



Effect of Factors Variation on the Adsorption of Cd²⁺ on Chemically Modified Agricultural Waste

*Musah, M., ¹Elele, U. U., ¹Umar, M. T. and ²Umar, A.

¹Department of Chemistry, Ibrahim Badamasi Babangida University, Lapai, Nigeria

²Department of Chemistry, Niger State College of Education, Minna, Nigeria

ABSTRACT

The effects of variation of time, adsorbent dosage, concentration and solution pH on the adsorption of Cd²⁺ from aqueous solution were determined using standard methods of analysis. Results indicate that 83.49 % of Cd²⁺ was adsorbed after 30 minutes interaction time and 0.2 g adsorbent dosage with concentration and pH kept at 10 mg/dm³ and 4 respectively; 92.11 % Cd²⁺ was removed from solution when adsorbent dosage was increased to 1.0 g while time, concentration and pH remained unchanged. The effect of adsorbent dosage on adsorption of Cd²⁺ positive and high (7.438) while the effects of concentration and pH were -6.622 and -4.532 respectively (negative effect). The experimental and calculated (predicted) value for each run falls closed to the straight line with residual value of ≤ 2.00 indicating a good fit of the model.

Keywords: Adsorption, time, dosage, concentration, pH, Agricultural waste

INTRODUCTION

Heavy metals enter the environment through natural processes or through human activities. These metals are known to persist in the environment creating problems of inaccessibility to clean water as result of contamination. The high cost of water treatment to remove heavy metals has necessitates the need for activated carbon prepared from low cost viable agricultural materials or wastes to meet the increasing need for heavy metal removal from wastewater. In Nigeria as in most other developing countries, most industries discharge their wastewaters without treatment and there seem to be very little or no supervision by relevant authorities on how the wastewater is discharged into the environment (Babatunde *et al.*, 2014).

The utilization of agricultural by-products for removal of heavy metals from aqueous solutions is getting much attention these days. Natural biopolymers are industrially attractive because of their capability of lowering transition metal ion concentration to parts per billion concentrations and may have potential to be used as low cost adsorbents, as they represent unused resources, widely available and are environmentally friendly (Ahmad *et al.*, 2014). The best known and most famous of such solids known is activated carbon (AC). AC is a microcrystalline carbonaceous material that has highly developed porosity and internal surface area of more than 500 m²/g. It consists of an irregular array of interconnected micro crystallite, each consisting of fused hexagonal ring of carbon similar in structure to graphite. It is predominantly an amorphous solid with large internal surface area and pore volume (Siki *et al.*, 2012). AC is one of the best discoveries that man ever made in

technological advancement. It has been recognized as one of the most widely used adsorbent in wastewater treatment (Bhatnagar *et al.*, 2013).

Adsorption has now become an important phenomenon in sensing and separation of ions and molecules. Any sorbent that has high adsorptive capability and good selective ability is very important in separation through adsorption. This study seeks to determine the effects of factor variation and contribution on the efficiency of adsorption of Cd²⁺.

MATERIALS AND METHODS

Cadmium Stock Solution (1000 mg/dm³) was prepared by dissolving 2.036 g of cadmium nitrate (Cd(NO₃)₂) in 1000 cm³ volumetric flask with distilled then made up to mark. The working solutions of 10, 20, 30, 40 and 50 mg/dm³ 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 with H₂SO₄ as activating agent.

Factorial design of the adsorption experiment

A 2⁴ factorial design was employed to study the adsorption of Cd²⁺ on activated carbon. Table 1 shows the low and high levels of the variables for the adsorption of Cd²⁺. Factorial design reduces the total number of experiments to be performed in order to achieve maximum optimization (Musah, *et al.*, 2018). It also reduces time and cost of overall process and better response is obtained (Geyikci and Buyukgungov, 2013).

*Corresponding author. E-mail: mkkoro22@gmail.com

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Table 1: Factor levels of variables for the adsorption of Cd²⁺

Factors	Low level	High Level
Time (mins)	30	150
Dosage (g)	0.2	1.0
Concentration (mg/dm ³)	10	50
pH	4	8

The rate of agitation was kept constant at 250 rpm.

Mathlab 2013A was employed to design the number and order of runs for the factorial experiment for time, adsorbent dosage, concentration and pH with their two-way interactions. It was also used to determine the predicted response of Cd (II) ion removal in comparison to the actual percent removal obtained from laboratory results. Graphs for variation of adsorption factors were plotted using Microsoft spreadsheet for windows 10.

RESULTS AND DISCUSSION

Effect of Factor Variation on Adsorption of Cd²⁺

Figures 1 – 4 present graphical representation of how change in two experimental conditions at a time (with others kept constant) can simultaneously affect the adsorption of ions. Figure 1 shows the effect of simultaneous variation in time

of interaction and adsorbent dosage on adsorption of Cd²⁺ while concentration and pH were kept unchanged. At 30 minutes interaction time and 0.2 g adsorbent dosage with concentration and pH held at 10 mg/dm³ and 4.0 respectively, 83.49 % of Cd²⁺ was adsorbed; while 92.11 % was removed at 30 minutes when adsorbent dosage was increased to 1.0 g. The increase in adsorption is due increase in number of sites resulting from increased adsorbent dosage not the time of interaction. When time was increased to 150 minutes and adsorbent dosage varied between 0.2 and 1.0 g, there is a corresponding increase in adsorption as dosage was increased from 0.2 to 1.0 g. These observations were similar to those reported for the removal Pb²⁺ (Tibet and Coruh, 2015).

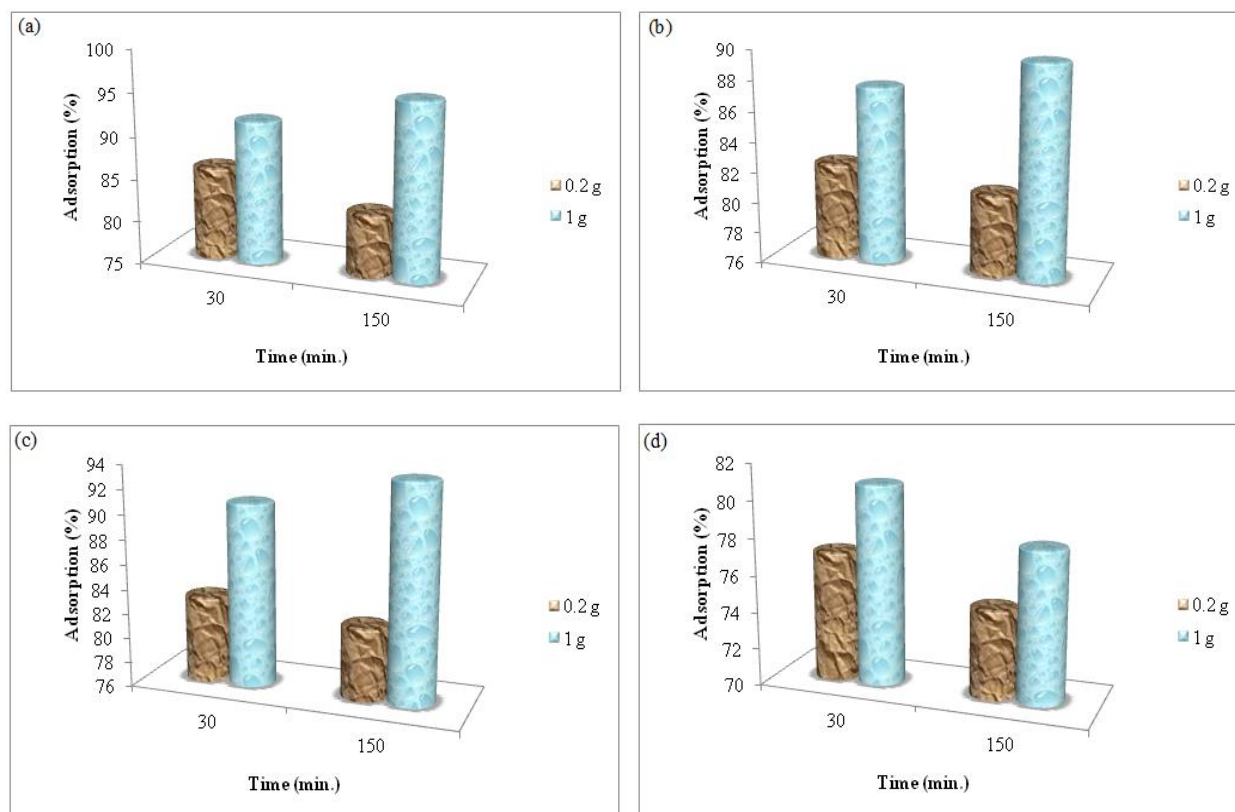


Figure 1: Effect of Time on adsorption of Cd²⁺ (a) conc. of 10 mg/dm³ and pH of 4, (b) conc. of 50 mg/dm³ and pH of 4 (c) conc. of 10 mg/dm³ and pH of 8 (d) conc. of 50 mg/dm³ and pH of 8

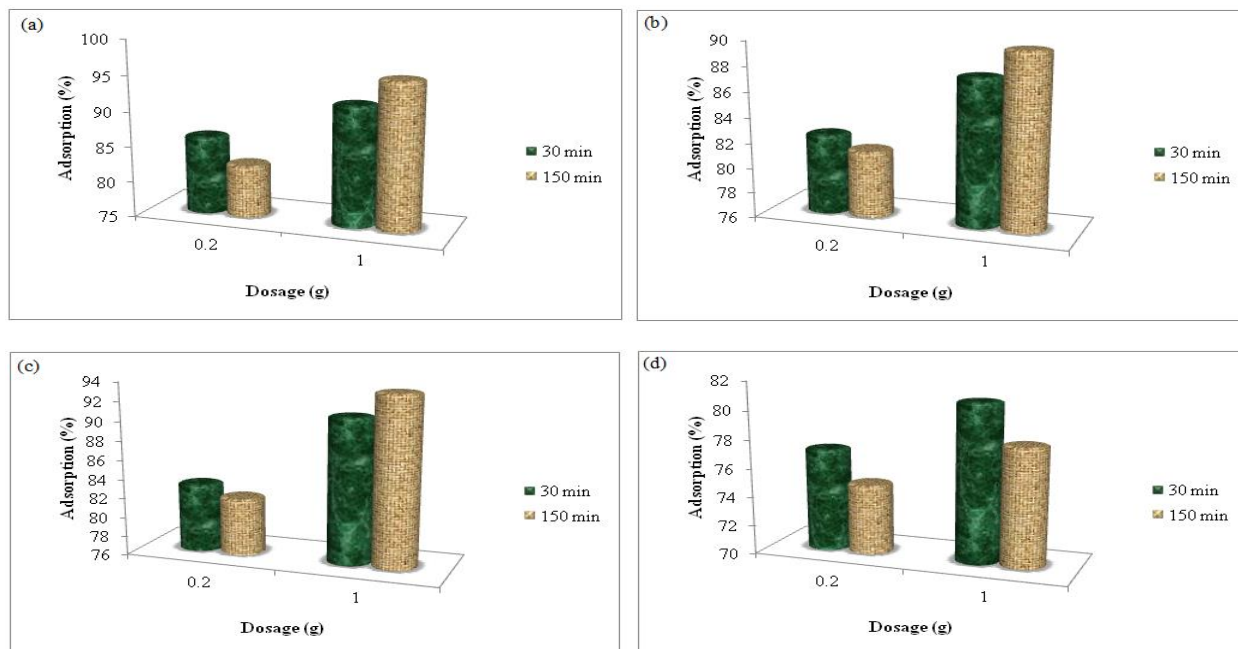


Figure 2: Effect of Dosage on adsorption of Cd²⁺ (a) conc. of 10 mg/dm³ and pH of 4, (b) conc. of 50 mg/dm³ and pH of 4 (c) conc. of 10 mg/dm³ and pH of 8 (d) conc. of 50 mg/dm³ and pH of 8

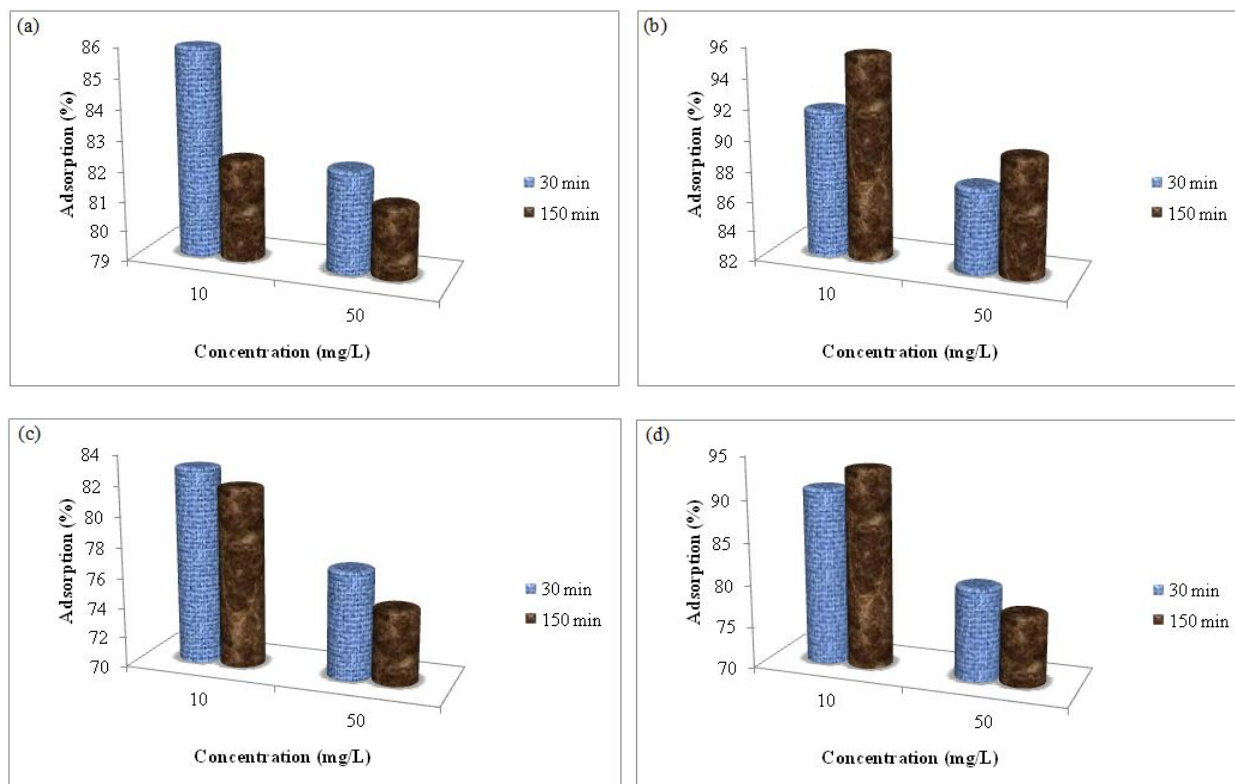


Figure 3: Effect of concentration on adsorption of Cd²⁺ (a) Dosage of 0.2 g and pH of 4, (b) Dosage of 1 g and pH of 4 (c) Dosage 0.2 g and pH of 8 (d) Dosage of 1 g and pH of 8

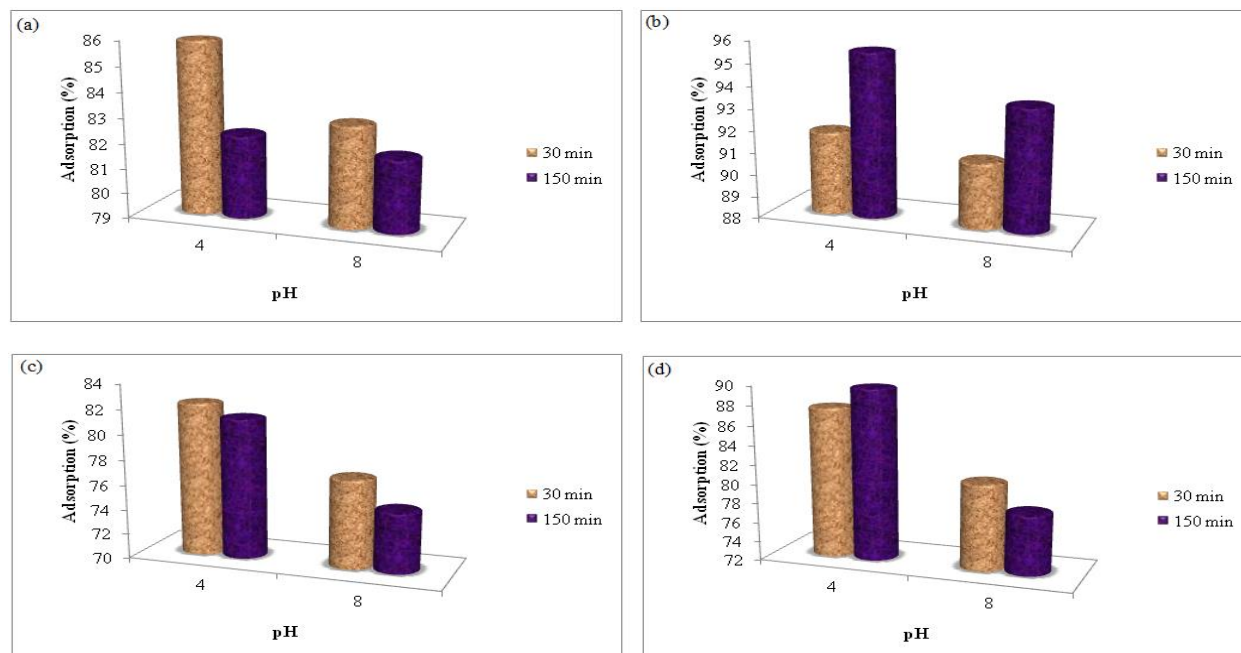


Figure 4: Effect of pH on adsorption of Cd²⁺ (a) conc. of 10 mg/dm³ and Dosage of 0.2 g (b) conc. of 50 mg/dm³ and Dosage of 0.2 g (c) conc. of 10 mg/dm³ and Dosage of 1 g (d) conc. of 50 mg/dm³ and Dosage of 1 g

Concentration of adsorbate is an important factor in adsorption. Varying concentration (10-50 mg/dm³) of solution and time of interaction (30-150 minutes) while keeping dosage and pH constant at 0.2 g and 4.0 respectively, significant adsorption of Cd²⁺ was observed when concentration was 10 mg/dm³ at 30 minutes as seen in figure 2a. On the other hand, when concentration was increase from 10 to 50 mg/dm³ at 30 minutes interaction time, there was a reduction in the amount of Cd²⁺ adsorbed. This is due to increased competition for the available binding sites on the adsorbent as more ions are present in 50 mg/dm³ solution competing for sites available in 0.2 g. The amount of Cd²⁺ adsorbed at concentration of 50 mg/L and interaction time of 150 minutes when adsorbent dosage and pH are kept constant (0.2 g and 4.0) was lower than adsorption of 10 mg/dm³ at 30 minutes. With limited binding sites and increased concentration, time of interaction may not significantly enhance the adsorption of Cd²⁺ from the solution.

Effect and Contribution of Factors on Adsorption Efficiency

The effects and percent contributions of each factor and interaction of factors on adsorption of Cd²⁺ ions are presented in Tables 2. While adsorbent dosage had the highest positive effect on the adsorption of Cd²⁺ from solution, concentration on the hand had the highest negative effect (-6.622). pH of solution also showed negative effect (-4.532) on sorption. The negative values means an increase in the parameter will cause a decrease in adsorption of Cd²⁺ (Santuraki and Muazu, 2015). Adsorbent dosage gave significant positive effect (7.438). This may be due increased surface area and pore volume in the adsorbent. An increase in adsorbent dosage will lead to a corresponding increase in the amount adsorbate removed as more surfaces become available and competition for adsorption sites is reduced (Shalna and Yogamorthi, 2015; Adie *et al*, 2012).

Table 2: Effect and Contribution (%) of Factors on the Adsorption of Cd²⁺

Term	Effect	Sum of Square	Contribution (%)
Time (A)	-0.287	0.340	0.060
Dosage (B)	7.438	221.040	39.060
Concentration (C)	-6.622	175.230	30.970
pH (D)	-4.532	82.040	14.500
AB	1.733	11.950	2.110
AC	-0.678	1.820	0.320
AD	-0.602	1.430	0.250
BC	-2.227	19.780	3.500
BD	-0.768	2.330	0.410
CD	-2.992	35.670	6.300

The percentage contribution of adsorbent dosage to adsorption of Cd^{2+} ion is 39.06 % and significantly higher than that of time, concentration and pH.

Verification of Model

Performance of adsorbents can be visualized by observing the plots of actual (experimental) response versus predicted response and residuals versus run number for the sorption of Cd^{2+} as depicted in figures 5 – 6. Figure 5 present values of plots of actual versus predicted responses of the adsorption

of Cd^{2+} , it showed that experimental and predicted values fall close to the straight line and their residuals are within $\leq \pm 2.00$. This suggests the suitability of the models and also indicates a good fit for the experimental data of the sorption of Cd^{2+} . The closer the actual and predicted values are to the line, the lower the residual value and the better the fit of the model. Davarnejad *et al.* (2015) also reported a good fit of model to experimental data using plots of actual versus predicted values.

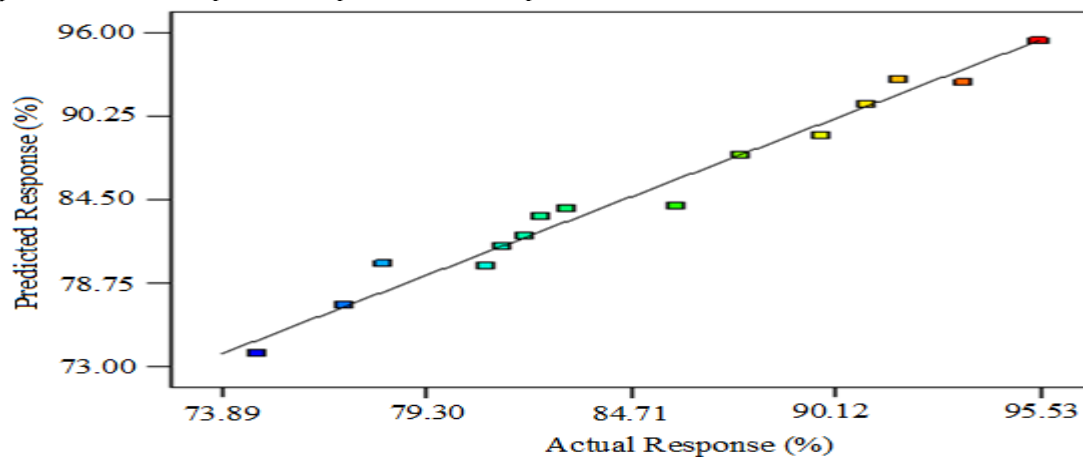


Figure 5: Predicted vs Actual Responses of Adsorption of Cd^{2+}

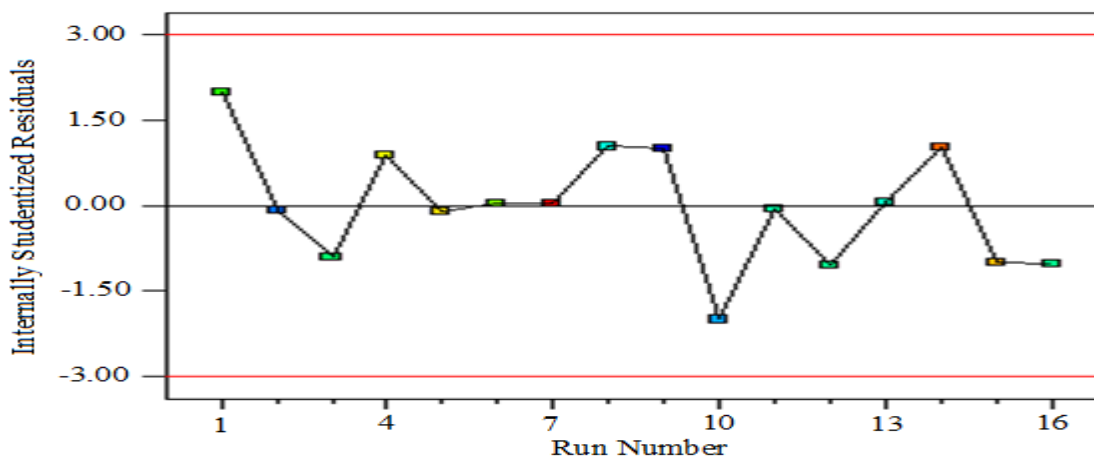


Figure 6: Residual vs Number of Run Response for Adsorption of Cd^{2+}

Plot of residuals versus experimental run order (figure 6) showing randomly scattered residual values can also be used to validate the model. Residuals are the difference between experimental and predicted values (Turan and Ozgonenel, 2013). Residual values obtained for the sorption of Cd^{2+} are within $\leq \pm 2.00$ which is an indication of a good fit of the model to experimental data. Result of plot for the removal of Cd^{2+} is lower than the residuals scattered around $\leq \pm 3.00$ reported for the adsorption of Pb^{2+} and Cu^{2+} onto Kenaf fiber based activated carbon (Chowdhury *et al.*, 2012).

CONCLUSION

The influence of adsorption factors on the removal of Cd^{2+} from aqueous solution was studied. Application of factorial design experiment enhanced the adsorption of Cd^{2+} and results of analysis indicate that adsorbent dosage had greater influence on sorption Cd^{2+} , hence the application of factorial design in removal ions from aqueous solution is encouraged.

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