FACTORIAL DESIGN ANALYSIS FOR THE SORPTION OF CHROMIUM (VI) ION ON MODIFIED CALYX OF GOLD COAST BOMBAX

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Abstract: The removal efficiency of Cr (VI) from aqueous solution onto modified calyx of gold coast bombax was studied. The effects of contact time, adsorbent dosage, solution concentration and pH of solution on adsorption of Cr (VI) were optimized using the 2^4 factorial design experiment. Optimum experimental adsorption was 96.53±0.03% with a predicted response of 97.75±0.19% and a residual value of -1.04 at 10 mg/dm^3 solution concentration. Main and interaction effects of the four adsorption parameters revealed adsorbent dosage and the interaction of adsorbent with solution concentration had the most significant influence on the removal of Cr (VI) from solution. Correlation coefficient of the experiment and predicted values indicate a good performance of the model.

Keywords: Adsorption, concentration, aqueous solution, adsorbent, calyx

Introduction

Pollution from heavy metals is a major concern in both developing and developed countries. The discharge of waste containing heavy metals into water ways, on land and underground is a serious pollution problem which could affect surface and underground water and eventually the quality of water supply (Najua *et al*., 2008). Increasing concentrations of these metals in water constitute severe health problems due to their toxicity and non biodegradable character.

Heavy metals in the environment may generally be a result of emissions from coal-burning plants, smelters, badly designed landfills, industrial waste and wastewater, and natural processes (Dike *et al*., 2004). Once released into the environment, heavy metals can remain for decades increasing the likelihood of human exposure. The commonly occurring heavy metals linked to human poisoning include nickel, lead, chromium and mercury. Chromium exists mostly as Cr^{3+} and Cr^{6+}. Cr^{3+} exists naturally in rocks, plants, animals, volcanic dust and gasses. Activities that increase the concentration of Cr^{6+} in the environment include steel and textile manufacturing. Other industrial sources of Cr^{6+} include chromate pigments in dyes, inks, paints, plastics and pharmaceutical wastes, particles released during smelting of ferrochromium ore, fumes from the welding of stainless alloys, the addition of chromates as anti-corrosive agents in paints and chromate plating by deposition of chromium metal onto the surface of materials when a solution of chromic acid is used (Ademiluyi and Nze, 2016; Ahmad *et al*., 2016)

Chromium strongly binds to soils, becomes immobile and very persistent. Cr^{3+} is an important nutrient that helps the body process sugars, fats and protein; it does not irritate the nose or mouth (Anyakora *et al.,* 2011). While Cr^{6+} on the other hand, is a known human toxin; ingesting high levels of Cr^{6+} can lead to irritation in nose lining, nose ulcer, runny nose and problems associated with breathing, such as asthma and cough. Skin contact can cause skin ulcer, skin irritation and allergic reactions consisting of severe skin redness and swelling. Prolong exposure to Cr^{6+} can cause damages to circulatory system, liver, kidney and nerve tissues. When dissolved in water, Cr^{6+} is extremely carcinogenic and can cause death if ingested above tolerable level (Orjuela and Gonzalez, 2011).

Major ill effects caused by heavy metals include inhibition of enzyme activity, dizziness, nausea and vomiting, kidney infection and cancer (Standard Organisation of Nigeria, 2007). Different physical and chemical processes are known and available for removal of heavy metals from wastewater; such processes include precipitation, coagulation, ultra filtration, ion exchange and reverse osmosis (Rajendra, 2010). A major drawback with precipitation is sludge formation, ion exchange is a better alternative technique for such purpose, but it is not economically appealing because of high operational cost. The use of activated carbon for the removal of toxic metal ion pollutants and numerous other organic materials from both gases and aqueous solutions is of considerable importance. Activated carbon has proven to be an efficient and cost effective adsorbent (Iyagba and Opete, 2009). This study is aimed at applying factorial design experiment in enhancing the adsorption of Cr (VI) ions from aqueous solution by activated carbon prepared from calyx of gold coast bombax.

Materials and Methods

Chromium Stock Solution (1000 mg/dm^3) was prepared by dissolving 2.829 g of potassium dichromate ($K_2Cr_2O_7$) in 1000 cm^3 volumetric flask with distilled then made up to mark. Working solutions were prepared by appropriate dilution of the stock solution. Activated carbon used for the adsorption experiment was prepared from the Calyx of Gold coast bombax by the two step method using H_2SO_4 and KOH as activating agents (Rahman *et al*., 2014) labelled as HAC and KAC, respectively.. pH of the solutions were adjusted using 0.1 mol/cm^3 HCl and 0.1 mol/cm^3 NaOH. Batch adsorption method was used for interaction of the solutions with the adsorbent.

Factorial design of adsorption experiment

A 2^4 factorial design was employed to study the adsorption of Cr^{6+} from aqueous solution onto the activated carbons. In this study, percentage adsorption of metal ions is the dependent variable while time (mins), dosage (g) of adsorbent, concentration (mg/dm^3) and pH of solution are the independent variables. Factorial design reduces the number of experiments to be performed in order to achieve maximum optimization. It also reduces time and cost of the overall process as well as better response (Geyikci and Buyukgungor, 2013). Table 1 shows the low and high levels of the variables for the adsorption of Cr (VI) ions.

Table 1: Factor levels of Variables for the Adsorption of Cr^{6+}

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

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Concentrations of heavy metal ions in the wastewater solutions were determined before and after interactions with the activated carbon using Atomic Absorption Spectrophotometer. The removal efficiency (%) was calculated as follows (Javadian *et al.*, 2015):

$$RE\,(\%) = \frac{(C_o - C_f) \times 100}{C_o} \tag{1}$$

Where: C_o is the concentration of heavy metal ion before interaction with the adsorbent; C_f is the concentration of heavy metal ion after interaction with the adsorbent

Statistical analysis

Mathlab 2013A was employed to design the number and order of runs for the 2^4 factorial experiments for time, adsorbent dosage, concentration and pH and their two-way interactions. It was also used to determine the predicted response of the heavy metal ions removal in comparison to the actual percent removal obtained from laboratory results and the equations of adsorption.

Minitab 16 version 14.12.0 was adapted for treatment of data obtained from the 2^4 factorial designed experiments in order to determine the estimated effects, standard deviations, coefficients, pareto charts, main effects and interaction plots for various responses. It was also used to calculate the P – and F – values in analysis of variance (ANOVA).

Experimental and predicted responses for adsorption of Cr^{6+}

The responses of the 2^4 factorial experimental design for the adsorption of Cr^{6+} onto H_2SO_4 modified (HAC) and KOH modified (KAC) activated carbons is presented in Table 2. Actual and predicted responses arranged in run order as influenced by independent variable: time of interaction (min), adsorbent dosage (g), concentration of solution (mg/dm^3) and pH of medium are presented in the Tables. Temperature and rate of agitation per minute (rpm) were maintained at 28 ± 2^oC and 200 rpm respectively. Columns 7 indicate the highest actual response in all cases. Percent actual responses of 96.53, 96.42 and 93.64% with predicted responses of 97.75, 95.52 and 93.76% were recorded for the adsorption of Cr^{6+} ions onto HAC and KAC (Table 2). The 96.53% obtained for adsorption of Cr^{6+} onto HAC is slightly higher than 91.05 and 92.30% obtained for adsorption of Pb^{2+} and Tl^{3+} (Kalantari *et al.*, 2014; Hamdzah *et al.*, 2013; Sheibani and Zare-Khormini, 2012). This could be due to increased pores, presence of carboxylic and hydroxyl functional groups on surface of HAC.

Table 2: 2^4 Factorial experimental design for adsorption of Cr^{6+} onto HAC and KAC

Run Order	Time (mins)	Dosage (g)	Concentration (mg/dm^3)	pH	Removal of Cr^{6+} (%)			
					HAC		KAC	
					Actual	Predicted	Actual	Predicted
1	30.00	0.20	10.00	4.00	83.49±0.19	81.79±0.90	81.77±0.20	83.38±0.79
2	30.00	0.20	50.00	8.00	80.39±0.12	79.42±0.68	71.59±0.12	72.90±0.51
3	30.00	0.20	10.00	8.00	82.71±012	84.28±0.49	71.54±0.04	70.51±0.71
4	150.0	1.00	50.00	4.00	91.22±0.03	89.96±0.14	74.67±0.18	75.30±0.35
5	30.00	1.00	10.00	8.00	92.56±0.06	91.05±0.07	90.02±0.03	89.39±0.55
6	30.00	1.00	50.00	4.00	89.53±0.02	88.48±0.74	76.49±0.07	76.71±0.13
7	150.0	1.00	10.00	4.00	96.53±0.03	97.75±0.19	96.42±0.11	95.52±0.27
8	30.00	1.00	50.00	8.00	78.39±0.05	79.30±0.67	81.02±0.12	81.37±0.41
9	150.0	0.20	50.00	8.00	76.10±0.06	74.41±0.92	78.52±0.12	78.06±0.48
10	150.0	1.00	50.00	8.00	77.59±0.12	79.34±0.04	84.65±0.05	83.45±0.77
11	150.0	0.20	10.00	8.00	79.85±0.16	80.95±0.34	81.73±0.10	81.91±0.30
12	150.0	0.20	10.00	4.00	80.50±0.04	79.54±0.49	92.06±0.17	91.30±0.62
13	150.0	0.20	50.00	4.00	76.91±0.04	78.47±0.68	80.45±0.13	81.48±0.51
14	150.0	1.00	10.00	8.00	93.92±0.10	92.77±0.46	93.23±0.12	94.71±0.36
15	30.00	1.00	10.00	4.00	93.11±0.09	94.75±0.59	90.65±0.14	90.70±0.16
16	30.00	0.20	50.00	4.00	81.30±0.11	82.40±0.54	81.69±0.01	79.81±0.27

Temperature = 28 ± 02^oC; Agitation = 200 rpm; HAC is Functionalized H_2SO_4 modified activated carbon; KAC is Functionalized KOH modified activated carbon

Table 3: Estimated effects and coefficients for response (%) of HAC Adsorption of Cr^{6+}

Term	Effect	Coef.	SE Coef.	T	P
Time (mins)	-1.108	-0.554	0.612	-0.91	0.407
Dosage (g)	8.950	4.475	0.612	7.32	0.001
Concentration (mg/dm^3)	-6.405	-3.202	0.612	-5.24	0.003
pH	-3.885	-1.943	0.612	-3.18	0.025
Time (mins) *Dosage (g)	2.528	1.263	0.612	2.06	0.094
Time (mins) *Concentration (mg/dm^3)	-0.840	-0.420	0.612	-0.69	0.523
Time (mins)*pH	-0.540	-0.270	0.612	-0.44	0.677
Dosage (g) *Concentration (mg/dm^3)	-3.443	-1.721	0.612	-2.81	0.037
Dosage (g)*pH	-3.097	-1.549	0.612	-2.53	0.052
Concentration (mg/dm^3)*pH	-2.737	-1.369	0.612	-2.24	0.075

$R^2 = 95.87\%$; R^2 (adj) = 87.61%; Key: HAC is functionalized H_2SO_4 modified activated carbon

Table 4: Estimated Effects and Coefficients for Response (%) of KAC Adsorption of Cr^{6+}

Term	Effect	Coef	SE Coef	T	P
Time (mins)	4.870	2.435	0.482	5.05	0.004
Dosage (g)	6.475	3.238	0.482	6.72	0.001
Concentration (mg/dm^3)	-9.042	-4.521	0.482	-9.38	0.000
pH	-2.237	-1.119	0.482	-2.32	0.068
Time (mins) *Dosage (g)	-1.422	-0.711	0.482	-1.48	0.200
Time (mins) *Concentration (mg/dm^3)	-3.245	-1.622	0.482	-3.37	0.020
Time (mins)*pH	1.870	0.935	0.482	1.94	0.110
Dosage (g) *Concentration (mg/dm^3)	-5.080	-2.540	0.482	-5.27	0.003
Dosage (g)*pH	5.660	2.830	0.482	5.87	0.002
Concentration (mg/dm^3)*pH	3.107	1.554	0.482	3.22	0.023

$R^2 = 98.07\%$; R^2 (adj) = 94.21%; KAC is functionalized KOH modified activated carbon

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Results of the 2^4 factorial design also indicate optimum sorption occurred at low concentration and pH, and at the upper level (1.0 g) of dosage as adsorption is generally favoured at low concentration. At low concentration, adsorbents remove available cations due to less competition for available binding sites (Santuraki and Muazu, 2015). This is similar to optimum adsorption of Ni^{2+} at concentration of 10 mg/l and the lowest adsorption at 50 mg/dm^3 as reported by Lakherwal *et al*. (2016). Wan-Ngah and Hanafiah (2008) also reported maximum adsorption of Cd^{2+} using different types of adsorbents at pH 4.5 because of the low competing effects of protons at this pH. When the pH of solution is higher than 4, the carboxylic group becomes deprotonated and the adsorbent surface will have negative charge resulting in high adsorption. At pH $\leq$ 3, the carboxylic groups become protonated and binding sites becomes less available for the attraction of cations (Farghali *et al.,* 2013; Wan-Ngah and Hanafiah, 2008).

Estimated effects and coefficients for the adsorption of Cr^{6+}
The effects of the main adsorption factors and their interactions, coefficients of the model, standard deviations of coefficients and probabilities for responses of HAC and KAC are presented in Tables 3 – 4.
Main effects and interactions which have probability (P) values less than 0.05 (P < 0.005) are considered to be statistically significant. Positive values of coefficients of main and interaction effects meant that metal ion uptake is favoured at high values; i.e an increase in their levels lead to increasing cations adsorption by the sorbents while negative values of coefficients lead to decrease in response when their level is increased (Lima *et al.,* 2007). Gaikwad *et al.* (2010) also posited that when a factor's effect on adsorption is positive, there will be an increase in percent adsorption as the factor moves from low to high level. On the contrary, reduction in percent adsorption will occur for high level of a factor if the effect is negative. This is corroborated by values on 'effects column' of Table 3 – 4. P – and T – values have been used as tools for checking the significance of factors (Tibet and Coruh, 2015). The significance of coefficients is directly proportional to T – value and inversely proportional to P – value. Large magnitude of the T – values and small P - values are indications of high significance of the corresponding coefficients (Al Mamum *et al.,* 2011). The value of coefficient is equal to one half the value of the corresponding effect. As the value of coefficient increases, T-values also increase while p-values decrease.

Close observation of Tables of effects and coefficients indicate that factors with T – values < $\pm$ 2.60 have P – values greater than 0.05 (P > 0.05) and hence are not significant in the sorption process. Adsorbent dosage and concentration showed significant effect on adsorption of Cr^{6+} onto HAC with P-value less than 0.05 (P < 0.05). This can be due to high surface area of HAC and the small ionic size of Cr^{6+} (58 pm). R^2 values obtained ranged between 0.9497 to 0.9823 for the removal of Cr^{2+} by HAC and KAC. The values indicate good agreement between experimental and predicted response. Adsorbent dosage showed a positive effect in all sorption processes with high t – values and low P – values indicating the high significance of dosage in the sorption process. Increase in the adsorbent dosage will lead to an increase in adsorption. Concentration and pH had negative T – values and negative effect values suggesting that any increase in these factors will lead to a decrease in the sorption of Cr^{2+}; hence adsorption is favoured at low levels of concentration and pH. Similar observations were reported by Geyikci and Buyukgungor (2013), Turan and Ozgonenel (2013) and Al Qahtan (2012) on the adsorption of Ag^+, Cu^{2+}, Cd^{2+} and Pb^{2+} onto montmorillonite clay and *Cyperus lavigatus,* respectively.

Analysis of variance for adsorption of Cr^{6+}
Results of analysis of variance (ANOVA) for the adsorption of Cr^{6+} onto HAC, ACK and CAC are presented on Tables 5 - 6. The results showed a total of 15 degrees of freedom (DF) in each case. Analysis of variance was used to reveal the main and interaction effects of factors that influence the efficiency of adsorption of Cr^{6+}.
Analysis of the main and interaction effects on adsorption depict estimated adsorption efficiency of Cr^{6+} as a function of contact time, adsorbent dosage, concentrated and pH of the solution their two-way interactions. Main effects that showed significant influence on adsorption with P-values less than 0.05 (P < 0.05) are dosage (0.001), concentration (0.003) and pH (0.025) for HAC; time (0.004), dosage (0.001) and concentration (0.000) for KAC. Fewer interaction effects showed significant influence when compared to effects of the main factors. Interaction of dosage and concentration (0.037) was significant for HAC; time and concentration (0.020), dosage and concentration (0.003), dosage and pH (0.002) were significant for KAC. Similar trends were observed in the removal of copper ions from acid mine (Gaikwad *et al.,* 2010) and biosorption of Copper (II), Nickel (II) and Lead (II) using factorial experimental design (Kalantari *et al.,* 2014).

Table 5: Analysis of variance for response (%) of HAC adsorption of Cr^{6+}

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	4	549.785	549.785	137.446	22.96	0.002
Time (mins)	1	4.906	4.906	4.906	0.82	0.407
Dosage (g)	1	320.410	320.410	320.410	53.53	0.001
Concentration (mg/dm^3)	1	164.096	164.096	164.096	27.41	0.003
pH	1	60.373	60.373	60.373	10.09	0.025
2-Way Interactions	6	145.248	145.248	24.208	4.04	0.073
Time (mins)*Dosage (g)	1	25.503	25.503	25.503	4.26	0.094
Time (mins)*Concentration (mg/dm^3)	1	2.822	2.822	2.822	0.47	0.523
Time (mins)*pH	1	1.166	1.166	1.166	0.19	0.677
Dosage (g)*Concentration (mg/dm^3)	1	47.403	47.403	47.403	7.92	0.037
Dosage (g)*pH	1	38.378	38.378	38.378	6.41	0.052
Concentration (mg/dm^3)*pH	1	29.976	29.976	29.976	5.01	0.075
Residual Error	5	29.930	29.930	5.986		
Total	15	724.964				

HAC = Functionalized H_2SO_4 modified activated carbon

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Table 6: Analysis of variance for response (%) of KAC adsorption of Cr^{6+}

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	4	609.663	609.663	152.416	41.00	0.001
Time (mins)	1	94.868	94.868	94.868	25.52	0.004
Dosage (g)	1	167.703	167.703	167.703	45.11	0.001
Concentration (mg/dm^3)	1	327.067	327.067	327.067	87.98	0.000
pH	1	20.026	20.026	20.026	5.39	0.068
2-Way Interactions	6	334.196	334.196	55.699	14.98	0.005
Time (mins)*Dossage (g)	1	8.094	8.094	8.094	2.18	0.200
Time (mins)*Concentration (mg/dm^3)	1	42.120	42.120	42.120	11.33	0.020
Time (mins)*pH	1	13.988	13.988	13.988	3.76	0.110
Dosage (g)*Concentration (mg/dm^3)	1	103.226	103.226	103.226	27.77	0.003
Dosage (g)*pH	1	128.142	128.142	128.142	34.47	0.002
Concentration (mg/dm^3)*pH	1	38.626	38.626	38.626	10.39	0.023
Residual Error	5	18.588	18.588	3.718		
Total	15	962.447				

KAC = Functionalized KOH modified activated carbon

The significance of the model was verified by F-test values. F-test is a statistical measure of how well a model describes the variation in the data about a mean (Kalantari *et al.*, 2014). The greater the F-test value the more the certainty of the model to adequately describe the variation in the data and the closer the estimated significant terms of adsorption variables are to the experimental value (Chowdhury *et al.*, 2012). A high F-value and low P-value (p<0.05) indicate that such main effects and/or interactions are significant at 5% significance level. From the Tables 5 - 6, F-values of 53.53, 27.41 and 10.09 were obtained for HAC; 11.33 was obtained for the interaction effect of time and concentration in the adsorption of Cr^{6+} by KAC.

Main and interaction effects having P-values less than 0.05 (P < 0.05) and F-value greater than 5.00 (F > 5.00) indicate the model is significant. From the results, main effects showed more statistical significance. These results indicate the model is in good prediction of the experimental result (Al-Mamun *et al.*, 2011), and similar to those reported by Tibet and Corah (2015) on full factorial design analysis of lead removal.

It can be seen from the Tables 5 − 6 that dosage had positive effect in all cases. This is because an increase in adsorbent dosage will lead to increase in the coverage of adsorbent surface and binding sites that are available for adsorption. Similar observation was reported by Nwankwo and Mogbo (2014) on the adsorption of cadmium from wastewater. On the contrary, increase in adsorbate concentration without corresponding increase in adsorbent dosage lead to negative effect as few binding sites were available for adsorption (Farghali *et al.*, 2013).
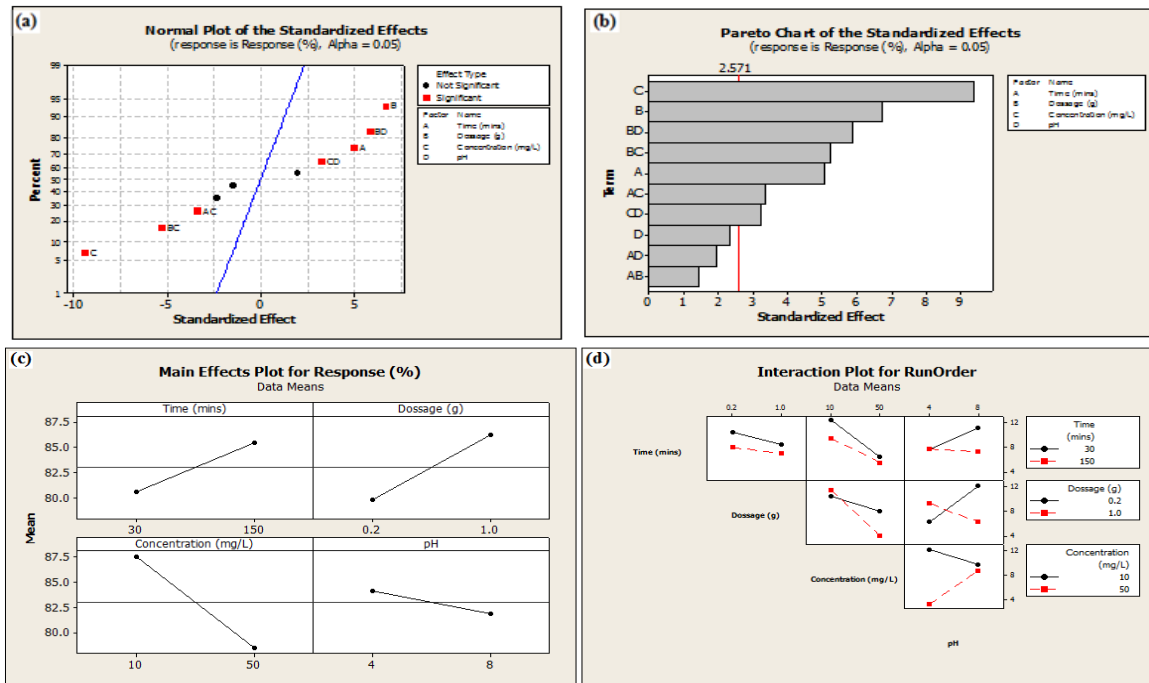
Main and interaction plots for adsorption efficiency
Results of the statistical analysis of main and interaction effects for adsorption of Cr^{6+} ions by HAC are presented in Figs. 1 - 2. From the normal plots of standardized effects in 'a' sections of Figs. 1 and 2 the points that are near the line represent factors that do not show significant effect on adsorption and points that are far from the line are those that have significant effect on adsorption. The farther the point is from the line the more its significance.

Adsorbent dosage and concentration are the most significant factors in the adsorption of Cr^{6+} as depicted in Figs. 1(a) and 2(a). These factors also appeared at certain level of significance in the adsorption of Mn^{2+} and Cd^{2+} by HAC and KAC. Interactions that showed strong influence in the sorption of Cr^{6+} are the interactions between adsorbent dosage with concentration (for HAC); adsorbent dosage with pH and adsorbent dosage with concentration (for KAC) as seen in Figs. 1(a) and 2(a). Factors on the positive side of the line have positive effects while those on the negative side of the line have a negative effect on adsorption (Tibet and Coruh, 2015). Similar observations were made by Al-Qahtani (2012) for the adsorption of Cd^{2+} and Pb^{2+} ions by *Cyperus laevigatus*.
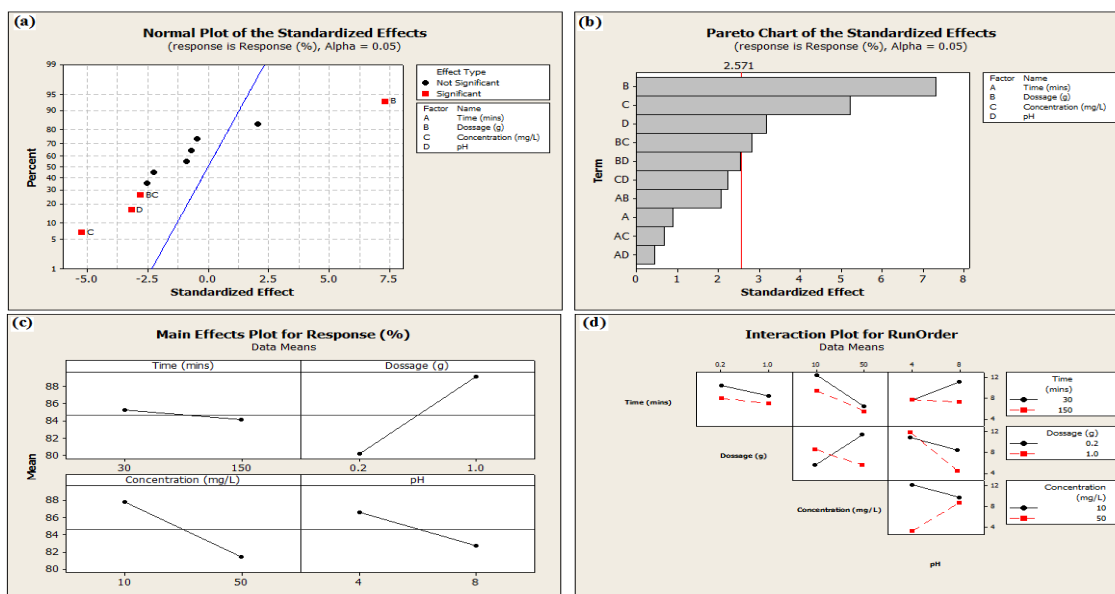
A = Time; B = Dosage; C = Concentration; D = pH
Fig. 1: Main and interaction plot for Adsorption of Cr^{6+} onto HAC

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A = Time; B = Dosage; C = Concentration; D = pH
**Fig. 2: Main and interaction plot for adsorption of Cr^{6+} onto KAC**

Student's t-test presented as Pareto chart of standardized effects was used to determine if calculated effects are notably different from zero. For a 95% confidence level and degrees of freedom, the t-value is equal to 2.571 (Gaikwad *et at*., 2010). These estimations are presented in Figs. 1(b) and 2(b) for HAC and KAC adsorption of Cr^{6+}, with the vertical line indicating the magnitude of the minimum statistically significant effect and values in the horizontal column represent the student's t-test value for each effect (Turan and Ozgonenel, 2013). 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 B, C, D and B*C were very important factors in the adsorption of Cr^{6+} by HAC. Similar factors, including A, A*C and C*D were significant in the sorption of Cr^{6+} onto KAC. These results are similar to those obtained for the effects concentration and pH by Lima *et al*. (2007).

Main effects plots for responses presented in Figs. 1 (c) and 2 (c) are useful in visualizing the factors that affect responses the most and each factor's level affects response differently. If the slope is close to horizontal, then the magnitude is small (Tibet and Coruh, 2015). The figures also showed that adsorbent dosage (B) at a high level with C and D at low level results in a high mean response of HAC. Time of interaction showed a very weak effect as it tends towards the horizontal line. High effect of adsorbent dose (B) in the adsorption of Cr^{6+} by ACH is similar to the response obtained by Turan and Ozgonenel (2013) for montmorillonite and high response for Cd^{2+} adsorption obtained at pH values of 3 and 6 as reported by Geyikci and Buyukgungor (2013); Turan and Ozgonenel (2013), respectively. Al-Qahtani (2012) noted that at lower pH (< 3), the adsorption of heavy metals usually takes place with low sorption efficiency. This is believed to occur as a result of the presence of high concentration of protons in the solution and these protons compete with the metal ions in forming bonds with the active sites (sites containing the functional groups) available on the surface of the adsorbents (Santuraki and Muazu, 2015). Dosage (B) gave high mean response at high level in comparison to the response at low level for 'C'. This is similar to observations reported by Geyikci and Buyukgugor (2013).
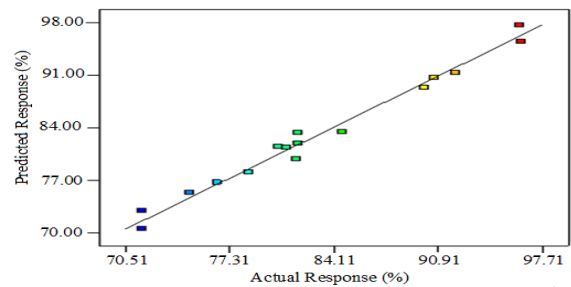
Interaction plots for responses presented in Figs. 1(d) and 2(d) depict the impact that the changing of one factor will have on another during adsorption process. If the lines of the two factors run parallel, then there is no interaction between the factors but if the lines are far from being parallel and seen to appreciably cross each other, then the two factors are said to interact (Tibet and Coruh, 2015). Interaction effect is done because one factor at a time experiment does not usually characterise the combined effect of all the factors involved in the experiment (Turan and Ozgonenel, 2013).

Verification of Model

Performance of the adsorbents on the adsorption of Cr^{6+} can be visualized by observing the plots of actual (experimental) response versus predicted response and residuals versus run number for the sorption of Cr^{6+} onto HAC and KAC as depicted in Figs. 3 – 4.
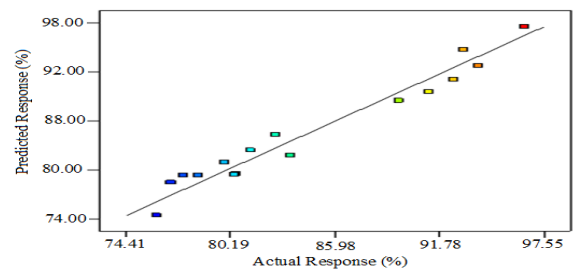
Fig. 3: Predicted vs actual responses of HAC adsorption of Cr^{6+}

Fig. 4: Predicted vs actual responses of KAC adsorption of Cr^{6+}

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Figures that present values of plots of actual versus predicted responses of Cr^{6+} by HAC and KAC showed that the values fall close to the straight line and their residuals are within $\leq \pm 2.00$. This suggests the suitability of the models and is corroborated by equations 3 and 5. The values indicate a good fit for the experimental data of the sorption of Cr^{6+}. The closer the actual and predicted values are to the line, the lower the residual value and the better the fit of the model.

Adsorption equations

To describe the behaviour of adsorption factors in relation to adsorption by HAC and KAC, regression model equations were used (equations 2 – 5). For the development of the model, 16 runs were used for calibration in each case; and percent adsorption of metal ions varied depending on adsorbent used, main factors and interaction of factors. Considering the student's t-test presented as Pareto charts in the 'b' parts of Figs. 1 – 2 and P-values in Tables 3 – 6, some factors were not statistically significance ($P > 0.05$) on the responses. On the bases of foregoing, the models were recalculated to eliminate the non significant effects and resultant model equations for adsorption Cr^6onto HAC and KAC are presented as the simplified final equations in term of significant factors. The significant factors are considered important because they indicate the limiting condition such that a variation in their value will affect adsorption (Al-Mamun *et al.,* 2011). Equations 3 and 5 represent the final equations for the adsorption of Cr^{6+} ion onto HAC and KAC, respectively.

Equation for the Adsorption of Cr^{6+}Ion onto HAC in Terms of Actual Factors:

Response (%) = +73.0569 – 0.016792 x Time + 24.52344 x Dosage + 0.20578 x Concentration + 1.41938 x pH + 0.052604 x Time x Dosage – 0.00035 x Time x Concentration – 0.00225 x Time X pH – 0.21516 x Dosage x Concentration – 1.93594 x Dosage x pH - 0.034219 x Concentration x pH   (2)

Final Equation in terms of Significant Factors for the Adsorption of Cr^{6+} onto HAC:

Response (%) = +73.05969 + 24.52344 x Dosage + 0.20578 x Concentration + 1.41938 x pH – 0.21516 x Dosage x Concentration   (3)

Equation for the Adsorption of Cr^{6+} onto KAC in Terms of Actual Factors:

Response (%) = 97.36344 + 0.056344 x Time – 1.09531 x Dosage – 0.13444 x Concentration – 4.53281 x pH – 0.03224 x Time x Dosage – 0.0013 x Time x Concentration + 0.0072708 x Time x pH – 0.32531 x Dosage x Concentration + 3.61562 x Dosage x pH + 0.037281 x Concentration x pH   (4)

Final Equation in terms of Significant Factors for the Adsorption of Cr^{6+} onto KAC:

Response (%) = + 97.36344 + 0.056344 x Time – 1.09531 x Dosage – 0.13444 x Conc. -0.0013 x Time x Conc. – 0.32531 x Dosage x Conc. + 3.61562 x Dosage x pH + 0.037281 x Conc. X pH   (5)

Coefficients having single variable of adsorbent dosage, time of interaction, concentration or pH represent the effect of that factor on sorption process. Coefficients with two factors indicate interaction of those factors and their effects on sorption. Positive sign preceding any factor indicate a synergistic effect of the factor while an antagonistic effect of factors is represented by negative sign in front of the factor (Chowdhury *et al.,* 2012). The models presented using equations is verified by the high R^2 and adjusted R^2 values presented in Tables of estimated effects and coefficients (Tables 3 - 4). Similar models of 2^3 and 2^4 factorial were designed and equations for the sorption of Pb^{2+} and Ag^+ were

reported by Tibet and Coruh (2015) and Geyikci and Buyukgungor (2013).

Conclusion

The effects of factors such as such as contact time (A), adsorbent dosage (B), initial metal concentration (C) and solution pH (D) on the removal efficiency of Cr (VI) were optimized. Factorial design experiment was found to be an appropriate method of optimising the main factors that control the adsorption process. Factors B and C, interactions B*C and B*D significantly influence the adsorption process. Results of analysis of variance (ANOVA) and estimated effects indicate the suitability of the model in adsorption of Cr (VI) from aqueous solution; hence the use of factorial design in removal metal ions from solutions is encouraged.

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