Highly Efficient Removal of Chromium (VI) from Water by Mesoporous Alumina

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ABSTRACT

Mesoporous Activated alumina (MAA) was used for removal of hexavalent chromium from water. The activated alumina was characterized for Powder X-ray diffraction (XRD), Scanning Electron Microscope (SEM).The characterized adsorbent was evaluated for the removal of chromium (VI) from water. The adsorption efficiency of activated alumina was studied by batch adsorption study. MAA exhibit highly efficient removal with more than 99% removal at initial concentration of 5 mg/l. The experimental data was fitted to Langmuir and Freundlich adsorption model and found that Langmuir model fits well confirming mechanism of monolayer adsorption on uniform surface. The adsorption kinetic data was well described by pseudo first order kinetics. The residual Cr(VI) concentrations after treatment with MAA were below the prescribed limits as per WHO and Indian Drinking water standards.

Keyword : - *Mesoporous , Alumina, Adsorption, Chromium(VI)*

1. Introduction

Chromium is one of the important industrial metal used in various products and process. About 60% chromium is used in electroplating industry and other steel fabrication, leather tanning, refractory product, fine chemicals etc.[1]. The contamination of heavy metal ion in surface and ground water has matter of concern due to increasing the level of metal ion like Cr, As, Cd, Hg and Cu in water and wastewater. Chromium has wide toxicity effect on environment and human health.[2]. Chromium mainly occurs in water and wastewater in trivalent and hexavalent form of which hexavalent form of chromium is more hazardous as compared to trivalent form as it has been associated with carcinogenic and mutagenic effects on human.[3]. Cr (VI) is highly mobile and mutagenic pollutants, which not only damages plant and animal tissues but also gives rise to varieties of diseases in humans even in small quantities. Therefore, it is necessary to remove Cr (VI) from contaminated water[4].According to Bureau of Indian Standard (BIS) the industrial effluent permissible discharge level of total Cr and Cr(VI) into inland water is 2 and 0.05 mg l^{-1},respectively.

The different methods used to remove hexavalent chromium from water include membrane filtration, chemical precipitation, solvent extraction, adsorption, etc. Among these method, adsorption is considered as an effective process for removing chromium from water.[4]

Various adsorbents have been reported for the removal of Cr(VI) from water namely natural adsorbents like clay, dolomite, bentonite [5], bio materials and agricultural wastes including tree barks[6], rice bran, wheat bran[7], coconut shell, leaves, algae, saw dust [8], activated alumina[9], activated carbon[10], modified chitosan [12], hydrocalcite, zero valent iron[11], bimetal oxides [12] etc. There are many disadvantages of existing adsorbents such as low efficiency, sludge generation and reusability. The highly porous activated alumina has many advantages over these limitations as it provides grains with diameter of 0.3 to 0.6 mm having both macro and microspores and high surface area for sorption. Mesoporous activated alumina is commonly used to remove different heavy metals from water. Therefore the highly mesoporous activated alumina (MAA) have been studied for the removal of chromium (VI) from water. The adsorption capacity of MAA was determined by computing the adsorption isotherm

2. Experimental

2.1 Material and Method.

All chemicals used were AR grade purchased from E Merck. The mesoporous activated alumina beads of Sasol (Germany) make were used. The alumina beads were wash with DI water and dried in oven at 80^0C temperature and was used for evaluation of chromium from water.

2.2 Characterisation of Activated alumina

Mesoporous Activated alumina (MAA) was characterised for the structural and morphological properties. X ray diffraction (Model Rigaku: Miniflex) was used to identify structural phase and crystalline nature. The PXRD patterns for the adsorbent were recorded at 2Θ range from $10^0$to 80^0.The AA was also characterized using Scanning electron Microscopy (SEM) JEOL instrument.

2.3Batch Adsorption studies

Chromium adsorption study was performed to determine the adsorption efficiency of MAA. The batch adsorption study was conducted using 1 to 5 gm/l dose of alumina beads in synthetic chromium(VI) water. Chromium (VI) solution of 5 mg/L of initial concentration was prepared from 1000 mg/L of chromium stock solution. The desired dose of adsorbent was taken in 250ml polycarbonate flask and kept for shaking in orbital shaker at 150 rpm on room temperature. The pH of sample was maintained between 6-6.5 using 0.1 M NaOH or 0.1 M HCl. The samples were withdrawn from orbital shaker after 24 h. The concentration of chromium (VI) in samples was determined by ICP-MS.The experiments were repeated twice and it was observed that the experimental error was within ±2%.
The amount of Cr(VI) adsorbed ($mg \cdot g^{-1}$) at time *t* was computed using following equation[2]:

$$= \frac{[C_0 - C_t]V}{m} \qquad [1]$$

3. Result and Discussion

3.1.Characterization of Alumina

The PXRD patterns of activated alumina is presented in Fig.1 which shows that the broad peaks obtained at about 35° 45.5° and 66° confirms the presence of γ alumina phases. Also the pattern of PXRD reveled the amorphous nature of alumina. Scanning electron micrograph of activated alumina is presented Fig.2 shows the highly porous structure of alumina may allow the diffusion in fine pores and create intimate contact of metal ion with the surface of alumina.

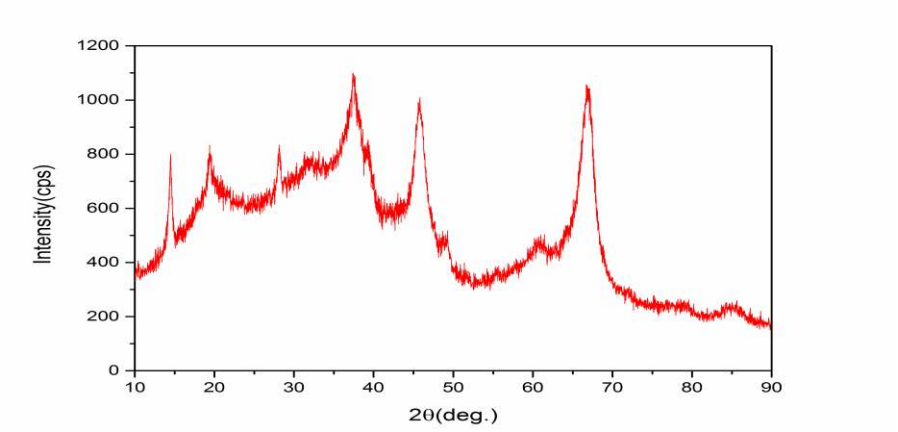

Fig.1-PXRD of MAA

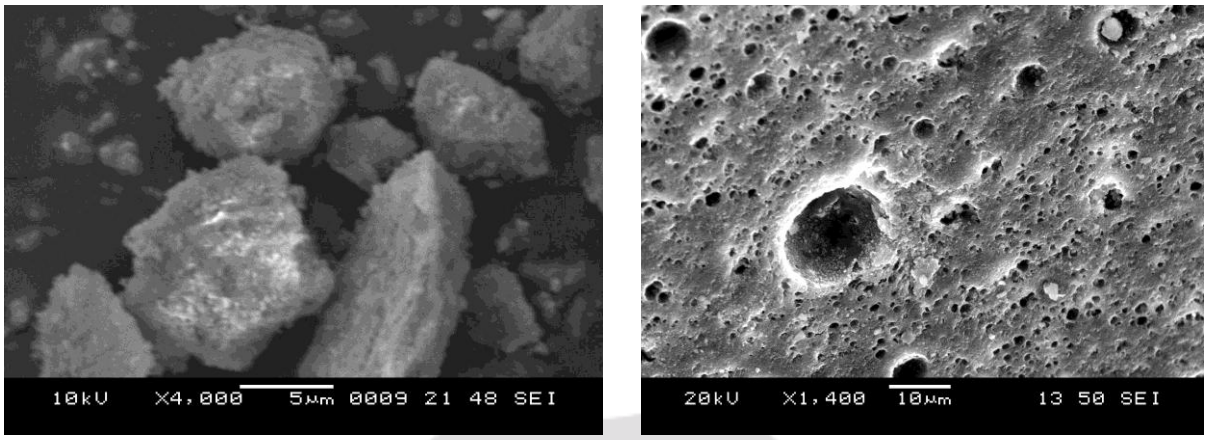

Fig.2- SEM of MAA

3.2 Adsorption studies

The percentage adsorption of Cr(VI) with initial concentration on activated alumina given in Fig.3.The maximum adsorption was 99% occur with 5mg/L initial Chromium(VI) solution using 0.5g/50 dose of alumina.

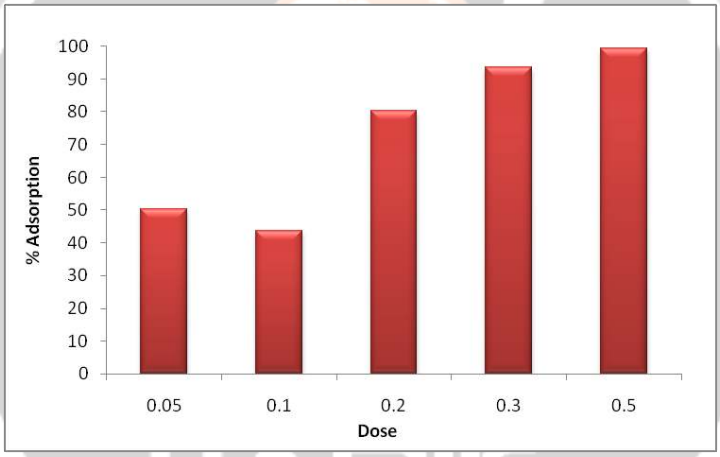

Fig. 3- Dose study of MAA

To study adsorption mechanism of activated alumina, two adsorption models were used Langmuir adsorption is based on Langmuir theory in which molecules are adsorbed at a fixed number of active sites with homogeneous distribution over the surface of the adsorbent. These active sites have same affinity for adsorption of a mono molecular layer and there is no interaction between the adsorbed molecules. The Langmuir isotherm plot is presented in Fig.4(a) based on linear form of Langmuir equation which can be written as:

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m} \qquad [2]$$

Freundlich isotherm model interprets the adsorption on heterogeneous surfaces with interactions between the adsorbed molecules and is not restricted to the formation of a monolayer. This model assumes that when the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases and correspondingly, the sorption energy exponentially decreases over the completion of the sorption centre of the adsorbent[13].The linear form for Freundlich equation, it is written as:

$$log(q_e) = log\, k + \frac{1}{n} log(C_e) \qquad [3]$$

where q_e is the amount of adsorbate adsorbed per unit weight of adsorbent at equilibrium (mg g^{-1}), q_m is the maximum adsorption capacity (mg g^{-1}), K_L is the Langmuir constant, C_e is the equilibrium concentration of adsorbate in solution (mg l^{-1}), K_f is the Freundlich constant, n is the Freundlich constant, which reflects the adsorption intensity. The plot for Freundlich isotherm is given in Fig.4(b).

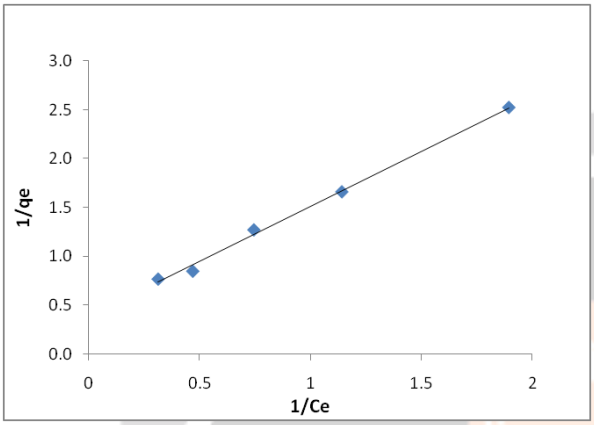

Fig.4(a)-Langmuir Adsorption Isotherm

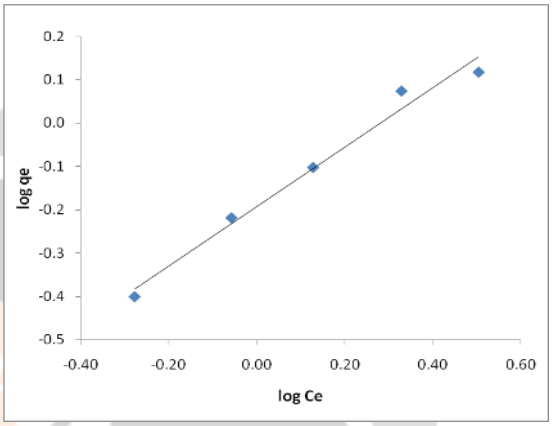

Fig.4(b)-Freundlich adsorption Isotherm

It was observed that the experimental data was well fitted to Langmuir model with correlation coefficient ($R^{2)}$ of 0.996 and the adsorption capacity obtained from Langmuir model was 2.64 mg/g.

3.4 Adsorption kinetics

During adsorption the adsorbate migrate from bulk solution to the outer surface of adsorbent by diffusion. To study the reaction kinetics pseudo-first-order and pseudo-second-order models were used. A simple pseudo-first-order kinetic model known as Lagergren equation is given as:[14]

$$\ln(q_e - q_t) = \ln q_e - k_{ad} t \qquad [4]$$

Where q_t is the amount of Chromium adsorbed at time t (mg g^{-1}) and k_{ad} is the equilibrium rate constant of pseudo-first-order adsorption (min^{-1}). The linearised plots of log (q_e–q_t) versus t will give the rate constants. The linear plots of (Eq. 5) are presented in Fig.5 (a).

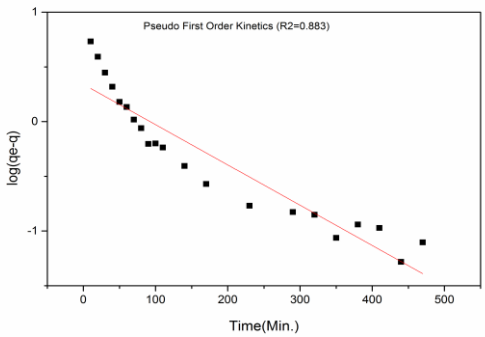

Fig. 5(a)-Pseudo First order kinetics

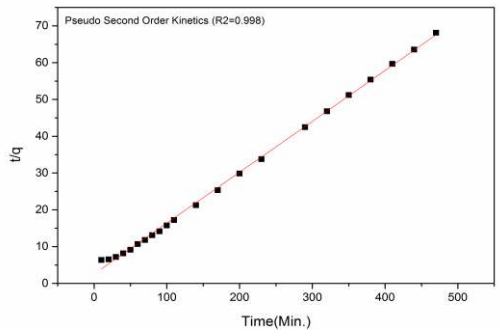

Fig.5(b)-Pseudo second order kinetics

The pseudo-second-order model is used to predict the kinetic parameters the linear equation for which is represented as[14] :

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \qquad [5]$$

Pseudo second-order (Eq. 6) models for Cr(VI) are presented in Fig.5(b).

$$\text{And} \quad h = kq_e^2 \qquad [6]$$

Where q_t is the amount of Chromium adsorbed at time t (mg g−1), q_e is the amount of Chromium adsorbed at equilibrium (mg g−1), h is the initial sorption rate (mg g−1 min−1). The values of q_e (1/slope), k (slope^2/intercept) and h (1/intercept) is obtained from the plots of t/qt versus tis presented in Table 1.

Table 1 - Kinetic parameters for chromium adsorption on Alumina

Pseudo first order		**Pseudo second order**		
$K_{ad}(min^{-1})$	r^2	$Kf\ (g\ mg^{-1}\ min^{-1})$	*1/n*	r^2
2.64	0.996	0.825	0.685	0.980

It is clear from the values of correlation coefficients that the pseudo-second-order model is better fitted as compared to pseudo-first-order model for Cr(VI). The values of correlation coefficient (r^2) indicate pseudo-second order model is fitted well which confirms that the prevailing mechanism is chemisorption.

3.5. Effect of pH

Several literatures have reported that the adsorption process is highly dependent on pH. The removal efficiency for Cr(VI) of MAA was evaluated at different pH range from 3 to 10. It was observed that adsorption capacity slightly vary with pH. The Fig.6 shows the effect of pH on adsorption of Cr(VI) on activated alumina. The removal of chromium (VI) in at pH 3 to 6 is higher than alkaline pH. The maximum removal (>95%) was obtained at pH 3 thereafter slight reduction in removal was obtained.

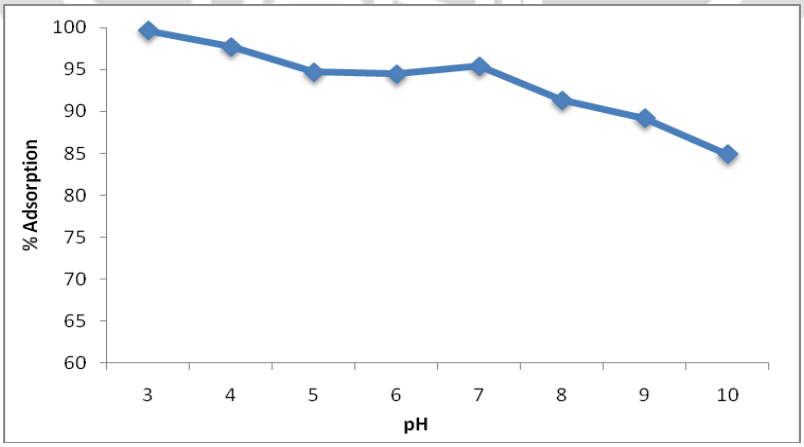

Fig.6- Effect of pH on Chromium (VI) adsorption

4.Conclusions

Modified Activated Alumina(MAA) has been used for the removal of Chromium (VI) which showed adsorption efficiency 99% with 5 mg/L of initial chromium(VI) concentration. The effect of pH shows that the removal capacity is maximum at pH 3 and slightly reduced with increase in pH but the removal was almost same from pH 3 to 6, hence the alumina is considered as efficient adsorbent at wide range of pH. Adsorption isotherm data were well fitted to Langmuir model and the adsorption capacity was found to be 2.64 mg/g. The kinetic studies confirms the applicability of second order kinetic model which is based on chemisorption as prevailing mechanism

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