REMOVAL OF HEXAVALENT CHROMIUM FROM AQUEOUS SOLUTION BY USING ACTIVATED RED MUD AS A ADSORBENT

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A B S T R A C T

The present work shows, removal of hexavalent chromium from aqueous solution by thermally activated acid neutralized red mud which is used as adsorbent successfully. The important findings revealed that, hexavalent chromium adsorption efficiency increases with increasing contact time until the state of equilibrium is reached. The increase in adsorbent dosage increased the percent removal of adsorbate. As the adsorbent dosage was increased from 10 to 100mg, the hexavalent chromium adsorption efficiency increased from 38% to 70% for ARM. The maximum adsorption efficiency of hexavalent chromium was obtained at pH 2 .At a contact time of 90 min, 70% maximum sorption occurred. The experimental data fitted well with Langmuir isotherm equation, as the homogenous adsorption occurred. The results of this study indicated that Activated Red Mud has the potential to be used as an alternative adsorbent material for the removal of hexavalent chromium from aqueous solution.

Keywords: Activated red mud, hexavalent chromium, waste water, Adsorption , Aqueous solution etc.

1.Introduction

Due to increased industrial and agricultural activities, have resulted in the generation of various types of toxic pollutants, which are the main cause of water pollution. The type of pollutants present in wastewater mainly depends on the type of the industry. However, some of the common pollutants generally present in effluents are metal ions, dyes, phenols, insecticides, pesticides, detergents and a wide spectrum of aromatics. Pollutants present in wastewaters can be toxic to aquatic life and can cause natural waters to be unfit as potable water sources. Amongst several water and wastewater treatment technologies, adsorption is considered as the most versatile process, the low-cost adsorbent, if developed, could reduce the pollution of wastewaters at a reasonable cost.

Each year, about 90 million tonnes of red mud are produced globally [1]. Depending on the origin, quality and composition of the bauxite, the amount of red mud left over from alumina refining can vary widely. For every tonne of alumina produced, the process can leave behind a third of a tone to more than two tones of red mud. Red mud is a highly alkaline waste material with a pH of 10–13 because of the sodium hydroxide solution used in the refining process. Red mud is mainly composed of fine particles containing aluminium, iron, silicon, titanium oxides and hydroxides. The red colour is caused by the oxidized iron present, which can make up to 60% of the mass of the red mud. Because of the alkaline nature and the chemical and mineralogical species present in red mud, this solid waste causes a significant impact on the environment, and proper disposal of waste red mud presents huge challenges where alumina industries are installed [2]. Red mud can be classified as hazardous waste because of its caustic/saline/sodic nature and before its use as an adsorbent, red mud needs to be neutralized [3]. Different neutralization methods have been reported in the literature. Neutralization of red mud results in a residue with a pH of 8.0–8.5. Adsorption potential of red mud as a low-cost adsorbent for the removal of different pollutants from water and wastewater is well reported.

Hexavalent chromium is one of the heavy mental contaminants found in the water which is used in a variety of applications including electroplating, steel production, leather tanning, mining and textile dyeing [4]. Chromium usually exists in both trivalent and hexavalent forms in water, and trivalent chromium is an essential trace element for human and plays a vital role in normal carbohydrate, lipid and protein metabolism [5]. It is poisonous only at high concentration [6]. Hexavalent chromiumis highly toxic, it can cause diseases like dermatitis, damage to liver, kidney circulation, lung cancer and even death [7]. According to the recommendation of The World Health Organization (WHO), the maximum allowable limit for total chromium in drinking water is at the levelof 0.05 mgL^{-1}[8].

2. Experimental

Red mud is an insoluble residue produced when refining of bauxite to finally obtain pure aluminum. Red mud, due to its high aluminum, iron, and calcium content, has been suggested as a cheap adsorbent for removal of toxic metals (e.g., As, Cr, Pb, Cd) as well as for water or wastewater treatment. The basic advantage of red mud is its versatility in application. Since it is composed of a mixture of useful adsorbents and flocculants, it can be used for treatment of several effluents [9] Red mud used in the present experiments was supplied from (Jawaharlal Nehru Aluminium Research Design and Development Centre) JNARDDC, Nagpur, Maharashtra. It has the following average chemical composition (%): Al_2O_3, 19.88; Fe_2O_3, 36.47; CaO, 2.33; SiO_2, 15.95; Na_2O, 10.03; TiO_2, 4.97; CO_2, 2.48; S, 0.09; V_2O_5, 0.074; P_2O_5, 0.041 and loss on ignition, % 8.04. After arrival in the laboratory, red mud was air dried and sieved by 250 mesh steal sieve. The studies were carried out with the red mud of particle size of 0.1-1.0 mm diameter. Sieved red-mud was stored at laboratory conditions until activation processes.In a 1000 ml beaker approximately 10 gm of red mud was added to 190 gm milipore water and stirred to form slurry, to which 18 gm of 31 wt% HCl was added. The resulting solution was heated at 60°C for 20 min and diluted with water to make total volume of 800 cm^3 with constant stirring. Liquid Ammonia solution (specific gravity ~0.880) was added slowly with constant stirring until a pH of 8 and resulting precipitate was heated at 50°C for 10 min with constant stirring. The precipitate was separated by filtration, washed 3 times with distilled water dried overnight in oven at 110°C and finally calcined at 700°C for 2 hours which is referred as an activated red mud (ARM).A stock solution (100 mgL^{-1}) of hexavalent chromium was prepared by dissolving analytical grade $K_2Cr_2O_7$ into distilled water. The test solution of hexavalent chromium used in each study was prepared by diluting the stock solution. Experimental solutions of the desired concentrations 10mg/l, 15 mg/l, 20mg/l, 25m g/l and 30mg/l of chromium were obtained by successive dilutions and Cr (VI) was determined via 1, 5-diphenylcarbazide (DPC) colorimetric method by measuring the absorbance at a wavelength of 540 nm using UV/VIS spectrophotometer (Shimadzu 1700 double beam spectrophotometer) at shivaji science college, Nagpur

3. Results and discussion

3.1 Effect of dosage

Adsorbent dosage is an important parameter because it determines the capacity of an adsorbent for a given initial concentration of the adsorbate. The effect of adsorbent has been studied on hexavalent chromium removal and the results have been illustrated in Fig. 1. In general, the increase in adsorbent dosage increased the percent removal of adsorbate. As the adsorbent dosage was increased from 10 to 100mg, the hexavalent chromium adsorption efficiency increased from 38% to 70% for ARM. Because number of active sites increases with respect to increase of adsorbent dosage.

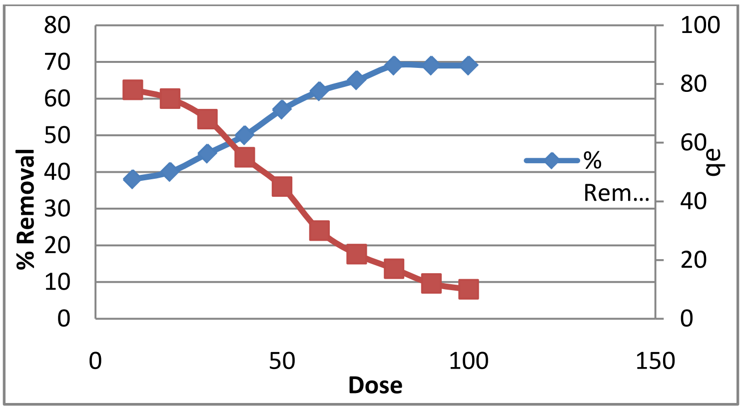

Fig. 1: Adsorbent dose versus percentage removal of Cr(VI) by Activated red mud

3.2 Effect of pH

The solution pH is another important parameter and it has a strong effect on the adsorption of hexavalent chromium on the surface of the ARM. Hexavalent chromium can be represented in various forms such as H_2CrO_4, $HCrO^{4-}$, $Cr_2O_7^{2-}$ and CrO_4^{2-} depending on the pH [10]. H_2CrO_4 predominates at pH less than about 1.0. While in the pH range of 1 - 6 different forms of chromium ions such as $HCrO4^-$ and $Cr2O_7^{2-}$ coexist, being $HCrO4^-$ predominant. As the pH increases, this form shifts to $Cr_2O_7^{2-}$ and CrO_4^{2-}. At pH greater than 7.5, $CrO_4^{2-}$is the only hexavalent chromium species in aqueous phase. The maximum adsorption efficiency of hexavalent chromium was obtained at pH 2 while the adsorption decreased when the pH increased as can be observed in Fig. 2. The decrease of adsorption efficiency in the alkaline pH range (pH > 8.5) may be due to the competition of the OH^- with the hexavalent chromium for surface sites on ARM or electrostatic repulsion of hexavalent chromium ion to the negatively charged surface.

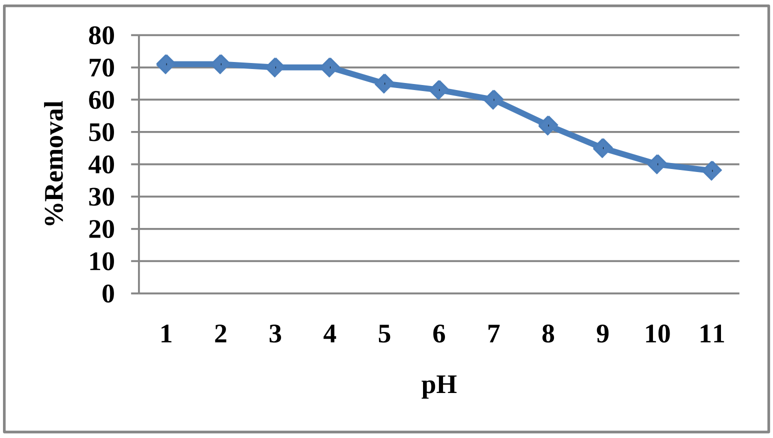

Fig. 2: Effect of pH on the removal efficiency of Cr (VI) by Activated red mud

3.3 Effect of contact time

The important findings were represented in Fig.3 which revealed that, hexavalent chromium adsorption efficiency increases with increasing contact time until the state of equilibrium is reached. It was clear that the removal of hexavalent chromium can be derived into two stages: the first stage showed high adsorption efficiency is very high, followed by a second stage with much lower adsorption efficiency. At a contact time of 90 min, 70% maximum sorption occurred. Thus, a period of 90 min is adequate for adsorption of hexavalent chromium by ARM.

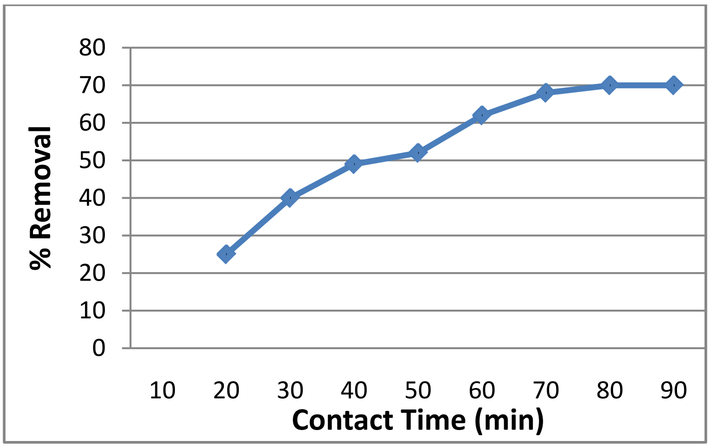

Fig. 3: Contact time versus adsorption capacity of Cr (VI) by Activated red mud

3.4 ***Effect of initial concentration***

Effect of initial concentrations of Cr(VI) on the removal efficiency of had been studied for 10mg/l, 20mg/l, 30mg/l, 40mg/l through batch experiment mode at pH=2, agitation rate of 3000 rotation per min, contact time of 2 to 80 minutes on activated red mud at dose of 100 mg/100ml at constant temperature 25±2°C and shown in Fig.4.The removal efficiency was found to be 75%,. The percentage adsorption increased rapidly up to the certain time duration and thereafter the increase becomes more and more insignificant. The decrease in the percentage removal of Cr (VI) can be explained with the fact that the activated red mud had limited active sites, which would have become saturated above a certain circumstance.

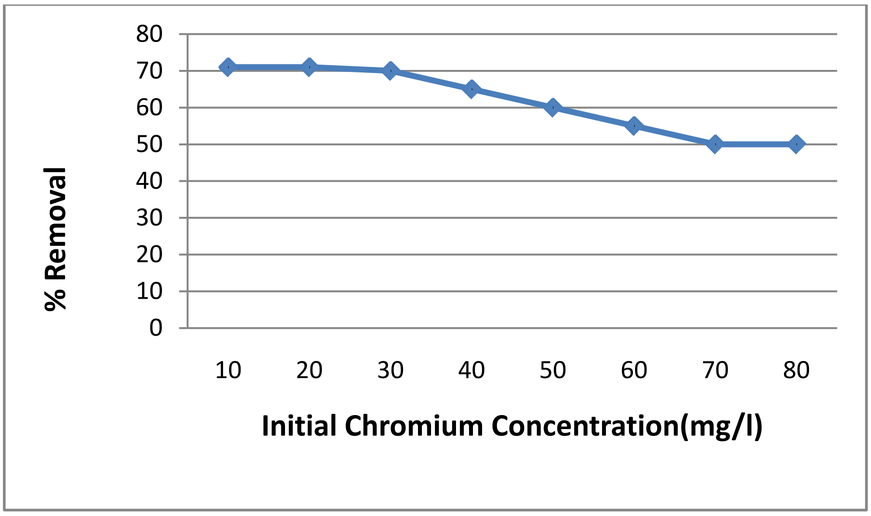

Fig. 4: Effect of initial Cr (VI) concentration on removal by ARM

3.5 ***Adsorption isotherm***

Thermodynamic parameter such as free energy change (ΔG°), enthalpy change (ΔH°) can be calculated using the equation described earlier in nitrate removal study. The Van't Hoff equation in chemical thermodynamics relates the change in the equilibrium constant (K_{eq}) of a chemical equilibrium to the change in temperature, T, given the standard enthalpy change, ΔH^0 for the process shown in Fig.5. With the increase in temperature, the adsorption increases which indicates the process is exothermic.

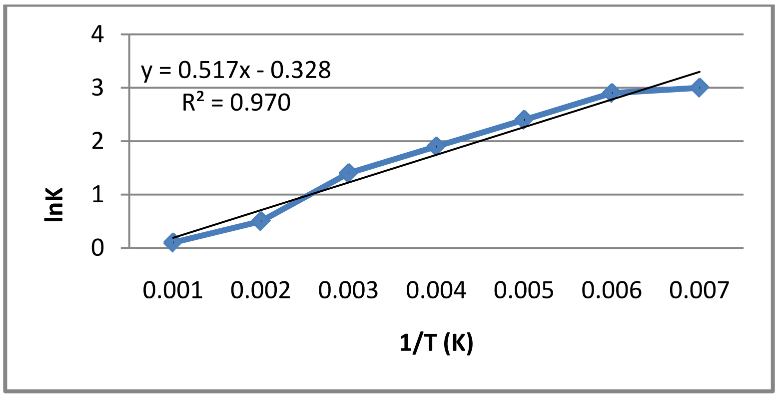

Fig. 5: Van't Hoff plot for Cr(VI) adsorption by ARM

Experimental data were analyzed with adsorption isotherm models including Langmuir and Freundlich isotherms. The linear plot of C_e/q_e versus C_e (Fig. 3.6) with correlation coefficient R^2 was found to be 0.993, 0.989, 0.976 for temperature 308, 318 and 328 K, indicates the accuracy of Langmuir isotherm shown in Fig 6.This indicates a monolayer adsorption of Cr(VI) onto the adsorbent surface. The equilibrium data was fitted to both Langmuir and Freundlich models. Fig 6 &7 indicates that both Freundlich and Langmuir models give good fit for the data. It can be inferred that Cr (VI) has greater affinity and is more favorable for adsorption on activated red mud. The Langmuir isotherm describes the experimental data better than Freundlich isotherm. The value of R (dimensionless parameter) (R< 1), also shows the favourable adsorption of Cr (VI) on activated red mud.

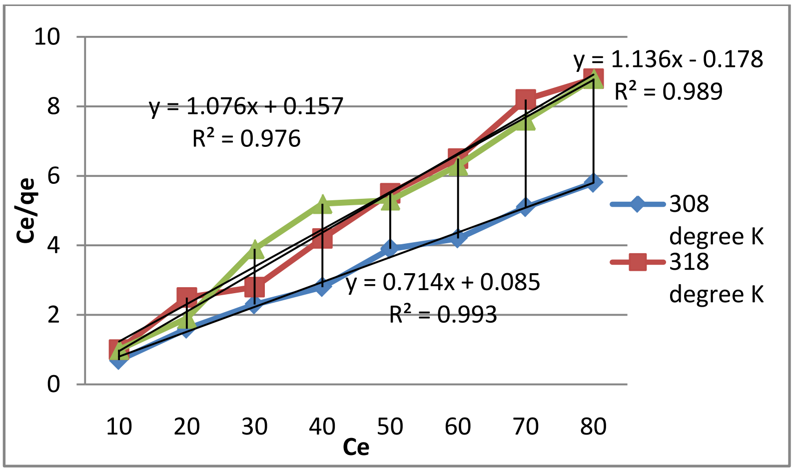

Fig 6: Langmuir isotherm for Cr (VI) adsorption by activated red mud

The Freundlich isotherm is employed to describe heterogenous system. where C_e is the adsorption capacity (mg/g) and n is the empirical parameter. The value of R^2 are 0.956, 0.947, and 0.929 at 308 degree K, 318 degree K and 328 degree K respectively (Fig 7). Higher value of correlation coefficient of Langmuir isotherm indicates that adsorption data fits better with Langmuir equation then by Freundlich's isotherm.

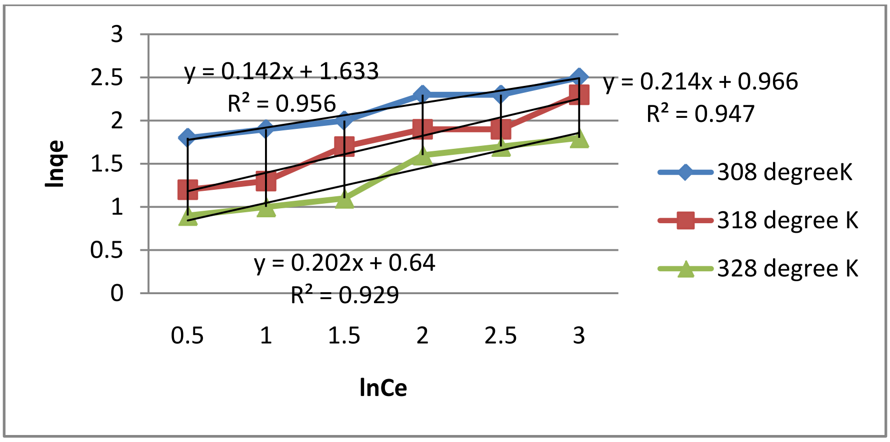

Fig. 7: Freundlich isotherm for Cr (VI) adsorption by Activated red mud.

4. Conclusion

The present work shows that thermally activated acid neutralized red mud can be used as adsorbent for the removal of hexavalent chromium from aqueous solutions successfully. The important findings revealed that, hexavalent chromium adsorption efficiency increases with increasing contact time until the state of equilibrium is reached. The increase in adsorbent dosage increased the percent removal of adsorbate. As the adsorbent dosage was increased from 10 to 100mg, the hexavalent chromium adsorption efficiency increased from 38% to 70% for ARM. The ARM has shown good adsorptive for hexavalent chromium. The maximum adsorption efficiency of hexavalent chromium was obtained at pH 2 . At a contact time of 90 min, 70% maximum sorption occurred. Thus, a period of 90 min is adequate for adsorption of hexavalent chromium by ARM. The experimental data fitted well with Langmuir isotherm equation, as the homogenous adsorption occurred. Adsorption of hexavalent chromium on ARM is a result of the electrostatic attraction and ligand exchange. Additionally, the red mud is discarded as waste in bauxite processing industry, its utilization as adsorbent for removal of hexavalent chromium is expected to be economical. The results of this study indicated that ARM has the potential to be used as an alternative adsorbent material for the removal of hexavalent chromium from water.

5. Acknowledgement

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