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REMOVAL OF HEXAVALENT CHROMIUM FROM SYNTHETIC WASTEWATER BY USING BIOCARBON

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ABSTRACT

Presence of toxic heavy metals in industrial effluents becomes a major human and environmental health problem. Particularly, hexavalent chromium is highly toxic in nature and is a major pollutant in the tannery wastewaters. For the removal of such heavy metals, number of cheap adsorbents has been developed from agricultural waste materials by different processes. In present investigation, "*Lantana camara* plant leaves," which is a medicinal plant material, was selected for the production of biocarbon as adsorbent for the removal of heavy metals in aqueous solutions. This adsorbent was used for the removal of chromium (VI) in batch mode in initial concentration and temperature of 100 mg/L and 28 ± 2°C, respectively. The influence of contact time, initial metal ion concentration, biocarbon dose and pH was studied. To know the properties of adsorbent different analysis such as FT IR, EDAX and SEM were studied. Evaluation of FTIR spectroscopy revealed the involvement of –OH, C=O, C–O groups on the biocarbon surfaces in chromium binding. The optimum biocarbon dose in this experimental study was 2.5g/100mL and the pH solution was 4.8. The analytical results suggest that, the adsorption capacity of the biocarbon as adsorbent was 95.80% for 100 mg/L solution at the contact time of 180 min. This study indicated that, the biocarbon generated from *Lantana camara* plant leaves can be used as an effective and environmentally friendly biosorbent for the treatment of Cr (VI) ions in aqueous solutions.

Keywords: *Lantana camara*, biocarbon, hexavalent chromium, tannery wastewaters.

INTRODUCTION

The modernization process and sustainable development goals lead to the rapid growth industrialization and urbanization. This process resulted in exponential discharge of industrial effluents and toxic heavy metals in to aquatic and terrestrial ecosystem [1]. Treatment of wastewater generated by industrial processes is a primary concern. Industrial processes such as electroplating, dichromate and basic chrome sulphate manufacturing, tannery, anodizing, cutting tools, and chrome mining are usually produce a large volume of wastewater with considerable amount of chromium [2].

Number of treatment methods has been developed and are available for the removal of toxic metal such as chromium from aqueous solutions and industrial wastewater [3]. Most of these methods have drawbacks such as high capital and operational cost [4, 5]. Therefore, there is a need for the development of a new methodology with low cost, easily available material by which chromium can be removed from industrial wastewaters. Recently, researchers have studied the removal of Cr (VI) from aqueous solution is by using natural and low cost materials as adsorbent [6, 7].

Adsorption process and method has many advantages. It is very simple, efficient and versatile method for removing chromium ions in industrial wastewater [8 – 10]. In many adsorption processes, commercial activated carbon (CAC) is used as adsorbent. Although it possesses large sorption capacity for the removal of heavy metal ions, the higher unit cost restricts their potential use for environmental protection applications. The present investigation deals with the application of biocarbon generated from *Lantana camara* plant leaves for the effective removal of chromium (VI) from synthetic wastewater.

MATERIALS AND METHODS

In this study, 1000ppm stock solution of Cr (VI) was prepared by dissolving 1.4143g of analytical grade potassium dichromate ($K_2Cr_2O_7$) substance in deionized water and diluted to 500mL. *Lantana camara* plant leaves were collected and washed several times with distilled water and shade dried for two days. The biocarbon was prepared by using standard procedures outlined in literature [11]. The resulting biocarbon was preserved and used as an adsorbent. The particle size of biocarbon between 90 and 125 µm was used in the batch biosorption studies.

The biosorption capacity of the biocarbon on removal of Cr (VI) in a synthetic wastewater was performed in this present study. For the purpose of optimization, 50mL of Cr (VI) solution (100mg/L) was placed in seven 250mL capacity Erlenmeyer flask with stopper. In the experimental flask, biocarbon dose of 0.5 to 3.5g was added and equilibrated at the speed of 250rpm for 3hours (pH = 4.8). At the end of the equilibrium time, the samples were filtered off and the concentration of Cr (VI) was determined using AAS procedure. In the similar way, the optimal contact time was established with the interval of 30min with the initial concentration of 100mg/L of Cr (VI) solution at the biocarbon dose rate of 2.5g/100mL. The effect of pH on the removal of Cr (VI) on biocarbon was established by varying the pH of the working solution in the range of 3.0 to 8.0. The pH of the solution was adjusted by using 1.0 N NaOH and 1.0 N HCl. All the experiment was carried out at 28 ± 2°C. The percentage removal of chromium (VI) from aqueous solution was computed from the following equation.

$$\%\ \text{Removal} = \left(\frac{C_o - C_e}{C_o}\right) \times 100 \qquad (1)$$

The metal uptake (q_e) at equilibrium time was calculated from the following equation

$$q_e = \left(\frac{C_o - C_e}{w}\right) \times V \qquad (2)$$

where q_e = amount of dissolved solids adsorbed (mg/g), V = volume of wastewater (mL), w = mass of biocarbon (g), C_o = initial dissolved solids concentration (mg/L) and C_e = concentration of dissolved solids at equilibrium (mg/L). The analytical data were analysed and standard deviations of the statistical tests were carried out using programme of analysis of variance (ANOVA) by using SPSS program.

RESULTS AND DISCUSSION

Characterization of biocarbon

The physico-chemical analysis and spectral characterization of the biocarbon is very essential to illustrate the biosorption capacity and behaviour of the biocarbon material. The surface area analysis of the biocarbon reveals that, its surface area is 328 (m^2/g). The bulk density is 0.67 (g/mL), It has very less moisture content of 5.92%. The yield of the biocarbon is 87.5%. These results supports that, the biocarbon has good potential for biosorption of heavy metals in wastewater system.

Surface analysis by SEM and EDAX spectra

The scanning electron micrographs (SEM) of pure biocarbon and after chromium (VI) adsorption are shown in Figure 1(a) and 1(b). The surface morphology of both materials was found to be irregular. The SEM micrographs showed that pores with different sizes and different shapes existed on external surface of biocarbon. The porous present in the material facilitates the adsorption of metal ions on different parts of the materials [12]. The micrograph of biocarbon after chromium (VI) adsorption shows a reduction of number of pores, pore space and surface area available. Hence it is confirmed that there is metal adsorption on the surface of adsorbent.

Furthermore, the EDS spectra of selected zone of biocarbon before adsorption and after adsorption were carried out to investigate the chemical constituents in the biocarbon matrix. It has been found from Figure 2(a) that biocarbon having the carbon, oxygen on its surface before interaction with Cr (VI) ions, whereas in Figure 2(b) new chromium peak was observed with the surface bearing groups of carbon and oxygen, which confirmed the Cr (VI) adsorption on the biocarbon matrix.

FTIR Spectral Analysis

The FTIR spectra of pure biocarbon and after adsorption of Cr were analysed (Figure 3). The result indicates that FTIR spectra of both biocarbon has a broad band between 3410.50 cm^{-1} and 3417.18 cm^{-1} (–OH), the band at 2862.06 to 2926.37 cm^{-1} (–CH_2 and –CH_3 asymmetric and symmetric stretching), the peak at 1630.06 – 1710.77 cm^{-1} (associated with C=O carbonyl), and the peak at 1113.94 to 1162.75 cm^{-1} (associated with the C–O bond). The peak at 1379.92 – 1394.37 cm^{-1} is due to presence of S–O bonding. There is no appreciable difference between the FTIR spectra of pure biocarbon and the biocarbon containing Cr. Evaluation of FTIR spectroscopy revealed the involvement of –OH, C=O, C–O and S–O groups on the biocarbon surfaces in chromium binding.

The removal of Cr (VI) with biocarbon is highly dependent on the pH of the solution which affects the uptake capacity of biocarbon. The influence of pH is presented in the Figure 4. The pH can significantly influence the removal behaviour of heavy metals, and there will be an optimum pH for maximum removal. Normally at the lower pH the metal uptake capacity of biocarbon is low [13]. The removal of Cr (VI) from aqueous solution by biocarbon was more efficient at a pH around 4.5 – 5.0. Further increase of pH leads the decrease in removal of Cr (VI) which might be the precipitate formation of chromium ions.

The effect of contact time on the removal of Cr (VI) ions by biocarbon is shown in the Figure 5. The time of contact has a significant influence on the adsorption process of Cr (VI) on biocarbon matrix. The results indicated that metal adsorption increases with contact time. The removal of Cr (VI) from aqueous solution increases progressively and reaches a maximum value of 95.80% at time of 150min. Further increase in contact time has a negligible effect on the percentage removal of Cr (VI). The possible mechanism of metal ions transfer to the solid includes diffusion through the fluid film and pores to the internal adsorption sites. Initially, the concentration gradient between the film and the solid surface is high, and hence the transfer of metal ions onto the solid surface is faster. As the contact time increases, intraparticle diffusion becomes predominant [14]. Hence, after 95.8% adsorption, metal ions take more time in the transfer process to internal adsorption sites through the pores. Therefore, the optimum time for adsorption of Cr (VI) on biocarbon is 150min for all batch studies.

The removal of Cr (VI) at different dose of biocarbon (0.5 – 3.5g) for the initial concentration of 100 mg/L is investigated. The result is presented in figure 6. The percentage removal of Cr (VI) increases with increasing adsorbent dose. This is due to the availability of rich active sites on the biocarbon matrix for adsorption process.

The effect of initial concentration of Cr (VI) ions from 10 to 100 mg/L is described in Figure 7. The removal of Cr (VI) increases with the increase in concentration of Cr (VI) ions. The rate of removal Cr (VI) is higher at the beginning due to larger surface area of biocarbon being available for the adsorption. Once saturation point is reached the capacity of the adsorbent gets exhausted and removal rate is controlled by the sorbate, transported from the exterior to the interior sites of the adsorbent particles. The results indicated that the initial Cr (VI) ions concentration determines the equilibrium concentration and also determines the rate of removal of Cr (VI) ions and its kinetic character [15].

Figure 1(a). SEM photograph of *Lantana camara* biocarbon.

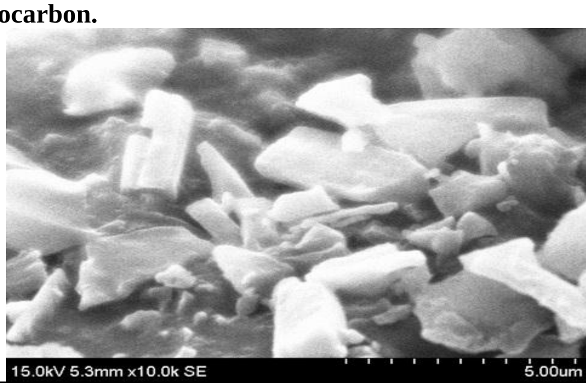


Figure 1(b). SEM photograph of *Lantana camara* biocarbon after Cr (VI) adsorption.

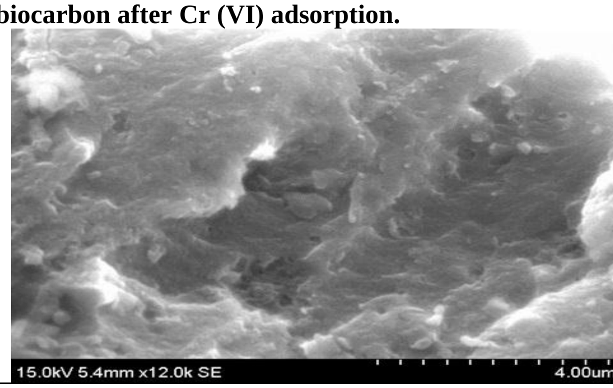


Figure 2(a). EDAX spectrum of pure *Lantana camara* biocarbon.

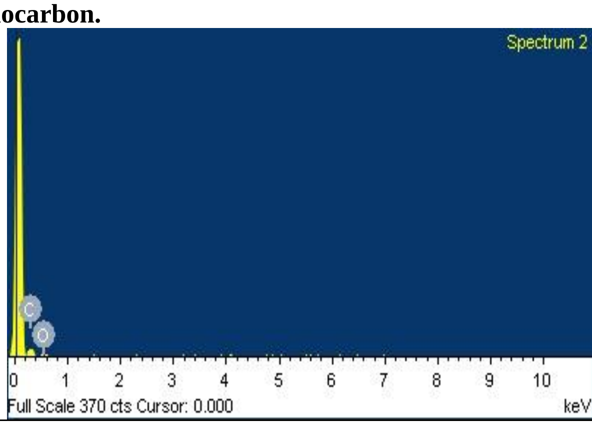


Figure 2(b). EDAX spectrum of *Lantana camara* biocarbon after Cr (VI) ions adsorption.

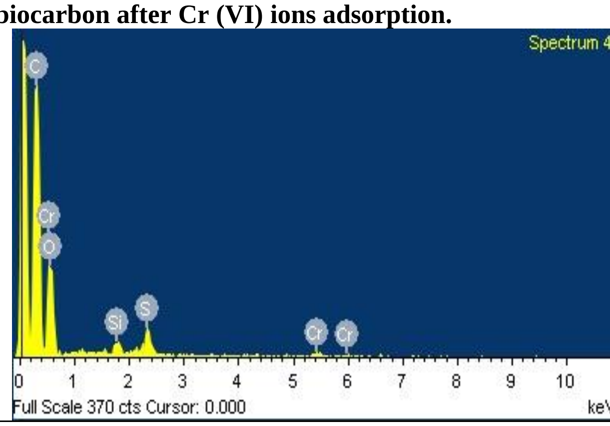


Figure 3. Combined FTIR spectrum (A) for pure LCBC and (B) for Cr (VI) ions adsorbed biocarbon.

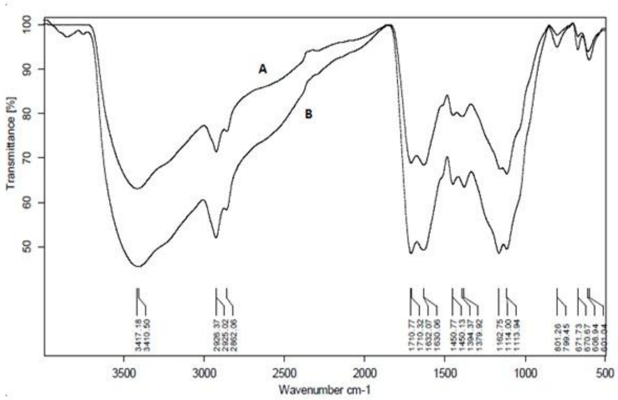


Figure 4. Effect of pH on the removal of Cr (VI) ions.

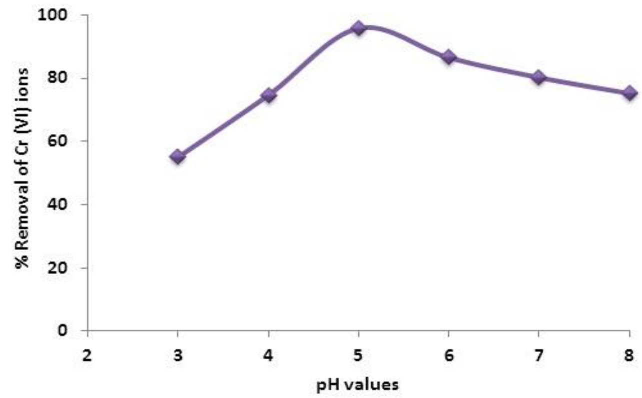


Figure 5. Effect of contact time on the removal of Cr (VI) ions.

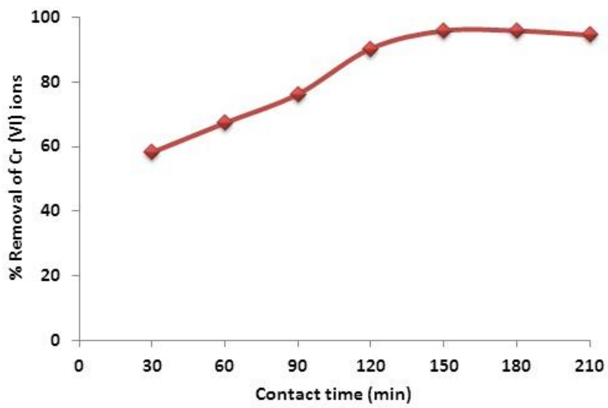


Figure 6. Effect of biocarbon dose on the removal of Cr (VI) ions.

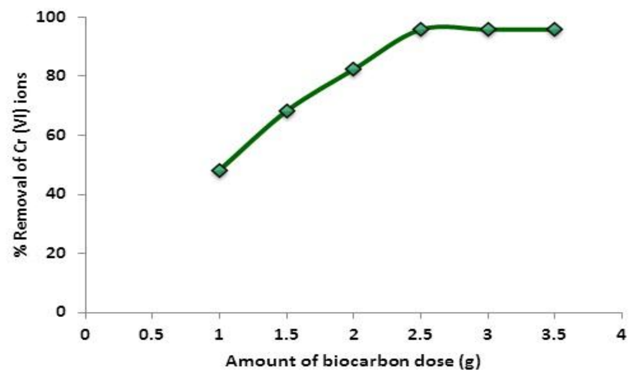
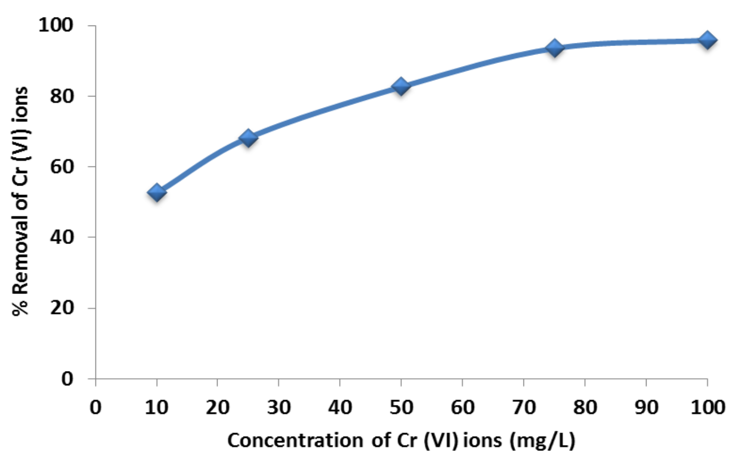


Figure 7. Effect of initial concentration on the removal of Cr (VI) ions.



CONCLUSION

The biocarbon generated from leaves of *Lantana camara* plant was found to be a better adsorbent based on its efficiency in the removal of chromium ions from synthetic wastewater. The biosorption results indicates that, the maximum removal of Cr (VI) ions was 95.80% under optimum condition such as pH of 4.8 and the biocarbon dosage of 2.5g/100mL and equilibrium contact time 150 minutes. Evaluation of FTIR spectroscopy revealed the involvement of –OH, C=O, C–O groups on the biocarbon surfaces in chromium binding. Hence the biocarbon can be rated as potential adsorbent for removal of chromium ions and other hazardous materials from industrial wastewater.

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