time and contact speed) were all statistical significance on the experimental response presented in Table 2.

The estimated BBD coefficients of the statistic model by the ANOVA for the responses were given in Table 3. The R^2-value of 0.8899 was obtained, which implies that the modeled response fit well with the experimental data and the equation is reliable and accurate. In addition, Table 3 also revealed that the linear terms were significant expect for the initial pH and contact speed. Also, it was observed that only the contact time is insignificant for the quadratic terms of the model, while the interactive terms; adsorbent dosage/ initial pH and initial pH / contact speed were found to be insignificant. Therefore, it can be deduced that the response regression equation is extremely statistically significant; as a result, the proposed regression model is appropriate. Based on the quadratic model, the predicted response for the percentage removal of Zn^{2+} ion from the prepared stock solutions in terms of coded and actual factors for the significant parameters were as follows:

$$Percentage\,Removal of\,Zn^{2+} = +98.22 + 3.77 \times A + 3.31 \times C - 7.71 \times A^2 - 11.34 \times B^2 - 6.95 \times D^2 + 5.33 \times AC + 5.16 \times BC - 9.63 \times CD \tag{12b}$$

$$Percentage\,Removal of\,Zn^{2+} = -455.2183 + 4.9857 \times A + 3.1908 \times C - 0.0493 \times A^2 - 2.8354 \times B^2 - 0.0111 \times D^2 + 0.0284 \times AC + 0.1719 \times BC - 0.0257 \times CD \tag{13}$$

3.4. Adsorption isotherm studies of Zn^{2+} ion onto as-prepared CNTs

The optimum optimization conditions (adsorbent dosage, 50 mg; time, 60 min; contact speed, 125 rpm) from the batch adsorption process in Table 3 were used in the isotherm's studies. The linear plots of the Langmuir, Freundlich and Temkin isotherm models for the adsorption of Zn^{2+}ion onto as-prepared CNTs are presented in Fig. 5(a)-(c) respectively. The straight lines plots confirmed satisfactory fits of the application of the models to the adsorption of Zn^{2+}ions onto the as-prepared CNTs. Base on the plot in Fig. 5(a), (b) and (c), the intercepts and slopes were computed for the Langmuir, Freundlich, and Temkin constants and the values obtained were presented in Table 4.

From Table 4, the R^2 value obtained for the Langmuir isotherm was 0.9915, and the values of Q_O and K_L were calculated to be 0.000164 mg/g and 61.52 L/mg respectively. Meanwhile, for the Freundlich isotherm, the R^2 value obtained was 0.9708, K_F and n were evaluated to be 2.5909 and 0.11447 respectively, while the R^2, A_T and β were calculated to be 0.8401,

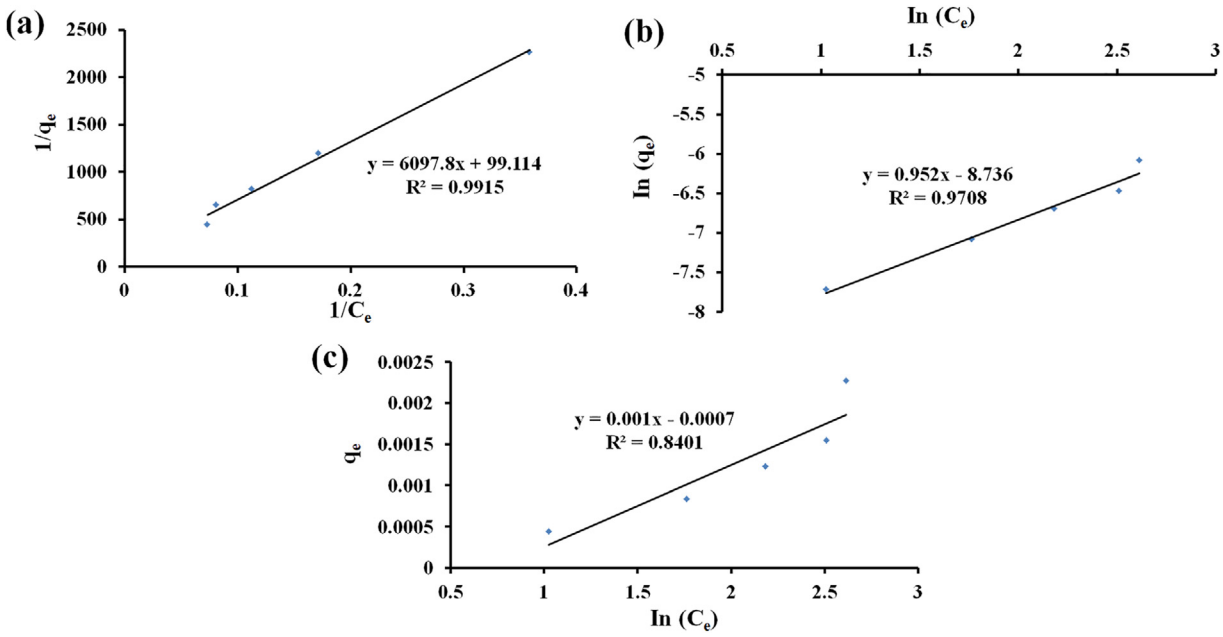

Fig. 5. (a) Langmuir (b) Freundlich and (c) Temkin Adsorption isotherms for Zn^{2+} ions adsorbed onto as-prepared CNTs.

Table 4
The results for both Langmuir and Freundlich models of Zn^{2+} ions.

ions	Langmuir isotherm			Freundlich isotherm			Temkin isotherm		
	Q_O (mg/mg)	K_L (L/mg)	R^2	K_F (mg^{-1})	n	R^2	A_T (L/g)	β	R^2
Zn^{2+}	0.000164	61.52309	0.9915	2.5909	0.11447	0.9708	0.4966	0.001	0.8401

0.4966 L/g and 0.001 respectively for Temkin model. The higher value obtained for the correlation coefficient of Langmuir model ($R^2 = 0.9915$) compared to that of the Freundlich model ($R^2 = 0.9708$) and Temkin model ($R^2 = 0.8401$), indicates that the Langmuir model is more appropriate to describe the adsorption characteristic of Zn^{2+} ions onto as-prepared CNTs in this study. The Langmuir, Freundlich and Temkin equations were developed to fit Zn^{2+} ions equilibrium adsorption capacity, q_e onto as-prepared CNTs. The Eqs. (14), (15) and (16) represent the developed Langmuir, Freundlich and Temkin equations for adsorption of Zn^{2+} ions onto as-prepared CNTs adsorbent.

The developed Langmuir Equation;

$$q_e = \frac{0.01009\ C_e}{1 + 61.52309\ C_e} \tag{14}$$

The developed Freundlich Equation;

$$q_e = 2.5909\ C_e^{8.735913} \tag{15}$$

The developed Temkin Equation;

$$q_e = 0.001\ In\ (0.4966\ C_e) \tag{16}$$

3.5. Adsorption kinetic studies of Zn^{2+} ion onto as-prepared CNTs

In order to investigate the controlling mechanism of adsorption processes (i.e. mass transfer and chemical reaction), the pseudo first order and pseudo second order equations are applied to model the kinetics of Zn^{2+} adsorption onto as-prepared CNTs. Fig. 6(a) shows a straight line plots of $In\ (q_e - q_t)$ against time (t) for different initial concentration of the Zn^{2+} ion stock solution while the plots of linearized pseudo second order reaction at different initial concentration of the Zn^{2+} ion stock solution were shown in Fig. 6(b).

The pseudo first order and pseudo second order rate constants from Fig. 6(a) and (b) for different Zn^{2+} ions concentrations were determined and the results are presented in Table 5 along with the corresponding correlation coefficients. The plot of the pseudo second order model in Fig. 6(b) yields very good fit straight lines with correlation coefficients, $R^2 > 0.99$ as compared to the plot of the pseudo first order model. More so, the theoretical values of q_e for the pseudo second order also agree very well with the experimental values. Based on these findings, it can be suggested that the adsorption

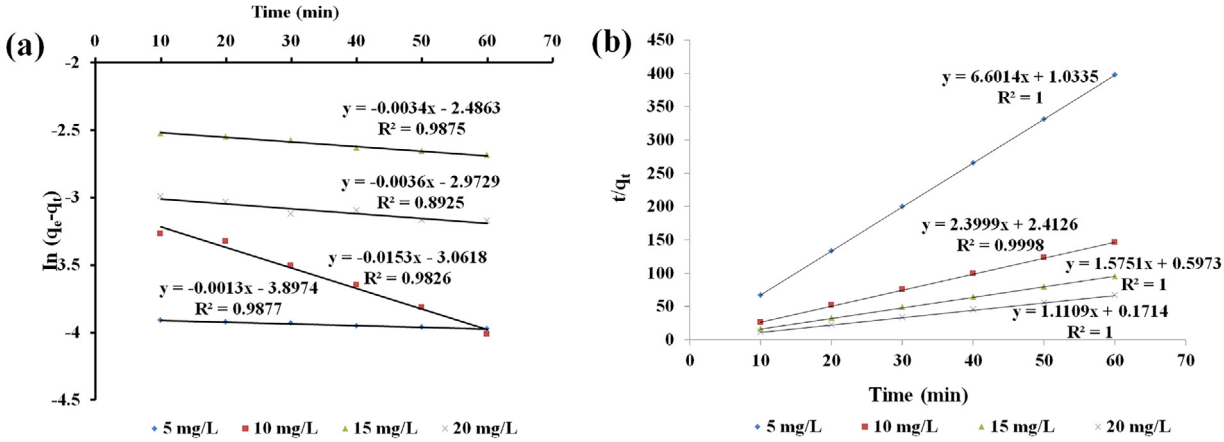

Fig. 6. (a) Pseudo first order reaction (b) Pseudo second order reaction for Zn^{2+} ions adsorbed onto as-prepared CNTs at different initial concentrations.

Table 5
Comparison between the adsorption rate constants, q_e, estimated and correlation coefficients associated with pseudo first order and pseudo second order rate equations.

Initial Zn^{2+}ion Conc. (mg/L)	Pseudo first order rate equation			Pseudo second order rate equation			q_e exp (mg/g)
	K_1 (min^{-1})	q_e (mg/g)	R^2	K_2 (g $mg^{-1}min^{-1}$)	q_e (mg/g)	R^2	
5	0.0013	0.0203	0.9877	42.1659	0.1515	1.0000	0.17
10	0.0153	0.0468	0.9826	2.3873	0.4167	0.9998	0.43
15	0.0034	0.0832	0.9875	4.1536	0.6349	1.0000	0.70
20	0.0036	0.0512	0.8925	7.2001	0.9002	1.0000	0.94

of Zn^{2+} ions onto as-prepared CNTs follows the pseudo second order kinetic model, which relies on the assumption that chemisorption may be the rate limiting step for this study. It is worth to mention that in chemisorption, the metal ions stick to the adsorbent surface by forming a covalent bond and tend to find sites that maximize their coordination number with the surface [25].

4. Conclusions

CNTs was successfully synthesized using $NiFe_2O_4$/kaolinite catalyst via conventional chemical vapor deposition method, acetylene as carbon source and argon as carrier gas. The HRTEM/SAED, HRSEM/EDX, BET, and DLS analyses results revealed that the as-prepared CNTs have good capability for Zn^{2+} ion removal from aqueous solution. The optimum percentage removal Zn^{2+} ion of 99.50% was obtained under the optimum conditions: 50 mg adsorbent dosage, 6 initial pH value, 60 mins contact time and 125 rpm contact speed. The equilibrium data were fitted by the Langmuir model ($R^2 = 0.9915$) better than the Freundlich model ($R^2 = 0.9708$) and Temkin model ($R^2 = 0.8401$). The kinetic adsorption parameters showed that the overall adsorption can be better described by the pseudo second order than the pseudo first order kinetic model. Finally, it was found that the as-prepared CNTs is a good adsorbent for Zn^{2+} ions removal from aqueous solution.

Conflict of interest

No potential conflict of interest relevant to this article was reported.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.sciaf.2019.e00069.

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