Available online www.jsaer.com

***Journal of Scientific and Engineering Research*, 2016, 3(3):188-193**

Research Article

ISSN: 2394-2630
CODEN(USA): JSERBR

Application of Factorial Design to the Adsorption Cd (II) ion from Aqueous Solution onto Chemically Modified *Bombax buonopozense* Calyx

Musah M*[1], Yisa J[1], Mann A[1], Suleiman MAT[1], Auta M[2]

[1]Federal University of Technology, Department of Chemistry, Minna, Nigeria
[2]Federal University of Technology, Department of Chemical Engineering, Minna,, Nigeria

Abstract The removal of cadmium ions from aqueous solution was studied using activated carbon prepared from *Bombax buonopozense* Calyx. The effects of variables such as contact time, adsorbent dosage, concentration and pH of solution were studied. A 2^4 factorial experimental design technique was used to study the adsorption of cadmium ions onto the adsorbent. The factorial design model allows the prediction of the extent of different adsorption conditions of the variables. Analysis of variance used to validate the model showed that there is no lack of fit at 95 % confidence level. The correlation coefficient between the experimental and calculated results showed a good performance of the model. Maximum experimental adsorption of 95.53 % was achieved under optimum condition.

Keywords Heavy metals, adsorption, concentration, adsorbent, aqueous solution

Introduction

Metals and their compounds are very important and indispensable part of any nation's industrial and technological advancement. Pollution derived from these metals has continued to increase as industrial activities increases. The annual toxicity resulting from heavy metals discharged into the environment is believed to exceed the total toxicity of organic and radioactive wastes [1].

Heavy metals are elements whose densities are relatively high (> 5g/cm^3) and could be toxic even at low concentrations [2]. These metals are not usually biodegradable, when released into the environment can persist for decades and if ingested above tolerable levels can have very harmful effects on human health. Despite the adverse effects of heavy metals on human health, exposure to these metals has continued and even increasing in areas.

Heavy metals of concern include cadmium, lead, mercury, nickel, silver, manganese, chromium and cobalt. This work focuses on the adsorption of cadmium from aqueous solution. Cadmium occurs naturally in soil, rocks, coal and in mineral fertilizers; it has also been found in several industrial wastes. Cadmium is widely used in metal plating, pigments, and metal coatings, as stabilizers in PVC products, rechargeable nickel-cadmium batteries and as anticorrosive agent.

Natural and anthropogenic sources of cadmium which include industrial discharge, application of sewage sludge and fertilizers on farmland has increased soil and water contamination. Its uptake by plants and consumption of such plants increases exposure to health effects of cadmium whose exposure over long term may cause skeletal damage [1]. Ingesting high dosage of cadmium severely irritates the stomach, causing vomiting and diarrhoea; and grave damage to the lungs could occur. Low level exposure over a long time will lead to a build up of cadmium in the kidneys and kidney disease, fragile bones and damage to the lungs [3].

Several research report on the adsorption of heavy metals from aqueous solution have used one variable at a time keeping others constant on the assumption that the variables are independent of each other. Geyekci and Buyukgungor [4] posit that the assumption is not true. This research uses the analysis in which more than one factor can be evaluated to study the adsorption (factorial analysis) of Cd (II) ion from aqueous solution onto the adsorbent.

Materials and Methods

Cadmium Stock Solution (1000 mg/L) was prepared by dissolving 2.036 g of cadmium nitrate ($Cd(NO_3)_2$) in $1000cm^3$ volumetric flask with distilled then made up to mark. The working solutions of 10, 20, 30, 40 and 50mg/L were prepared by appropriate dilutions of the stock solution. Adsorbent used for adsorption experiment was prepared from *Bombax buonopozense* Calyx using the two step method and further functionalized with 32.5 % nitric acid [5-6].

Factorial Design of the Adsorption Experiment

A 2^4 factorial design was employed to study the adsorption of Cd^{2+} onto the activated carbon. Whenever factorial design is used, there is reduction in the total number of experiments performed in order to attain maximum optimization of a system. It reduces time and also saves cost of overall process and gives better response [7]. In this study, percentage adsorption of metal ions is the dependent variable while time (mins), dosage (g), concentration (mg/L) and pH are the independent variables. Table 1 shows the low and high levels of the independent variables for the adsorption of the Cd (II) ion. 0.1 $moldm^{-3}$ of HCl and NaOH were used to adjust pH of the solution.

Table 1: Factor Levels of Independent Variables for the Adsorption of Cd^{2+}

Independent Variables	Low level (-1)	High Level (+1)
Time (mins)	30	150
Dosage (g)	0.2	1.0
Concentration (mg/dm^3)	10	50
pH	4	8

Results and Discussion

Experimental and Predicted Adsorption of Cd (II) Ion

Table 2 presents the percent adsorption of cadmium using the 2^4 factorial experimental design. The result showed the actual and predicted adsorption as well as residuals of adsorption arranged in run order as influenced by the independent variables: time (mins), adsorbent dosage (g), concentration (mg/L) and pH.

Table 2: 2^4 Full Factorial Experimental Design

Run Order	Time (mins)	Dosage (g)	Concentration (mg/L)	pH	Adsorption (%)		Residual
					Actual	Predicted	
1	30.00	0.20	10.00	4.00	85.95	84.07	1.88
2	30.00	0.20	50.00	8.00	77.12	77.18	-0.06
3	30.00	0.20	10.00	8.00	83.04	83.89	-0.85
4	150.00	1.00	50.00	4.00	89.79	88.94	0.85
5	30.00	1.00	10.00	8.00	90.97	91.05	-0.08
6	30.00	1.00	50.00	4.00	87.62	87.58	0.04
7	150.00	1.00	10.00	4.00	95.53	94.47	0.06
8	30.00	1.00	50.00	8.00	80.89	79.90	0.99
9	150.00	0.20	50.00	8.00	74.84	73.89	0.95
10	150.00	1.00	50.00	8.00	78.18	80.06	-1.88
11	150.00	0.20	10.00	8.00	81.90	81.94	-0.04
12	150.00	0.20	10.00	4.00	82.33	83.32	-0.99
13	150.00	0.20	50.00	4.00	81.32	81.24	0.08
14	150.00	1.00	10.00	8.00	93.54	92.57	0.97
15	30.00	1.00	10.00	4.00	91.81	92.76	-0.95
16	30.00	0.20	50.00	4.00	82.36	83.33	-0.97

Columns 7 (table 2) showed the highest experimental adsorption value of 95.53% with predicted values of 94.47%. Optimum adsorption of Cd (II) ion occurred at upper levels of time and dosage; and lower concentration and pH as depicted in figure I. The residuals value of 0.06 indicates a good agreement between the experimental and predicted adsorption for Cd (II) adsorption with R^2 equals 0.9749 also suggesting a good fitting of the model. The good correlation observed between the predictive and experimental values indicate a good predictive ability of the model. The adsorption obtained in this study are similar to those reported for Cu (II) adsorption at upper level contact time and dosage and at lower level of concentration and pH [8].

Estimated Effects and Coefficients for Adsorption of Cd (II)

Estimated effects and coefficients of the experimental factors are presented in Table 3. The table shows the main and interactive estimated effects, coefficients of the model and probability for adsorption of HAC adsorption of Cd (II) ion. The correlation coefficient of 97.49% was obtained for HAC. The coefficient equals one-half of the corresponding effect and every coefficient has a standard deviation shown in column 4 of the estimated effects. The results of 'student's t-test' labelled 'T' and P-value indicate that three main individual factors effects (dosage, concentration and pH) and the 2-factors interactions (dosage*concentration and concentration*pH) are significant at 95% confidence level.

Table 3: Estimated Effects and Coefficients for Cd (II) Ions Adsorption (%)

Term	Effect	Coef	SE Coef	T	P
Constant		84.826	0.4217	201.14	0.000
Time (mins)	-0.287	-0.144	0.4217	-0.34	0.747
Dosage (g)	7.438	3.719	0.4217	8.82	0.000
Concentration (mg/L)	-6.622	-3.311	0.4217	-7.85	0.001
pH	-4.532	-2.266	0.4217	-5.37	0.003
Time (mins) *Dosage (g)	1.733	0.866	0.4217	2.05	0.095
Time (mins) *Concentration (mg/L)	-0.678	-0.339	0.4217	-0.80	0.458
Time (mins)*pH	-0.602	-0.301	0.4217	-0.71	0.507
Dosage (g) *Concentration (mg/L)	-2.227	-1.114	0.4217	-2.64	0.046
Dosage (g)*pH	-0.768	-0.384	0.4217	-0.91	0.405
Concentration (mg/L)*pH	-2.982	-1.491	0.4217	-3.54	0.017

R-Sq = 97.49%   R-Sq(adj) = 92.47%

Positive effect of dosage meant that Cd (II) ion uptake is favoured at high value as corroborated by values on the 'effect column'. This observation is similar to those made on the biosorption of Cd^{2+} and Pb^{2+} [9] and the adsorption of Ag^{+} onto montmorillite [7]. On the other hand, the negative effect values of concentration, pH and dosage*concentration, concentration*pH implies these factors contribute to adsorption at low values. When the effect of a factor is positive, there is an increase in percent adsorption as the factor changes from low to high levels. On the contrary, reduction in percent adsorption occurs for high level of a factor if the effect is negative [10].

Analysis of Variance for Adsorption of Cd (II) Ions

Table 4 present the results of Analysis of Variance (ANOVA) for the adsorption of HAC adsorption of Cd (II) ion using the factorial design.

Analysis of the main and interaction effects on adsorption showed significant parameters and estimated adsorption efficiency of Cd (II) ion as a function of interaction of time, dosage of activated carbon, concentration and pH of solution as main effects and their interactions. Main effects; dosage (0.000), concentration (0.001) and pH (0.003) showed significant effect on adsorption of Cd^{2+} onto HAC. Few interaction effects were significant with only the interactions of dosage*concentration (0.046) and concentration*pH (0.017) been significant. Similar trends were observed in the removal of copper ions from acid mine [10] and biosorption of chromium using factorial experimental design [11].

Table 4: Analysis of Variance for *Adsorption of Cd (II) Ions*

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	4	479.200	479.200	119.800	42.10	0.000
Time (mins)	1	0.331	0.331	0.331	0.12	0.747
Dosage (g)	1	221.266	221.266	221.266	77.76	0.000
Concentration (mg/L)	1	175.430	175.430	175.430	61.65	0.001
pH	1	82.174	82.174	82.174	28.88	0.003
2-Way Interactions	6	73.079	73.079	12.180	4.28	0.066
Time (mins)*Dosage (g)	1	12.006	12.006	12.006	4.22	0.095
Time (mins)*Concentration (mg/L)	1	1.836	1.836	1.836	0.65	0.458
Time (mins)*pH	1	1.452	1.452	1.452	0.51	0.507
Dosage (g)*Concentration (mg/L)	1	19.847	19.847	19.847	6.97	0.046
Dosage (g)*pH	1	2.356	2.356	2.356	0.83	0.405
Concentration (mg/L)*pH	1	35.581	35.581	35.581	12.50	0.017
Residual Error	5	14.228	14.228	2.846		
Total	15	566.507				

Statistical Analysis of Adsorption of Cd (II) Ions

F-value is the mean of the variation of the data about the mean. A high F-value and low p-value ($p<0.05$) indicate that such main effects and/or interactions are significant at 95% significance level. From the results, F-values of 77.76, 61.65 and 28.88 having p-values less than 0.05 indicate the model is significant with main effects showing more statistical significance. These results indicate the model is in good prediction of the experimental result [9], and similar to those reported for lead adsorption [12].

From the normal plots of standardized effects in Figure 1a, the points that are near the line represent factors whose effect on the response is small and points that are far from the line indicate those that have significant effect on the response. The farther the point is from the line the more its significance. Factors on the positive side of the line have positive effects while those on the negative side of the line have negative effect on the response [12].

In figure 1b, dosage (B), concentration (C), pH (D) and interactions B*D, B*C and C*D showed significant effect on the response with main effect B having the highest positive significance while effect C had the highest negative effect on HAC adsorption of Cd (II) ion as corroborated by effects and P-values in Table 3.. This result is similar to that obtained in the adsorption of silver ions from water were dosage, pH and concentration had significant effect on the response [7].

Student's t-test presented as pareto chart of standardized effects was used to determine if the calculated effects are notably different from zero. For a 95% confidence level and 15 degrees of freedom, the t-value is equal to 2.571 [10]. These estimations are presented in figure 1b with the vertical line indicating the minimum statistically significant effect magnitude, values in the horizontal column represent the student's t-test value for each effect [8]. All standardized effects are in absolute values. Factors that showed significance from the chart are those whose values are ≥ 2.571. From the results, it can be inferred that main effects B, C, D and 2-way interactions B*C and C*D are important factors in the adsorption of Cd (II) ions onto the adsorbent. These results are similar to those obtained for the effects concentration and pH by Lima et al [13].

Main effects plot for adsorption is presented in Figure 1c. This plot is useful in visualizing the factors that affect adsorption the most and each factor's level affects response differently. If the slope is close to horizontal, then the magnitude of the effect is small [12]. The effect of factor dosage (B) at high level with dosage (B) and concentration (C) at low levels results in high mean response. Factor A (time) showed a very weak positive effect indicating insignificant effect of the factor on the sorption process. Effects of concentration (C) and pH (D) at low levels showed that the process is favoured at low concentration (C) and pH (D). This observation is similar to the report on the adsorption of Ag^{+} [7].

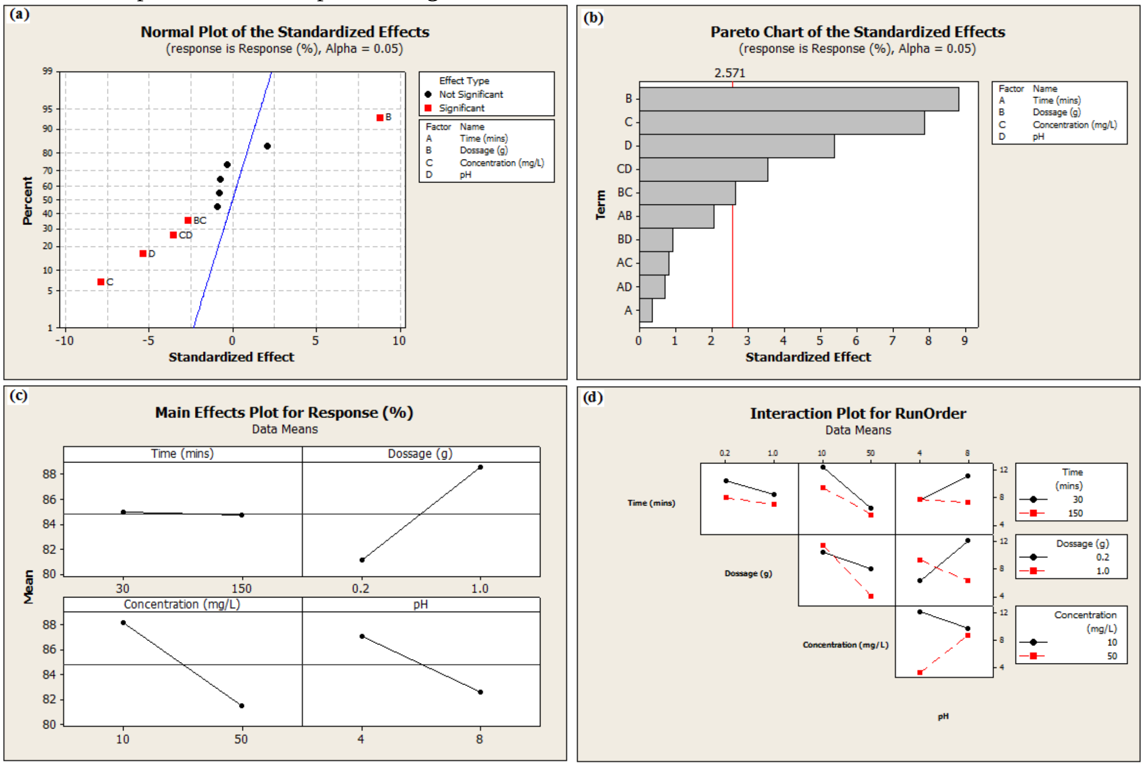

Figure 1: Statistical Analysis of Adsorption of Cd (II) Ions

The factors interaction plot for adsorption of Cd^{2+} presented in figure 1d depicts the impact changing of a factor will have on another during sorption. If the lines of the two factors run parallel, then there is no interaction between the factors but if the lines are far from being parallel and seen to appreciably cross each other, then the two factors are said to interact [11]. Interaction effect is done because one factor at a time experiment does not usually characterise the combined effects of all the factors involved in the experiment [8]. The results showed B*C and C*D as the significant 2-way interactions in the adsorption of Cd^{2+} from aqueous solution onto the adsorbent.

Equations in Terms of Factors for Adsorption of Cd (II)Ions

A model equation was used to describe the behaviour of adsorption factors in relation to adsorption of Cd^{2+}. For the development of the model, 16 runs were used for the calibration; and percent adsorption of metal ions varied depending on main factors and 2-way interaction of factors. Considering the student's t-test presented as Pareto charts in Figures 1b some factors were not statistically significance on the adsorption. On the bases of foregoing, the model was recalculated to eliminate the non significant effects and the resultant model equation for adsorption process is presented in simplified form as equation 1.1.

Adsorption (%)

= +80.12516 + 13.08438 x Dosage + 0.16716 x Concentration + 0.036016 x pH – 0.13898 x Dosage x Concentration – 0.037328 x Concentration x pH

When the effect of a factor is positive , adsorption increases as the factor changes from low to high level, but if the effect is negative, reduction in adsorption occurs for high level of same factor [10].

Conclusion

From the study, factorial design for experiment has proved to be a good technique for studying the influence of main factors and interactions of factors on adsorption by reducing the number of experiments. The use of factorial design experiments allows the identification of the most significant factors in adsorption and mathematically determines the significant factors among several factors in one experiment that predicts where the optimum adsorption is likely to be obtained. The most significant effect for Cd^{2+} adsorption in this study is due the main effects; dosage, concentration and pH. The 2-way interactions that had significant influence on the sorption process are dosage and concentration, with concentration and pH.

Acknowledgement

Authors are grateful to STEP-B (Science and Technology Education Post Basic) and the laboratory technologists of the Departments of Chemistry, Federal University of Technology, Minna and Ahmadu Bello University, Zaria, Nigeria for their assistance.

References

[1]. Badmus, M.A.O., Audu, T.O.K. & Anyata, B.U. (2007). Removal of lead ion from industrial wastewaters by activated carbon prepared from periwinkle shells (*Typanotonus fuscatus*). *Turkish Journal of Engineering and Environmental Science*. 31:251-263.

[2]. Nwankwo, O .D. & Mogbo, T. C. (2014). Preliminary study on use of urea activated melon (*Citrulus colocynthis*) husk in the adsorption of cadmium from wastewater. *Animal Research International,* 11(2):1917-1924.

[3]. Martin, S. & Grisworld, W. (2009). Human health effects of heavy metals. *Environmental Science and Technology Briefs for Citizens*, 1-6.

[4]. Geyikçi, F. And Büyükgüngör, H. (2013). Factorial Experimental Design For Adsorption Silver Ions From Water Onto Montmorillonite. *Acta Geodyn. Geomater*, 10(3),363–370.

[5]. Rahman, M. M., Adil, M., Yusof, A. M., Kamaruzzaman, Y. B. and Ansary, R. H. Removal of heavy metals ions with acid activated carbons derived from oil palm and coconut shells. *Materials*.2014; 7:3634-3650.

[6]. Albishri, H. M. andMarwani, H. M. Chemically modified activated carbon with tris(hydroxymethyl)aminomethane for selective adsorption and determination of in water samples. *Arabian Journal of Chemistry*. 2011. doi:10.1016/j.arabjc.2011.03.017.

[7]. Geyikçi, F. And Büyükgüngör, H. (2013). Factorial Experimental Design For Adsorption Silver Ions From Water Onto Montmorillonite. *Acta Geodyn. Geomater*, 10(3),363–370.

[8]. Turan, N. G. and Ozgonenel, O. (2013). Study of Montmorillonite Clay for the Removal of Copper (II) by Adsorption: Full Factorial Design Approach and Cascade Forward Neural Network. *The Scientific World Journa*,l-11.

[9]. Al-Mamun, A., Alam, Z., Mohammed, N.A.N. & Rashid, S.S. (2011). Adsorption of heavy metal from landfill leachate by wasted biosolids. *African Journal of Biotechnology*,10(81):18869-18881.

[10]. Gaikwad, R.W., Sapkal, R.S. & Sapkal, V.S. (2010). Removal of copper ions from acid mine drainage wastewater using ion exchange technique: Factorial design analysis. *Journal of Water Resources and Protection*, 2:984-989.

[11]. Carmona, M.E.R., Pereira da Silva, M.A. & Leite, S.G.F. (2005). Biosorption of chromium using factorial experimental design. *Process Biochemistry*, 40:779-788.

[12]. Tibet, Y. & Coruh, S. (2015). Lead release from lead-acid batteries slag using waste materials: Full factorial design analysis. Proceeding of the 14th International Conference on Environmental Science and Technology, Rhodes, Greece.

[13]. Lima, E. C., Royer, B., VAghetti, J. C. P., Brasil, J. L., Simon, N. M., Dos Santos, A. A., Pavan, F. A., ……… Da Silva, E. A. (2007). Adsorption of Cu (II) on *Araucaria angustifolia* waste: Determination of the optimal conditions by statistic design of experiment. *Journal of Hazardous Materials*, 140:211-220.