



EVALUATION OF OPTIMUM CONDITIONS FOR THE REMOVAL OF SELECTED HEAVY METALS IN TANNERY EFFLUENTS FROM NILEST USING CARBONISED SWEET DATTOCK SHELLS

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ABSTRACT

The optimum conditions for the adsorption of Ni, Cd, Cr and Pb ions onto modified sweet dattock shells (Sd) from tannery effluents were investigated and analysed. Three adsorption variables (pH, adsorbent dosage and contact time) were studied using central composite design (CCD) a subset of response surface methodology (RSM). The cheap, nontoxic and locally available adsorbent (sweet dattock shells) was subjected to carbonisation and subsequently the digestion of the sample was done using a standard method. In RSM study, the individual and interactive effects of the three critical variables including pH of the solution, Sd dosage and contact time on the adsorption capacity were optimised. Quadratic models were developed for both metals percentage removal. The prime adsorption conditions obtained were pH 4, Sd dosage of 0.8g at 20 mins with desirability of 0.925. These results were statistically significant and this shows that the conditions obtained could be used for treatment of tannery effluents.

Keywords: Heavy metals, Effluent, Sweet dattock shell, RSM.

INTRODUCTION

The major characteristics of developed countries and primary desires of third world countries or developing nations are industrialisation and urbanisation. This, though brought development but economic solution to its disadvantages has become a global problem. A high degree of urbanisation and industrialisation have substantially enhanced the degradation of aquatic environments through the discharge of industrial waste water and domestic wastes. Industries like tannery, electroplating, textiles e.t.c have large quantities of heavy metal ions in their

effluents which are toxic for human beings. Presence of these heavy metals in water stream and ground water is very serious environmental concern since these metal ions are toxic to life forms; therefore, removing them as well as controlling their level levels in waste water is very crucial (Kumar and Jena, 2017).

Biosorption process through utilisation of biomass/ biosorbents in the removal of heavy metal ions from tannery effluents is one of the most promising alternatives in substituting conventional methods like precipitation, membrane filtration, electrolyte or liquid extraction, electrolysis

and reverse osmosis. Sorption methods are flexible and easy to operate with much less sludge disposal problems (Garba and Afida, 2014; Maksin, *et al* 2012). Various adsorbents with local availability, high adsorptive capacity as well as economic suitability are still needed. This prompted the search in the investigation of the Sd shells (*Detarium microcarpum*) as the new and explorable adsorbents.

The term heavy metal refers to any metallic chemical element that has a relatively high density and is very toxic or poisonous at low concentrations. A heavy metal is defined as a metal whose density is above 5gcm^{-3} or 50gmol^{-1} . Examples of heavy metals include mercury (Hg), cadmium (Cd), nickel (II), chromium (Cr), thallium (Tl), and lead (Pb).

Heavy metals are natural components of the Earth's crust. This cannot be degraded or destroyed. To a small extent they enter our bodies via food, drinking water and air. As trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning of life forms. Heavy metal poisoning could result, for instance, from drinking-water contamination (e.g. lead pipes), high ambient air concentrations near emission sources, or intake via the food chain. Heavy metal toxicity is one of the major current environment health problems and is potentially dangerous because of bio-accumulation through the food chain (Maksin, *et al* 2012) and this can cause hazardous effects on livestock and human health (El Haddad, *et al.*, 2013). In general, the hazardous effects of these toxic

elements depends upon the dietary concentration of the element, absorption of the element by the system, homeostatic control of the body for the element and also the species of the animal involved (Yusuf and Tekin, 2017).. Heavy metal pollution has become a serious health concern in recent years, because of industrial and agricultural development. The toxic heavy metals of great concern are Cd, Pb and Hg which are usually associated with harmful effects in humans and animals. It is recognized that heavy metals may exercise a definite influence on the control of biological functions, affecting hormone system and growth of different body tissues (Slimani, *et al.*, 2014). Many heavy metals accumulate in one or more of the body organs with differing half-lives. These heavy metals apart from acute or chronic poisoning can be transferred to next generation and have potential toxicity from the viewpoint of public health (Baccar, *et al.*, 2013). This research is aimed at carrying out the optimization of the paramount parameters for an effective adsorption of Ni (II), Cd (II), Cr (II) and Pb (II) from tannery effluents of NILEST using *Detarium microcarpum*. The objectives of this research include to;

- i. collect, prepare and characterize carbonised *Detarium microcarpum* adsorbent
- ii. collect, digest and determine metal contents in NILEST tannery effluent
- iii. carry out adsorption experiment using response surface methodology
- iv. optimize the paramount parameters in the metal ion adsorption experiment and develop a model

- using response surface methodology.
- v. validate the model by carrying out experiment to confirm the optimization parameters obtained from the model.

MATERIALS AND METHODS

The sample was bought from Samaru market Zaria, Kaduna state, it was taken to Department of Botany at the Ahmadu Bello University, Zaria, and identified as *Detarium microcarpum*.

Preparation of biosorbents

The pericarps were removed and de-shelled, then the edible part and the shell was washed off with distilled water, Air dried for seven consecutive days to dehydrate it completely, and then grounded to smaller forms with mortar and pestle (Musah *et al.*, 2016).

The pre-treated sample was carbonized in a muffle furnace at a temperature of 300°C for 4 hrs. The charred material was allowed to cool to room temperature, soaked in H₃PO₄, washed with distilled water until a pH of 7 was obtained, the sample was then ground and sieved using 0.2 mm mesh. The sieved 0.2mm particle size material for carbonised sample was weighed and the particles were then dried in an oven at 25°C for 48hrs before being packed in an air tight sample bags for use (Garba, 2016).

Characterization of the Biosorbent

Scanning Electron Microscope (SEM) Analysis

The effect of metal biosorption on the surface properties of the biomass *Detarium*

microcarpum was analyzed using SEM. Surface micrographs of the Native and different Heavy metal treated algal biomass powder were recorded using SEM apparatus before and after adsorption.

Fourier Transform Infrared (FTIR) Analysis

To study the mechanism of Cd²⁺, Cr⁺⁶, Pb²⁺ and Ni²⁺ removal by biomass *Detarium microcarpum*, the active chemical groups on the biomass surface before and after respective metal sorption were evaluated by FTIR Spectroscopy. 30mg of finely grounded algal biomass was encapsulated in 300mg of KBr (sigma) in order to prepare the translucent sample disks used for the FTIR spectra analysis.

Digestion of sample

50 mL of the sample was measured into a beaker, after which 5 mL of conc. HNO₃ was added and heated gently, until the volume reduced to 20–25 mL in a fumehood. This was cooled; 5 mL of concentrated HNO₃ was added and reheated for gentle reflux to occur until digestion is complete, it was then evaporated to <5 mL and cooled. After cooling, beaker wall was washed down with water, filtered and the filtrate transferred to a 100 mL flask adjusted to volume using distilled water (APHA, 1999).

Design of Experiment

Central Composite Design (CCD) was used in designing the experiment with the aid of Design Expert software version 11.0.6 (Stat-Ease, Inc., Minneapolis, MN 55413, USA). Factors such as contact time, adsorbent dose and pH were varied and the response of the experiment was the

extraction efficiency of the metal ions from the collected tannery effluent. The concentrations of the un-extracted heavy metals were determined using Microwave Plasma Atomic Emission Spectrometer (MP-AES).

Sorption Experiment

The sorption experiment was carried out by batch method. The method reported by Garba *et al.*, 2016 was adopted. An adsorption experiment was carried out in order to study and evaluate the significance of variables on the percentage removal of Ni (II), Cd (II), Cr and Pb (II) according to the pH, time as well as the adsorbent dose as shown in table 1 below. **Table 1** shows the whole experimental runs as it was generated by the software on the basis of the 3 optimised conditions which are pH, adsorbent dosage and time. In each of the four Heavy metals there was certain % removal of metals from the tannery effluents using using *Detarium microcarpum* as the cheaply and most available adsorbent. The data presented Showed various adsorption efficiencies for respective metal ions in the tannery effluents using Sd as an adsorbent. Ni ranges from 87.17 to 99.74, Cd from 88.70 to 98.22, Cr from 87.12 to 99.54 and Pb from 88.70 to 90.47.

The experiment was carried out at ambient temperature (25°C) on a mechanical shaker

using 100cm³ conical flask as the reactor. 50cm³ solution of the tannery effluent was measured into the flask. The pH of the solution was adjusted to the required value throughout the experiment with 0.1M NaOH and 0.1M HNO₃. These gave only nitrate ion and sodium ion which are already in the medium without altering the chemistry of the ions of interest. An amount of the adsorbent was transferred into each of these conical flasks; Each set was agitated on the shaker at the different time, the samples were filtered, digested and analysed for residual metals concentrations. The adsorption efficiency or the percentage removals were obtained using the expression below

$$\% \text{Removal or adsorption efficiency} = \frac{c_o - c_t}{c_o} \times 100 \quad (1)$$

Where c_o = initial concentration

C_t = final concentration

The gram of a particular metal adsorbed per unit gram of adsorbent otherwise known as adsorption capacity after a given time was calculated using the expression below:

$$q_t = \frac{(c_o - c_t)V}{W} \quad (2)$$

Where: V = Volume of the solution

W = Mass of the adsorbent

Table 1: Experimental runs with responses

Run	pH	Adsorbent dose (g)	Time (min)	Ni removal (%)	Cd removal (%)	Cr removal (%)	Pb removal (%)
1	6	0.55	24.0908	99.6444	96.2331	99.5417	90.2331
2	6	0.55	14	98.6444	95.9358	98.5417	89.9358
3	4	0.3	20	99.7444	97.4709	99.0834	90.4709
4	6	0.129552	14	99.3424	95.9358	98.5417	89.9358
5	8	0.3	8	93.6203	92.5089	93.5251	88.5089
6	8	0.8	8	93.6203	92.7467	93.0843	88.5089
7	6	0.55	14	98.6324	94.9358	98.5236	89.9358
8	8	0.3	20	94.1763	93.9358	96.0843	89.9358
9	9.36359	0.55	14	87.1763	88.7087	87.1234	88.7087
10	6	0.55	14	98.6203	95.2224	97.5417	89.2224
11	6	0.55	3.90924	99.6324	95.5577	97.5417	89.5577
12	6	0.970448	14	98.6324	96.893	96.0843	89.893
13	4	0.8	8	98.1763	98.2224	99.6251	90.2224
14	8	0.8	20	93.6203	94.2331	93.5417	90.2331
15	2.63641	0.55	14	96.687	97.0333	94.1502	90.0333
16	6	0.55	14	98.6203	95.9845	97.5423	89.9845
17	6	0.55	14	98.1763	95.2224	97.5417	89.2224
18	4	0.3	8	99.7407	98.1094	98.0834	90.1094
19	6	0.55	14	98.7407	95.5577	97.5417	89.5577
20	4	0.8	20	99.6369	98.082	99.0834	90.082

The experiment was carried out at ambient temperature (25°C) on a mechanical shaker using 100cm³ conical flask as the reactor. 50cm³ solution of the tannery effluent was measured into the flask. The pH of the solution was adjusted to the required value throughout the experiment with 0.1M

NaOH and 0.1M HNO₃. These gave only nitrate ion and sodium ion which are already in the medium without altering the chemistry of the ions of interest. An amount of the adsorbent was transferred into each of these conical flasks; Each set was agitated on the shaker at the different

time, the samples were filtered, digested and analysed for residual metals concentrations. The adsorption efficiency or the percentage removals were obtained using the expression below

$$\% \text{Removal or adsorption efficiency} = \frac{C_o - C_t}{C_o} \times 100 \quad (1)$$

Where C_o = initial concentration

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The gram of a particular metal adsorbed per unit gram of adsorbent otherwise known as adsorption capacity after a given time was calculated using the expression below:

$$q_t = \frac{(C_o - C_t)V}{W} \quad (2)$$

Where: V = Volume of the solution

W = Mass of the adsorbent

Development of Model for Adsorption Process Parameters

A quadratic model in form of expression below was developed for the adsorption of the metal as it was influenced by the parameters considered during the experimental runs;

$$Y = b_o + \sum_{i=1}^n b_i x_i + (\sum_{i=1}^n b_{ii} x_i)^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n b_{ij} x_i x_j + \epsilon \quad (3)$$

Where: Y = Predicted response

b_o = Constant coefficient

b_i = Linear coefficient

b_{ii} = Quadratic coefficient

b_{ij} = Interaction coefficient

x_i and x_j = Factors or parameters considered

ϵ = Random error

Coefficient of Determination (R^2) was used to determine the quality of the model as it compared the data from predicted model with data gotten from experimental runs (Anilkumar *et al.*, 2016). Fisher variation ratio (F-value) was employed to explain the adequacy and significance of the predicted model.

Effects of each factor on adsorption were studied and presented in curves, while effects of interaction between factors on adsorption were presented in three-dimension (3-D) curves or contour plots (i).

RESULTS AND DISCUSSION

Scanning electron micrograph

The SEM images of the carbonised Sd before and after adsorption are shown in plates 1 and 2 respectively. Both plates were found to to be maintained its fibrous nature with different porosities. The formation of the pore system of the Sd resulted from the rapid emission of species during carbonisation process and from the development of new micropores induced by H_3PO_4 . It was suggested that H_3PO_4 could promote both the generation of new micropores and the enlargement of as-existing micropores to mesopores (Adeyinka, 2017). Furthermore, the image ($\times 500$ magnification) of the Sd after adsorption (plate 2) shows metal precipitate appearing as flakes and grain-like structures on the surface of Sd.

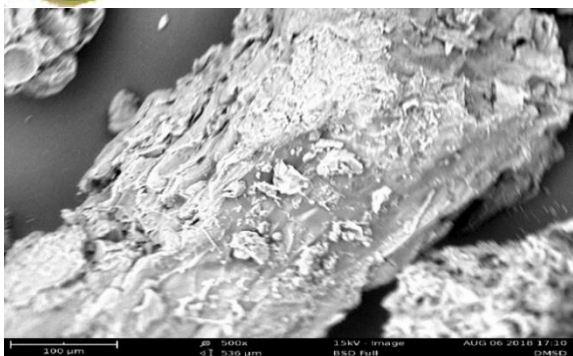


Plate 1. SEM image of Sd before adsorption

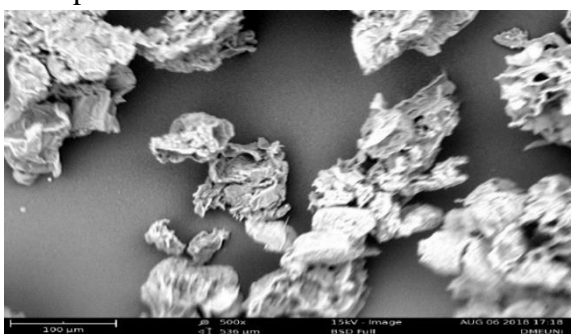


Plate 2. SEM image of Sd after adsorption

FTIR

From the IR spectra of the Sd presented in fig. 1 there is presence of -OH group which is attributed to the adsorption at 3276cm^{-1} . Strong adsorption at 2922cm^{-1} indicates the presence of C-H of alkanes while adsorption at 1606cm^{-1} portray the presence of C=C and lower adsorption at 1028cm^{-1} identified C-O as the functional group in the adsorption process (Absorption table, 2014; Spectroscopic tools, 2018). Adsorption was facilitated by various functional groups present on the surface of the Sd ; this is due to the presence of electronegative atom as well as electron cloud density at the multiple bonds of carbons. Hence, there is preferential adsorption of metal ions which are electropositive (Anilkumar., Chitti and Kavitha, 2016).

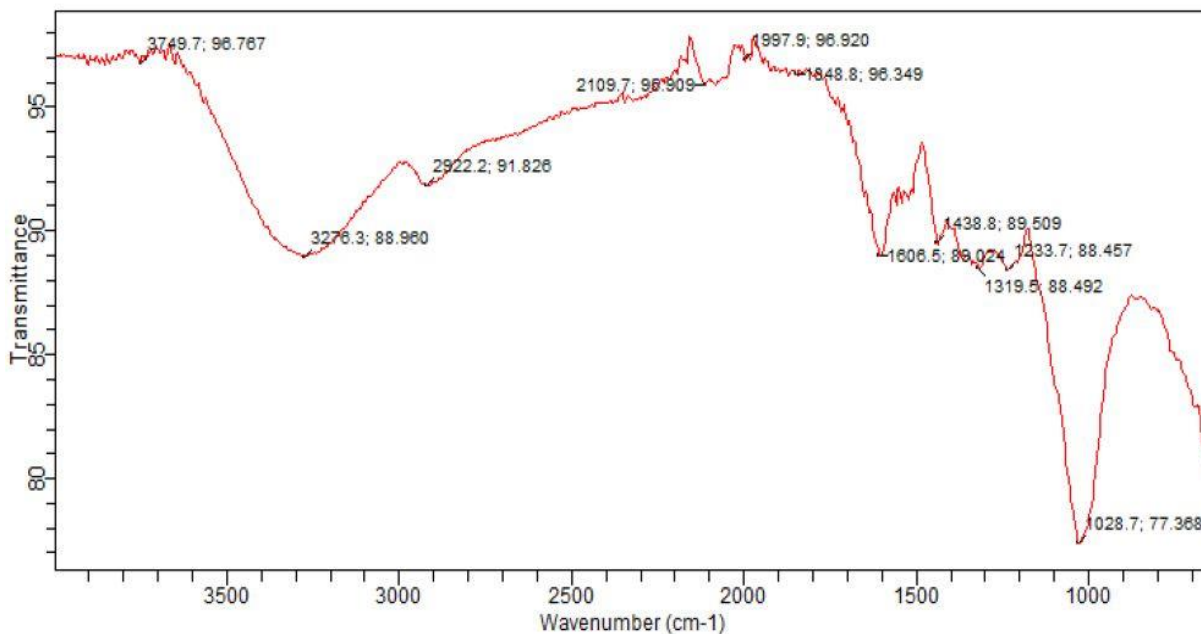


Figure 1a: FTIR spectra of the adsorbent after adsorption.

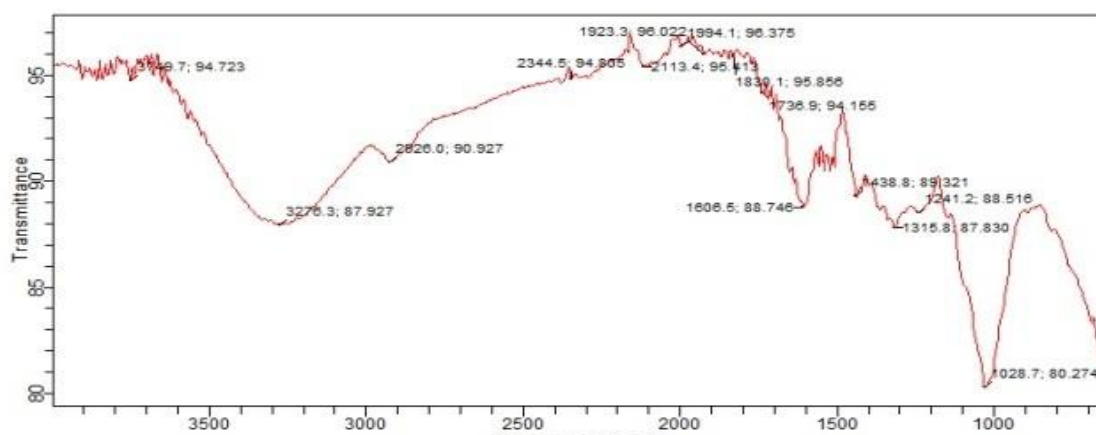


Figure 1b: FTIR spectra of adsorbent before adsorption

Statistical parameters to evaluate the quality of the models

The relationship between predicted and actual values as shown in Table 2 gives the Coefficient of Determination (R^2) which shows the quality of the model as it compared the data from predicted model with data gotten from experimental runs. The R^2 values of all the heavy metals were high which is a good achievement showing how valid are the models.

Table 2: gives the Coefficient of Determination (R^2) which shows the quality of the model

Metal	R^2
Ni	0.8329
Cd	0.8718
Cr	0.9087
Pb	0.8547

Table 3: Optimisation solution

S/N	pH	Adsorbent dose	Time	Ni removal	Cd removal	Cr removal	Pb removal	Desirability
1	4.558	0.800	20.000	99.657	97.622	99.307	90.097	0.926
2	4.531	0.800	20.000	99.647	97.632	99.292	90.098	0.926
3	4.591	0.800	20.000	99.667	97.609	99.323	90.095	0.926
4	4.620	0.800	20.000	99.675	97.597	99.337	90.094	0.925
5	4.645	0.800	20.00	99.681	97.586	99.348	90.093	0.925

The table shows the subsequent optimised values upon which the best % removal were

re- obtained at different set conditions as compared to Table 1.

Model and Statistics of % Metals removed

The data presented in table 1 showed various adsorption efficiencies for respective metal ions in the tannery effluents using Sd as an adsorbent. Ni ranges from 87.17 to 99.74, Cd from 88.70 to 98.22, Cr from 87.12 to 99.54 and Pb from 88.70 to 90.47.

The models (in coded forms) for the respective metal adsorptions are presented in equations(4)-(7) with positive sign(+) of the coefficient indicating the term affecting adsorption positively while the negative sign indicates the adsorption been affected negatively by the term in the model equations. The main contents of Table 2 include the results of the analysis of variance (ANOVA) fitted to the second order polynomial equations and the corresponding regression coefficients. Statistical significance and adequacy of the models can be identified via high F, low p-value, correlation coefficient (R^2) close to 1, and the results of lack of Fit (LOF) test.

$$\text{Ni adsorbed(\%)} = 98.58 - 2.30A - 0.2506B + 0.1494C + 0.1395AB - 0.1135AC + 0.1126BC - 2.39A^2 + 0.1032B^2 + 0.3334C^2 \dots\dots\dots(4)$$

$$\text{Cd adsorbed(\%)} = 95.46 - 2.38A + 0.2101B + 0.2395C - 0.0236AB + 0.4615AC + 0.0697BC - 0.7885A^2 + 0.4643B^2 + 0.2808C^2 \dots\dots\dots(5)$$

$$\text{Cr adsorbed(\%)} = 97.83 - 2.30A - 0.4082B + 0.5007C - 0.5656AB + 0.3198AC - 0.4554BC - 2.31A^2 + 0.0473B^2 + 0.4817C^2 \dots\dots\dots(6)$$

$$\text{Pb adsorbed (\%)} = 89.64 - 0.4165A + 0.0137B + 0.3127C + 0.1014AB + 0.3365AC - 0.0553BC - 0.0843A^2 + 0.1079B^2 + 0.1012C^2 \dots\dots\dots(7)$$

The LOF value parameter showed the variation of response around the fitted model; this parameter appears insignificant if the model fits data well. According to the stated standards for the analysis, the high F-values of all the four models are greater than 0.0001 as presented in Table 2 suggests the statistical significance of the models. The p-values of all the models lack of fit are greater than 0.05 showing they are not significant. It was further confirmed by the difference in p-values of less than 0.2 between the adjusted and predicted R^2 of the lack of Fits (design expert version 11, 2018).

The first five solutions of the optimum factors predicted by the software for maximum adsorption of the four metals were presented in Table 3. It was further validated by comparing experimental with predicted results. High coefficient of determination (R^2) ranging from 0.8329 to 0.9087 as shown in Table 4 as obtained, signifying less variation between predicted and actual values.

Table 4: Described how close between the experimental values (actual) to the values generated by the software (predicted). It actually signifies the validity of the data.

Solution	% Ni removal		%Cd removal		% Cr removal		% Pb removal	
	Actual	Predicted	Actual	Predicted	Actual	Predicted	Actual	Predicted
1	99.657	99.657	97.61	97.622	99.875	99.307	90.100	90.097
2	99.540	99.647	97.613	97.632	99.292	99.292	90.100	90.098
3	99.660	99.667	97.601	97.609	99.333	99.323	90.090	90.095
4	99.680	99.675	97.567	97.597	99.297	99.337	90.090	90.094
5	99.800	99.681	97.569	97.586	99.320	99.348	90.090	90.093

Effects of factors on adsorption

pH

This played a vital role in the removal of the individual ion as indicated by fig .2a, b, c and d. Ni, Cd, Cr and Pb adsorption were affected mostly by pH as shown by the steepness of pH curves in fig.2 above, this could be due to reduction in solubility as well as possible precipitation of the metals (Ahujat *al.*,1999 sun *et al.*,2012). This can also be as a results of hydrogen ions reduction struggling for the available sites as pH increases (Luet *al.*, 2017). These increase in adsorption with pH agree with typical cations adsorption behaviour (Oyetade et al.; 2017).

Contact time

The adsorption efficiencies of the metals increase with time which was attributed to the available sites during the experiment and enabled the adsorption process as designed in the matrix.

Adsorbent dosage

Adsorption efficiencies of all the metals increase with adsorbent dosages which was

due to the addition in active sites available for adsorption (Xu *et al.*, 2017).

Interactive effects on adsorption conditions

The interactive effects of pH, adsorbent dosage and time on the adsorption of Ni, Cd, Cr and Pb, respectively are presented in fig.3 using 3-D plot as this shows the interactive and synergistic effects of both factors during the adsorption process and pH been the best contributor of metals removal.

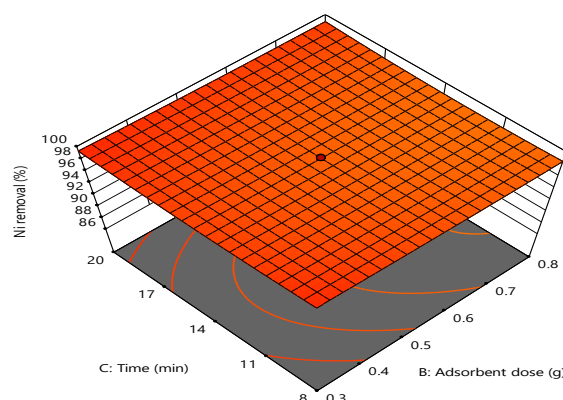


Figure 2a: Effect of Adsorbent Dose and Time on Adsorption.

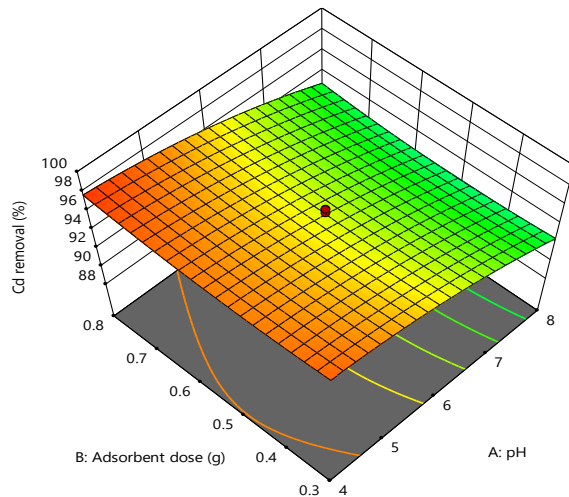


Figure 2b: Effect of pH and Adsorbent Dose on Adsorption

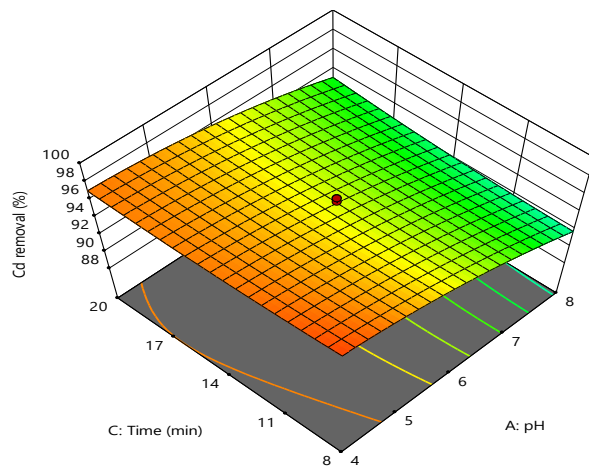


Figure 2c: Effect of pH and Time on Adsorption

CONCLUSION

The carbonised Sd shells (sweet dattock) adsorbent was found to be an effective adsorbent for the removal of Ni, Cd, Cr and Pb from tannery effluents. The RSM involving was succesfully CCD successfully

applied to examine the impact of independent variables, including pH, time and adsorbent dosage on the removal of Ni, Cd, Cr and Pb from and to determine the optimum adsorption condition. The quadratic equations developed to model the adsorption of all the four metals on the carbonised Sd shells were found to be statistically significant.

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