



Application and Optimization of Chitosan Beads Production for Adsorption Study of Arsenic and Copper ions from Simulated Waste Water

Raliat Yusuf Yakubu, Abdulsalami Kovo
Department of Chemical Engineering,
Federal University of Technology, Minna

ABSTRACT

This research is aimed at Chitosan beads synthesis, characterization and application for Arsenic and Copper removal from simulated waste water, which was achieved by developing chitosan beads under alkaline and acidic mediums. The Functional group, Pore size and Surface area of the synthesized beads were studied using the Brunauer Emmette Test and Fourier Transform Infrared Spectroscopy. The developed adsorbent was then used for Arsenic and Copper removal from simulated waste water. The effect of all parameters influencing the adsorption capacity such as adsorbent dosage, initial concentration, activation temperature and activation time were studied based on Experimental Design Matrix using Surface Response (SR) methodology. It was found that the functional present in this case is - CONH- CH₂ stretching the N - H bending and there was absence of the strong Amide II group due to the high degree of de - acetylation of produced chitosan beads. The surface area, pore size and pore volume were found to be 376m²/g, 6.52nm and 0.134cm³/g which also shows a good absorptive property resulting to high percentage removal of the heavy metals. The combined effect of all the operating parameters was found to have greatest adsorption efficiency on copper than arsenic from simulated waste water at the same operating conditions based on their F- values which was 98.03% for Copper and 96.22% for Arsenic

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INTRODUCTION

In recent years there has been an increase in the release of heavy metals into our surroundings leading to the contamination of ground water as a result of advancement in industrialization and urbanization. This has led to a great problem even to the world at large. (Oguzie and Okhagbuzo 2009). The presence of heavy metals in minute concentrations plays an important role in the metabolic activities and growth of plants and animals. However, increased concentrations of heavy metals may have several toxicological effects on many life forms (Purushotham *et al.*, 2013).

The most hazardous chemical industries are those that deal with heavy metals such as chromium (Cr), Nickel(Ni), Cadmium (Cd), Arsenic (As), Lead (Pb) and Copper (Cu). These industries released large amount of heavy metals which contaminates potable clean water and kill aquatic organism due to their high rates of solubility. As reported by (M.A Barakat *et al* 2010), the adsorption of heavy metals at concentrations above threshold limit into food chains by ingestion can result to serious health

related problems. Hence, the treatment of heavy metal contaminated – wastewater is a very important step prior to the emission or release to the environment.

Conventional treatment processes such as ion exchange, electrochemical removal and precipitation can be employed in the elimination of heavy metal from inorganic effluent. It is noteworthy to mention that each of these processes have their various disadvantages which includes: creation of toxic sludge, partial removal and sometimes high energy consumption. (Barakat and Eccles 2010).

Recent study for the quest of effective and inexpensive technologies which utilized low cost adsorbent has been intensified. One of such alternative for effluent treatment is adsorption (Barakat and Eccles 2010). Adsorption process is a suitable technique for inorganic and organic pollutants removal from wastewater, because of the significant advantages like low-cost, availability, profitability, ease of operation, efficiency, and effectiveness than other techniques (Gupta *et al.*, 2011). Adsorption process involves separation of a

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substance from one phase and its accumulation at another surface. This technique is easy to operate and equally effective in the removal of toxic pollutants, even at low concentrations (Amuda and Edewor, 2013). Though many techniques can be used for the treatment of inorganic effluent, the ideal treatment should be not only suitable, appropriate and applicable to the local conditions but also able to meet the Maximum Contaminant Level (MCL) standards established.

The various adsorbent may be in different forms which could be organic or may have biological origin, minerals, industrial by – product, biomass, polymeric materials and agricultural waste. (Kurniawan *et al.*, 2006). The commercial activated carbon most widely used as an adsorbent has become economically less feasible owing to its relatively high cost. Recently, different low cost bio sorbent sourced from natural materials and biological wastes from industrial processes has been studied for the development of cheap and effective metal sorbents (Sethu *et al.*, 2010). Also, the development of carbon has produced a variety of activated carbon with far better adsorption capacity (Amuda *et al.*, 2007). Among these low cost adsorbents, chitosan has the highest sorption capacity for several metal ions (Amuda *et al.*, 2009).

Chitin (2-acetamido-2-deoxy- β -D-glucose-(N-acetylglucan) is the main structural component of molluscs, insects, crustaceans, fungi, algae and marine invertebrates like crabs and shrimps. Chitosan (2-acetamido-2-deoxy- β -D-glucose-(N-acetyl glucosamine) is a partially deacetylated polymer of chitin and is usually prepared by deacetylation of chitin with a strong alkaline solution (Amuda *et al.*, 2009). It has been reported that approximately 49000 tons of scales per year rounding up to about 2% of fish weight are produced during de – scaling process of fish (Bin wang, 2013). Fish scales contains connecting tissues, protein, collagen embodied with calcium salt 41% - 84% protein content and the remaining contents are calcium carbonate and phosphate (Nagai *etal* 2004). There has been alternative usage of fish by – products such as skin, bones, scales for the preparation of collagen; this is based on their high rate of availability, the absence of high risk of disease transmission and religious beliefs. (Nagai *et al*, 2004)

Chitin is found in marine invertebrates, fungi, insects and yeast. Chitin which is a bio polymeric substance obtained from crustaceous

shell, a homo polymer of β (1 \rightarrow 4) linked *N*-acetyl-d-glucosamine and it is also a biopolymer that is synthesized by a large number of living organisms (Suneeta and Pradip, 2014). Chitin is one of the most abundant and most important natural polysaccharide which has been described to be produced on a yearly basis as much as cellulose found in shells and cell walls of fungi (Benabid and Zouai, 2016). Chitin in most cases is not widely used industrially; this is based on the fact that it is highly insoluble in most solvents which make it more difficult from natural source in its purest form thereby making its reproducibility more tasking under normal or sound condition (Suneeta and kumari, 2014).

Yang and Zall (1984) reported that chitosan can chelate three times greater concentrations of metals than chitin. They further reported this property to be related to the free amino groups exposed in chitosan because of deacetylation of chitin. Chitosan is slightly soluble at low P^H and possesses problems for developing commercial applications. Also, the active binding sites of chitosan are not readily available for sorption. The sites are reported to be soft and have a tendency to agglomerate or form gel in aqueous solutions. Transport of metal contaminants to the binding sites plays a very important role in process design. Therefore, it is necessary to provide physical support and increase the accessibility of the metal binding sites for process applications. This is what necessitated this research study based on chitosan synthesis from croaker fish scale for the adsorption of heavy metals (Arsenic and copper metal ion) from simulated wastewater. Also, investigation of adsorption parameters such as pH, contact time, adsorbent dosage, and temperature on removal efficiency are presented as well.

MATERIALS AND METHODS

The major starting material used in this research work during the experimental work include chitosan obtained from china, Sodium hydroxide (NaOH), Sodium, Acetic Acid and Heavy Metals (Copper Sulphate ($CuSO_4$) and Arsenic III Oxide) of analytical grades.

Hydrochloric acid, Sodium Hydroxide, Sodium Hypochlorite, Arsenic Oxide, and Copper Sulphate solution of various concentrations were prepared by dissolving calculated quantity of these chemicals of analytical grade into de – ionized water

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of which metal ions of desired concentrations were freshly prepared from the stock solution.

Preparation of Chitosan Beads

2 grams of chitosan powder was dissolved in 50ml of 5% (v/v) acetic acid solution and heated to a temperature of 90°C with simultaneous stirring speed of 200 rpm for 2 hours until complete dissolution of the chitosan nanoparticles was achieved.

The above mixture of chitosan nanoparticles and glacial acetic acid solution (Jelly) was filled into a 5ml syringe pump and precipitated by the drop wise addition into a 1M NaOH solution. This was actually carried out in a water bath by exerting equal pressure at distance of approximately 3cm. The beads formed were left for 45 – 60 mins for proper formation of the beads. The beads formed were washed with distilled water until neutralization occurs using a buffer solution of PH 7.0 as reference. Wet beads were sieved, dried at atmospheric condition for 48hours, weighed then packaged for further studies.

CHARACTERIZATION OF THE ADSORBENT

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR characterization of chitosan was performed with a Nicolet Magna 550 FT-IR instrument. Chitosan samples were prepared in the forms of thin film. For the preparation, 2% w/v

chitosan was dissolved in 2% acetic acid solution, poured on a petri dish, and finally dried at 60 °C for 16 hours under vacuum, the important thing is maintenance of equal sample thickness all thru. The spectra of the chitosan sample (in the forms of thin film) were obtained with a frequency range of 4000–400 cm^{-1} at 4 cm^{-1} resolutions and the major vibrations were identified associated with the main chemical groups.

Brunauer, Emmette Teller (BET)

The BET was carried out by nitrogen adsorption – desorption method using nitrogen temperature (-196°C) with an autosorb BET apparatus, Micrometrics ASAP 2020, surface area and porosity analyzer. The analysis procedure was automated and operated with static volumetric techniques. The samples were first degassed at 200 °C for 2hours before each measurement was recorded. These were carried out to determine the surface area and porosity of the adsorbent after production.

RESULTS AND DISCUSSION

Characterization of the Adsorbent

FTIR technique is used mainly to identify functional groups such as carboxyl, hydroxyl, and amine group that are capable of adsorbing pollutants. FTIR analysis of Chitosan beads depicted in the Figure1

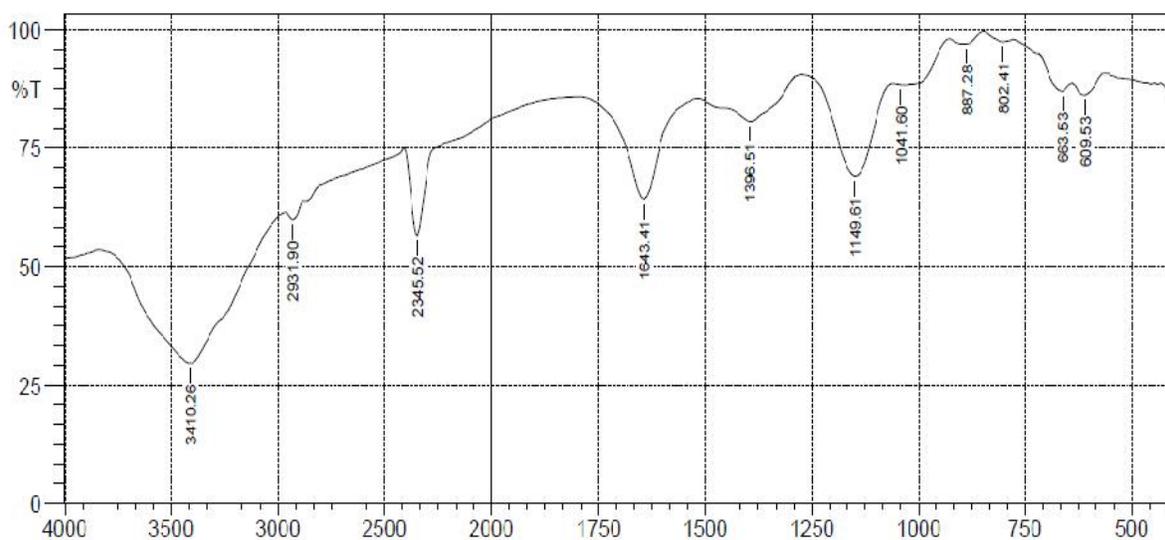


Figure 1: FT-IR result for Chitosan beads

Figure 1, for Chitosan beads peak at 1040 cm^{-1} and 1150 cm^{-1} correspond to N–H bending of the secondary amide II band of –CONH– whereas,

the amide I band is generally observed at 1643.41 cm^{-1} . In the present case, the amide I band is not found. Further bands that are observed in the region

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of 1380–1460 cm^{-1} are attributed to the symmetric and asymmetric bending vibrations of the methyl groups. Li *et al.*, (1998) also found that the peak at 1415 cm^{-1} indicates the C–H bending vibrations of –CH₂. A small peak around 2931.52 cm^{-1} relates to –CH₂, and –CH₃ functional groups. The C–O stretching vibrations of the structure are observed at 1041.60 cm^{-1} . The peak near 3410 cm^{-1} is usually attributed to intermolecular –H bands. This result is in agreement with Choi *et al.*, (2007) who observed similar characteristic peaks for chitosan from fish scale at 2940 cm^{-1} (–CH₃, –CH₂), 1655 (C=O stretch

vibration of secondary amide I band), 1555 cm^{-1} (N–H bending vibration of amide II band), 1570 cm^{-1} (N–H bending vibration of primary amides) and 1070 cm^{-1} (C–O stretching). Strong amide II bands are not present in this case, due to the high degree of deacetylation of the produced chitosan.

Table 1 shows the BET surface area, pore volume and pore size of Chitosan beads. The Chitosan beads have surface area of 376.40 m^2/g , pore volume of 0.134 cm^3/g and pore size of 6.522 nm

Table 1: BET analysis results for Chitosan Beads

Samples	Surface area (m^2/g)	Pore volume (cc/g)	Pore size (nm)
Chitosan beads	376.40	0.134	6.522

Table 2 shows the design matrix consisting of types of runs, coded and actual factors as

randomized by the software and respective responses obtained from the experiment

Table 2: Experimental design matrix using RSM for Copper and Arsenic removal onto chitosan beads

RUNS	A (g)	B (mg/L)	C ($^{\circ}\text{C}$)	D (min)	% Cu	% As
1	0.50	0.50	30.00	40.00	90.34	88.90
2	1.50	0.50	30.00	40.00	92.33	90.89
3	0.50	1.50	30.00	40.00	84.44	83.89
4	1.50	1.50	30.00	40.00	87.89	82.67
5	0.50	0.50	50.00	40.00	92.67	90.56
6	1.50	0.50	50.00	40.00	91.16	91.88
7	0.50	1.50	50.00	40.00	91.22	84.89
8	1.50	1.50	50.00	40.00	84.56	86.11
9	0.50	0.50	30.00	80.00	92.56	80.67
10	1.50	0.50	30.00	80.00	96.10	83.22
11	0.50	1.50	30.00	80.00	93.22	80.44
12	1.50	1.50	30.00	80.00	86.67	82.78
13	0.50	0.50	50.00	80.00	98.03	84.56
14	1.50	0.50	50.00	80.00	97.67	96.22
15	0.50	1.50	50.00	80.00	95.61	84.67
16	1.50	1.50	50.00	80.00	88.02	91.40
17	0.50	1.00	40.00	60.00	94.34	93.24
18	1.50	1.00	40.00	60.00	91.56	93.56
19	1.00	0.50	40.00	60.00	92.56	88.90
20	1.00	1.50	40.00	60.00	82.70	89.05
21	1.00	1.00	30.00	60.00	89.89	89.40
22	1.00	1.00	50.00	60.00	92.35	90.04
23	1.00	1.00	40.00	40.00	90.87	92.00
24	1.00	1.00	40.00	80.00	91.66	89.33
25	1.00	1.00	40.00	60.00	92.01	89.56
26	1.00	1.00	40.00	60.00	91.33	92.01
27	1.00	1.00	40.00	60.00	91.08	90.00
28	1.00	1.00	40.00	60.00	90.01	91.00
29	1.00	1.00	40.00	60.00	88.99	88.90
30	1.00	1.00	40.00	60.00	91.01	90.20

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The six centre points, run 25- 30 were conducted to determine the experimental error and the reproducibility of the data. From the results obtained, it could be observed that the highest percentage removal of copper and Arsenic on Chitosan beads were 98.03 and 96.22 % The highest removal efficiency on adsorbent (Copper and Arsenic) could be as a result of the processes employed which may also result to high adsorption surface area and active sites present in the structure of the adsorbent. In comparison, recent studies by Agata *et al.* (2017) on Zeolite modified by Chitosan

as an adsorbent for environmental applications shows that the removal efficiency of 100 % for Copper was obtained.

Table 3 shows that the quadratic model percentage removal for Copper and Arsenic on Chitosan beads. The result shows a relatively small standard deviation of 1.17 and relatively R^2 value of 0.9726 in reasonable agreement with adjusted R^2 (0.9512) for Copper and standard deviation of 1.77 which was relatively small, R^2 value of 0.9627 with adjusted R^2 (0.9414) for Arsenic on chitosan beads.

Table 3: Statistical parameters obtained from the analysis of variance (ANOVA) on Chitosan beads

Variable	Copper removal	Arsenic removal
Standard deviation	1.17	1.77
Coefficient of variation (%)	1.95	2.01
R- Squared (R^2)	0.9726	0.9627
R^2 - Adjusted	0.9512	0.9414
Adeq. Precision	11.388	11.219
Mean	91.09	88.36

The accuracy of the model developed can be understood by the value of R^2 , adjusted R^2 and standard deviation. R^2 indicates the ratio between sum of the squares (SSR) with total sum of the square (SST) and it describes up to what extent perfectly the model estimated experimental data points. Correlation coefficient and standard deviation were used to evaluate the fitness of the models developed. The closer the R^2 value to unity and the smaller the standard deviation, the better the model in predicting the response (Busetty and Ashutosh, 2014). The R^2 values can be attributed to the four factors (A- Adsorbent dosage, B- Initial metal concentration, C- Activation temperature and D- Activation time) considered.

The ANOVA was used to further emphasize the adequacy of the models and their significance. The mean squares in the ANOVA for the surface response quadratic models were obtained by dividing the sum of the squares of each of variation sources, the model and the error variance by the respective degrees of freedom. The ANOVA suggests that the equation and the actual relationship between the response and the significant variables represented by the equation were adequate. The larger the value of F and the smaller the value of p, the more significant is the corresponding coefficient term (Kalavathy *et al.*, 2009).

Table 4: ANOVA response surface cubic model on Copper removal for Chitosan Bead

Source	Sum of square	Degree of freedom	Mean square	F- Value	Prob> F
Model	320.39	14	22.88	7.27	0.0002
A-Dosage	15.07	1	15.07	4.79	0.0449
B- Conc.	133.88	1	133.88	42.54	<0.0001
C-Temp.	17.70	1	17.70	5.62	0.0315
D-Time	64.45	1	64.45	20.48	0.0004
AB	27.59	1	27.59	8.77	0.0097
AC	21.51	1	21.51	6.83	0.0195
AD	4.23	1	4.23	1.35	0.2643
BC	0.064	1	0.064	0.020	0.8887
BD	0.38	1	0.38	0.12	0.7347
CD	2.38	1	2.38	0.76	0.3983
A ²	14.87	1	14.87	4.72	0.0462
B ²	22.16	1	22.16	7.04	0.0181

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Source	Sum of square	Degree of freedom	Mean square	F- Value	Prob> F
C ²	0.83	1	0.83	0.26	0.6152
D ²	1.31	1	1.31	0.42	0.5288
Residual	47.21	15	3.15	-	-
Lack of fit	41.46	10	4.15	3.61	0.0847
Pure error	5.74	5	1.15	-	-

Table 5: ANOVA response surface cubic model on Arsenic removal for Chitosan bead

	Sum of square	Degree of freedom	Mean square	F- Value	Prob> F
Model	422.45	14	30.18	9.58	<0.0001
A-Dosage	40.23	1	40.23	12.77	0.0028
B- Conc.	49.67	1	49.67	15.77	0.0012
C-Temp.	78.00	1	78.00	24.77	0.0002
D-Time	19.01	1	19.01	6.04	0.0267
AB	4.46	1	4.46	1.42	0.2524
AC	14.57	1	14.57	4.63	0.0482
AD	24.93	1	24.93	7.91	0.0131
BC	0.32	1	0.32	0.10	0.7556
BD	23.26	1	23.26	7.38	0.0159
CD	32.06	1	32.06	10.18	0.0061
A ²	6.56	1	6.56	2.09	0.1687
B ²	20.76	1	20.76	6.59	0.0214
C ²	11.27	1	0.83	3.58	0.0780
D ²	3.37	1	3.37	1.07	0.3173
Residual	47.24	15	3.15	-	-
Lack of fit	41.22	10	4.12	3.42	0.0933

The value of prob>F lower than 0.05, indicates that the model may be considered to be statistically significant. For the removal of Copper on Chitosan beads, the ANOVA results (Table 5) indicated the model F-value of 7.27 which implied that it was significant and had only a 0.02% chance that its magnitude could occur due to noise (induced variation under normal operating conditions by uncontrollable factors). As expected, non-significant lack of fit was obtained with lack of fit F-value of 3.61 implying its non-significance relative to the pure error and the chances that 8.47 % of its value also occurred due to noise. As shown in Table 4, model terms A, B, C, D, AB, AC, A², B² were found significant. The ANOVA results for Table 5 for the removal of Arsenic on Chitosan beads also indicates the model F-value of 9.58 which implied that it was significant and had only a 0.01% chance that its magnitude could occur due to noise (induced

variation under normal operating conditions by uncontrollable factors). As expected, non-significant lack of fit was obtained with lack of fit F-value of 3.42 implying its non-significance relative to the pure error and the chances that 9.33 % of its value also occurred due to noise.

The data were also analyzed to check the correlation between the experimental and predicted percentage removal, as shown on Table 6. The experimental values were the result obtained, while the predicted values were obtained by calculation from the quadratic equation. It is shown in Figure 2 that the data points on the plot are distributed near to the straight line, indicating a good relationship between the experimental and predicted values of the response. The result also suggests that the selected quadratic model was adequate in predicting the response variables for the experimental data.

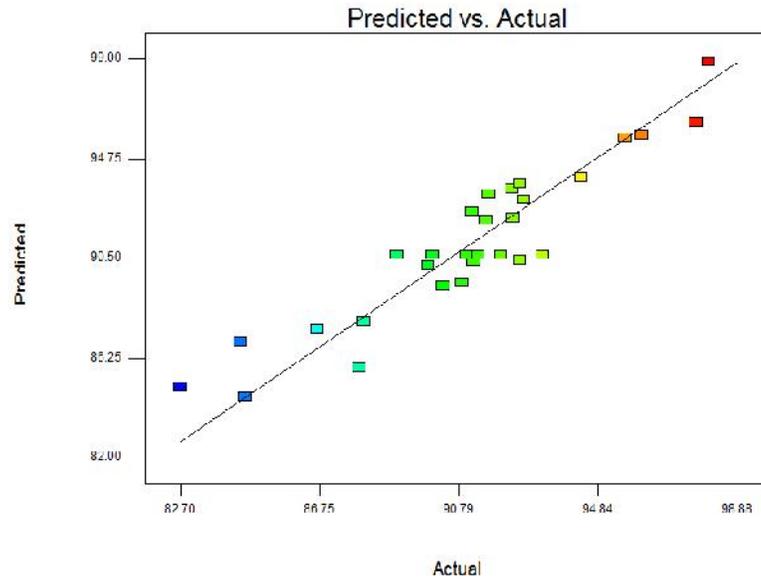


Table 6: Actual- predicted values and residual for Chitosan Bead responses.

Runs	Copper removal (%)			Arsenic removal (%)		
	Actual	Predicted	Residual	Actual	Predicted	Residual
1	90.34	89.33	1.01	88.90	89.85	0.95
2	92.33	93.48	1.15	90.89	89.49	1.40
3	84.44	86.96	2.50	83.89	85.45	1.56
4	87.89	85.83	2.06	82.67	82.98	0.31
5	92.67	92.99	0.32	90.56	89.55	1.01
6	91.16	92.50	1.34	91.88	93.01	1.13
7	91.22	90.34	0.88	84.89	84.59	0.30
8	84.56	84.60	0.038	86.11	85.94	0.17
9	92.56	93.68	1.12	80.67	80.05	0.62
10	96.10	95.77	0.33	83.22	84.69	1.47
11	93.22	90.67	2.55	80.44	80.48	0.039
12	86.67	87.52	0.84	82.78	83.00	0.22
13	98.03	98.88	0.85	84.56	85.42	0.86
14	97.67	96.33	1.34	96.22	93.87	2.35
15	95.61	95.62	0.012	84.67	85.28	0.61
16	88.02	87.82	0.20	91.40	91.62	0.22
17	94.34	93.96	0.38	93.24	91.14	2.10
18	91.56	92.13	0.57	93.56	94.13	0.57
19	92.56	90.45	2.11	88.90	89.87	0.97
20	82.70	84.99	2.29	89.05	86.55	2.50
21	89.89	90.22	0.33	89.40	86.87	2.53
22	92.35	92.20	0.15	90.04	91.04	1.00
23	90.87	89.46	1.41	92.00	90.93	1.07
24	91.66	93.25	1.59	89.33	88.87	0.46
25	92.01	90.65	1.36	89.56	91.04	1.48
26	91.33	90.65	0.68	92.01	91.04	0.97
27	91.08	90.65	0.43	90.00	91.04	1.04
28	90.01	90.65	0.64	91.00	91.04	0.042
29	88.99	90.65	1.66	88.90	91.04	2.14
30	91.01	90.65	0.36	90.20	91.04	0.84

Design-Expert® Software
 % Cu

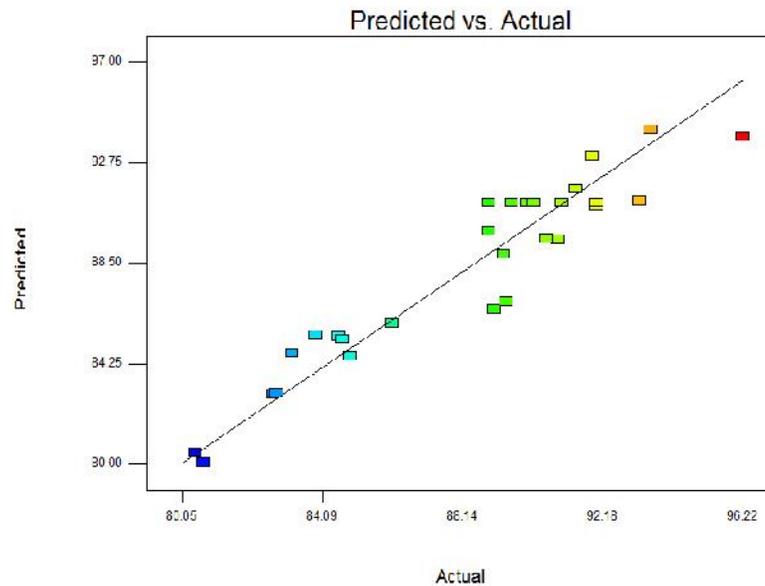
Color points by value of
 % Cu
 96.03
 82.7



(a)

Design-Expert® Software
 % As

Color points by value of
 % As
 96.22
 80.44



(b)

Figure 2: Actual – predicted value plot on percentage adsorption of (a) Copper (b) Arsenic on Chitosan Beads.

The interaction effects of adsorbent dosage, initial metal concentration, temperature and time

parameters for Copper removal catalyst on chitosan beads as shown in Figure 3 (a-f)

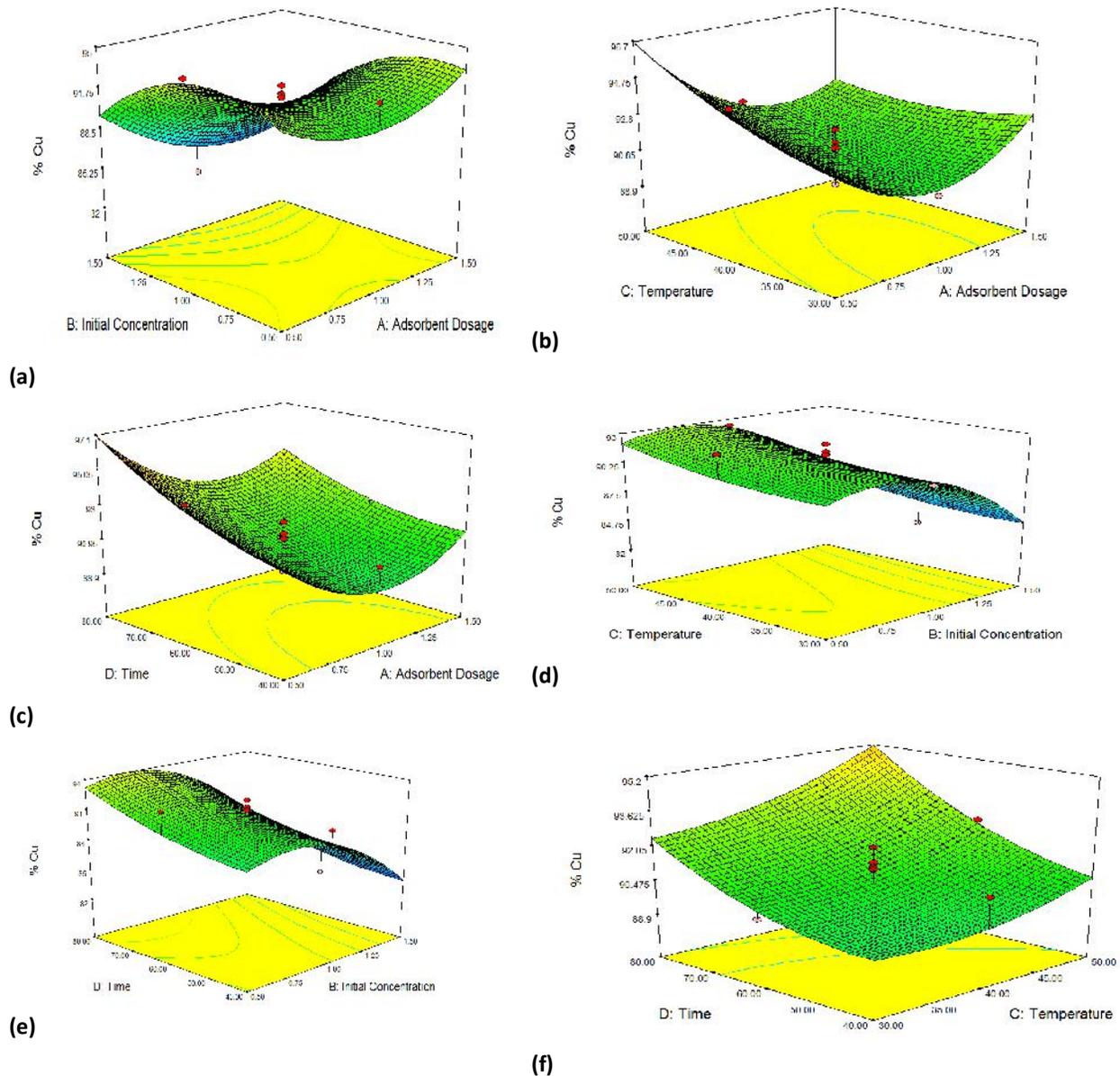


Figure 3: 3D Surface plots for effects of Copper adsorption parameters on Chitosan Beads

The effect of initial concentration (A) and adsorbent dosage (B) is given in Figure 3a. The plot indicates that both parameters have significant effect on Copper removal with the linear (A, B) and interaction AB terms having a marked effect ($p < 0.05$) as seen on Table 4. The resultant effect of both parameters on copper removal may be attributed to the enhanced surface area and the availability of more active binding sites in adsorbing the solute. The concentration of Copper ensued increasing of the mass transfer driving force and the rate of Copper passing the bulk solution to the

particle surface. At a concentration of 0.5 mg/L and adsorbent dosage of 0.5 g, the maximum percentage removal of copper was 98.03 %. The sloppy nature of the 3D plot as a function of adsorbent dosage (A) and time (C) depicted in Figure 3b, shows that the two terms have significant effect on Copper removal with the linear (A, C) and interaction AC term having a marked effect ($p < 0.05$) as seen on Table 5. The Copper percentage removal increased from 82.7-98.03 % as the temperature increased and remained approximately same with lower adsorbent dosage. Figure 3c represents the 3D plot for time (D) as a

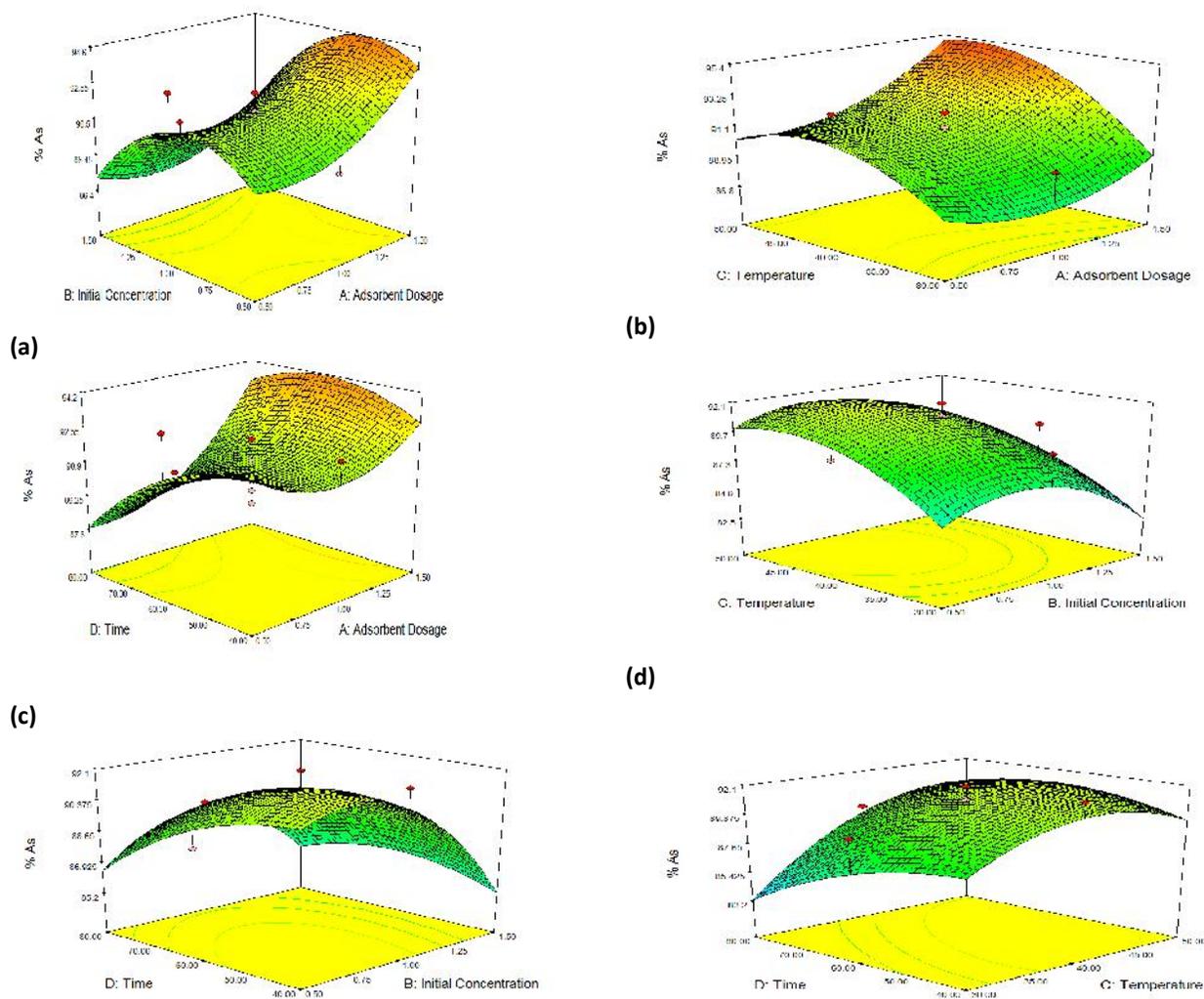
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function of adsorbent dosage (A) for Copper removal. According to the plot, the two terms have significant effect on Copper removal; however adsorbent dosage has a much higher effect, this behavior is attributed to the availability of more active site and surface area which is largely determined by adsorbent dosage.

An adsorbent dosage of 0.5 mg/L is observed to give a Copper removal of over 98 % at a time of 80 min. The surface plot for the interaction of temperature (C) and initial concentration (B) on the synthesized Chitosan beads used in the removal of Copper is displayed in Figure 3d. The plot shows that both terms significantly influenced Copper removal with the linear (C, B) having a marked effect on the removal. This trend could be as a result of initial concentration due to the saturation of metal binding sites of the adsorbent and at maximum temperature (50 °C), maximum removal of Copper

was favoured. The relationship between time (D) and initial concentration (B) is illustrated in the 3D plot of Figure 3e. The curvature nature of the plot suggests that a significant individual interaction exists between the two terms. It shows that the combination of low initial concentration and high adsorption time favours maximum Copper removal. Figure 3f represents the 3D plot for time (D) as a function of temperature (C) for Copper removal. According to the plot, the two terms have significant individual effect on Copper removal; however adsorption time has a much higher effect. An increased in temperature (30-50 °C) and increased in time (40-80 °C) result to an increased in the maximum removal of Copper.

The interaction effects of adsorbent dosage, initial metal concentration, temperature and time parameters for Copper removal catalyst on chitosan beads as shown in Figure 3.4(a-f)



*Corresponding author: Raliat Yusuf Yakubu ✉ rallyusuf@yahoo.com ✉ Department of Chemical Engineering, Federal University of Technology, Minna. © 2019 Faculty of Technology Education, ATBU Bauchi. All rights reserved

(e)

The effect of initial concentration (A) and adsorbent dosage (B) is given in Figure 4a. The plot indicates that both parameters have significant effect on Arsenic removal with the linear (A, B) terms having a marked effect ($p < 0.05$) as seen on Table 5. The resultant effect of both parameters on copper removal may be attributed to the enhanced surface area and the availability of more active binding sites in adsorbing the solute. At lower concentration of Arsenic and higher adsorbent dosage, the removal of Arsenic was maximum (96.22 %). The sloppy nature of the 3D plot as a function of adsorbent dosage (A) and time (C) depicted in Figure 4b, shows that the two terms have significant effect on Arsenic removal with the linear (A, C) and interaction AC term having a marked effect ($p < 0.05$) with temperature having the highest effect based on their F-values as seen on Table 5. The Percentage removal of Arsenic increased from 82.67- 96.22 % as the adsorbent dosage increased and remained approximately same with decreased initial concentration due to the binding sites of the adsorbent. Figure 4c represents the 3D plot for time (D) as a function of adsorbent dosage (A) for Arsenic removal. According to the plot, the two terms have significant effect on Arsenic removal; however adsorbent dosage has a much higher effect, this behaviour is attributed to the availability of more active site and surface area which is largely determined by adsorbent dosage. An adsorbent dosage of 1.5 mg/L is observed to give an Arsenic removal of over 96.22 % at a time of 80 min. The surface plot for the interaction of temperature (C) and initial concentration (B) on the synthesized Chitosan beads used in the removal of Copper is displayed on Figure 4d. The plot shows that both terms significantly influenced Copper removal with the linear (C, B) having a marked effect on the removal. This trend could be as a result of initial concentration which is due to the saturation of metal binding sites of the adsorbent. The relationship between time (D) and initial concentration (B) is illustrated in the 3D plot of Figure 4.e. The curvature nature of the plot suggests that a significant interaction exists between the two terms and based on their F-value, initial concentration has the highest effect on the percentage removal. It shows that the combination of lower initial concentration (0.5 mg/L) and higher adsorption time (80 min) favours maximum Arsenic

(f)

Figure 4: 3D Surface plots for effects of Arsenic adsorption parameters on Chitosan Beads

removal. Figure 4f represents the 3D plot for time (D) as a function of temperature (C) for Copper removal. According to the plot, the two terms have significant interaction effect on Arsenic removal; however, adsorption temperature has a much higher effect. An increased in temperature (30-50 °C) and increased in time (40-80 °C) result to an increased in the percentage removal.

CONCLUSION

- i. IR spectrum analysis suggested the different functional groups which are present in the Chitosan beads to be $-\text{CONH}-$, $-\text{NH}-$, $-\text{CH}_3$, C-O, stretching N-H bending
- ii. The BET shows the surface area, pore size and pore volume of the Chitosan beads to be $376.40\text{m}^2/\text{g}$, 6.522nm , and 0.134cc /respectively.
- iii. Central composite design was used to optimize the percentage removal of Copper and Arsenic on Chitosan beads produced at various parameters such as: adsorption temperature, initial concentration, adsorbent dosage and adsorption time under study. The optimal conditions obtained for Copper removal on Chitosan beads were 0.5 g, 0.5 M, 50 °C and 80 min which translated to 98.03 and 99.78%.
- iv. The combined effect of adsorbent dosage and temperature and the combined effect of temperature and time from the four parameters studied for Chitosan beads were found to have the greatest impact on Copper and Arsenic removal while the combined effect of initial concentration and time and that of adsorbent dosage and initial concentration were also found to have the greatest impact on both Copper and Arsenic removal based on their F-values.

REFERENCES

- Agata, P., Dorota, K., Paulina M. G., Małgorzata F., Zbigniew H. (2017). The zeolite modified by chitosan as an adsorbent for environmental applications. *Research Article* 35, 9-10.
- Amuda O. S., Edewor T. I. (2007). Steam-activated carbon prepared from *Chrysophyllum albidum* seed shell for the adsorption of cadmium in wastewater:

*Corresponding author: Raliat Yusuf Yakubu ✉ rallyusuf@yahoo.com ✉ Department of Chemical Engineering, Federal University of Technology, Minna. © 2019 Faculty of Technology Education, ATBU Bauchi. All rights reserved



- kinetics, equilibrium and thermodynamic studies. *Int. J. Environ. Waste Manage.* 12(2):213-229.
- Barakat M.A (2010) New Trend in removing heavy metals from Industrial Waste Water. *Arabian J. of Chemistry Review Article.* 363 – 368
- Busette Subramanyam and Ashutosh Das (2014). Linearise and non – linearized isotherm models optimization analysis by error functions and statistical means. A Research Article, *Journal on Environmental Health and Science Engineering* 2014.12:92
- Benabid F. Z. and Zouai F. (2016). Natural Polymers, Cellulose, Chitin, Chitosan, Gelatin, Starch, Carrageenan, Xylan and Dextran. *Algerian Journal of Natural Products* 4:3(2016)349 - 350
- Choi, C. Y., Kim, S. B., Pak, P. K., Yoo, D. I. & Chung, Y. S. (2007). Effect of Nacylation on structure and properties of chitosan fibers. *Carbohydr. Polym.* 68(1), 122-127.
- Gupta, A., Yunus, M. and Sankaramakishnan, N., (2011). *International Conference on Environment Science and Engineering, Singapore*, 29–32. IACSIT press: Singapore.
- Kurniawan T.A, Chan G.Y, Lo W. H, Babel S. (2006). Comparisons of low – cost adsorbents for treating wastewaters laden with heavy metals. Department of Applied Biology and Chemical Technology, the Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong. *Review Article. Sci. Total Environ* 1:366(2 – 3).
- Kalavathy, M. H., Regupathi, I., Pillai, M. G. & Miranda, L. R. (2009). Modelling, analysis and optimization of adsorption parameters for H₃PO₄ activated rubber wood sawdust using response surface methodology (RSM). *Colloids Surf B*, 70(1), 35–45.
- Li, Q., Weng, S., Wu, J. & Zhou, N. (1998). Comparative study on structure of solubilized water in reversed micelles. 1. FT-IR spectroscopic evidence of Water/AOT/n-Heptane and Water/NaDEHP/n-Heptane systems. *J. Phys. Chem. B* 102(17), 3168-3174.
- Nagai Takeshi, Masami Izumi, Masahide Ishii (2004) Fish scale collagen preparation and partial characterization. *International Journal of Food Science and Technology and Amp; Technology* 39(3):239
- Oguzie F. A. and Okhagbuzo G.A (2009). Concentration of heavy metals in Effluent Discharges Downstream of Ikpoba river in Benin City, Nigeria. Department of Fisheries, University of Benin, Benin City Edo State, Nigeria. *African Journal of Biotechnology*, 9(3):319
- Purushotham D., Mehnaz Rashid, Mahjoor Ahmad Lone, Narsing Rao.A., Shakeel Ahmed, Nagaiah E. and Farooq Dar. A. (2013). Environmental impact assessment of air and heavy metal concentration in ground water of Maheswaram watershed, Ranger Reddy District, Andhra Pradesh. CSIR – National Geophysical Research Institute Hyderabad-500606 Department of Geology, Osmania University Hyderabad – 500 007
Email: dasu_purushotham@yahoo.co.in
- Sethu VS, Goey KS, Iffah FR, Khoo CM, Andresen JM (2010). Adsorption Characteristics of Cu (II) Ions in Aqueous Solutions using *Mangifera Indica* (Mango) Leaf Biosorbents. *J. Environ. Res. Develop.* 5(2), 262-278.
- Suneeta Kumari, Pradip Kumar Rath (2014). Extraction and characterization of chitin and chitosan from (Labeo rohita) fish scales. *Third International conference on Materials Processing and Characterization (ICMPC 2014) Proceedia Material Science* 6 (2014) 482 – 484
- Yang C. Tony and Zall Robert R. (1894). Adsorption of Metals by Natural Polymers generated from Seafood processing waters. *Industrial and Engineering Chemistry Product Research and Development* 23(1) 322.