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Adsorption of Hexavalent Chromium using Levigated Alumina GRM-1909

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Abstract

Use of commercially available levigated alumina GRM-1909 for adsorption of Hexavalent chromium is investigated. In this study, the adsorption of Cr(VI) was carried out in a batch mode and rate of adsorption was evaluated at varying conditions viz. pH, adsorbent dose, initial concentration and contact time. The maximum removal of Cr(VI) (98%) was observed at pH 4 with an adsorbent dose 1 gm/100 ml and chromium concentration of 10 mg/l. The adsorption study revealed that pH and adsorbent dose play significant roles towards Cr(VI) adsorption. Langmuir and Freundlich adsorption isotherm models were applied. The Langmuir isotherm fitted the equilibrium adsorption data better with a correlation coefficient of R2 = 0.971. The present study reveals that the commercially available levigated alumina can be an ideal candidate for the removal of chromium (VI) metal ions from waste water.

Keywords: Adsorption, Chromium (VI), Levigated alumina, Langmuir isotherm and Freundlich isotherm

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I. INTRODUCTION

Chromium is considered as one of the highly toxic heavy metal which is widely used in industries viz. metallurgical, electroplating, leather tanning, pigments, dyeing, paper etc [1]. Effluents coming out of these industries contain chromium in two oxidation state, i.e. Cr (III) and Cr (VI) in soluble form. Hexavalent chromium is present in the form of chromate (CrO_2^{4-}) form and dichromate (CrO_2^{7-}) ions [2] and it is highly toxic, and carcinogenic to the living organisms. Chromium has high potential to give rise to various health effects like bronchitis, dermatitis, carcinoma, liver damage, ulcer formation etc [3]. According to Bureau of Indian standards (BIS) the industrial effluent standard, permissible discharge limit for total chromium Cr and Cr(VI) into inland water is 2 and 0.05 mgl^{-1} [4]. Looking into current scenario it is necessary to remove chromium in order to prevent deterioration of ecosystem and human health. In view of the stringent regulation on chromium discharge industries are forced to look for the best technologies for chromium removal. Several treatment technologies are available to eliminate Cr(VI) from waste water which includes chemical oxidation and reduction, ion exchange, electrochemical treatment, filtration, membrane separation, solvent extraction, reverse osmosis, biosorption etc. [3]. However, these methods have high capital and operation cost, incomplete removal and toxic sludge generation and its disposal [5]. Compared to all above three methods adsorption techniques prove to be one of the most economical and efficient method for removal of chromium from waste water [6].

Several adsorbents have been reported for adsorption of heavy metal ions from waste water. Among these varieties, activated carbon, chitosan, mesoporous silica, zeolites, nano particles etc. are found to have good chromium adsorption properties[7]–[11]. Other various bio adsorbents such as activated carbon [12], rice husk and neem bark [13], algae [14], tea industry waste[15], areca [16], apple pomace [17] etc. has been reported for adsorption of Cr (VI) from water, however there are several disadvantages using these bio adsorbents like regeneration, sludge formation and low removal efficiency.

Activated alumina (Al_2O_3) is a highly porous dehydroxylated product of aluminum hydroxide. It has surface area over 200 m^2/gm. Activated alumina has several applications as an adsorbent for the removal of metals like F, Cl, As, Cu, Ni, S etc [18]–[21], it is also used as a catalyst and catalyst support for various chemical reactions. Many researchers have reported activated alumina as a successful absorbent for removal of heavy metals. Ikhlass Marzouk et al. has reported adsorption percentage of Cr(VI) removal using activated alumina as 97 % and adsorption capacity as 2.807 mg/gm [3]. Suman Mor et al. reported adsorption efficiency of 99 % and adsorption capacity of 7.44 mg/gm for absorbing chromium on activated alumina [22]. Nilima et al has reported removal of Cr(III), Ni(II) and Cu(II) using activated alumina with a removal efficiency of 99.4% for Cr(III), 99.1% for Ni(II) and 99.8% for Cu(II) [23].

Although myriad of adsorbents works well in lab scale, most of them fails in scale up. This happens owing to the addition of binders and few other chemicals during bulk synthesis. In such cases, working with a commercially available adsorbent proves to be a better choice.

Hence in present study commercially available levigated alumina has been studied for the removal of chromium (VI) from water. Batch adsorption studies were carried out. In addition, the behavior of activated alumina was investigated for several parameters such as pH, adsorbent dose, initial Cr(VI) concentration and time of contact. The results clearly show that levigated alumina GRM 1909 could be an ideal candidate adsorbent for Cr(VI) removal.

II. MATERIALS AND METHODS

A. Materials

All the chemicals used in this study were purchased from Merck. Reagents used in present study were, $K_2Cr_2O_7$, HCL and NaOH. Levigated alumina GMR-1909 used in this study was purchased from Himedia.

B. Material synthesis

In present study, alumina powder (molecular weight 101.96 g mol^{-1}) was washed with distilled water and dried in an oven at 80 °C to remove adhered impurities for 2 hours. A synthetic stock solution of Cr(VI) was made by dissolving known amount of $K_2Cr_2O_7$ in a distilled water.

C. Analysis

The quantification of Cr(VI) from the samples were carried out using UV-Visible spectrophotometer (Systronics spectrophotometer-166) at a wavelength of 540 nm.

D. Batch adsorption studies

Batch experiments were performed to study the Cr(VI) removal using commercial alumina at room temperature. 1 g activated alumina and 100 ml Cr(VI) solution at 10 mg/l were mixed and agitated at 100 rpm using a mechanical shaker for 2 hours. The filtrate was then collected and filtered through Whatman (No. 1, 0.45 µm) filter paper. The filtrated samples were analyzed for Cr(VI) concentration by recording absorbance using a UV-Visible spectrophotometer.

III. RESULTS AND DISCUSSION

Batch experiments were carried out to study the effect of pH, Cr(VI) concentration, adsorbent dose and contacting time on chromium removal efficiency.

A. Effect of pH

Removal efficiency for Cr(VI) on activated alumina was evaluated over a pH range of 2-10, keeping adsorbent dose constant at 1 gm/100ml at an initial concentration of 10 mg/l. The contact time was 120 min. pH was adjusted using 0.1 M NaOH and 0.1 M HCL. The results show that the % removal (Fig. 1) increases with rise in pH upto pH 4, later declines with further increase in pH. A maximum removal of 98% was obtained at pH 4. The higher removal of chromium at low pH might be due to presence of H^+ ions which supports neutralization of negative charged particles, thereby reducing resistance for adsorbate diffusion [24], [25]. Similarly with increase in pH, the number of negative charged ions ($HCrO_4^-$, $CrO_4^{2-,}$ $Cr_2O_7^{2-}$) increases at alumina surface which retards the approach of these ions towards the adsorbent surface [26].

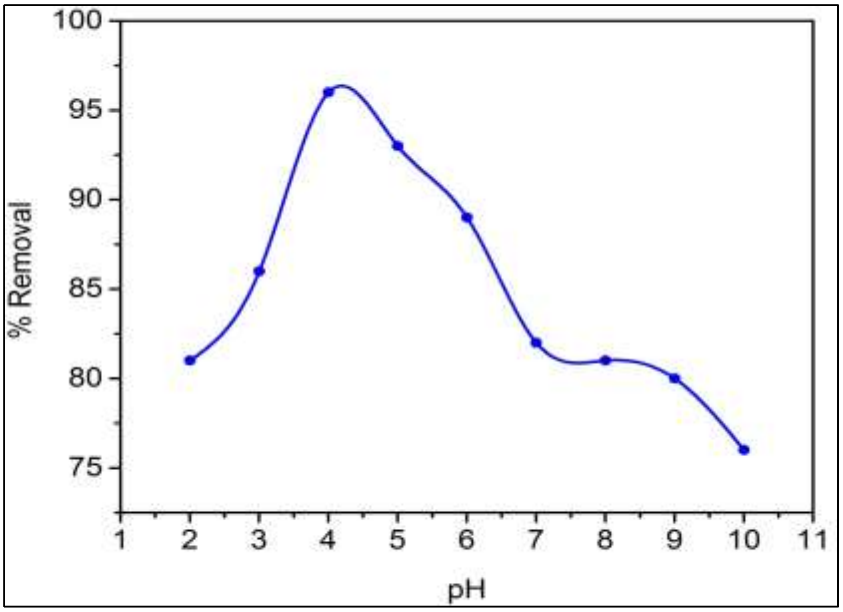

Fig. 1: Effect of pH on the removal of Cr(VI) ions at concentration of 10 mg L-1 and adsorbent dose of 1 g.

B. *Effect of initial concentration*

Influence of initial Cr(VI) concentrations on adsorption was studied with fixed doses (1gm/100ml) of alumina from 10 to 50 mg/l. It was found that initial concentration of Cr(VI) is highly responsible for adsorption. From Fig. 2 it can be seen that percent removal decreases with increase in initial concentration. On increasing the concentration from 5 to 50 mg/l removal efficiency decreases from 99% to 87%. The increase in Cr(VI) concentration actually increases number of metal ions in the solution, However due to limited availability of adsorbent sites the adsorbent has been saturated which results in decline in further adsorption [27].

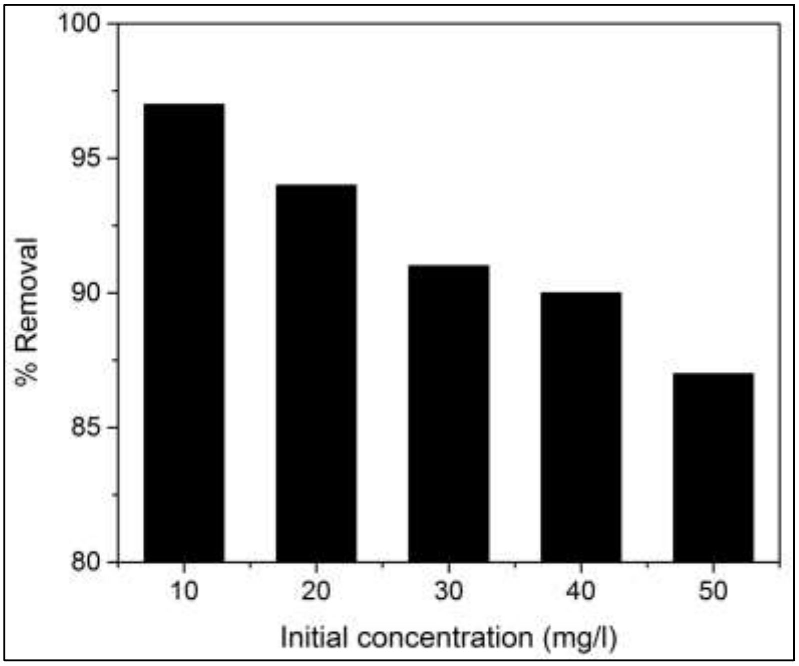

Fig. 2: Effect of initial concentration on removal of Cr (VI) at pH 4 and adsorbent dose of 1 g.

C. *Effect of adsorbent dose*

The adsorption of Cr(VI) on activated alumina was investigated using different adsorbent doses (1-10 g/100ml) at different initial Cr(VI) concentrations (10, 50 and 100 mg/l). From Fig. 3 it is evident that an adsorbent dose of 1 gm is sufficient to remove 97% Cr(VI) metal ions at lower concentration of 10 mg/l in a given contact time. With the increase in metal ion concentration from 50 to 100 mg/l, the requirement of adsorption sites increases, Hence the amount of adsorbent dose required to reach gradually increases.

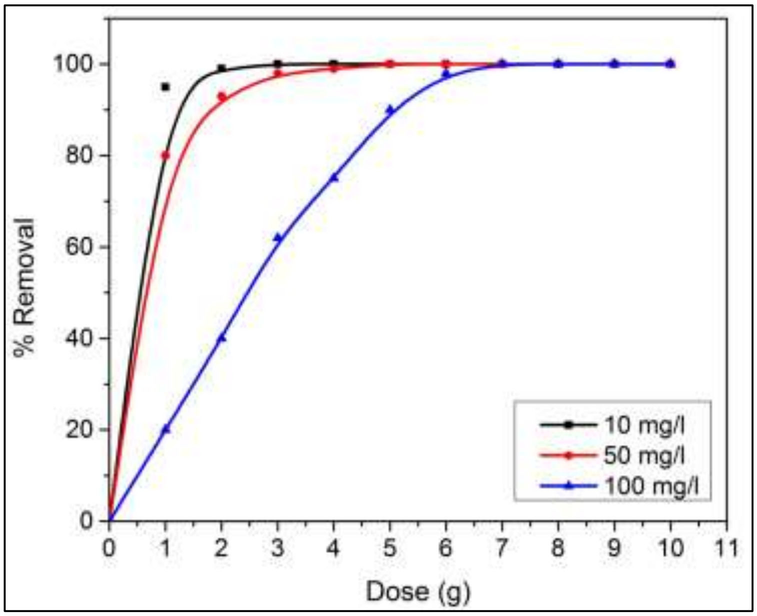

Fig. 3: Effect of adsorbent dose on removal of Cr (VI) at various concentrations and pH 4

D. Effect of contact time

We studied the effect of contact time at a dose of 1 gm/100ml adsorbent dose at 10 mg/l Cr(VI) concentration. Samples were taken in for an interval of 20 min upto 2 hours. Time profile for metal ions adsorption was plotted in Fig. 4. The results clearly shows that adsorption of Cr(VI) increases with time. The maximum removal of (98%) was obtained at 100 min, after which the removal is approximately constant.

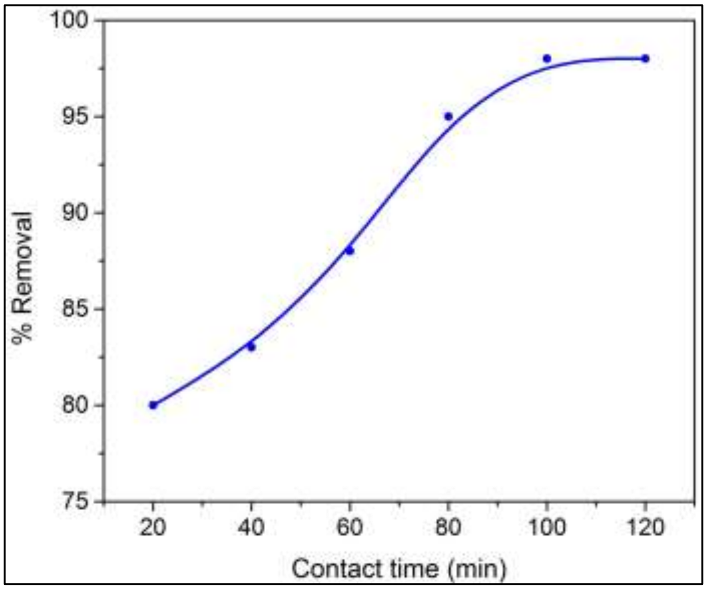

Fig. 4: Effect of contact time on removal of Cr (VI) ions at pH 4, Cr(VI) concentration of 10 mgl-1 and adsorbent dose of 1 g.

IV. ADSORPTION ISOTHERM

Adsorption isotherm studies were carried out to estimate the ultimate adsorption capacity of an adsorbent and to study the mechanism of chromium adsorption on levigated alumina [3]. Experimental data were generated for various concentrations with an adsorbent dose of 1 gm/100ml and contact time of 120 min. The data were fitted to Langmuir and Freundlich isotherms and their results were analyzed.

The Langmuir model is given in eq. (1).

$$\frac{Ce}{qe} = \frac{1}{q_{max} b} + \frac{Ce}{q_{max}} \qquad (1)$$

In the above equation, Ce is the equilibrium chromium concentration (mg/l) of the solution, q_e is the amount of solute adsorbed on the alumina per unit weight of adsorbent (mg/g), q_{max} is the maximum adsorption capacity (mg/g) and b is the Langmuir constant. The Values of q_{max} and b were determined from plot of C_e/q_e versus C_e (Fig. 5). Where $1/q_{max}$ is the slope and $1/q_{max}b$ is the intercept.

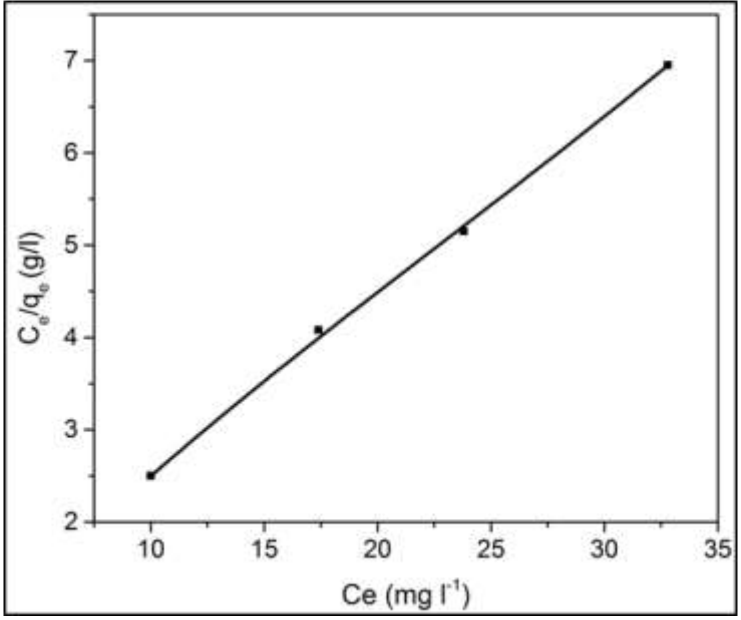

Fig. 5: Langmuir adsorption isotherm for adsorption of Cr(VI) on levigated alumina

The Freundlich isotherm model is given in eq. 2.

$$\log q_e = \log K + \frac{1}{n}\log Ce \qquad (2)$$

In the above equation, q_e is the amount of solute adsorbed per unit mass of adsorbent (mg/g), Ce is the equilibrium chromium concentration (mg/l) in the solution, K and 1/n are the Freundlich constants which represents adsorption capacity and adsorption intensity. Empirical constants K and n can be determined by plotting the log (q_e) versus log (C_e) as shown in Fig. 6.

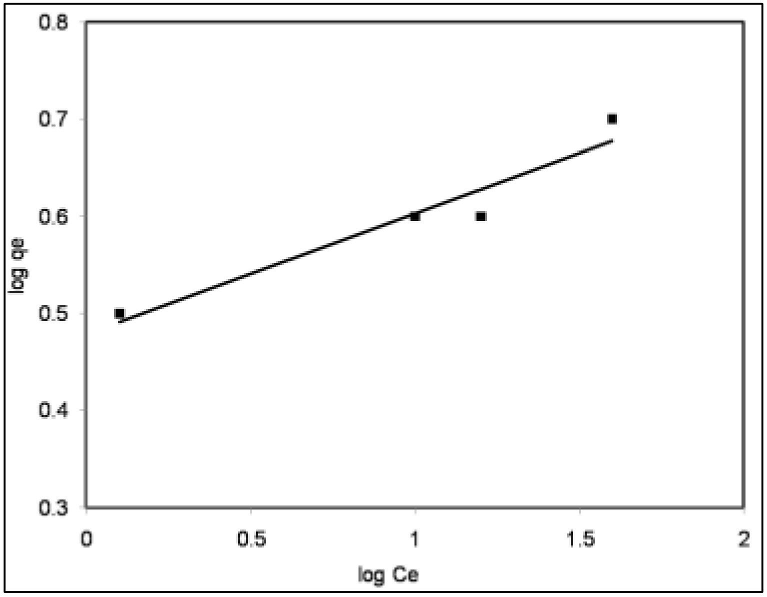

Fig. 6: Freundlich adsorption isotherm for adsorption of Cr (VI) on levigated alumina

The Langmuir constant and the Freundlich constants are shown in Table 1. It is evident from the coefficient of regression that, the Langmuir isotherm fits better than the Freundlich isotherm for the equilibrium data. This confirms the homogenous nature of levigated alumina surface. The correlation coefficient (R^2) for Langmuir isotherm was found to be 0.971, which signifies the monolayer adsorption of Cr(VI) at the outer layer of alumina. The maximum adsorption capacity for monolayer saturation was recorded to be 0.614 (mg/g).

Table – 1
Langmuir and Freundlich isotherm parameters for Cr(VI) adsorption onto levigated alumina

Langmuir			*Freundlich*		
R^2	Q_{max} (mg/g)	b (l/mg)	R^2	K	n
0.971	*0.614*	*3.26*	*0.931*	*3*	*8.06*

V. CONCLUSION

The results clearly depicts that the commercially available levigated alumina GRM-1909 is a potential adsorbent for removal of Cr(VI). The maximum uptake of Cr(VI) on levigated alumina was found at pH 4. The langmuir isotherm explained the adsorption phenomenon better than Freundlich isotherm. The ultimate uptake capacity of Cr(VI) on levigated alumina was found to be 0.614 mg/g.

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