

Effect of pH on the Removal of Cr (VI) from Aqueous Solution by Using Agricultural Adsorbents

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ABSTRACT

The metal cations such as Cr (VI) is one of the highly toxic heavy metals. It is priority toxic and carcinogenic chemical when present in excess amount in waste water. It is widely used in a number of industries like metallurgical, electroplating, paints, pigments, inks, fungicides and photography. It enters into the natural water bodies through the industrial effluents creating water pollution. Therefore its removal from waste water is considered to be very important. The removal of Cr (VI) by using agricultural waste as sugarcane bagasse from aqueous solution was investigated as a function of change in pH at temperature $28 \pm 1^\circ\text{C}$, concentration $1.987 \times 10^{-4}\text{M}$ and particle size $< 55\mu\text{m}$. The removal of Cr (VI) on chemically modified sugarcane bagasse (MSB) was nearly 10% higher against unmodified sugarcane bagasse (USB). So the acidic pH of the medium promoted the rate of Cr (VI) removal on the adsorbent while inhibited at neutral or alkaline pH and gave good fit for adsorption kinetics equation during the study.

Keywords: - Adsorbents, Chromium (VI), Sugarcane Bagasse, Heavy metals

INTRODUCTION

The toxicity of heavy metals in water/ waste water has been a major cause of water pollution which concern for environmental engineers in the ecosystem. The industrial and domestic wastewater is mainly responsible for causing several damages to the environment and adversely affecting the health of the human beings. Due to industrialization, the heavy metal contaminations in aquatic environment increased the awareness about the heavy metal toxicity these elements discharge in the effluents which will be absorbed and accumulated by microorganisms which are considered as

environmental priority pollutants which are targeted for cleanup processes by removal/adsorption methods. So the removal of toxic metals from sewage and industrial waste water is a matter of great interest in the field of water pollution, which is a serious cause of water degradation¹. Chromium is commonly found in large quantities in tannery wastewater and also in small and medium scale industries. Therefore the removal of Cr(VI) from wastewater/polluted water bodies is a major problem and challenge at global level for the scientists. The metallic chromium and salts are widely used in industry in a variety of chemical processes. It is used in electroplating industry where it oxidizes electroplated metal surfaces to provide smooth, shiny and clean finishes. Some other products which contain chromium include paints, pigments, inks, wood preservatives, rubber ceramics, photography and textiles from where it is discharged into natural water bodies of water and lands in the environment.

The excess amount of chromium is in leather industry where it is used as a tanning agent chromium in waste water exists in two oxidation states viz Cr(III) which normally exist in the form of $\text{Cr}(\text{OH})_2^+$, $\text{Cr}(\text{OH})_4^-$ and Cr(VI) which exists in the form of $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-} depending on the pH of the solutions. Cr (VI) is considered to be highly toxic compared to Cr(III). Due to its high oxidation potential it can easily penetrate biological membranes and cause health hazards. On contract Cr(IV) causes irritation, corrosion of skin and respiratory tract and lung carcinoma. Various physico-chemical procedures are available for chromium removal from aqueous solution viz., precipitation, chemical reduction, ion-exchange electro chemical, evaporation, reverse osmosis and adsorption. However, among these, adsorption is found to be highly effective in expensive to operate at low concentration present in the waste waters^{2,3}. India is an

agricultural country and generates a considerable amount of agricultural wastes such as sugarcane bagasse, coconut juts nut shell, rice husk ash, rice straw, wheat straw, waste tea leaves, ground nut husk, peanut nulls and fertilizer wastes. The sugarcane bagasse one of the easily available agricultural waste which applied to removal of chromium as a adsorbent. Hence there exists a scope to try locally available low cost adsorbents for treatment of effluents containing Cr(VI). The various low cost adsorbent/agricultural adsorbents used for chromium removal reported by many investigators⁴⁻¹². So on the use of agricultural waste/agricultural byproducts as sugarcane bagasse as a good substrate for removal of metal cations from aqueous solutions and waste water. Chemical modification by the use of adsorbents increasing the efficiency of adsorbents¹⁴. The present works explains on the study of the kinetics of metal cations as Cr(VI) adsorption (K_1) at different pH values. The role of pH in Cr (VI) adsorption from aqueous solution in order to find out an appropriate pH range for maximum efficiency by using agricultural waste/byproducts as sugarcane bagasse under chemically modified and unmodified condition were investigated during research work by adsorption technique.

EXPERIMENTAL

MATERIALS AND METHODS:

The adsorption processes in which agricultural waste as sugarcane bagasse which used as adsorbent was collected local market cane juice seller and the pith was separated manually. It initially was light yellow in colour. The sugarcane bagasse was boiled with water for 30 minutes in order to remove soluble sugars present. Then the waste water to be used in the investigation was prepared by dissolving a known amount

of $K_2Cr_2O_7$ (Potassium dichromate) in a known volume of distilled water in the order to have waste of uniform characteristics and to avoid the interference with other elements. To evaluate the potential of bagasse to remove Cr (VI) batch experiments were carried out. Then wastewater containing known concentrations of Cr (VI) were prepared from the stock solution and taken separately in the glass stoppered conical flasks. Then known quantities of the adsorbent were added to the waste water. The system was equilibrated by shaking the contents of the flask at room temperature. So that adequate contact time between adsorbent and the metal ion was maintained. The suspension was filtered through Whatman No.41 filter paper and the filtrate was analysed to evaluate the concentration of Cr(VI) metal in the treated waste water. All the analyses were performed according to standard methods¹⁵ and the Cr (VI) metal analysis was carried out by using Atomic Adsorption spectrometry. All the chemicals were used of analytical reagent grade during the research works.

Adsorption Kinetic Study:

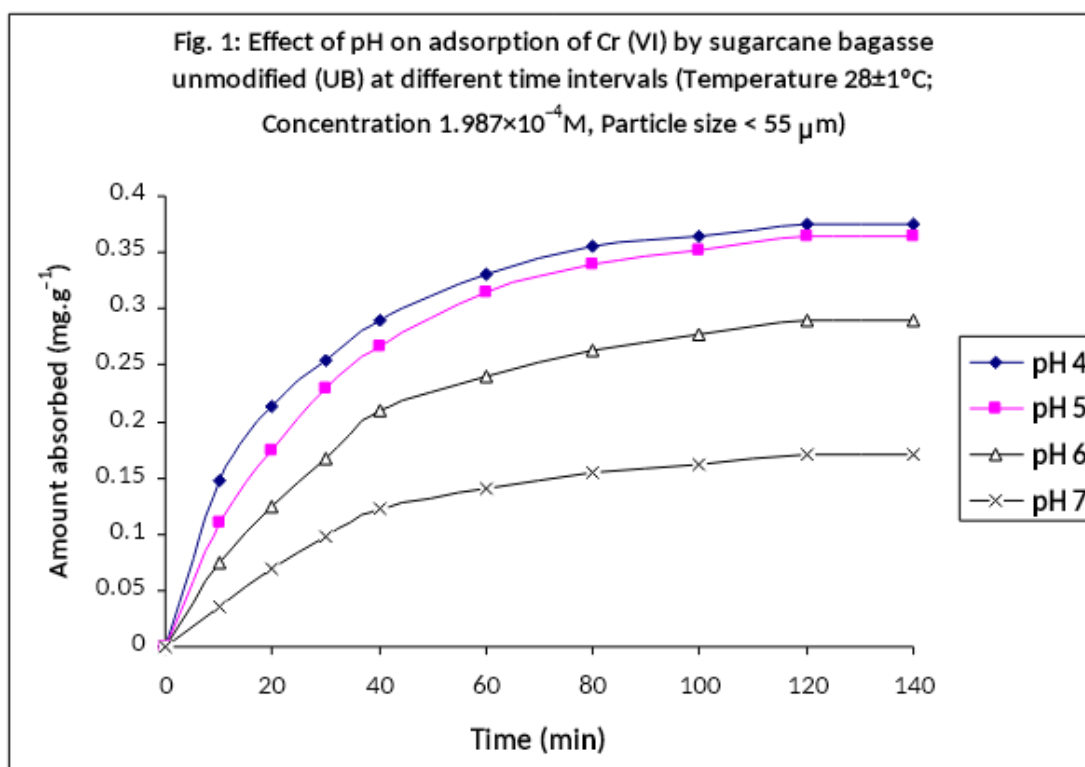
The batch mode adsorption studies were carried out to determine the adsorption of chromium metal. The kinetics of metal cations studies of Cr(VI) were carried out for each adsorbent at different pH with initial concentration of metal ion solution was $1.987 \times 10^{-4} M$, particle size of the adsorbent was $< 55 \mu m$ and temperature $28 \pm 1^\circ C$. Then a known amount of solution (100 ml) was taken in 250 ml Erlenmeyer flask, adsorbent (0.5gm each) was soaked separately in the flask and agitated in a shaker for a fixed time and constant speed (90 rpm). After agitation for an equilibrium period, the supernatant solution was filtered through whatman No.41 filter paper and uptake was

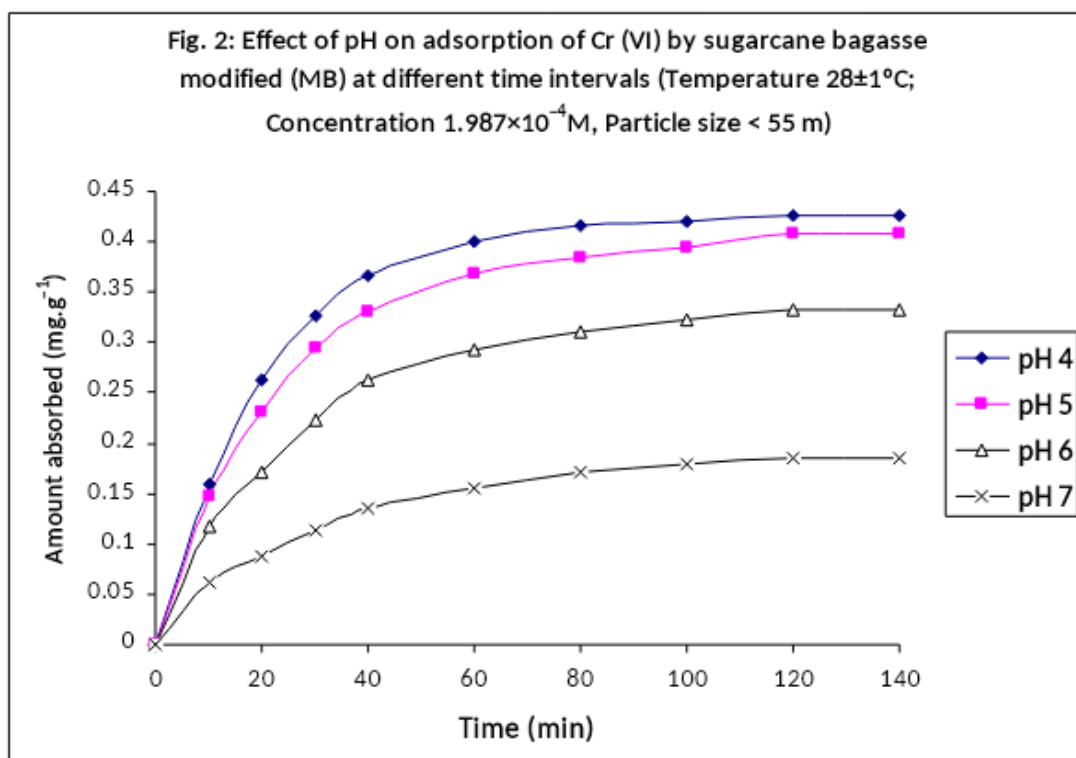
determined spectrophotometrically by using filtrate. Then adsorption dynamics was calculated by taking adsorption rate constant. So the first order reversible reaction kinetics was used for the rate of reaction in kinetic adsorption.

RESULTS AND DISCUSSION

Effect of pH on adsorption

The pH value is an important factor for controlling the process of adsorption as it affects the surface charge of the adsorbents, the degree of ionization and the species of the adsorbate. The effect of pH on adsorption of Cr (VI) by agricultural waste as sugarcane bagasse^{13,16,17} (using chemically modified and unmodified) is presented in Fig.-1 and Fig.-2.





The adsorption of chromium(VI) on adsorbent (sugarcane bagasse) depends upon the nature of adsorbent surface and species distribution of the metal cations Cr(VI). So, the change in pH of the solution has no effect on the basic nature of the time growth adsorption curves and period of saturation. The time growth adsorption of Cr (VI) by two adsorbents suggested that the removal was initially rapid and finally become constant due to the slow removal near saturation. This variation in percent adsorption at different pH by each adsorbent. The change in pH of the solution has no effect on the basic nature of the time growth adsorption curves and saturation periods as shown in Fig.-1 and Fig.2. However, the extent and rate of adsorption vary significantly with change in pH of the medium and modification of the sugarcane bagasse adsorbent. The adsorption of Cr (VI) on unmodified (normal) sugarcane bagasse (UB) the extent of removal changes from 74.9% to 33.8 pH 4 and pH 7 respectively with optimum velocity

at pH 4. However, the percent adsorption was significantly increased with chemically modified sugarcane bagasse (MB) at the same pH as in (Fig.-1 and Fig.-2). The adsorption was decreased from 85.30% to 37.30% at pH 4 and 7 respectively.^{18,19,20}

Conclusion

The present work explain the ability of sugarcane bagasse to adsorb Cr(VI) from aqueous solution has been explored. So, it is obvious from the results that pH of the medium affected the rate constant in accordance with extent of adsorption. The maximum adsorption has been noticed at pH 4. So there is an exponential decrease in the extent of adsorption with increase in pH (4 to 7). At pH 4 where maximum uptake of Cr (VI) has been noticed in both the conditions of the adsorbents (UB & MB) there exists a significantly high electrostatic attraction between protonated adsorbent surface and negatively charged adsorbate species. So the results in a high driving force for the formation of surface complex or their presence as chromates on the surface adsorbents. At pH 4 where maximum uptake of Cr (VI), there is an possibility of the dissolution of substrate and whose constituents cause surface precipitation of chromate. During in acidic condition the uptake of Cr (VI) by these adsorbents (UB & MB) is expected due to solid solution interface. Therefore, more adsorption of Cr (VI) by chemically modified

sugarcane bagasse (MB) might be due to increase in surface area which has great effect on sorption capacities of adsorbents. The Cr(VI) adsorption capacity was strongly depends on the pH of the solution by use agricultural byproducts as sugarcane bagasse.

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