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Factors that Influence Adsorption using 2^k Factorial Experiments

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Abstract: In this study a report on statistical evaluation of some operational factors that influence efficacy of adsorption as a treatment process was presented. A standard 2^4 factorial matrix was developed and four factors (stirring speed, adsorbent dose initial concentration of the adsorbate and co-ion concentration) were evaluated based on ability of the absorbent to remove cadmium from synthetic waste waters. The study revealed that cadmium adsorption was not significantly influenced by stirring speed of the solution to be treated. On the other hand, initial cadmium concentration, co-ion concentration and adsorbent dose significantly influenced efficiency of the process at 90% confidence level. Mathematical model for cadmium removal was found to be $Y = 84.53 - 1.83A + 2.59B - 4.18\,C + 3.07D$. The predictions given by the factorial experiments model agreed with the experimental data. It was then concluded that factorial experiments provide a comprehensive understanding of the impact of operational variables on process performance. Utilization of the 2^K matrix taking into account all interaction effects and appeared to be efficient in giving a mathematical model that conformed to criteria validity.

Key words: Factorial experiments, adsorption efficacy, co-ion concentration, adsorbent dose, stirring, initial concentrations

INTRODUCTION

Over the last decade several studies have been conducted on the performance of adsorption as a treatment method for heavy metals (pollutants) removal. It has been successfully utilized for various water and wastewater pollutants such as Cooper (II) and Chromium (VI) (Schmubi *et al*., 2001), Cadmium (II) (Krishnan and Anirudhan, 2003); fluoride (Jamode *et al*., 2004); Chromium (VI) (Erhan *et al*., 2004; Saswati and Ghosh, 2005). Previous studies have stated the effect of initial concentration of the pollutants; absorbent doses, stirring speed, pH and concentration of co-ions and time on the performance of adsorption process and various kinetic models for the adsorption process using these factors have been developed (Schmubi *et al*., 2001; Krishnan and Anirudhan, 2003; Jamode *et al*., 2004; Erhan *et al*., 2004; Saswati and Ghosh, 2005). The use of a statistical method to establish significance of these factors and their interactions has not been well documented. Considering the cost of producing and regenerating some adsorbents such as chitosan and activated carbon, there is a need to identify factors that influence efficacy of adsorption significantly as a treatment process. The main purpose of this work was to utilize a factorial type experimental design, (2^K) to establish effect of each experimental parameter (factors and interactions) on the performance of adsorption process using synthetic wastewater made from cadmium salts and to establish a mathematical model with a minimum number of experiments, which may be utilized to explain the phenomenon.

MATERIALS AND METHODS

A standard factorial design matrix was developed (Table 1). The factors studied are initial concentration of the adsorbate, concentration of co-ion, adsorbent dose and speed of stirring. The experiments were carried out in a cylindrical reactor. The adsorbent utilized was commercial activated carbon manufactured by BDH laboratory supplies Poole, BH 151TD England. A synthetic cadmium wastewater solution was prepared with distilled water and a known mass of cadmium salt (2.7442 g of $Cd(NO_3)_2$-4 H_2O in 1000 mL of distilled water), (APHA, 1998). Working cadmium concentration of the wastewater solutions studied was in the range of 1.50 to 4.50 mg L^{-1}. The advantage of working with this high concentration is that it adds very little volume (on the

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Table 1: 2^K fractional factorial design matrix

	Codified factors				Natural factors				
Experiments	A	B	C	D	A (rpm)	B (mg)	C (mg L^{-1})	D (mg L^{-1})	Combinations
1	-	-	-	-	30	250	1.0	1.50	Mean
2	+	-	-	-	60	250	1.0	1.50	A
3	-	+	-	-	30	850	1.0	1.50	B
4	+	+	-	-	60	850	1.0	1.50	BA
5	-	-	+	-	30	250	8.0	1.50	C
6	+	-	+	-	60	250	8.0	1.50	AC
7	-	+	+	-	30	850	8.0	1.50	BC
8	+	+	+	-	60	850	8.0	1.50	ABC
9	-	-	-	+	30	250	1.0	4.50	D
10	+	-	-	+	60	250	1.0	4.50	AD
11	-	+	-	+	30	850	1.0	4.50	BD
12	+	+	-	+	60	850	1.0	4.50	ABD
13	-	-	+	+	30	250	8.0	4.50	CD
14	+	-	+	+	60	250	8.0	4.50	ACD
15	-	+	+	+	30	850	8.0	4.50	BCD
16	+	+	+	+	60	850	8.0	4.50	ABCD

Table 2: Parameters used in the establishment of the factors, interactions and mathematical model

		Levels	
Code	Parameters	Low (-1)	High (+1)
A	Stirring (rpm)	30.00	60.00
B	Adsorbent dose (mg)	250.00	850.00
C	Co-ion concentration (mg L^{-1})	1.00	8.00
D	Initial concentration (mg L^{-1})	1.50	4.50

order of a microlitre) to the reactor containing the cadmium solution (Drouichel *et al*., 2001). The adsorbent mass utilized varied between 250 to 1000 mg. Effect of stirring speed as a parameter on the process performance was studied at various speeds ranged between 30 and 60 rpm. The effect of co ions concentration was studied by dissolving various amounts of lead (II) and iron (II) salts in the reactor vessel. Co-ion concentration was in the range of 1.00 to 8.00 mg L^{-1} was studied. In the establishment of the factorial design using a 2^K matrix, extreme levels (+1: high level and -1: low level) were chosen for each experimental parameter used in this study (Table 2). The supernatants from the wastewater were filtered with filter number 40 to prevent particles in the wastewater solutions. Samples were taken after 3 h and analyzed. The cadmium concentration was measured by using AAS method specified in APHA (1998). The amount of solute remove (adsorbed) at a given was computed using Eq. (1). The percentage of cadmium ion removed (R_c%) from the solution was calculated using Eq. (2).

$$q_t = \frac{(C_0 - C_t)}{M}V \qquad (1)$$

$$R_c = \frac{(C_0 - C_t)x100}{C_0} \qquad (2)$$

The factors were further studied to verify the result from 2^4 factorial experiments.

RESULTS AND DISCUSSION

Table 3 contains results of the factorial experiments, total, Yates, algorithm (analysis) divisors, estimated effect and sum of squares. The Yates, algorithm was obtained using procedures specified in Guttman *et al.* (1971). The divisors were computed using an expression stated in Gardiner and Gettinby (1998):

$$Y_r = r2^{k-1} = \frac{1}{2}\left(r2^k\right) \qquad (3)$$

$$SSQ = ef^2\left(r2^{k-2}\right) \qquad (4)$$

Estimated effects were obtained from column 15 in Table 3 divided by the divisor. The estimated effects show influence of each of the factors and interactions on the efficacy of an adsorption system. From the table the effects can be grouped into two, namely:

- Factors and interactions with negative effects (A, AB, C, AD, BD, ABD, BCD and ABCD)
- Factors and interactions with positive influences (B, D and others).

Factors and interactions with negative influence indicate that these are factors and interactions that reduce efficacy of the adsorption (the higher the values of these factors and interactions the lower the efficacy of an adsorption system). Similarly, factors and interactions with positive influence indicate that these are factors and interactions that increase efficacy of the adsorption (the higher the values of these factors and interactions the higher the efficacy of an adsorption system). The significant analysis of the result was carried out and the result of significant test is as shown in Table 4. The table shows that factors such as B, C and D have significant

Table 3: Factorial experiments analysis, effect and sum of squares

	Codified factors					Results					Yates' algorithms						
Experiments	A	B	C	D	Combinations	Run 1	Run 2	Run 3	Run 4	Total	1	2	3	4	Divisors	Effects	Sum of squares
1	-	-	-	-	Mean	89.55	89.25	87.06	83.78	349.64	685.36	1391.41	2606.8	5409.72	64	84.53	114316.50
2	+	-	-	-	A	85.77	85.67	83.78	80.50	335.71	706.05	1215.39	2802.92	-116.91	32	-3.65	213.57
3	-	+	-	-	B	91.94	91.74	89.85	86.17	359.69	554.12	1447.13	-41.09	165.87	32	5.18	429.87
4	+	+	-	-	BA	88.46	88.46	86.47	82.98	346.36	661.28	1355.79	-75.82	-27.56	32	-0.86	11.87
5	-	-	+	-	C	71.54	71.64	69.85	67.06	280.09	723.86	-27.26	127.86	-267.36	32	-8.35	1116.87
6	+	-	+	-	AC	70.45	69.95	68.36	65.27	274.02	723.27	-13.83	38.01	69.75	32	2.18	76.02
7	-	+	+	-	BC	85.47	85.37	83.48	80.20	334.52	658.59	-66.07	-1.09	125.67	32	3.93	246.76
8	+	+	+	-	ABC	83.48	83.38	81.59	78.31	326.76	697.20	-9.75	-26.47	-19.60	32	-0.61	6.00
9	-	-	-	+	D	96.12	96.52	94.23	90.45	377.30	-13.93	20.70	-176.02	196.11	32	6.13	600.95
10	+	-	-	+	AD	88.85	87.66	86.76	83.28	346.56	-13.33	107.16	-91.34	-34.73	32	-1.09	18.84
11	-	+	-	+	BD	96.91	96.81	94.62	90.94	379.29	-6.07	-0.60	13.43	-89.85	32	-2.81	126.14
12	+	+	-	+	ABD	87.86	87.76	85.87	82.49	343.97	-7.76	38.61	56.32	-25.37	32	-0.79	10.06
13	-	-	+	+	CD	83.28	83.58	81.29	78.11	326.26	-30.75	0.60	86.47	84.67	32	2.65	112.03
14	+	-	+	+	ACD	81.09	81.09	79.2	90.94	332.33	-35.32	-1.69	39.20	42.88	32	1.34	28.74
15	-	+	+	+	BCD	91.14	90.84	89.05	85.47	356.51	6.07	-4.58	-2.29	-47.26	32	-1.48	34.90
16	+	+	+	+	ABCD	87.06	86.96	85.07	81.59	340.69	-15.82	-21.89	-17.31	-15.02	32	-0.47	3.53

Table 4: Significant analysis of the factors and interactions

Factors	Sum of squares	Degree of freedom	Mean sum of squares	F- values	Critical F-values at 90% confidence limit
A	213.57	1	213.57	2.24	3.46
B	429.87	1	429.87	4.51	3.46
C	1116.87	1	1116.87	11.72	3.46
D	600.95	1	600.95	6.31	3.46
Total	3409.33	15	227.29		
Error	1048.07	11	95.28		
Interactions					
AB	11.87	1	11.87	0.12	3.46
AC	76.02	1	76.02	0.80	3.46
AD	18.84	1	18.84	0.20	3.46
BC	246.76	1	246.76	2.59	3.46
BD	126.14	1	126.14	1.32	3.46
CD	112.03	1	112.03	1.18	3.46
ABCD	3.53	1	3.53	0.04	3.46
ABC	6.00	1	6.00	0.06	3.46
ACD	28.74	1	28.74	0.06	3.46
BCD	34.90	1	34.90	0.37	3.46
ABD	10.06	1	10.06	0.11	3.46

effects on efficacy of an adsorption system, while factors such as A and interactions such as AC, BD and CD have effect on efficacy of an adsorption system but their effects are not significant because their F values were found to be lower than critical value at 90 % confidence level. The mathematical model for cadmium adsorption using those factors was found to be Y = 84.53- 1.83 A + 2.59 B- 4.18C + 3.07 D.

EFFECT OF ADSORBENT DOSE

Experiments were conducted in order to establish results from factorial experiments. The kinetic data for the removal of cadmium by adsorption against contact time for a fixed initial concentration of 5.00 mg dm^{-3} (C_0) with five different adsorbent doses of activated carbon varying between 0.250 and 1.00 g dm^{-3} are presented in Fig. 1. From the figure the rate of cadmium uptake was very high initially and decreased markedly after sometime. It was noted that at any time for a given C_0 value of cadmium removal increased with increase in adsorbent doses. This is because at higher dose of adsorbent due to increased surface area, more adsorption sites are available causing higher removal of cadmium. The cadmium removal from its solution is influenced by adsorbent doses and this result agrees with result from factorial experiments.

EFFECT OF INITIAL CONCENTRATION

Experiments at different initial concentrations and a constant adsorbent dose (0.7 g) were carried out to establish effect of initial concentration. In all cases the shape of the curves were similar (Fig. 2). The dependence of the process of cadmium removal from different initial concentrations (1.50 to 5.00 g dm^{-3}) with the same adsorbent dose is illustrated in Fig. 2. From Fig. 2 an increase in initial cadmium concentration decreased the percentage removal and increased the amount of cadmium uptake per unit mass of the adsorbent (mg g^{-1}). It was observed that removal of cadmium ions decreased from

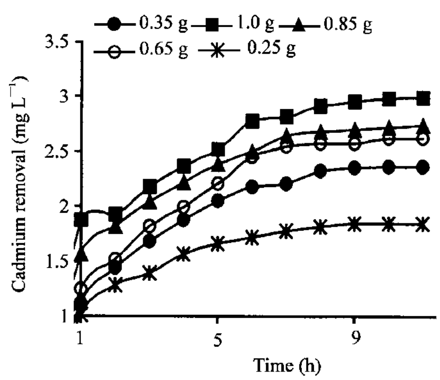

Fig. 1: Adsorption of cadmium at various doses

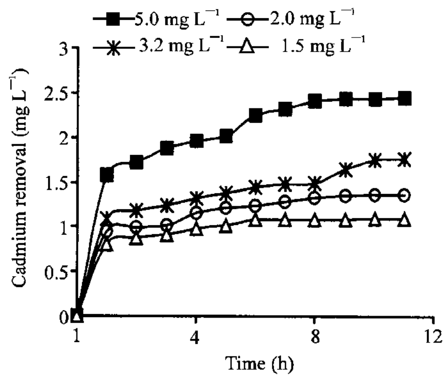

Fig. 2: Adsorption of cadmium at various initial concentrations

73.3 to 44.4% by increasing the concentrations from 1.50 to 5.00 mg dm^{-3} at an adsorbent dose of 0.70 g dm^{-3}. This indicates that at higher initial concentrations the ratio of initial number of moles of cadmium to the available surface area is high; hence fractional adsorption becomes dependent on initial concentration. For fixed adsorbent dose, the total available adsorption sites are limited thereby adsorbing almost the same amount of sorbate thus resulting in a decrease in percentage removal of the adsorbate corresponding to an increase initial sorbate concentration.

EFFECT OF CO-IONS

Effect of Pb(II) and Fe(II) on the uptake of cadmium by the commercial activated carbon was investigated at a constant pH. Batch experiments were conducted using 300 cm^{-3} of Cadmium solution having co-ions in the molar ratio of 1:1, 2:1 and 1:2 (Fig. 3). The percentage adsorption of cadmium from solution was 98.8% at an equilibrium time of 7 h in the absence of any co-ions (o) and decreased to 80.8% when Pb(II) and Fe(II) ions are present (in the 1:1 ratio). As the molar ratio increases

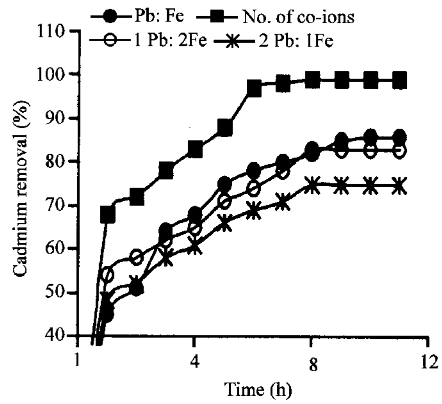

Fig. 3: Adsorption of cadmium at co-ion ratios

to 1:2 more reduction of cadmium removal was noticed (78.2 % in cadmium removal was observed when Pb(II) and Fe(II) ions present at a molar ratio of 1:2). As the molar ratio increases to 2:1 more reduction of cadmium removal was noticed (71.6% reduction in cadmium removal was observed when Pb(II) and Fe(II) ions present at a molar ratio of 2:1). This reduction in cadmium adsorption might be due to a competitive ion effect between cadmium and co-ions for the adsorption sites on the carbon. Based on these experimental results, the Pb(II) ion may be a stronger competitive ion than Fe(II) ions for cadmium removal by the adsorbent. The results can also be explained by the selectivity sequence of the most common cations on the adsorbent surface. It was observed that amongst the cations used, interference of Pb(II) ion is highest, followed by Fe(II). The observed order of interference was the same as that of their increasing ionic radii (their decreasing hydrated ionic radii). The smaller the hydrated ionic radius, the greater its efficiency to active groups of the adsorbent. This suggests that the energy required in the dehydration of the metal ions, in order that they could occupy a site in the adsorbent, plays an important role in determining the selectivity series for the metal ions (Heys, 1981).

EFFECT OF THE STIRRING SPEED

Effect of stirring speed on uptake of cadmium by the commercial activated carbon was investigated. Batch experiments were conducted using 300 cm^{-3} of cadmium solution (1.50 mg L^{-1} of cadmium ion with constant adsorbent dose of 1.0 g). Effect of three speeds was investigated: 20, 40 and 60 r•min^{-1} (Fig. 4). From the figure it appeared that stirring speed has no significant influence on the adsorption of cadmium. Higher stirring speed slightly increased the rate of cadmium solution.

Table 5: summary of significant test and discussions on selected factors

Factors	Effect	Remarks	Sources
Initial concentrations	Positive influence on cadmium removal by carbon from sugar cane	Significant effect, increase adsorption but decreases percentage removal	Krishnan and Anirudhan (2003)
Initial concentrations	Positive influence on chromium removal by carbon from sugar cane	Significant effect, increase adsorption but decreases percentage removal	Erhan *et al.* (2004)
Initial concentrations	Positive influence on chromium removal by hazelnut shell activated carbon .	Significant effect, increase adsorption but decreases percentage removal	Kobya (2004)
Stirring speed	Positive influence on chromium and copper removal by chitosan.	No significant effect	Schmuhi *et al.* (2001)
Adsorbent dose	Positive influence on cadmium removal by carbon from sugar cane	Significant effect, increase adsorption but decreases percentage removal	Krishnan and Anirudhan (2003)
Co-ion concentration	Negative influence on cadmium removal by carbon from sugar cane	Significant effect, decrease adsorption but decreases percentage removal	Krishnan and Anirudhan (2003)

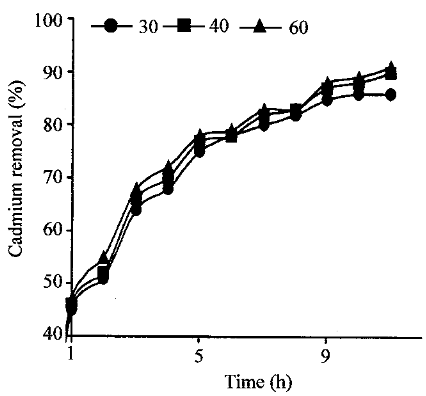

Fig. 4: Adsorption of cadmium at various stirring speeds

COMPARISON OF RESULTS WITH LITERATURE

In previous studies by Krishnan and Anirudhen (2003); Jamode *et al.* (2004); Erhan *et al.* (2004); Saswati and Ghosh (2005) discussions were made on these factors, these discussions as well as the significant analysis result from this study are presented in Table 5. In literature quantitative results on significant tests for the factors could not be found but pictorial or discussions on concentration data for the factors on chromium and cadmium adsorption onto chitosan and other low cost adsorbents are available. This means that the practical and industrial applications of significance of these factors are essential because low cost adsorbent such as chitosan (adsorbent capable of adsorbing copper to a non-detectable level) has been found relevant in these two important areas. Indicating that economically, speaking it is necessary to establish significance of key factors and their interactions that can influence efficacy of adsorbents because some adsorbents are more expensive than others.

CONCLUSIONS

The following conclusions were drawn from the study on factors that influence efficacy of adsorption as a treatment method:

- Utilization of the 2^K matrix taking into account all interaction effects on adsorption;
- The method appeared to be efficient in giving a mathematical model that conformed with the experimental data;
- adsorption was not significantly influenced by stirring speed of the solution to be treated but significantly influence by initial cadmium concentration, co-ion concentration and adsorbent doses at 90% confidence level; and
- Studies should be carried out on significant of others factors such as pH, time, particle size just to mention a few.

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NOMENCLATURE

q_e The adsorption capacity at equilibrium (mg g^{-1})
q_t The adsorption capacity at time t (mg g^{-1}),
M Adsorbent mass added (mg)
C_0 Initial concentration of arsenic in the solution (mg L^{-1})

C_e Experimental concentration in the solution at equilibrium (mg L^{-1})
C_t Experimental concentration in the solution at time t (mg L^{-1})
V Volume of solution (L)
Y_r Divisors
R Number of replication (4)
K Number of the factors examined (4)
ef^2 Effect squared
SSQ Sum of squares
(R_c%) Percentage of cadmium ion removed

REFERENCES

APHA, 1998. Standard Method for the Examination of Water and Wastewater, 20th Edn., America Water Works Association and Water Pollution Control Federation, Washington DC.

Drouiche1, M., H. Lounici1, N. Mameri1, D.L. Piron and M. Kharroune, 2001. Utilisation of factorial experiments for the UV/H2O2 process in a batch reactor. Water SA., 27: 551-558.

Erhan, D., M. Kobya, S. Elif and T. Ozkan, 2004. Adsorption kinetics for the removal of chromium III from aqueous solutions on the activated carbonaceous prepared from agricultural wastes. Water SA., 30: 533-540.

Gardiner, W.P. and G. Gettinby, 1998. Experimental Design Techniques in Statistical Practice, 2nd Edn., Harwood Publishing, Chichester.

Guttman, I., S.S. Wilks and J.S. Hunter, 1971. Introductory Engineering Statistics. 2nd Edn., John Wiley and Sons Inc, New York.

Heys, L., 1981. Physical Chemistry. 3rd Edn., Pitman Press, London.

Jamode, A.V., V.S. Sapkal, V.S. Jamode and S.K. Deshmukh, 2004. Adsorption kinetics of defluoridation using a low cost adsorbent. Adsorption Sci. Technol., 22: 65-73.

Kobya, M., 2004. Adsorption, kinetic and equilibrium studies of Cr(VI) by hazelnut shell activated carbon. Adsorp. Sci. Technol., 22: 51-64.

Krishnan, K.A. and T.S. Anirudhan, 2003. Removal of cadmium II from aqueous solutions by steam activated sulphonised carbon prepared from sugar-cane bagasse pith: Kinetic and equilibrium studies. Water SA., 29: 147-156.

Saswati, G. and U.C. Ghosh, 2005. Studies on adsorption behaviour of CrVI onto synthetic hydrox stannic oxide. Water SA., 31: 597-602.

Schmubi, R., H.M. Kneg and K. Keizer, 2001. Adsorption of CU(II) and Cr(VI) ions by chitosan, kinetic and equilibrium studies. Water SA., 27: 1-5.