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REMOVAL OF CADMIUM FROM SURFACE WATER OBTAINED AT THE OIL EXPLORATION SITE OF NIGER-DELTA REGION, NIGERIA: OPTIMIZATION OF THE BATCH-SORPTION PROCESS.

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ABSTRACT

The aim of the study was to determine the efficiency of cadmium contaminant removal from surface water situated near oil exploration sites in Niger-Delta Region. And to optimize the conditions, that is parametric factors for batch-sorption process of cadmium removal by studying as a function of the contact time, temperature, dosage (sorbent loading) and agitation speed using already synthesized bimetallic supported multi-walled carbon nanotube sorbents. The batch-sorption process was fully optimized in a system using 2^4 *factorial model. The optimum values of the parametric factors were found to be contact time 59.729 min, temperature 30.989* ^oC*, dosage 0.112 g and agitation 594.988 rpm, respectively. The removal efficiency, in this case, that is the maximum value of 99.071 % was obtained by the empirical model having desirability of 1.000 (and 98.96 % was experimentally verified). Therefore, this study showed the validity of the empirical model and sorption-capability of carbon nanotubes to effectively remove cadmium ions from the polluted surface water obtained at the oil exploration sites in the Niger-Delta region of Nigeria.*

1.0 INTRODUCTION

Human habitation has recently expanded to near frequent oil and gas explorations. There are an estimated 600 - 700,000 oil fields in a hundred or more countries with 1600 billion of known crude oil reservoir, globally (CIA, 2017; Bentley, 2002). Operational oil fields have emerged to possibly impact the health and environment of fewer than 1 million people in the world (O'Callaghan-Gordo *et al.,* 2016). Exploration has a destructive influence as a result of industrial progress and economic development. Niger-Delta Region Nigeria has overly 200 oil fields and 160 flow stations with resulting environmental pollution and this has become a persistent problem to both the aquatically and terrestrial expanding populations, as people become nearer to exploration activities (Osuji, 2002). Such behavior could have a negative impact on people's health. It is further evident that exploration and production activities introduced among others, many heavy metal contaminants into the ecosystems to include soil and groundwater (boreholes) in places where such activities are operated (Asia *et al.,* 2007). Heavy metal concentrations have been evaluated with respect to extraction of oil and that crude oil contains metals such as vanadium (V), nickel (Ni), lead (Pb) and cadmium (Cd). In addition, drilling fluids employed during the activity may contain other metals like chromium and zinc in varying fraction to the capacity of the oil field (Johnston et al., 2019; Lord, 1991).

During exploration, the formation waters that accompanied the crude oil, that is produced water (PW), drilling cuttings and wastes, are also another point sources of heavy metal contaminants entering the water bodies from functional drilling operations (Norwegian Oil and Gas, 2013). According to Lauer *et al,* wastewaters from drilling processes contained a high concentrations of toxic metal contaminants which include barium (Ba), cadmium (Cd), nickel (Ni), manganese (Mn) and lead (Pb) (Lauer *et al.,* 2016). The oil or water-base fluids, for example, can be discharged into oil field pits with the potentials to leach directly into the groundwater or soil. This in turn, may harmfully expose to local populations. Even, the surface water (streams, rivers, lakes etc.,) are disturbed by these anthropogenic sources and land mining that is discharged into the water basin. Johnston *et al.,* have reviewed the roles of oil extraction activities on local surface water quality and the impact of drilling oil wastewater discharge into a water basin, to adversely affect the quality of the surface water (Johnston et al., 2019).

For example, cadmium, which is present in oil and drilling fluids, is the second most toxic heavy metal and major pollution in oil drilling wastewater. FAO recommended that cadmium levels not exceed 0.01 mg/L in industrial effluents (Antil et al, 2001) and 0.003 - 0.005 mg/L in potable water (Venkateswarlu and Yoon, 2015; WHO, 2011). Other studies have reported its health challenges to include kidney failures, nausea, lung damages, hypertension to mention a few (Adelabu et al, 2020; Esvandi et al 2019). Cadmium in wastewater has been treated with different processes such as coagulation, precipitation, membrane separation, filtration, ion exchange, redox reaction and adsorption (Zhu et al., 2019). Adsorption process with materials on nanoscale metric has been recently, over two decades, designed as a method for wastewater treatment due to high efficiency, low operational cost and simplicity; reusability of adsorbent and pollutants (Foroutan *et al.,* 2020; Snoussi *et al.,* 2016). And amongst the nanoscale adsorbents, carbon nanotubes have been extensively explained and used in the remediation of cadmium ions from wastewater (Gupta and Saleh, 2013). Carbon nanotubes (MWCNTs) possess good electrical, mechanical, chemical and physical properties that lead to possible utilization in adsorption process. The appreciable thermal and chemical stability as well as large surface area (< 100 nm) make them better materials for adsorptive kinetics study (Wang *et al.,* 2002) MWCNTs possess high sorption capacity in relation to activated charcoal in a sorption process. This is a result of strong contacts between sorbates and MWCNTs that exist on the surfaces of carbon nanotubes during the adsorptive process (Long and Yang, 2001). MWCNTs have an abundant potential application of removing heavy metal pollutant, for example copper and lead ions, from surface water bodies (Peng *et al.,* 2005; Li *et al.,* 2006).

Previously, studies have discussed impacts of heavy metals pollution from oil drilling activities on the soil and boreholes in the Niger Delta, with little or no work on heavy metal contaminants in surface waters near drilling activities as reviewed by Johnston *et al.,* (2019), and the implication of remediating the surface water. Our previous study has identified the presence of lead (Pb) and its remediation in surface water near oil drilling sites in Delta State, Nigeria (Gbajabiamila *et al.,* 2020). Therefore, the present study aims at removing cadmium Cd, contaminants in the surface water flowing behind oil exploration sites in the state. It also proposes to optimize the efficient removal of cadmium ions with a full factorial model.

A full factorial model is used to achieve overall process optimization (Brasil et al., 2005; Montgomery, 2001). The model determines the influence of individual factors on the response and how the effect of a single factor varies with the variation in the level of the other factors (Arenas *et al.,* 2006), and to understand the interaction effects among the different factors, the Design of Experiment (DoE) technique was employed in the case. This technique was employed to limit the number of experiments, process time, as well as overall cost and to achieve a better response. The benefits of the factorial model over one-factor-at-a-time (OFAT) experiments are to obtain efficient processes and detect interactions (Erper et al., 2011). Other studies employing design of experiment (DoE) have shown the importance of the methodology (Torrades and Garcia-Montaño, 2014; Barka et al., 2014). Therefore, process optimization for the removal of Cd^{2+} ions present in surface water near oil exploration sites using 2^4 factorial model design was experimented with bimetallic supported carbon nanotubes (MWCNT).

2.0 MATERIALS AND METHODS

In this work, all chemicals used were of analytical grades and high percentage purity of 95-99.9% without any prior purification. The distinctive properties of bimetallic/Kaolin support in this study have been reported (Kariim et al., 2015)

2.1 Production of multi-walled carbon nanotubes (MWCNT)

The method used in the production of carbon nanotubes has been reported in our previous study. (Gbajabiamila *et al.,* 2020). One 1.0 g bimetallic catalyst was transferred into a crucible and placed in the center of the chemical vapour deposition (CVD) reactor. The reactor was purged at a stream rate of 50 ml/min at a steady heating rate until the temperature reached 700 ºC. Acetylene gas was released at 100 ml/min as the initial nitrogen stream was raised, being a carrier gas, to 100 ml/min for response (reaction) time of 45 min. The stream of nitrogen was then declined to 50 ml/min after the response time and the acetylene gas was stopped. The instrument was allowed to cool to 25 ºC. The carbon nanotubes were obtained and kept for further analysis.

2.2 Collection of Sample (Surface water)

The surface water sample was collected in polythene bottles from five (5) different strategic points within the breadth of a river near oil drilling sites. 5.0 ml HNO_3 was added to the 100 mL of water collected to check metals sticking to the bottle wall.

Still, 10 ml water samples were digested with 5 ml HNO_3 and 2 ml HCl. Then, distilled water, DI 15 ml was added to the digest and filtered using Whatman paper No. 45. The filtrate was made up to a 50 ml volumetric flask with DI water. The initial level of Cd^{2+} pollutants was analyzed using Shmadzu Atomic Absorption Spectrometer, AAS (Buck Scientific Model210VGP).

2.3 Adsorption Studies

The batch-sorption process was employed in this work and the multi-walled CNT sorbents were applied for the process, as described in the previous study (Gbajabiamila *et al.,* 2020). The relative effects of control factors, that is contact time (min), temperature (°C) dosage (g) and agitation (rpm) were studied on the %removed cadmium ions, Cd^{2+} by the multi-walled CNT sorbents.

$$\%R = \left(\frac{C_O - C_e}{C_o}\right) \times 100 \quad (1)$$

Where R is the removal efficiency, C_o is the initial metal ions level and C_e is the final metal ions level after the response (reaction) time.

2.4 Experimental Design and Statistical Analysis

A statistical method was adopted to optimize the Cd^{2+} batch-sorption process. A factorial model is composed of coefficients that were multiplied by corresponding factors. Equation (2) expresses relationship between factors and response variables. It is a polynomial function that describes this relationship.

$$f(Y) = a_0 + \sum_{i=1}^{k} a_i x_i + \left(\sum_{i=1}^{k} a_{ii} x_i\right)^2 + \sum_{i=1}^{k-1} \sum_{j=2}^{k} a_{ij} x_i x_j + \varepsilon \quad (2)$$

Where Y denotes the response, a_0 is the intercept, a_i is the coefficient of linear factor effects, a_{ij} is the interaction coefficient, a_{ii} is the quadratic coefficients and ε is the error terms. In a 2^K factorial design, four *(k)* factors were varied over two (2) levels. Therefore, the total number of runs is derived by: $N = 2^4 = 16$. The equation based on the model with four variables (A, B, C, D) and their interaction terms can be given in the form of the following derivation:

$$Y = b_0 + b_1 A + b_2 B + b_3 C + b_{12} AB + b_{13} AC + \cdots \quad (3)$$

The Y is the response, bn is the coefficient related to factor n, and the letters, *A, B, C, ...* represent each variable in the model. The removal efficiency of Cd^{2+} was considered as a response. Table 1 illustrates the variables and their corresponding levels for the experiment. The levels were coded as *-1 (low) and +1 (high)*. Design variables of the full factorial model for the batch-sorption process include contact time (30–60 min), temperature (30–60 °C), dosage (0.1–0.2 g) and agitation speed (300–600 rpm).

Table 1: Experimental ranges and levels of independent variables for the factorial design

		Experimental Fields	
		Min.value	Max.value
Coded variables	Description	-1	+1
A	Contact time (min)	30	60
B	Temperature (°C)	30	60
C	Dosage (g)	0.1	0.2
D	Speed (rpm)	300	600

2.5 Optimization of Parameters

The experimental study is partly to evaluate possibly optimization parametric factors, singly or in combination, of a given level that will maximize the %removal of Cd^{2+} ions in the oil-polluted surface water, in order to remediate the environmental challenges posed. Accordingly, the optimization component in Design-Expert® 12 (Stat Ease Inc., 2020) was employed.

3.0 RESULTS AND DISCUSSION

Table 2: Design matrix in actual, coded units and experimental response results

Runs	Contact time	Temperature	Dosage	Speed	Coded values				Cd Removal (%)
1	30	60	0.1	600	-1	+1	-1	+1	26.89
2	30	30	0.1	600	-1	-1	-1	+1	44.34
3	60	30	0.1	300	+1	-1	-1	-1	89.93
4	30	60	0.1	300	-1	+1	-1	-1	29.17
5	60	30	0.2	600	+1	-1	+1	+1	96.68
6	60	60	0.1	600	+1	+1	-1	+1	89.44
7	30	30	0.2	600	-1	-1	+1	+1	27.37
8	60	30	0.2	300	+1	-1	+1	-1	87.03
9	60	60	0.1	300	+1	+1	-1	-1	91.24
10	60	30	0.1	600	+1	-1	-1	+1	98.96
11	30	60	0.2	300	-1	+1	+1	-1	28.68
12	30	60	0.2	600	-1	+1	+1	+1	26.41
13	30	30	0.1	300	-1	-1	-1	-1	29.79
14	30	30	0.2	300	-1	-1	+1	-1	27.58
15	60	60	0.2	300	+1	+1	+1	-1	92.96
16	60	60	0.2	600	+1	+1	+1	+1	72.41

Table 3: Analysis of variance (ANOVA) for the factorial model

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	14826.55	6	2471.09	126.53	<0.0001	significant
A-Contact Time	14305.36	1	14305.36	732.48	<0.0001	
B-Temperature	123.65	1	123.65	6.33	0.033	
C-Dosage	103.23	1	103.23	5.29	0.0471	
D-Speed	2.34	1	2.34	0.1199	0.7371	
BD	224.4	1	224.4	11.49	0.008	
CD	67.57	1	67.57	3.46	0.0958	
Residual	175.77	9	19.53			
Cor Total	15002.32	15				

Std.Dev.	4.42	**R^2**	0.9883
Mean	59.93	**Adjusted R^2**	0.9805
C.V%	7.37	**Predicted R^2**	0.9630
PRESS		**AdeqPrecisin**	28.0671

3.1 Mathematical model development

The MWCNTs Cd(II) ions adsorption and %removed are shown in Table 2. The MWCNTs showed high affinity for Cd (II) removed with 98.96% at contact time 60 min, temperature 30 °C, dosage 0.1 g, and speed 600 rpm respectively. The mathematical correlation between the responses and control factors in terms of the coded and actual values of the variables is presented in Equations *(4)* and *(5)*. Hence, three factors contact time A, temperature B, dosage C and interactions between temperature and speed BD were regarded as significant at a p <0.05, 95% confidence level. Therefore, discarding the insignificant terms from the model, the resulting model is expressed as:

$$\% \ Removed = +59.93 +29.90A -2.78B -2.54C +0.3825D -3.75BD -2.06CD \quad (4)$$

The equation in terms of coded values is given in Equation *(4)* which is useful for translating the relative impact of the factors by comparing the factors coefficients. It is deduced from the equation that contact time (A) has more significant impact on the % Cadmium removal than temperature (B) and dosage (C).

$$\% \ Removed = -67.16125 + 1.99342 \ Contact\ Time + 0.563667 \ Temperature + 72.50000 \ Dosage + 0.118550 \ Speed - 0.001664 \ Temperature * Speed - 0.274000 \ Dosage * Speed \quad (5)$$

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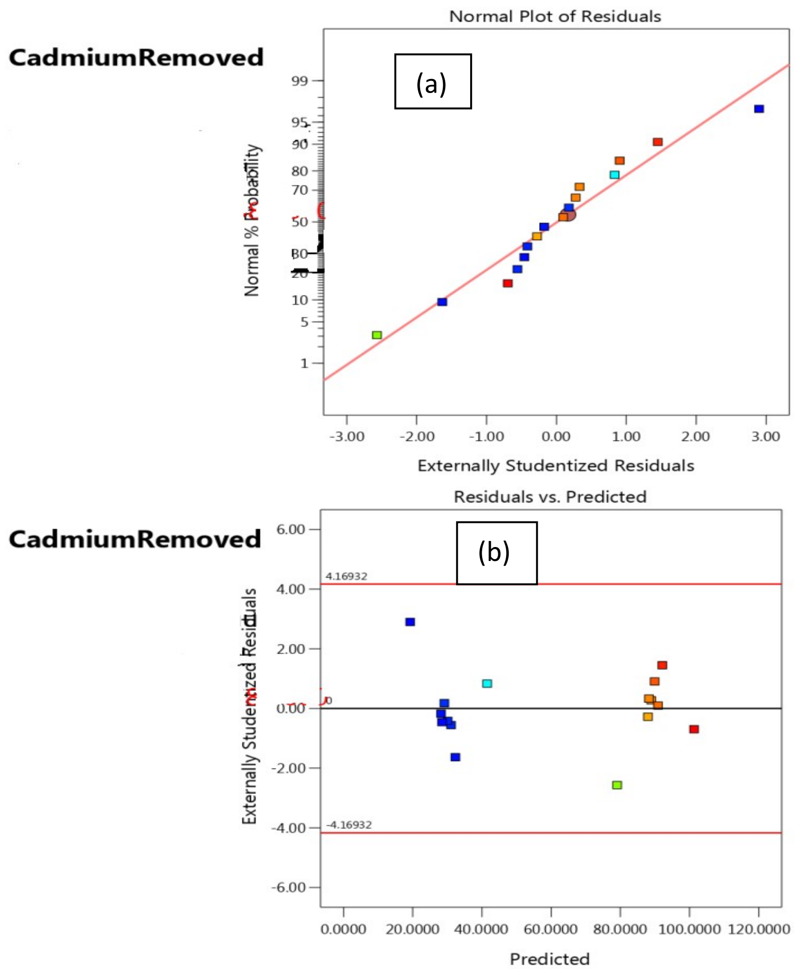

Figure 1. (a) Normal Plot of Residuals (b) Residuals vs. Predicted for the %Removal of Cd^{2+} ions Response

The equation in terms of the actual values of the factors is shown in Equation *(5)*. The equation is employed to predict the response for given levels of each of the control factors. The model is valid in the region of the experimental design, that is the applied range of the experimental control parameters of this research. Figure 1(a), the normal plot of the residual is almost linear supporting the condition that error terms are normally distributed. The random patterns shown in Figure 1(b) also indicate that a linear model affords a decent fitting to the data.

3.2 Analysis of variance of the fitted model (ANOVA).

The statistical significance of the factorial model was estimated using the ANOVA technique, and results were presented in Table 3. The ANOVA proved that the factorial model is significant. This indicated by the high F-value (126.53) with a corresponding low p-value (<0.0001). Hence, three factors contact time A, temperature B, dosage C and interactions between temperature and speed BD were regarded as significant at a $p < 0.05$, 95% confidence level. Temperature did not vastly influence other factors; this fact can be explained as the initiation step of radical mechanism requires low energy for activation (Rivas *et al.,* 2001). The experimental model fit was checked by the coefficient of determination, R^2. The R^2 value is constantly between 0 and 1, the closer the value to 1 the better the model will predict the response (Fu *et al.,* 2007). A correlation was found, dependently between the observed and predicted efficiency of about 0.9883. That is, 98% of results are explained by the model.

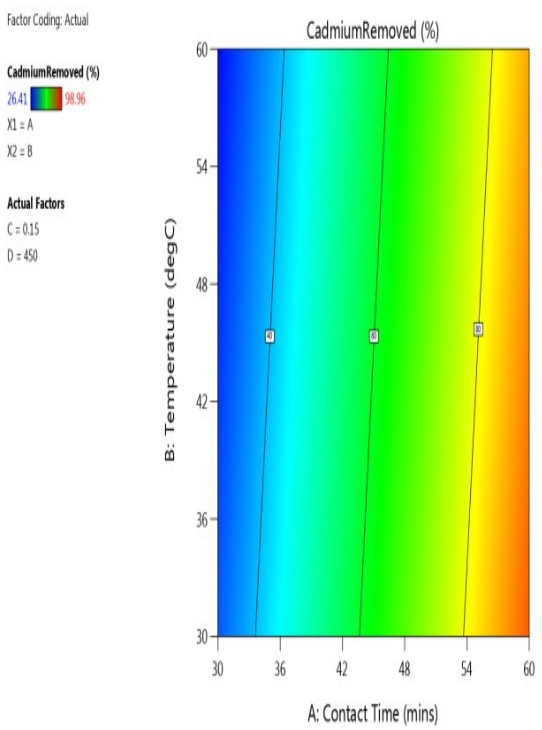

Figure 3: 2D Plot of the %Removal of Cadmium.

3.3 The factor effects and Response variable

A graphical illustration of relations between the factors and the response is presented as contour plots in Figure 3. The plot showed the three factors that have a single effect on the response, %removal of Cd^{2+} ions. Thus, variation in two factors to include a higher contact time A will adequately result in changes in the response values. The contour plots in Figure 6 indicate that no interaction effects between factors A, B, and C. The interaction effects were only observed between factors B and D as well as between C and D (Table 3). The linear variation effect is more pronounced with three-dimensional plots shown in Figure 6(a-c). The figure shows the 3D surface response presented as a function of contact time (min) and temperature (°C); temperature (°C) and Speed (rpm); dosage (g) and speed (rpm) respectively. Figure 4(a-b) shows that the % removal of Cd^{2+} ions increases with increase in contact time and decreases as the temperature increases.

(c)

(d)

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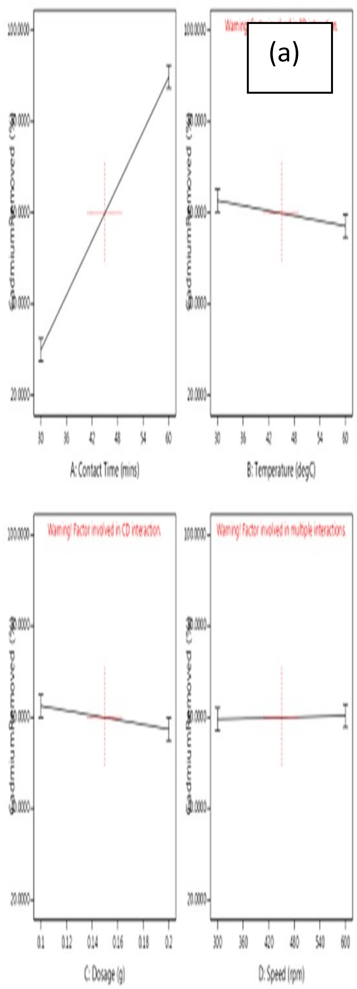
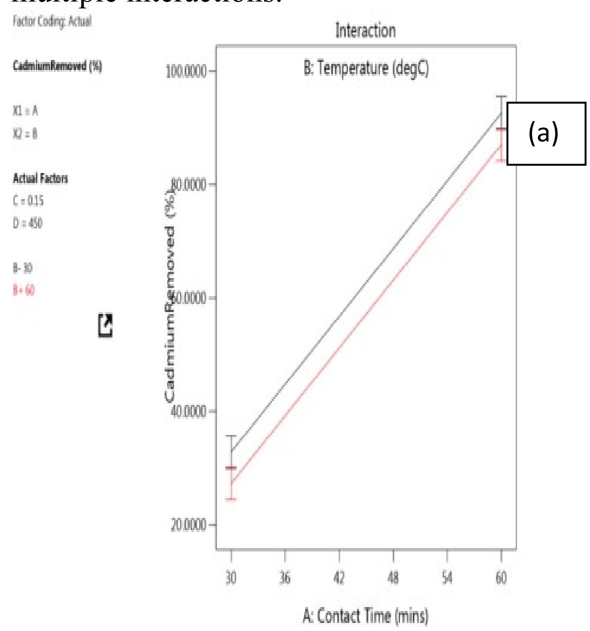


Figure 4: Main Effect Plots of the Factors

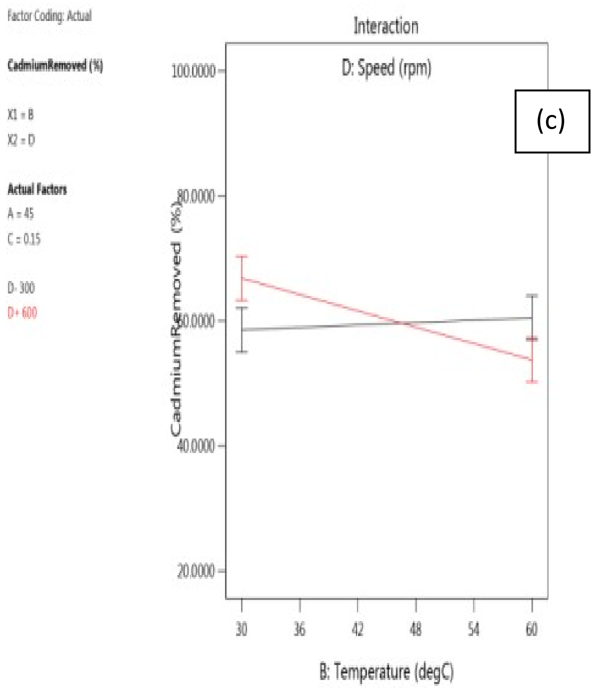
3.4 Main effect plots

The experiment is studied to understand the influence control factors; time, temperature, dosage, and speed have on the cadmium ions percent removal, such that percentage sorption is varied with varying factors. With this, a highest percent of Cadmium is expectedly removed. Thus, the main effect plot was used to study the effects of each factor on the %removal of Cd^{2+} ions. This is presented in Figure 4(a-d). It shows the main effects of the factors on the response which provides the effects of contact time, temperature, dosage and speed respectively. Fig. 4(a) the increasing relationship linearly from 30 to 60 min suggests that the contact time mostly aids the %removal of Cd^{2+} ions, with the highest removal of 98.96% at the time (60 min). This result is consistent with the previous finding of %removal of lead in oil contaminated surface water by Gbajabiamila *et al.,* (2020). However, temperature, dosage and speed slightly decrease in Figure 4(b-d) from minimum values (30 ºC, 0.1 g, 300 rpm) to maximum values (60 ºC, 0.2 g, 600 rpm) of the experimental levels respectively. This indicates insignificant aid on the %removal of Cd^{2+} ions by increasing the levels. Although, this insignificant relationship of each factor may occur as a result of multiple interactions.

(b)



(b)



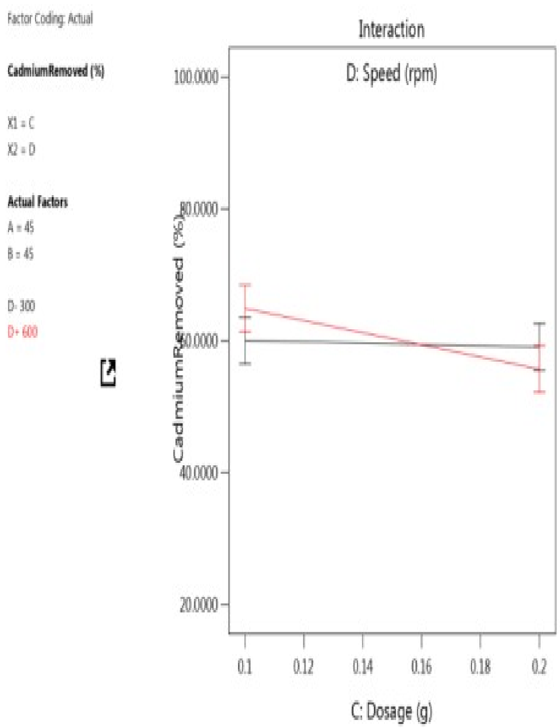
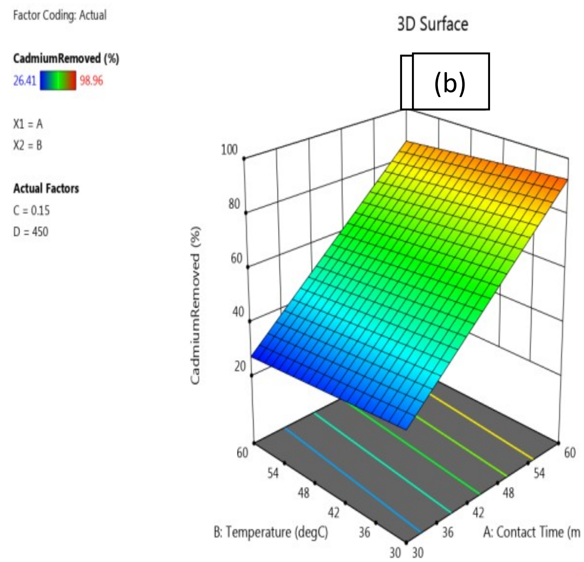
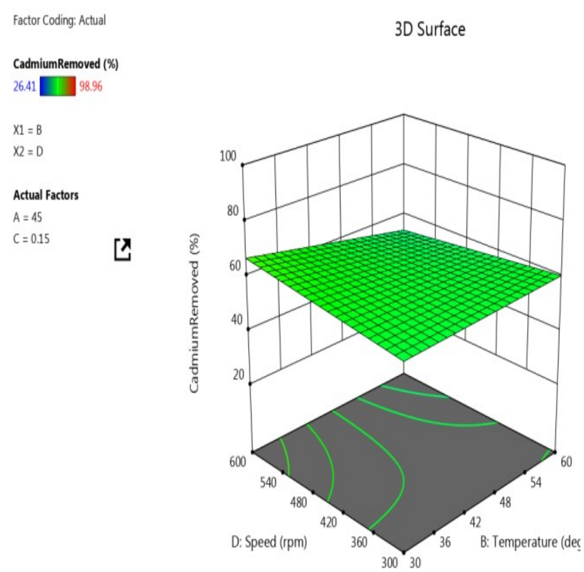


Figure 5: Effects of Interactions between the Factors (a)B and A (b)D and B (c)D and C

3.5 Interaction effects between factors.

The interaction effect between two factors is illustrated in Figure 5(a-c). It shows the effects in the two experimental levels that is, the low and high levels of any factor. Figure 5(a) indicates that A-B interaction is the most important because the lines are not parallel. Other interactions have some intersects which are practically parallel.





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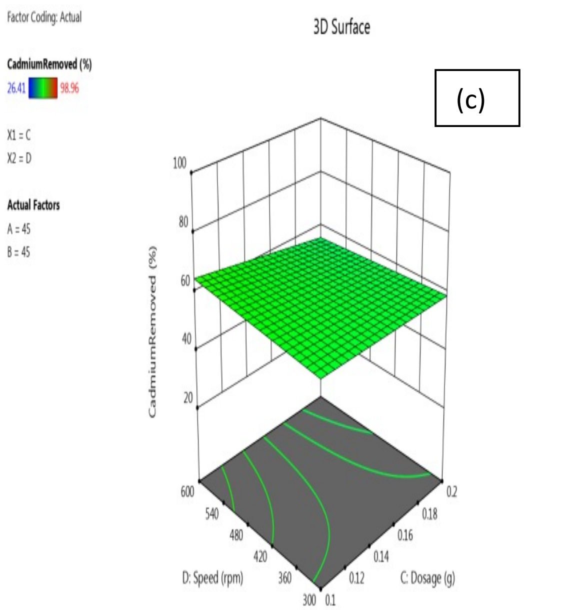

Figure 6: 3D Surface Plots for variation effects of factors (a)B and A (b)D and B (c)D and C

3.6 Optimization Criteria with solution

The %removal of Cd^{2+} ions were maximized and put to the highest decision of significance. The control factors were put at same options of significance, within the range. The result obtained from the optimization is shown in Table 2. The optimum solution for contact time, temperature, dosage, speed and the %removal of cadmium is 59.729 min, 30.989 ºC, 0.112 g, 594.988 rpm and 99.071% respectively, with a desirability of 1.000. The 3D plots of the desirability and percentage removal of cadmium of the optimization are presented in Figure. 7.

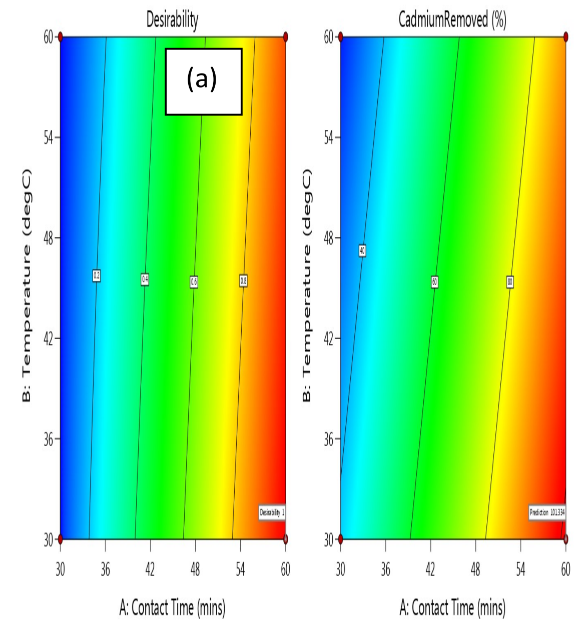

Figure 7: 3D Plots of the Optimized Desirability and %Removal of Cadmium

3.7 MODEL VALIDATION

The results obtained have shown that higher contact time and speed will increase the %removal of Cadmium and low temperature and dosage, all within the set levels, is necessary in order to obtain desirably highest %removal of Cd^{2+}ions. The correlation between predicted and observed %removal is highly significant $R^2 = 0.9883$ and $R^2_{adj} = 0.9805$ values, suggesting better accord between the model and experimental data that confirmed the validity and practicality of the adopted model. Therefore, this study showed the validity of the empirical model and sorption-capability of carbon nanotubes for effective removal of cadmium ions from the polluted surface water obtained at the oil exploration sites in the Niger-Delta region of Nigeria.

4.0 CONCLUSION

This study examined the removal of cadmium contaminants and the effect of control factors; contact time, temperature, dosage and speed, in the optimization process on removal of Cadmium, Cd^{2+} ions in surface water located around oil exploration sites in the Niger Delta region, Nigeria. The experimental design based on full two-factorial model was used to optimize the effective removal of Cd^{2+} ions and to predict the optimum factor combinations for highest removal of cadmium. This experimental study has provided a baseline for optimization of batch-sorption process factors in the remediation of surface water cadmium contaminants from around oil exploration sites. It also provides a reference for the use of bimetallic supported multi-walled carbon nanotubes, MWCNTs as effective materials for batch-sorption process of toxic metal ions.

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