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RESEARCH ARTICLE

KINETIC STUDIES OF ADSORPTION PROCESS OF CHROMIUM IONS FROM AQUEOUS SOLUTION.

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Granular activated carbon, adsorption, chromium, kinetics models.

Abstract

The adsorption efficiency of granular activated carbon was investigated for removal of Cr(VI) ions in a lab scale fluidised bed reactor. The effect of various parameters like pH, contact time and initial metal ion concentration on adsorption process were investigated. More adsorption was observed at lower pH and optimum pH was found to be 3.0.The equilibrium time was observed at 420 min. With the increase in initial Cr(VI) ion concentration, the percentage adsorption decreases while the adsorption capacity (q_e) increases. Maximum adsorption of 96.02 % and 63.28 % was found at concentration of 10 mg/L and 50 mg/L respectively. The kinetic study was performed using pseudo-first and pseudo-second order kinetic model. The process of adsorption of Cr(VI) ions was found to follow pseudo-second order kinetic model.

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Introduction:-

Environmental pollution in water bodies is due to the enormous quantity and variety of chemical compounds found in the industrial wastewaters. Large amount of effluent laden with toxic heavy metals from industries is discharged into the environment posing threat to public health due to their toxic and persistent nature.High concentrations of chromium are found in wastewater released from the chemical industries especially electroplating and leather tanning industries [1]. Othersources include pigment, paper, paints, steel fabrication, mining and textile dyeing industries. Chromium salts also found their use in wood preservatives and ceramic, fungicides and rubber manufacturing [2]. In aqueous phase chromium exists in two forms: trivalent and hexavalent. Cr(III) is required for nutrition but upto a certain limit only. However, Cr(VI) is toxic and is found to be carcinogenic. The tolerance limit for Cr(VI) in potable water is 0.05 mg/L. For releasing the hexavalent chromium into the inland waters, the tolerance limit is 0.1 mg/L. The safe limit for chromium containing effluent discharge into the surface water is also 0.1 mg/L as set by the Ministry of Environment and Forest [MoEF] [3]. According to EPA, chromium inhalation causes shortening of breath, asthmatic problems, wheezing and nose and throat irritation. Continuous exposure leads to bleeding of stomach and intestine and circulatory, kidney and liver damage. Skin contact causes skin allergy, ulcers and skin irritation [4]. Ion exchange, Reverse osmosis, Chemical reduction, Electrolysis, Precipitation, Flocculation, Coagulation andNano-filtration are the most popular conventional methods used for the removal of chromium ions from the industrial wastewater. Most of the processes have one or more drawbacks and they cannot be used for removing lower concentrations of heavy metal ions. It is challenging task for the environment scientists and engineers to develop new technologies for removing heavy metals which are effective and economic [5]. Adsorption process is efficient in removing very low concentrations of metal ions and is considered more effective

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technology as compared to other methods. In the present study Cr(VI) is removed from the aqueous solution using granular activated carbon (GAC) in Fluidised bed reactor and the various factors affecting the process of adsorption are studied.Activated carbon is widely used adsorbent because of its larger surface area high adsorption capacity. GAC has a great potential to adsorb a wide range of pollutants efficiently.

Experimental:-

Materials:-

Granular activated carbon:-

Granular activated carbon (GAC) supplied by the Brillex Chemical Ltd. Punjab was probed in the present experiment for Cr(VI) removal as an adsorbent. It was sieved and then stored in an air-tight container.

Reagents:-

2.828 g of potassium dichromate was dissolved in 1 L of distilled water to prepare 1000 mg/L stock solution of Cr(VI). The prepared standard stock solution of Cr(VI) was diluted to get the required initial concentration of Cr(VI) for further experiments. 0.1 M HCl and NaOH were used to adjust the pH of the solutions.

Methods:-

Adsorption experiments in FBR:-

Experiments were conducted in lab scale fluidised bed having internal diameter of 5cm and 116 cm height. The experimental setup include FBR column, feed tank containing Cr(VI) solution, rotameter and centrifugal pump. 50 g of granular activated carbon was added to the FBR and Cr(VI) solution was pumped into column from the bottom at a constant flowrate of 150 L/h, so that the process of fluidisation can take place. Working volume of 2 L was taken. The samples were taken after a regular interval of 1 h and the residual concentration of Cr(VI) was determined using atomic adsorption spectrophotometer (AAS). The amount of Cr(VI) ions adsorbed per unit mass of the GAC was calculated from the following expression:

$$q_e = \left(\frac{C_0 - C_e}{W}\right) \times V$$

Where, q_e(mg/g)is the amount of metal ion adsorbed per unit weight of adsorbent, C_0 (mg/L) is the initial metal ion concentration, C_e (mg/L) is the equilibrium concentration, W (g) is the weight of the adsorbent used and V (L) is the volume of the metal solution.

Result and Discussions:-

Effect of pH:-

To study the influence of pH on adsorption of Cr(VI), experiments were run in FBR varying the pH between 1 and 10 with concentration of 50 mg/L chromium solution and adsorbent dose of 50 g. The flow rate was kept constant at 150 L/h. It is quite evident from Figure 2 that the adsorption characteristics of GAC are highly dependent on pH of the solution. It was observed that removal ofCr(VI) ions decreased with the increasing pH. The optimal pH for the adsorption of Cr(VI) was 3.0 as maximum removal of 74.49 %was observed at this pH. This is due to the fact that at lower pH the Cr(VI) exists as $HCrO_4^-$. The adsorbent at low pH is protonated having H^+ and attract negatively charged $HCrO_4^-$ ions which get adsorbed on GAC surface. With increasing pH, surface of adsorbent gets deprotonated and the Cr(VI) exists as chromate (CrO_4^{2-})ions resulting in electrostatic repulsion. This decreases the percentage adsorption of Cr(VI) [6, 7]. All the further experiments were conducted at pH 3.0.

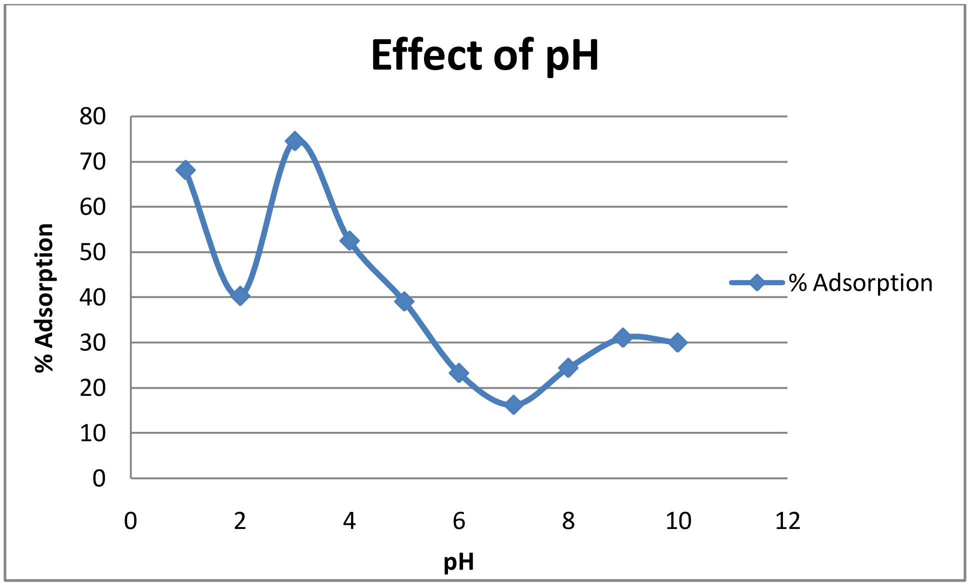

Figure 1:- Effect of pH on adsorption of Cr(VI).

Effect of contact time:-

The effect of contact time on Cr(VI) adsorption was measured by conducting experiment at initial Cr(VI) ion concentration of 50 mg/L, GAC dose of 50 g and flow rate of 150 L/h. the pH was maintained at 3.0.There was a noticeable increase in the percentage adsorption of Cr(VI) up to 240 min. After 240 min the process of removal slows down showing very little change in removal percentage reaching equilibrium at around 420 min. The removal recorded was 56.45 % at 240 min and reaches 63.28 % at 420 min. The initial speedy adsorption can be attributed to the enormous active sites available for adsorption. With time these active sites got filled and hindered the Cr(VI) ions to get adsorbed on GAC due to steric effect and delay the equilibrium time to 420 min. [8, 9]. The influence of contact time is shown in Figure 3. Based on the results, all the experiments were performed for 420 min to reach equilibrium.

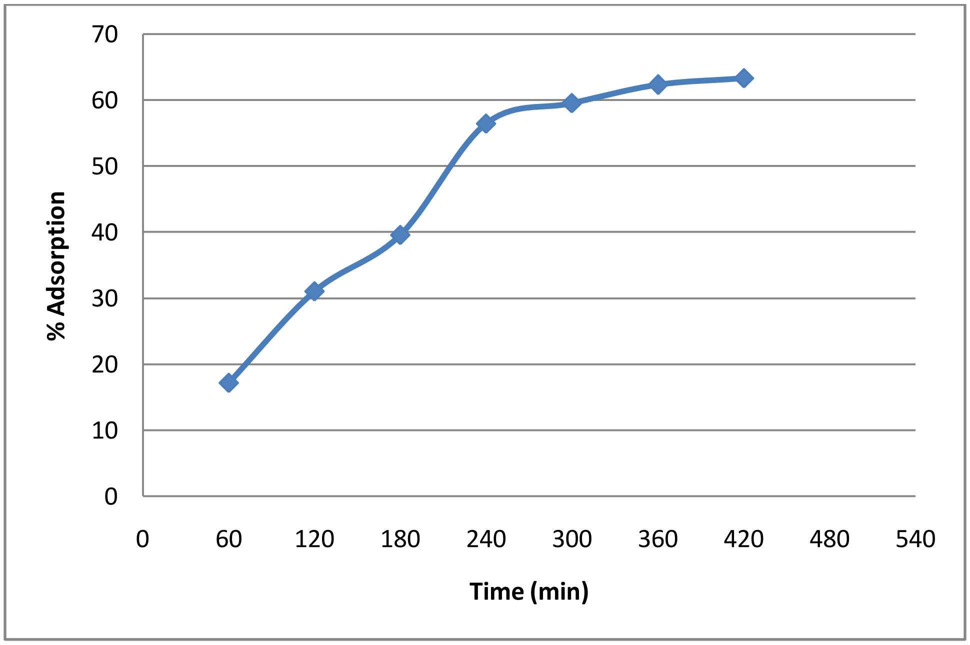

Figure 2:- Effect of contact time on adsorption of Cr(VI).

Effect of initial ion concentration:-

The initial Cr(VI) ion concentration was varied between 10 mg/L and 50 mg/L to know its effect on removal of chromium ions. All other parameters were kept constant. The adsorption of Cr(VI) is concentration-dependent which can be clearly proven from Figure 4 showing effect on percentage adsorption and amount of Cr(VI) ions adsorbed per unit mass of GAC (q_e). It was visualised that as the initial Cr(VI) ion concentration is increased from 10 mg/L to 50 mg/L, the percentage adsorption decreases and on the other hand the adsorption capacity (q_e) or the amount of Cr(VI) ions adsorbed per unit mass of GAC increases. The removal decreased from 96.02 % at 10 mg/L to 63.28 % at 50 mg/L while the adsorption capacity (q_e) increased from 0.768 mg/g at 10 mg/L to 2.531 mg/g at 50 mg/L of Cr(VI) concentration. The decrease in percentage adsorption is due to the reason that the active adsorption sites get saturated as the concentration is increased for the same amount of adsorbent dose [10, 11].

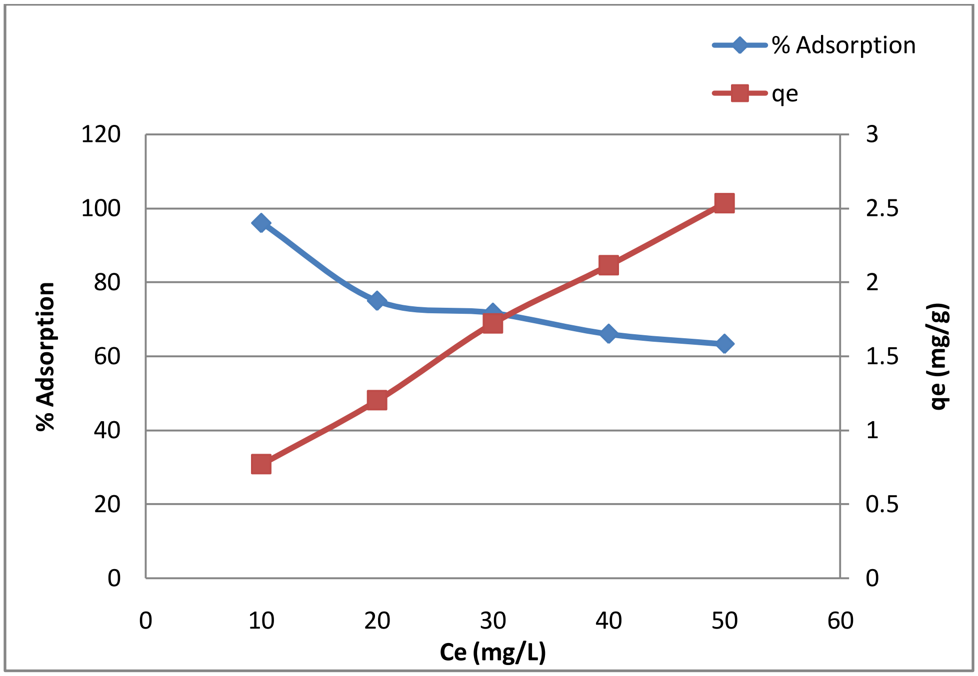

Figure 3:- Effect on initial CR(VI) ion concentration on percentage adsorption and adsorption capacity (q_e).

Kinetic studies:-

Kinetic study is important to analyse the mechanism of adsorption and pathway of reactions taking place during the process of adsorption. Kinetic study also helps in designing the efficient adsorption system. The kinetics of adsorption of Cr(VI) ions onto GAC in a FBR was tested using pseudo-first order kinetic model and pseudo-second order kinetic model proposed by Lagergren. The conformity between theoretical and experimental data was evaluated using value of correlation coefficient, R^2 [12].

The linear form of pseudo-first order equation is expressed as:

$$log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303}t$$

Where q_e the adsorption capacity (mg/g) at equilibrium, q_t is the adsorption capacity (mg/g) at time t and K_1 (1/min)is the pseudo-first-order rate constant of adsorption. The slope and intercept of $\log(q_e - q_t)$ vs. time, t gives the value of K_1 and q_e.

The pseudo-second order equation is given by:

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

WhereK_2 (mg/g min) is the second order rate constant of adsorption. The initial sorption rate can be calculated from the equation:

$$h = K_2 {q_e}^2$$

The values constants K_2, h and correlation coefficient R^2 is determined by plotting t/q_tagainst time, t [13, 14].

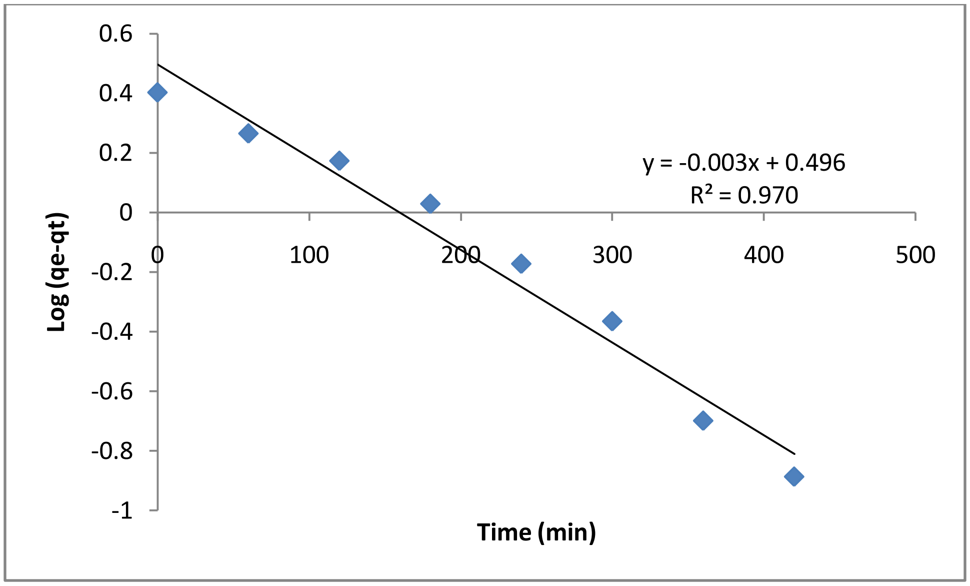

Figure 4:- Pseudo-first order kinetic plot for adsorption Cr(VI) onto GAC.

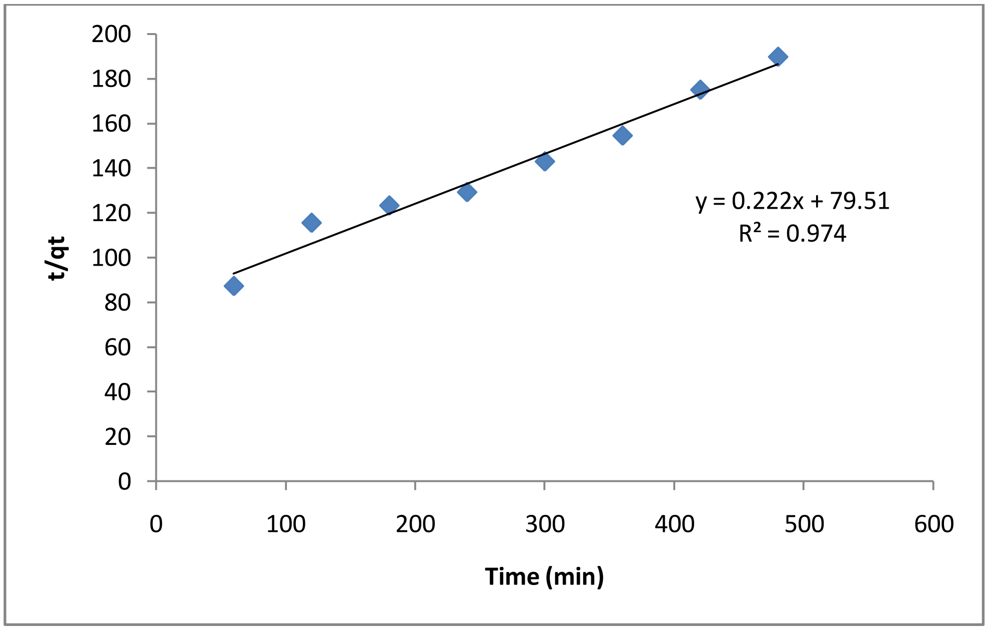

Figure 5-:- Pseudo-second order kinetic plot for adsorption Cr(VI) onto GAC

The linear plots of log(q_e – q_t) vs. t and t/$q_t$vs. t for pseudo-first order and pseudo-second order are shown in Figure 4 and 5 respectively. The values of constant $K_{1,}$ K_2, h and correlation coefficient are tabulated in Table 1 and 2 for pseudo-first order and pseudo-second order.

Table 1:- Kinetic constant parameters obtained for Pseudo-first order kinetic model.

Pseudo-first order constants		
R^2	k_1 (min^{-1})	q_e (mg/g)
0.9704	0.0071	3.1376

Table 2:- Kinetic constant parameters obtained for Pseudo-first order kinetic model.

Pseudo-second order constants			
R^2	k_2	q_e (mg/g)	h (mg/h min)
0.9743	0.00062	4.4943	0.01257

The value of R^2 is >0.95 for both the kinetic models but higher R^2 value is observed for pseudo-second order kinetic model [15, 16]. This shows that the experimental data fits better to pseudo-second order kinetic models for the adsorption of Cr(VI) ions onto granular activated carbon in a fluidised bed reactor.

Conclusion:-

Adsorption of Cr(VI) ions is highly dependent on pH, contact time and initial metal ion concentration. Maximum adsorption capacity was found to be 2.531 mg/g at initial Cr(VI) ion concentration of 50 mg/L. The experimental data is in correlation with pseudo-first order kinetic model. Granular activated carbon can be evaluated as effective adsorbent for removing chromium ions in fluidised bed reactor.

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