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Adsorptive Removal of Cr (VI) from Aqueous Solution onto Charred Sugar Cane Bagasse

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Abstract

Charred sugar cane bagasse was prepared by chemical modification of sugar cane bagasse with conc. H_2SO_4*. The adsorption of Cr(VI) ions on charred sugar cane bagasse (CSCB) has been studied through batch adsorption techniques to evaluate the influence various parameters such as pH, contact time, initial concentration and adsorbent doses. The adsorbent surface was characterized by using Scanning Electron Microscopy (SEM) and functional group was detected by Fourier Transform Infrared (FTIR) spectroscopy. The optimum pH was found to be 1 and the reaction followed pseudo-second order kinetics. The adsorption percentage of chromium by charred sugar cane bagasse decreased at the higher initial metal concentration and lower adsorbent doses. The equilibrium adsorption isotherm was best fitted with Freundlich adsorption isotherm. This result indicates that SCB can be used as economical and efficient material for the adsorption of Cr(VI) from the aqueous solution.*

Keywords: *Modified Sugar Cane Bagasse (MSCB), Langmuir Isotherm, Freundlich Isotherm, SEM, FTIR*

Introduction

The pollution of heavy metal ion in the environment is a critical problem because of their toxicity and other effects. Chromium is a toxic metal of widespread use in many industries and mixing into the environment as a result of metal plating facilities, mining operation, leather tanning, metallurgy, fly ash from incinerators, manufacture of electrical equipments paints, alloys, batteries pesticides, fertilizers. Chromium has two stable oxidation states Cr(III) and Cr(VI). The trivalent form is less harmful but hexavalent chromium is toxic, and mutagenic in nature[1]. Chromium is hard steel-gray metal that is highly resistant to oxidation, even at high temperature. Industries wastages are quite responsible for the spreading the heavy metals in aquatic environment and parallel into the terrestrial environments too[2]. The problem is created due to the contamination of the waste water of urban areas with toxic heavy metals ions. Contamination of these metals and metalloids in lake, stream, and other resources of the drinking water leads to horrendous health problems in animals, plants including human beings[3].

If the concentration of the Cr (VI) is slightly greater than its tolerance limit (land surface water 0.1 ppm and potable water is 0.05 ppm), it becomes toxic and its ingestion can cause pain, vomiting. Classically, chromic metal can be removed by precipitation lime coagulation, solvent extraction,

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electrolysis, ion-exchange, reverse osmosis, evaporation, chelating, centrifugation, electro-dialysis methods[1]. These techniques are economically expensive and involve incomplete metal removal process. To overcome those problems and to obey more efficient method, it was needed to be practiced efficient and environment friendly methods. Biosorpotion is an efficacious and versatile method for removing chromium and copper and other heavy metals from industrial and other drain wastage. The modified carbon is most frequently used adsorbent for the removal of Cr(VI) present in water and wastewater that can be employed for the treatment of trace concentration of pollutant[4]. Modified carbon has been prepared from various agricultural waste materials like coconut husk, peat moss, wool, husk of Bengal-gram, exhausted coffee, waste tea, banana bark, sawdust, sugarcane dust, rice husk, alpine etc. are the low cost of such carbon precursors[1]. The modified material thus prepared from agricultural wastes however can be modified by various methods like chemical activation, steam activation, thermal activation etc. The effective surface area of the modified charcoal gets modified due to the fractionalization of the raw materials by the chemical modification process[5,6]. The main aim of this study is to explore the adsorption capacity and the kinetics of Cr(VI) ions onto the sugarcane bagasse.

Experimental Methods

Preparation of adsorbent

The raw sugarcane bagasse was collected from juice shop of Kathmandu, was washed with distilled water and dried on sunlight about one week. Then it was grinded by mechanical grinder and was sieved into 250 µm mess size. Thus obtained raw sugar cane bagasse is poor efficient for the removal of Cr(VI) metals. To increase its adsorption efficiency thus obtained raw sugarcane bagasse was subjected with chemical modification by conc. H_2SO_4[7-10].

Buffer solution

Buffer solutions of pH 4.0, pH 7.0 and pH 9.2 were prepared by dissolving buffer tablets in 100 ml conical flasks for each single tablet in distilled water by shaking process.

Preparation of solutions

1000 mg/L of standard stock solution of Cr(VI) was prepared by dissolving potassium dichromate crystal in distilled water and further diluted with 0.1 N nitric acid solution to prepare working solutions of desired concentrations of 20 mg/L, 50 mg/L, 100mg/L, 200 mg/L, 500 mg/L, 600 mg/L , 700 mg/L[9].

Effect of pH

The pH of 50 mg/L of Cr(VI) metal ion was maintained in the range pH 1-5 using 0.1 N HNO_3 and 0.1 N NaOH solutions. 25 mg adsorbent along with 20 ml working solution of Cr(VI) ion with different pH was taken and shaken at room temperature for 24 hr to reach equilibrium.

Effect of adsorbent concentration

The study on effect of adsorbent concentration was carried out using Cr(VI) ion concentration from 20 mg/L to 700 mg/L at optimum pH. After shaking the sample bottles at room temperature for 24 hr and filtering, the equilibrium concentration of Cr(VI) ion were measured. From the Cr(VI)l concentration measured before and after adsorption (c_i and c_e, respectively) and dry weight of adsorbent (W) as well as the volume of aqueous solution (V), the amount of Cr(VI) adsorbed in mg/g at equilibrium are computed by using equation (1),

$$q = \frac{c_i - c_e}{w} \times V \qquad (1)$$

Batch equilibrium time studies

Equilibrium time of the adsorbents for the sorption of Cr(VI) was investigated at optimum pH values at room temperature. 25 ml of 20 mg/L concentration of Cr(VI) solutions were taken in 125 ml reagent bottle with 25 mg adsorbents and was shaken in a mechanical shaker for 10 min, 20 min, 30 min, 40 min, 50 min, 60 min, 70 min, 80 min, 90 min, 100 min, 120 min, 4 hrs, 5 hrs, 6 hrs and 24 hrs respectively. The metal ion [Cr(VI)] concentration was determined by spectrophotometric method.

Batch kinetic studies

The adsorption kinetic experiments were carried out at optimum pH for Cr(VI) adsorption by equilibrating 25 mg of adsorbents in 125 ml stopper bottles containing 25 ml of 20 mg/L Cr(VI) solution in each. Separate sets of various samples were kept on mechanical shaker and shaken vigorously. Samples were filtered through filter paper and concentration before and after the adsorption were determined by spectrophotometric method by analyzing the filtrate. The data obtained was tested with pseudo first order, pseudo second order and second order kinetic model.[27]

Results and Discussion

The sorption of Cr(VI) in aqueous solution was examined by optimizing various physiochemical parameters such as initial pH, initial adsorbate concentration, contact time, adsorbent dose, desorption study. The absorbance of red-violet Cr(VI)-diphenylcarbazide complex at maximum wavelength 520 nm, i.e., λ_{max} is 520 nm.

Removal of Cr(VI) was found to be decreased with increase in pH. The maximum removal value was obtained at pH 1 which is an optimum pH for CSCB as shown in Figure 1. Figure 2 depicts the study of adsorption was carried out in measuring the effect of contact time on the batch adsorption of 50 mg/L metal solution with 25 mg adsorbent for different time intervals ranging from 10 minutes to 360 minutes. The required time equilibrium for adsorption of Cr(VI) onto CSCB was found to be 250 minute.

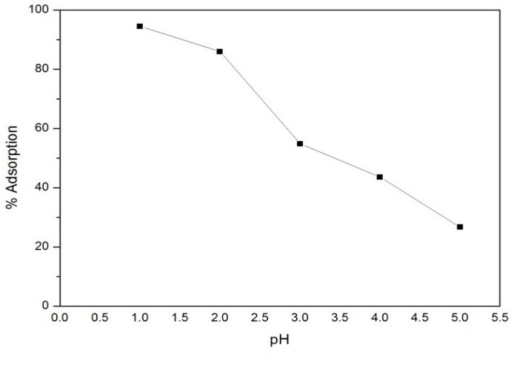


***Figure 1:** Effect of pH on Cr(VI) adsorption by CSCB*

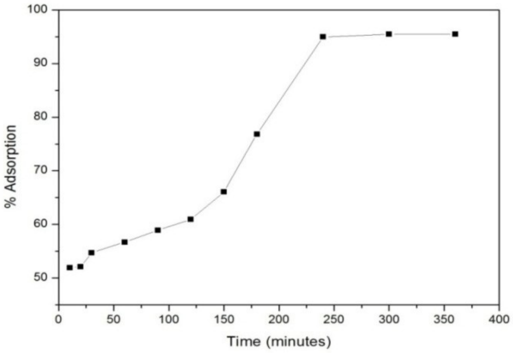


***Figure 2:** Effect of contact time for the adsorption percentage of Cr(VI) onto CSCB*

The effect of adsorbent dose for adsorption of Cr(VI) onto CSCB was studied at room tempreture at optimum pH 1 was studied by varying the adsorbent amounts from 25 mg to 200 mg which is graphically shown in Figure 3. The maximum adsorption capacity Cr(VI) onto CSCB is found to be 100 mg with 93.2 % adsorption.

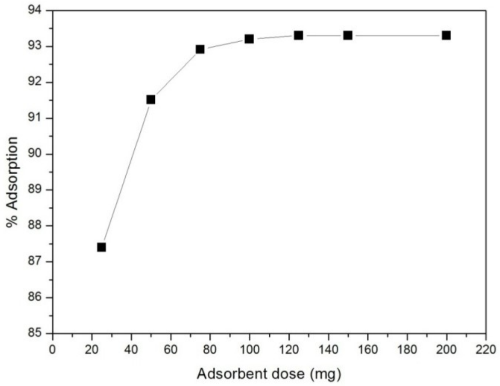


***Figure 3:** Effect of adsorbent dose for the adsorption percentage of Cr(VI) onto CSCB*

Adsorption of Cr(VI) onto CSCB gives linear relationship with Freundlich and Langmuir isotherms. Freundlich adsorption isotherm is more applicable than Langmuir adsorption isotherm. The values of Langmuir and Freundlich parameters are determined and tabulated in investigated at various concentration from 20 mg/L to 700 mg/L. Freundlich isotherm plot for the adsorption of Cr(VI) onto CSCB is shown in Figure 4 as given by equation 2.

$$\log q_c = \log K + 1/n \log c_e \qquad (2)$$

Where q_e is the amount adsorbed per unit pass of adsorbent (mg/g), c_e is the equilibrium concentration of the adsorbent mg/L, K and n are Freundlich equilibrium co-efficient, which are considered to be relative indicators of adsorption capacity and adsorption intensity. The value of 1/n varies between 0.1 and 1.0 indicates the favorable adsorption and heavy metal ions[11].

Table 1: Langmuir and Freundlich parameters for the adsorption of Cr(VI) onto CSCB

Adsorbent	**Expt. q_{max}(mg/g)**	**Langmuir isotherms**			**Freundlich isotherms**		
		q_m (mg/gm	**b (L/mg)**	**R^2**	**K (mg/gm)**	**1/n**	**R^2**
CSCB	319.75	418.41	0.0096	0.958	3.093	0.559	0.987

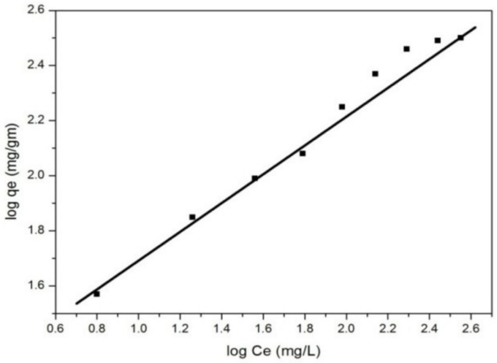


Figure 4: *Freundlich isotherm plot for the adsorption of Cr(VI) onto CSCB*

The kinetic data for the adsorption of Cr(VI) onto CSCB was studied by using pseudo-first order, pseudo-second order and second order kinetics model. From these result, the experimental data were better described by pseudo second order kinetics. The plot of pseudo-second order model is shown in the Figures 5. The data for all kinetic models are tabulated in the Table 2. Previous research work is also reported pseudo-second order[12].

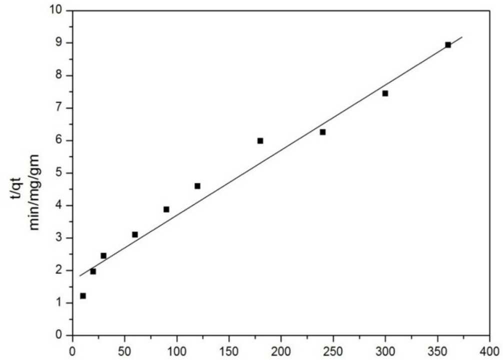


Figure 5: *Pseudo-second order kinetic plot for the adsorption of Cr(VI) onto CSCB*

Table 2: *Kinetic parameters for the bisorption with correlation coefficient*

Order	Rate Constant (g/mg/min)	R^2
Pseudo first order	1.06×10^{-2}	0.890
Pseudo second order	2.315×10^{4}	0.974
Second order	1.613×10^{-3}	0.64

In present research work, FTIR analysis is performed to investigate the surface functional groups of RSCB and CSCB. The FTIR spectra of both adsorbents (RSCB and CSCB) are shown in Figures 6 and 7, respectively which were used to determine the vibration frequency changes the functional group in the adsorbents of SCB. The adsorption peak around 1635 cm^{-1} indicates the presence of C=O stretching. This is due to the hemicelluloses and lignin aromatic groups. The peak around 1616 cm^{-1} indicates the C=O stretching of aromatic groups, that may be attributed to the hemicelluloses and lignin aromatic groups. This confirms that the changes in vibration of carbonyl group of charred and non- charred sample. The peak around 806 represents the C=C alkenes. The peak around 3313 cm^{-1} represents the free –OH stretching group[13-14].

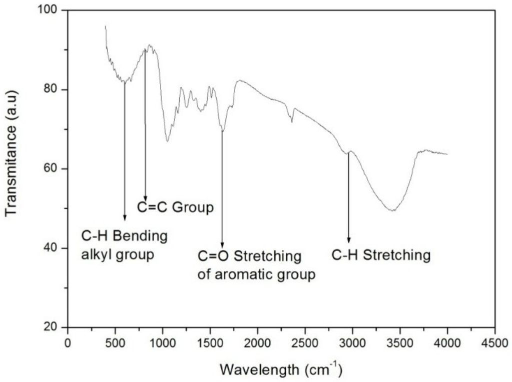


***Figure 6**: FTIR spectra of RSCB*

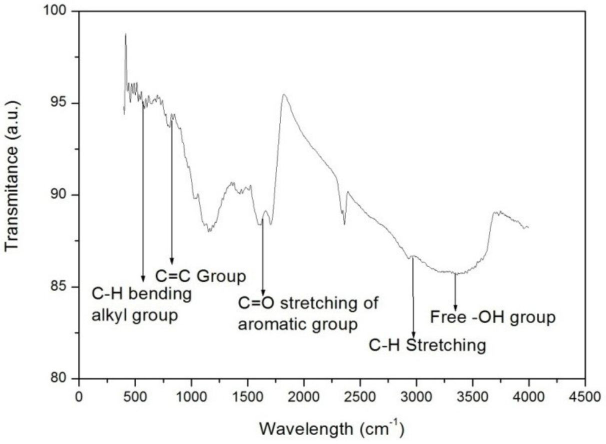
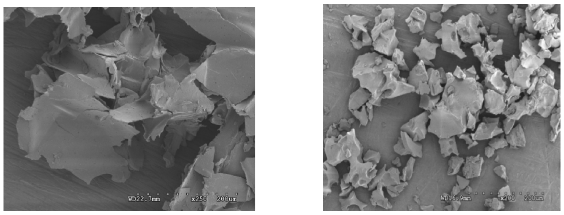


***Figure 7:** FTIR spectra of CSCB*

The Figures 7(a) and 7(b) show SEM images of the raw sugarcane bagasse and charred sugarcane bagasse.



(a) *(b)*

Figure 7: *SEM images of (a) raw sugarcane bagasse and (b) charred sugarcane bagasse*

SEM images of charred sugar cane bagasse has smaller particle size with larger surface area and so has greater efficiency to the adsorptive removal of heavy metal ion from aqueous solution as compare to the raw sugar cane bagasse.

Conclusions

The chemically modified SCB can be used in the separation of Cr(VI) metal ion from the aqueous solutions which results of the present research work are the optimum pH 1 for the adsorption of Cr(VI) and the Freundlich adsorption isotherm model with correlation coefficient R^2 of 0.987 was more applicable than Langmuir isotherm model (R^2=0.958). The maximum adsorption capacity of Cr(VI) onto charred sugarcane bagasse (CSCB) was found to be 100 mg. The required time equilibrium for the adsorption of Cr(VI) onto CSCB was found to be 250 minutes. The experimental data were better described by pseudo-second order kinetics. FTIR spectrum defines different functional group. SEM image of charred sugar cane bagasse has greater efficient of the adsorption capacity as compared to the raw sugarcane bagasse.

Acknowledgements

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