

Isotherm studies for adsorption of Cr (VI) using activated carbon

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Abstract

In the present study, efficiency of commercially obtained Powdered Activated Carbon as adsorbent in the removal of Cr(VI) ions was investigated under controlled laboratory Batch conditions. The experiments were carried out for kinetic studies on the removal efficiency by monitoring for variation with contact time, p^H and strength of adsorbent-adsorbate. The removal efficiency was found to increase from 27.50 to 99.38%, with increase in the activated carbon dosage from 1 to 30gm/l. It however shared an inverse relationship with initial chromium (VI) concentration and p^H , with the optimum being 2. Adsorption isotherm studies revealed that the Langmuir and Freundlich models confirmed well with the removal process, while Dubinin-Radushkevich (D-R) did not fit the equilibrium data. The plot of $\log q_e$ versus $\log C_e$, unraveled value of 'n' value to be 9.81, thereby indicating good adsorption. The removal process followed mono-layer adsorption, under the influence of Vander-Waals forces. The overall study indicated adsorption by activated carbon as an alternative and reliable technique in efficient hexavalent chromium removal.

Key words: Chromium, kinetics, adsorption, Langmuir, Freundlich, isotherm.

Introduction

Environmentally persistent Chromium concentration in aquatic bodies has always

been a major cause of concern in Environmental management due to the rapid industrialization. Severely affecting the human interface and habitat, at higher concentration chromium is known to be toxic, mutagenic and carcinogenic

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to living forms⁶. Elevated levels of the heavy metal is distinctively found in effluents from sources such as electroplating industries, chrome tanneries, dye manufacturing, ink and pigment units, textiles, pickling industry⁴ etc. The commonly used procedures for removing metal ions from effluents include chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction⁷. Amidst these removal measures, the process of adsorption is the most versatile and widely used². With the aid of isotherm studies, several researches have confirmed that among most adsorbents, activated carbon have a higher metal adsorption capacity⁵. Hence, Isotherm studies are of great importance in the wastewater treatment, as it provides an approximate estimation of the sorption capacity of adsorbents.

Experimental Methodology

The Batch scale laboratory studies at room temperature determined the removal efficiency with variation of contact time, p^H , adsorbent dosage and initial concentration of adsorbate. All the chemicals used for the current research were of analytical grade and qualitative analysis techniques were referred from 'Standard Methods' (19th edition, 1991). The Adsorption experiments were carried out in Jar Test Apparatus and samples were withdrawn at regular intervals of 1, 5, 10, 15, 20, 25 and 30 minutes respectively. Commercially available Powdered Activated Carbon [PAC] of size 20 μ was used throughout the study. The withdrawn samples were filtered through Whatmann filter paper no. 42 and the filtrate was analyzed for residual chromium concentration by s-diphenyl carbazide method. The amount of material adsorbed was then determined

as a function of adsorbate concentration at equilibrium. The results were then fitted to the Freundlich, Langmuir and Dubinin-Radushkevich (D-R) isotherm models. The validity of Adsorption isotherm models for chromium (VI) adsorption concluded the study.

Result and Discussion

The results were expressed as the removal efficiency of adsorbent was defined as equivalent of $(C_0 - C_1)/C_0 \times 100$, where C_0 and C_1 are the Initial and Equilibrium concentrations respectively.

Effect of contact time on the removal process:

Chromium adsorption by PAC for an initial concentration of 10mg/l as a function of stirring time for varying dosages of activated carbon [1 to 30gm] was carried out initially at neutral p^H . This task was conducted to optimize the contact time for further removal/ adsorption studies. From figure 1, it is evident that as the contact time increased, the percentage removal also increased. The general observation envisaged sorption of Cr(VI) to be rapid in the early stages, with a maximum attained by 20 minutes. After 30 minutes and then on, it was almost constant or observed to reduce. Consequently, the current experiment was restricted to only an hour. The percentage removal is higher in the initial stages as adequate surface area of the activated carbon was available for the adsorption process and that during the initial stages of the process the absorptive ions preferentially occupied many of the active sites in a random manner, hence as a result of which, the rate of uptake was faster. As time elapsed, some of the active sites get blocked resulting in conflicts between

adsorption and desorption. Hence the rate of uptake became slower in the later stages. Henceforth, all further experimental setup envisaged half an hour interval only.

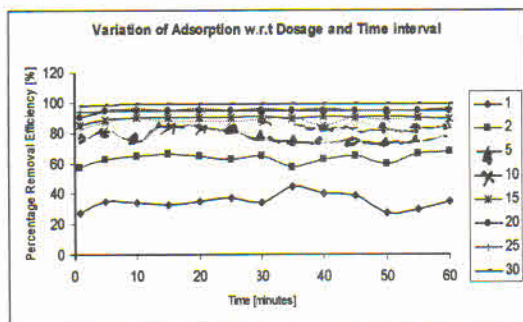


Figure 1. Effect of contact time and activated carbon dosage on removal process

Effect of activated carbon dosage on removal process :

This analysis was inevitable in pursuit of establishing the trade-off between the adsorption capacity and percentage removal of hexavalent chromium to ascertain optimal adsorbent dose. Cr(VI) adsorption trend by activated carbon as a function of activated carbon dosage at neutral p^H is also indicated in figure 1. It is apparent that the rate of adsorption increased with increase in dosage. The percentage removal increased up to 99.38% for dosage of 30gm/l, while it was a paltry 27.50% for a dosage of 1gm/l. The steep increase in adsorption rate with increased dosage may be attributed to the increase in surface area and availability of more binding sites for adsorption of chromium. The equilibrium time observed was again around 20 minutes and after that percentage removal was more or less stagnant after an optimum period. Based on economics and rate of removal efficiency, an optimum dosage of PAC as

10gm/l was considered further on.

Effect of p^H on the removal process :

p^H is the most important parameter in the adsorption of heavy metals, since p^H dependence of metal adsorption can be credited to type and ionic state of the functional group present in the adsorbent⁸.

Chromium adsorption by PAC for detention time of 1-30 minutes as a function of p^H for activated carbon dosage of 10gm/l and initial chromium concentration of 10mg/l has been revealed graphically in figure 2. The percentage removal was boosted from a paltry 65% to a maximum adsorption of 99%, when the p^H was reduced from 12 to 2. The chief cause for better adsorption at low p^H may be attributed to the large number of H^+ ions present at low p^H , which in turn neutralize the negatively charged adsorbent surface, thereby reducing the inference to the diffusion of dichromate ions. At an acidic p^H , the predominant species of Chromium include $Cr_2O_7^{2-}$, $HCrO_4^-$, $Cr_3O_{10}^{2-}$ and $Cr_4O_{13}^{2-}$ ⁹. Above p^H 8, only CrO_4^{2-} is found to be stable and as the p^H further increases, the equilibrium shifts to dichromate according to the overall equilibrium. At higher p^H , the reduction in adsorption may hence be due to OH^- ions as it being more dominant species creates hindrance to diffusion of chromate and dichromate ions. Consequently, the net positive surface potential of adsorbent decreases, resulting in the weakening of electrostatic forces between adsorbent and adsorbate, which ultimately leads to reduced adsorption capacity. Hence all further experiments were incepted at p^H 2.

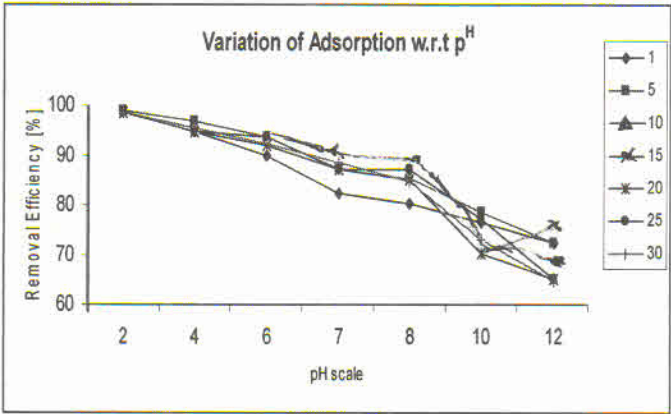


Figure 2. Effect of p^H on adsorption process

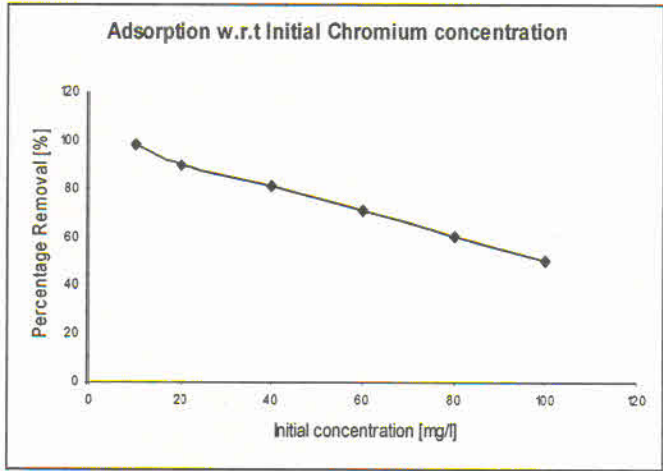


Figure 3. Effect of Initial concentration on adsorption process.

Effect of initial chromium concentration on removal process :

The effect of initial concentration of chromium on the sorption potential of the activated carbon was investigated over a wide range of chromium concentration ranging from 10 to 100mg/l. The plot of percentage removal at various initial chromium concentrations has been depicted in figure 3. From the plot, it's

evident that the removal efficiency decreased with increased initial concentration and the removal efficiency was found to drop from 50.30 to 98.75% over the experimental range. The logical explanation for the decreasing trend points to the fact that all the adsorbents possess a limited number of active sites, which over a period of time become saturated, for and above certain sample strength.

Figure 4 shows the plot of percentage removal and amount adsorbed per unit weight of activated carbon. As the initial concentration increases, the amount adsorbed per unit weight of PAC also increased. When the initial concentration was increased from 10 to 100mg/l, the amount adsorbed increased from 0.99 to 5.03mg/gm respectively. Such a development can be attributed to the fact that as the initial chromium concentration increases, the number of chromium molecules available will also be more, thereby enhancing greater opportunities for contact with adsorbent.

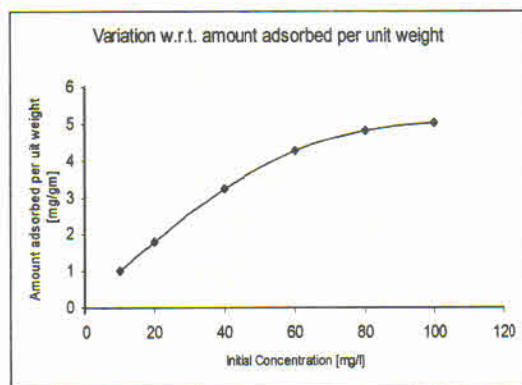


Figure 4. Amount adsorbed per unit weight of adsorbent

Isotherm Modeling :

The equilibrium of adsorption is one of the most important physico-chemical aspects for the evaluation of the process, as the distribution of Cr(VI) between the liquid phase and the solid adsorbent phase is a measure of the position of equilibrium in the sorption process and thereby is critical in optimizing the use of adsorbent. Expressed as a mathematical model, adsorption isotherms are also of great importance for they provide vital inputs in the

description of how adsorbate interacts with an adsorbent. As a requisite, in the present investigation the kinetics of the adsorption data was analyzed, with the conformity between experimental data and the model predicted values being expressed by the correlation coefficient (R^2). A relatively high R^2 value indicates successful applicability of the model in describing the kinetics of the adsorption (Krim Louhab, 2010). For the current research, the results of the concentration dependence of chromium adsorption on activated carbon over initial chromium concentrations 10-100 mg/l were fitted to the 3 equilibrium models namely the Langmuir, Freundlich and Dubinin-Radushkevich (D-R). These were applied to evaluate feasibility of adsorbate-adsorbent interaction and subsequently analysed for validity of the study.

Langmuir model :

The Langmuir model (equation 1) suggests monolayer sorption on a homogeneous surface, without interaction between sorbed molecules. In addition, the model assumes uniform energies of sorption onto the surface and no transmigration of the sorbate (Peavy et al., 1985).

$$C_e/q_e = C_e/q_m + 1/K_L q_m \quad (1)$$

Where, q_e is the equilibrium adsorption capacity on the adsorbent (mg/g) and C_e is the equilibrium solute (or metal ion) concentration in the solution (mg/l). Langmuir constants q_m represents the monolayer adsorption capacity of the adsorbent (mg/g) and K_L is the energy of adsorption (l/mg) respectively. The values of q_m and K_L were obtained from the slope

and intercept of a plot of C_e versus C_e/q_e . The greater the value of K_L , higher is the adsorption energy, reflecting a rapid increase in adsorption at low concentrations of adsorbate¹².

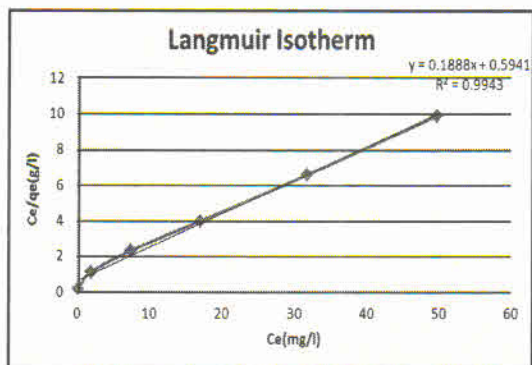


Figure 5. Langmuir isotherm plot.

When the Langmuir equation (equation 1) was applied to quantify maximum adsorption capacity, the plot of $C_e/[1/q_e]$ versus C_e (figure 5) indicated a linear relationship with the correlation coefficient (R^2) value as 0.9943. It may hence be deduced that the adsorption process closely follows the Langmuir isotherm model. The study hence confirmed the monolayer coverage of Cr(VI) at the outer surface of activated carbon. The parameter 'a' and 'b' were 0.86 and 6.84 respectively.

Freundlich isotherm :

Unlike the Langmuir isotherm model, the Freundlich isotherm is a nonlinear sorption model (equation 2) and advocates a multilayer sorption with a heterogeneous energetic distribution of active sites, accompanied by interaction between sorbed molecules¹².

$$\log q_e = \log K_F + 1/n \log C_e \quad (2)$$

Where, q_e is the amount of solute adsorbed per unit weight (mg/g) of the adsorbent used, C_e is the equilibrium solute concentration in the solution (mg/L), K_F is a constant relating the adsorption capacity (mg/g) and $1/n$ is an empirical parameter relating the adsorption intensity which varies with the heterogeneity of the material. The values of K_F and are obtained from the slope and intercept of a plot of $\log(q_e)$ versus $\log C_e$ (figure 6). Both the parameters K_F and $1/n$ affect the adsorption isotherm, by sharing a direct proportional relationship with the adsorption capacity¹².

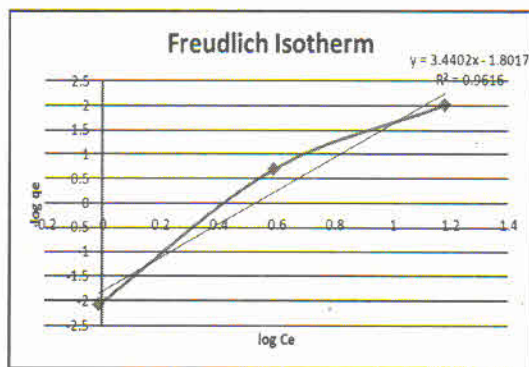


Figure 6. Freundlich isotherm plot

Though the plot of $\log(q_e)$ versus $\log(C_e)$ (figure 6) indicated good adsorption as the 'n' value for Cr(VI) was found to be 9.81, with the value of ' K_F ' upon computation as 0.364, yet the R^2 value was found to be 0.9616, which was lower than that for Langmuir Isotherm. Though both the models fit the adsorption equilibrium data satisfactorily, Langmuir fit had better correlation. Hence, it may be deduced

that the Freundlich model faltered in describing the relation between the amount of hexavalent chromium adsorbed and its equilibrium concentration in the solution.

Dubinin-Radushkevich (D-R) isotherm model :

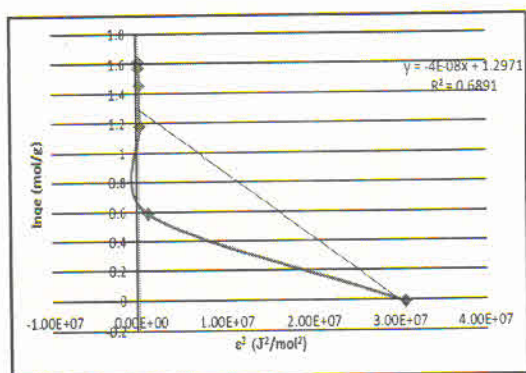


Figure 7. Freundlich isotherm plot

The equilibrium data was further subjected to the D-R isotherm model to identify the nature of adsorption processes. The linear form of D-R isotherm equation is given by the equation 3.

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (3)$$

Where, q_e is the amount of metal ions adsorbed on per unit weight of adsorbent (mol/L), q_m is the maximum adsorption capacity (mol/g), β is the activity coefficient related to adsorption mean free energy (mol^2/J^2) and ε is the Polanyi potential (equation 4).

$$\varepsilon = RT \ln (1 + 1/C_e) \quad (4)$$

As can be confirmed from the plot

(figure 7), the D-R isotherm model did not fit the equilibrium data as the R^2 value was found to be 0.6891. This though was obviously lower than Freundlich and Langmuir adsorption isotherm models, was used to find adsorption mean free energy, determined via equation 5.

$$E = 1/\sqrt{-2\beta} \quad (5)$$

Where E is mean free energy (KJ/mol). The adsorption mean free energy gives information about adsorption mechanisms. If value of E is between 8 and 16 KJ/mol, the adsorption process followed chemical ion exchange and if E was lesser than 8 KJ/mol, the adsorption process is of physical nature. For the present study, the mean adsorption energy was computed to be 0.6211 KJ/mol, thereby suggesting that the driving forces for Cr(VI) adsorption was of physical nature such as Van-der-Waals forces¹⁰⁻¹¹.

Conclusion

Batch adsorption studies carried out demonstrated the removal of Hexavalent Chromium using commercially obtained Powdered Activated Carbon to be strongly dependent on pH, adsorbent dose, contact time and initial Cr(VI) concentration. Equilibrium time was attained at 20 minutes with the maximum adsorption 99.38% attained at an optimized adsorbent loading of 30gm/l. As initial hexavalent chromium concentration was increased from 10 to 100mg/l, the removal efficiency had reduced from 98.75 to 50.30%, while the amount adsorbed per unit weight of activated carbon increased from 0.99 to 5.03 mg/gm. Equilibrium studies depicted percentage removal sharing an inverse relationship with change in p^H , with a high affinity at p^H 2. The

isotherm studies confirmed monolayer adsorption with applicability of Langmuir model. On the whole, the present study affirmed that activated carbon was sufficiently efficient in removing Cr(VI).

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