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Removal of Chromium (III) Ions from Aqueous Solution by Natural Clays

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Abstract: One of the important, hazardous and toxic heavy metal is Chromium (III) especially found in industrial effluents. Removal of Chromium (III) from industrial waste is of vital importance. In the present study adsorption of chromium (III) from aqueous solution by equivalent mixture of Bentonite and China clay had been investigated as a function of pertinent parameters like contact time, concentration of adsorbents and chromium (III), effect of pH, shaking frequency and effect of concentration of Ca^{+2},Na^{+1} and K^{+1}. The results had been verified on Langmuir isotherm model. The spectrophotometric method had been used to determine the concentration of chromium (III) ions with the help of reagent 2-hydroxybenzaldeminoglycine. Maximum adsorption 99% was observed under optimized conditions of variables.

Key words: Adsorption · Chromium (III) ions · Bentonite clay · China clay · Spectrophotometer

INTRODUCTION

The determination of trace elements in waste water environment samples is one of the most important tasks [1] requires highly sensitive as well as standard analytical methods. Heavy metals are toxic inorganic contaminants in the waste water streams can be readily absorbed by marine animals and directly enter into food chains [2]. Unlike organic contaminants they cannot be degraded by microorganisms and must be removed from wastewater before being discharged to the environment. Hexavalent form of chromium is toxic and is thought to be a carcinogenic to humans. Cr (VI) can straightforwardly pass through cell membranes, often via sulfate transport systems and is reduced to Cr (III) inside the cell. The reduced Cr (III) can bind to DNA and cause various unwanted changes during replication and the radicals produced during the reduction can cause oxidative damage inside cells. Cr (III) is less toxic to humans, due to its affinity to adsorb to solids or precipitate out of solution and its incapability to pass through cell membranes. Cr (III) is considered a vital micronutrient and carcinogenic to mammals, where it is thought to aid in glucose metabolism [3].

Conventional methods for the removal of toxic heavy metals from industrial effluents includes chemical precipitation, filtration, electrochemical treatment, electrodialysis is an electrically driven process involving the use of ion-selective membranes [4] ion exchange [5] coagulation [6], solvent extraction [7], electrolysis [8], membrane separation [8], absorption [9] and inclusion [10], solid formation [11] which were all distinguished by the type of association between metal and host mineral. These processes have many disadvantages such as incomplete removal, high energy and reagents costs and disposal of toxic sludge. Adsorption as an alternative method, to be a highly effective, cheap and easy method among the physicochemical treatment processes [12]. The surface attachment can be physical, chemical or exchange adsorption. In the present study of adsorption to eliminate Cr(III) from waste water and the effect of various parameters, such as contact time of adsorbate and adsorbents, pH of metal solution and initial metal ion concentration, presences of other metal ions have been investigated. Equilibrium modeling was carried out using the Langmuir adsorption isotherms. The objective of this study was to optimize the parameters for the removal of Cr (III) metal from aqueous solution.

MATERIALS AND METHODS

Adsorbents: The mixture of Bentonite clay and China clay in equal proportion was used as an adsorbent for the study of adsorption for chromium (III). The samples of Bentonite clay and China clay were obtained from market. The Bentonite sample had hydrated oxides of aluminum,

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silicon, calcium, magnesium, uranium, sodium and potassium while China clay sample contains quartz mica and hydrous silicate.

Experimental Condition: All adsorption experiments were carried out at room temperature. Solutions were placed in glass flasks and gently agitated on electric shaker. The effect of contact time (5-120 min), pH (2-10), concentration of Cr(III) (20-70ppm), concentration of clay (adsorbents) (0.01-1.5g), number of revolutions per minute, concentration of (Na^+, K^+ and Ca^{2+}) were investigated by varying any one of the process parameter and keeping the other parameters constant. Distribution coefficient (K_d) and % adsorption (P %) were calculated according to the following equation [13]

$$K_d = \frac{C_0 - C_{eq}}{C_{eq}} \times \frac{V}{M} (cm^3/g) \quad (1)$$

$$P(\%) = \frac{100 \times K_d}{K_d + V/M} \% \quad (2)$$

Where

C_0 = Initial concentration of Cr (III),
C_{eq} = Concentration in supernatant after filtration
V = Volume of the solution added (cm^3)
W = Weight of the adsorbent (g).

The Langmuir adsorption model (1) can be presented in the following form [13]

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \quad (3)$$

Where, C_e is the equilibrium concentration (mg/L) of chromium as dependent variable, q_e is the amount of Chromium adsorbed as independent variable at equilibrium time (mg/g), Q_o and b are Langmuir constants related to the adsorption capacity and energy respectively.The model (3) was fitted by using regression analysis and significance is checked at 5% level of significance. The model adequacy is determined on the basis of coefficient of determinant (R^2).

RESULTS AND DISCUSSION

Effect of Amount of Clay (Adsorbent): Amount of the adsorbents (clay) affected the efficiency of the adsorption keeping other parameters constant and varying amount of Bentonite from 0.01 to 1.5 g. It was clear from the results (Table 1) that % adsorption increases with increasing the amount of clay up to 0.4 g and then remained constant up to 1.5 g.

Effect of Chromium (III) Concentration: For the effect of chromium concentration on the adsorption process was studied under the optimized conditions of shaking time, pH and the amount of adsorbent. The concentration of chromium was varied from 20 to 70 ppm. All the values obtained are given in Table 1. The results showed that the adsorption of chromium was almost constant up to 60 ppm of chromium. Beyond this concentration the adsorption gradually decreased with an increase in the concentration of chromium. It can be assumed that at low concentrations, metal was absorbed by particular sites, while by further increment of metal ion concentrations, the specific sites were filled.

Effect of Contact Time: The effect of different shaking time on percent adsorption of chromium (III) over the range of 5 to 120 minutes was studied keeping other parameters constant (Table1). It was seen that the percent adsorption increases with shaking time. Maximum adsorption was observed at 30 minute time, beyond which there was no further increase in the adsorption. The 30 minutes contact time was considered to be sufficient for the adsorption of chromium (III) on mixture of China and bentonite clay.The adsorption data of contact time was further analyzed with Langmuir adsorption isotherm model present in equation (3), pH and amount of clay was fixed 7.5 and 0.4 g respectively. The regression model between equilibrium concentration of chromium and the amount of chromium adsorbed (Table 2) is significant ($p<0.05$) the significance of individuals parameters is also presented in Table 2. The regression coefficient (2.051) was found significant ($p<0.05$) and indicate a positive relationship between the transformed independent and dependent variables and ultimately same conditions holds between the original variables. On the basis of these results, the form of the fitted model is as,

$$\frac{Ce}{qe} = -0.022 + 2.051 \frac{Ce}{qe} \quad (4)$$

The high value of R^2 indicates that the fitted model is significant and confirms the relationship between the variables.

Table 1: Variation of Various Condition

Sr.		Q^0 (μg)	C_e (μg)	q_e (μg)	K_d	P (%)	C_e/q_e	Sr.		Q^0 (μg)	C_e (μg)	q_e (μg)	K_d	P (%)	C_e/q_e
Sr.	Amount of Clay (g)	Effect of amount of clay (adsorbent) on the adsorption of Cr (III)						Sr.	Concent ration of Ca^{+2} Cation	Effect of Ca^{+2} on the adsorption of Cr (III)					
1	0.2	600	466.46	133.53	14.31	22.26	3.490	1	2	600	49.741	550.259	550.259	91.709	0.090
2	0.4	600	357.35	242.64	44.97	80.44	1.470	2	4	600	19.757	580.242	580.242	96.707	0.034
3	0.6	600	223.36	376.64	29.09	62.77	0.590	3	6	600	18.358	581.641	581.641	96.940	0.031
4	0.8	600	169.21	430.79	31.82	72.00	0.390	4	8	600	18.181	581.818	581.818	96.969	0.031
5	1.5	600	85.128	514.87	40.28	75.81	0.160	5	10	600	16.666	583.333	583.333	97.222	0.028
	Concentration of Cr (III)	Effect of amount of Cr (III) on the adsorption of Cr (III)							Concentration of Na^+ Cation	Effect of Na^+ on the adsorption of Cr (III)					
1	1.0	2.50	0.0259	0.974	940.0	97.41	0.0265	1	2	600	43.523	556.476	319.642	92.746	0.078
2	1.5	3.75	0.0309	1.469	1186.60	97.94	0.0210	2	4	600	24.771	575.229	580.555	95.871	0.043
3	2.0	5.00	0.0428	1.957	1142.30	97.86	0.0218	3	6	600	21.746	578.253	664.772	96.376	0.038
4	2.5	6.25	0.0534	2.446	1145.50	97.86	0.0218	4	8	600	44.024	644.024	740.384	107.34	0.068
5	3.0	7.50	0.0628	2.937	1269.73	98.11	0.0213	5	10	600	19.163	580.837	757.758	96.806	0.033
	Revolution per min.	Effect of different revolutions per minutes on the adsorption of Cr (III)							Concentration of K^+ Cation	Effect of K^+ on the adsorption of Cr (III)					
1	25	600	28.698	571.30	497.222	95.21	0.0502	1	2	600	38.298	561.702	366.666	93.617	0.068
2	50	600	16.518	583.48	883.333	97.24	0.0283	2	4	600	20.642	579.358	701.666	96.559	0.036
3	100	600	62.01	537.99	867.647	89.66	0.1152	3	6	600	251.23	348.768	34.7058	58.128	0.720
4	150	600	4.524	595.48	3291.66	99.24	0.0075	4	8	600	15.075	584.924	970	97.487	0.026
5	200	600	5.296	594.70	2812.5	99.11	0.0089	5	10	600	15.859	584.141	920.833	97.356	0.027
	Contact Time (min)	Effect of shaking time on the adsorption of Cr (III)							pH	Effect of pH on the adsorption of Cr (III)					
1	5	600	25.728	574.27	562.50	95.71	0.044	1	2	600	534.72	65.283	3.05225	10.880	8.190
2	10	600	13.764	586.24	1065.0	97.70	0.023	2	3	600	223.57	376.42	42.093	62.738	0.593
3	20	600	301.50	298.50	24.752	49.75	1.010	3	4	600	190.26	409.735	53.8377	65.289	0.464
4	30	600	9.8040	590.20	1505.76	98.36	0.016	4	5	600	131.64	468.363	88.9502	68.060	0.281
5	60	600	14.538	585.46	1006.81	97.57	0.024	5	6	600	63.096	536.904	112.735	75.264	0.011
6	90	600	4.7940	595.21	3105.55	99.20	0.008	6	7	600	274.41	325.585	160.661	80.484	0.842
7	120	600	10.266	589.73	1436.9	98.28	0.017	7	7.5	600	121.79	550.210	235.624	90.478	0.223
Q_0= Initial Cr(III) concentration, C_e = Final Cr(III) concentration								8	8	600	109.79	490.210	111.625	83.701	0.223
q_e = Cr(III) Adsorbed, K_d = Distribution coefficient,															
P (%)= Percent adsorption							9	10	600	43.979		556.020	216.071	85.670	0.079

Table 2: Langmuir Isothermal Model Fitting

Effect of Contact Time	Coefficient	S.E	t-test	p-value	Effect of pH	Coefficient	S.E	t-test	p-value
Constant	-0.022	0.005	-4.398	0.007	Constant	-1.82	0.730	-2.49	0.047
D	2.051	0.026	77.768	0.000	d	9.649	1.783	5.412	0.002
Q_o=600		R^2=0.999			Q_o=600		R^2=0.830		
b= -0.07575		Adjusted R^2 = 0.999			b= -0.0000914		Adjusted R^2 = 0.802		

Effect of Ca^+ Cation	Coefficient	S.E	t-test	p-value	Effect of Na^+ Cation	Coefficient	S.E	t-test	p-value
Constant	-0.003	0.000	-22.479	0.000	Constant	-0.002	0.00	-11.080	0.002
D	1.124	0.003	413.230	0.000	d	1.104	0.005	228.405	0.000
Q_o=600		R^2=0.999			Q_o=600		R^2=0.999		
b= -0.5555		Adjusted R^2 = 0.999			b= -0.8333		Adjusted R^2 = 0.999		

Effect of K^+ Cation	Coefficient	S.E	t-test	p-value	Effect of Different revolutions per minutes on the adsorptions of Cr (III)	Coefficient	S.E	t-test	p-value
Constant	-0.027	0.007	-3.920	0.030	Constant	-0.002	0.001	1.906	0.153
D	1.781	0.036	49.195	0.000	D	1.124	0.018	63.074	0.000
Q_o=600		R^2=0.999			Q_o=600		R^2=0.999		
b= -0.06172		Adjusted R^2 = 0.998			b= -0.8333		Adjusted R^2 = 0.999		

Effects of pH: The removal of chromium (III) from waste water was found to be highly dependent on the pH of the solution which affects the surface charge of the adsorbent and the degree of ionization. The adsorption behavior of chromium ions was studied in aqueous solutions at different pH values (2 to 10) keeping all the other parameters at their optimum level (Table). The maximum adsorption of chromium (III) occurred at pH 7.5, which gradually increased with the increase in pH. The removal of chromium could probably be due to the mixed effect of "ion exchange" and "surface complexation" phenomena on the surface of China and bentonite clay. The Langmuir adsorption isotherm model also fitted and found significant ($p<0.05$) with high value of R^2. The regression coefficient (9.649) showed significant positive relationship between the variables (Table 2). On the basis of the results, t he form of the fitted model was as:

$$\frac{Ce}{qe} = -1.823 + 9.649\frac{Ce}{qe} \quad (5)$$

Effect of Revolution per Minute (RPM) of Orbital Shaker: The change in percent adsorption was studied by varying revolutions per minutes (RPM) over the range of 25 to 200, keeping other parameters constant. Maximum adsorption was observed at 150 RPM, beyond which there was no further increase in the adsorption and 150 RPM was considered to be sufficient for the adsorption of chromium (III) on mixture of China and bentonite clay and was used for all subsequent experiment (Table 1). The adsorption data of RPM were further analyzed with Langmuir isotherm model. The transformed regression model is found significant ($p<0.05$) with high value of R^2 (Table 2). The regression coefficient (1.124) was found positive and significant ($p<0.05$), indicating a positive relationship. The fitted Langmuir isotherm model was as:

$$\frac{Ce}{qe} = -0.002 + 1.124\frac{Ce}{qe} \quad (6)$$

Effect of Ca^{2+}, Na^+ and K^+: The effect of Ca^{2+}, Na^+ and K^+ was studied under the optimized conditions of shaking time, pH and the amount of adsorbent (Table 1). The results showed that the sorption of Cr (III) on mixture of China and bentonite clay (adsorbent) was influenced to a significant extent b y the cations in the solution. This indicated that cations can alter the surface properties of China clay and bentonite clay and hence influence the sorption of Cr (III) on adsorbents surface. The effect of these cations in reducing the adsorption of chromium (III) followed the order $K^+ < Na^+ < Ca^{2+}$ at pH 7.5. It was clear from these results that chromium (III) adsorption was mainly controlled by sodium (Na^+) and calcium (Ca^{2+}).

Application of Langmuir Adsorption Isotherm Model to Effect of Ca^{2+} Cation: Langmuir adsorption isotherm model was employed to check the effect of Ca^{+2} Cation on adsorption of Cr (III) by bentonite and China clay mixture. The regression model was found to be significant ($p<0.05$) (Table 2) with high coefficient of determination. The individual regression coefficient was found significant. With these results, the fitted model was

$$\frac{Ce}{qe} = -0.003 + 1.124\frac{Ce}{qe} \quad (7)$$

In the same way, the effect of sodium (Na+) and potassium (K+) on adsorption of Cr (III) was determined by fitting Langmuir adsorption isotherm model separately. Both regression models were found significant ($p<0.05$) and explained 99% of the total information. The regression coefficient for both models were 1.104 and 1.780 respectively and significant also (Table 2). The resultant Langmuir adsorption isotherm models are as under:

$$\frac{Ce}{qe} = -0.002 + 1.104\frac{Ce}{qe} \qquad \textit{For sodium}(Na^+) \quad (8)$$

$$\frac{Ce}{qe} = -0.027 + 1.781\frac{Ce}{qe} \qquad \textit{For potassium}(K^+) \quad (9)$$

CONCLUSION

The adsorption technique was found rapid, simple and selective in the present study hence it could be used for removal of chromium (III) from domestic and industrial waste water by using Bentonite and China clay. The effect of pH, contact time, shaking speed, concentration of clay, concentration of chromium and concentration of Ca^{2+}, Na^+ and K^+ were studied to achieve the optimum adsorption condition for the removal of chromium(III) and their effects were found significant. Ninety nine percent (99%) adsorption was achieved at pH 7.5 in 30 minutes by mixing 0.4 gm of adsorbent (mixture of China and bentonite clay) and 10 ml of 60ppm solution of Cr (III) at 150 RPM of electric shaker.

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