

Batch adsorption studies of chromium(III) onto commercial grade granular activated carbon: Equilibrium and Kinetic Studies

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Abstract - Batch adsorption studies were carried out for the removal of chromium using commercial grade granular activated carbon. Synthetic chromium effluent solutions were prepared using chromium chromium chloride. The effects of various factors such as pH, agitation rate, and initial concentration were examined. The adsorption capacity was found to increase with increase in initial concentrations ranging from (300,400,500 mg/l) and was found to be maximum between the pH ranges 4-5. From the kinetic and isotherm studies Pseudo second order and Langmuir model was found to fit best with the experimental data's with R2 values greater than 0.99. The goodness of fit was checked using MATLAB @2009a.

Index Terms: Granular activated carbon, chromium chloride, adsorption capacity, isotherm, kinetics.

I. INTRODUCTION

Chromium, a natural element found in rivers, seawater, soils and rock. They are widely used in Electroplating process, Paints and inks, Wood Preservatives, Leather tanning, Textiles, Refractories etc., In nature chromium always exists in combination with other elements. To mention few chromium sulphate, chromium nitrate, chromium oxide, chromium trioxide, chromium acetate, sodium dichromate, chromite etc. All these compounds are used in any of the above said manufacturing process. Chromium enters the sewage through several ways that includes industrial activities, run –off, service activities, water supply and also through food chain since chromium is present in food source.

There exists two important forms of chromium that is hexavalent and trivalent, hexavalent chromium is man-made whereas trivalent occurs naturally.[7].The man-made chromium is more soluble than Cr(III) but Cr(III) precipitates at an average pH. There are many methods available for the removal of chromium that includes filtration, chemical precipitation, electrodepositions, membrane system etc.,[8].

Adsorption is one of the effective process for the removal of soluble chromium present in waste water. There are several low cost adsorbents available processed and even several studies are carried out for obtaining low cost adsorbents. Several adsorption studies are carried out for the removal of heavy metals. [11, 12].

In this work, batch adsorption studies of Cr (III) was carried out onto commercial grade activated carbon. The adsorption kinetics and isotherms equations are fitted using MATLAB@R2009a.

II. MATERIALS AND METHODS

A. Chemicals Used

Chromium chloride was used as a source of Cr(III) and purchased from Central drug house (CDH), India.,as CrCl₂.xH₂O and commercial grade GAC was bought from Sudhakar Biologicals (Suppliers),Chennai, India. The synthetic effluent solutions of Cr (III) was prepared by dissolving 1g of chromium chloride in 1000 ml (1g/l) of distilled water and the pH was varied using 0.1N HCl or 0.5N NaOH.

B. Determination of Cr (III)

Initially using wavelength scan mode the maximum wavelength of Cr (III) was identified to be 520nm.The concentration of Cr(III) was directly measured using double beam UV-VIS spectrophotometer (UV Pharmspec 1700, Shimadzu) at 520nm.The Beer's law is valid for concentration range of (0.1-1g/l). For the experimental conditions the same method was followed.

C. Batch Studies

Batch experiments were conducted in 250ml Erlenmeyer flasks at room temperature. The experiments were carried out with a working volume of 200ml and 1g of adsorbent, as a function of pH, agitation, contact time and initial concentration. The experiments were conducted in order to develop kinetics and isotherms.

III. DATA ANALYSIS

A. Uptake rate of Cr (III)

The uptake rate of Cr(III) was calculated using

$$Q = v * (C_0 - C_f) / M \quad (1)$$

where, Q is the adsorption capacity (mg g⁻¹), v is the volume of the Cr(III) solution (ml), C₀ is the initial concentration of the solution (mg l⁻¹), C_f is the final concentration (mg l⁻¹) of the solution and M is the mass of the adsorbent in (g).

B. Removal Efficiency of Cr (III)

The removal efficiency of Cr(III) from the solution was calculated using the following equation

$$\text{Removal Efficiency (\%)} = \frac{C_0 - C_f}{C_0} * 100$$

where, C_0 is the initial concentration of the solution (mg l^{-1}), C_f is the final concentration (mg l^{-1}) of the solution.

C. Adsorption Kinetic Studies

The process of adsorption is highly time dependent and thus the of rate of Cr(III) adsorption is crucial to understand the kinetics of adsorption. Various adsorption kinetic models are available but the most preferred and widely used kinetic models are Pseudo I order and Pseudo II order kinetic models to understand the mechanism of adsorption [7] .The integrated form of Pseudo I order and Pseudo II order equations are given below as Eq.3 &4 respectively.[9,10]

$$\ln(q_e - q_t) = \ln q_e - (K_1 t / 2.303)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$$

where q_e is the equilibrium adsorption capacity of Cr(III) (mg g^{-1}), q_t is the adsorption capacity at time t , K_1 is Pseudo first order rate constant (min^{-1}), K_2 is the second order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$). The linear plot of $\ln(q_e - q_t)$ versus t gives the slope of $-K_1/2.303$ and an intercept of $\ln q_e$ and the plot of (t/q_e) versus t gives a slope of $(1/q_e)$ and intercept of $(1/K_2 q_e^2)$

D. Adsorption Isotherms

Experimental data's were fitted using Langmuir and Freundlich isotherm models. The isotherms are used to generate equilibrium curves that would be helpful to optimize the adsorption system.

The linear expression for Langmuir Isotherm Model is shown in Eq.5

$$\frac{C_e}{q_e} = \frac{1}{Q_L K_L} + \frac{C_e}{Q_L}$$

where, C_e was the equilibrium concentration (mg L^{-1}), Q_L (mg g^{-1}) and K_L (l g^{-1}) are the Langmuir's constants. A linear plot of C_e/q_e versus C_e gives the slope of $1/Q_L$ and intercept of $1/Q_L K_L$ respectively

The linear expression for Freundlich Isotherm Model is shown in Eq.6

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$$

where, K_f (mg g^{-1}) and n are Freundlich constants. The measure of surface heterogeneity [9] can be obtained from the slopes. The type of adsorption can be identified from the values of $1/n$ obtained.

E. Curve Fitting using MATLAB@ R2009a

The kinetic models and isotherm studies for the experimental datas were done using MATLAB@ R2009a using cftool. The coefficients with 95% confidence bounds ,slope ,intercept and the goodness of fit were analyzed. The regression coefficient R^2 and the root mean square error (RMSE) were estimated for the given expressions.

IV. RESULTS AND DISCUSSION

A. Effect of pH

The effect of pH for the removal of Cr(III) was studied at pH (2,3,4 and 5).The experimental data's showed that the adsorption of chromium was found to be maximum between the pH (4-5). At low pH the adsorption rate was poorer and steadily increased till pH 5. As shown in Fig.1 there is no much difference in the adsorption rate of chromium between pH 4 and 5, a similar pattern was observed in [1,2].

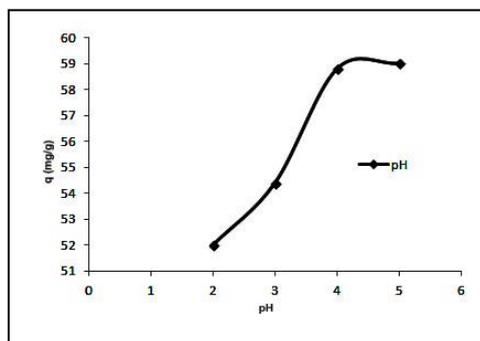


Figure 1.Effect of pH on adsorption capacity

B. Effect of initial concentration of Cr(III)

The results showed that the increase in initial concentrations increased the adsorption capacity of the process. The rate of adsorption varied for different concentrations but towards the end, the adsorption capacity was found to be more or less the same.

C. Effect of agitation rate

The adsorption rate of chromium was checked at different RPM's (50,100,150,200 & 250) for an initial concentration of 300mg/l for 300 minutes. The effect of agitation on adsorption rate of Cr(III) was shown in Fig.3.As can be seen the adsorption rate was highly influenced by the agitation rate. There was a high correlation between agitation and adsorption. The agitation increased the contact rate between the adsorbate and adsorbent. Agitation increased the mobility of the system [3] and thereby the adsorption rate was also increased ,if agitation was nil ,it would be difficult to reach the saturation point. The adsorption capacity was found to be 59mg/g and was almost the same between 250-300 RPM.

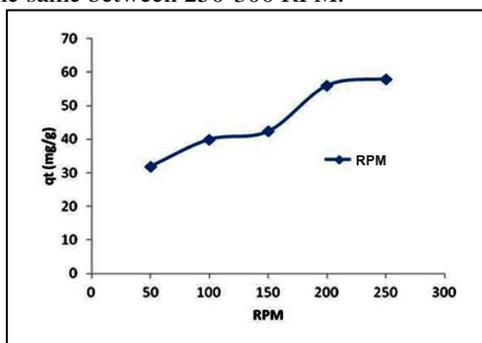


Figure 2.Effect of RPM on Adsorption Capacity

D. Effect of contact time

The effect of contact time on the adsorption rate of Cr(III) was studied at three different concentration (300,400 &500 mg/l).The experiments were conducted at 250 RPM until equilibrium was achieved. .Samples were collected at a regular interval of 30 minutes and from the observation it was clear that the adsorption progressively increased as the contact time was increased between the adsorbent and the adsorbate. Further kinetic analysis were done on the experimental data's.

E. Adsorption Kinetics Studies

The adsorption kinetics of Cr(III) was checked for various initial concentrations. From the observation it was clear that as the concentration of Cr(III) was increased the rate of adsorption also progressed in increasing order. The same datas were analyzed using kinetic equations. The linear form of the equations was fixed using MATLAB@R2009a , 'cftool' along with certain fixed values at the initial conditions. The goodness of fit was verified using the R² values and also with the values of the parameters obtained.

The values of the kinetic parameters were shown in (Table. 1-2). From the values listed in the table shows that Pseudo I order kinetic model did not fit to a great extent and also the parameters were not in good match with the experimental values. whereas the Pseudo II order kinetics shows a fine match with the experimental values. The R² value for an initial concentration 300 mg/l was > than 0.99.The theoretical adsorption capacity obtained increased with the decrease in the rate constant values. The trends of both the kinetic models were given in Fig.3[a-f]

Table 1 Parameters of Pseudo First order Kinetics

Parameters	Pseudo First order kinetics		
Concentration (mg/l)	300	400	500
K ₁₁ mg g ⁻¹ min ⁻¹	0.04692	0.01818	0.02433
q _e (mg/g)	87.33	62.7	82.16
R ²	0.9493	0.8442	0.8968
RMSE	0.4137	0.3267	0.3453

Table 2 Parameters of Pseudo Second order Kinetics

Parameters	Pseudo Second order kinetics		
Concentration (mg/l)	300	400	500
K ₁₂ mg g ⁻¹ min ⁻¹	1.71 * 10 ⁻⁴	5.17*10 ⁻⁵	1.210*10 ⁻⁵
Q _{cal} mg g ⁻¹	76.42	91.99	160.4
R ²	0.9917	0.8998	0.8264
RMSE	0.1155	0.3495	0.2752

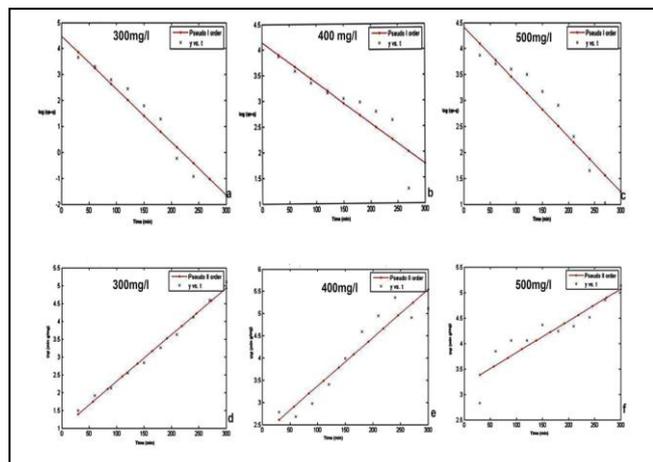


Figure 3. Pseudo I order Kinetics a) 300mg/l, b) 400mg/l, c) 500mg/l. Pseudo II order Kinetics d) 300mg/l, e) 400mg/l, f) 500mg/l. [y vs. t; y axis vs. x axis]

E. Equilibrium Adsorption Studies

According to Langmuir’s isotherm model, the surface of the adsorbent is considered to have a number of active sites [4] in to which the adsorbate make a contact and attaches themselves either physically or chemically, such interactions are termed as physisorption and chemisorptions respectively. When the adsorbent reaches a saturation point there would be no further space for the adsorbate [5]. The experimental data’s were fitted to Langmuir’s equation using ‘cftool’. The equilibrium parameters of Langmuir adsorption isotherm were given in Table.3 From the goodness of fit it could be seen that Langmuir suits to the best with R² value of 0.985. Furthermore the adsorption

Adsorption Isotherm Model					
Langmuir adsorption Model	Q _{cal} (mg/g)		K _L (l/g)	R ²	RMSE
	60.51		5.673	0.985	0.1986
Freundlich adsorption model	N	K _f (mg/g)	R ²	RMSE	
	6.281	26.6	0.7923	0.2549	

capacity achieved theoretically was much higher than that achieved experimentally. The Freundlich isotherm model assumes that the surface of the adsorbent has unequal sites and heterogeneous. The R² value was 0.7923 and this showed that the model did not suit well for the experimental data’s. The value of n obtained was 6.281 that showed a favorable adsorption process [6]. The goodness of fit of both the models were exhibited graphically in Fig.4 [a-b].

V. CONCLUSIONS

Commercial grade granular activated carbon was found to be a good adsorbent for minimum concentrations of chromium. The maximum adsorption capacity of Cr(III) was around 59mg/g that was achieved between pH 4-5. The saturation time was found to be 300 minutes after which a steady state was achieved. The influence of agitation was a key factor to accomplish excellent adsorption rate, and experiments carried out at various RPM showed that at 250 RPM the adsorption rate was found to be maximum. The adsorption rate increased with increase in initial concentration. The experimental data fitted well for Pseudo II order kinetics and Langmuir isotherm model with R² value greater than 0.99. Further column studies would bring a clear idea about the real-time application of the adsorbent.

Nomenclature

- C₀, C_f, C_e Initial, final and equilibrium concentration (mg l⁻¹)
- K₁ pseudo 1st order rate constant (min⁻¹)
- K₂ pseudo 2nd order rate constant (g mg⁻¹ min⁻¹)
- K_F Freundlich isotherm constant related to adsorption capacity (mg g⁻¹)
- K_L Langmuir isotherm constant relating to affinity of binding (l mg⁻¹)
- M mass of adsorbent (g)
- N Freundlich isotherm constant related to adsorption intensity (l/mg)
- Q adsorption capacity (mg/g)
- q_e equilibrium adsorption capacity (mg g⁻¹)
- Q_L monolayer coverage capacity at equilibrium (mg g⁻¹)
- T time (minutes)

REFERENCES

- [1] A.B. Perez Marin, M.I. Aguilar, V.F. Meseguer, J.F. Ortuno, J. Sáez, M. Lloréns Biosorption of chromium (III) by orange (*Citrus cinensis*) waste: Batch and continuous studies, Chem. Eng. J.155 (2009) 199–206.
- [2] Xiu-Wen Wu , Hong-Wen Ma , Yan-Rong Zhang ,Adsorption of chromium(VI) from aqueous solution by a mesoporous aluminosilicate synthesized from microcline, Appl. Clay Sci. 48 (2010) 538–541.
- [3] Mohammad A. Al-Ghoutia, Majeda A.M. Khraisheh, I. Mohammad N.M. Ahmadc, Stephen Allenc, Adsorption behaviour of methylene blue onto Jordanian diatomite: A kinetic study, J. Hazard. Mater. 165 (2009) 589–598
- [4] Parimalam Ramachandran, Raj Vairamuthu, and Sivakumar Ponnusamy, Adsorption isotherms, kinetics, thermodynamics and desorption studies of reactive orange16 on activated carbon derived from *ananas comosus* (L.) carbon, J. Eng.Appl.Sci. 6 (2011).
- [5] L.S.Chan, W.H. Cheung, S.J.Allen, G.McKay, Error Analysis of Adsorption Isotherm Models for Acid Dyes onto Bamboo Derived Activated Carbon, Chin.J.Chem.Eng. 20(3) (2012) 535– 542.
- [6] R.Subha,C.Namasivayam ,Zinc chloride activated coir pith carbon as low cost adsorbent for removal of 2,4-dichlorophenol:Equilibrium and Kinetic studies .Indian J. Chem.Technol.16, (2009) 471-479.
- [7] A.R. Rahmani, M.T. Samadi, R. Noroozi Hexavalent Chromium Removal from Aqueous Solutions by Adsorption onto Synthetic Nano Size ZeroValent Iron (nZVI), World Acad. Sci. Eng. Technol. 50, (2011)
- [8] Abdul rehman, Farah r. Shakoori and Abdul Rauf shakoori, Heavy metals resistant rotifers from a chromium contaminated wastewater can help in environmental clean-up, Pakistan j. Zool. 40(5), (2008) 309-316.
- [9] Nahid Ghasemi, Sara Mirali, Maryam Ghasemi, Somaye Mashhadi, Mohammad Hadi Tarraf, Adsorption isotherms and kinetics studies for the removal of Pb (II) rom aqueous solutions using Low-cost adsorbent, IPCBEE. 32 (2012).
- [10]Zahid Ahmed Al-Anber, Mohammed, A.S.Al-Anber, Thermodynamics and kinetic studies of Iron (III) adsorption by olive cake in a batch system, J. Mex. Chem. Soc. 52(2) (2008) 108-115.
- [11]Babel S , Kurniawanta ,Low-cost adsorbents for heavy metals uptake from contaminated water: a review,J.Hazardous Mater. 97 (2003) 219-243.
- [12]Bailey Se, Olin TJ, Bricka RM ,Adrian ,DD ,A review of potentially low-cost sorbents for heavy metals. Water Res. 33 (1999) 2469-2479.