Removal of Cr(VI) by Adsorption on Kala Jamun (*Syzygium cumini* L.) Bark Powder

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Abstract—*The work describes the removal of hexavalent chromium, Cr(VI) from aqueous solution using a natural biomass, Kala Jamun bark powder (Syzygium cumini L.), KBP. The biosorbent KBP was characterized with FTIR, SEM, surface area, cation exchange capacity and anion exchange capacity measurements. KBP was found to have very good potential for Cr(VI) removal by adsorption on the surface of the particles. The data were fitted into Langmuir and Freundlich isotherms and the adsorption capacities were found along with the kinetic parameters.*

1. INTRODUCTION

In this universe, water is the base of all forms of life and energy. However, this precious resource has been contaminated almost everywhere due to discharge of effluents by the industries introducing a large number of harmful pollutants into water having adverse effects on human health and the ecology in general. In the last century, dramatic changes have been experienced on the natural environment. In addition to industrialization, growing population, mechanization at increased speed, rapid urbanization and the accompanying unplanned expansion and growth of towns and cities, have also been among the major factors for polluting the water resources. The contamination of soil, sediments, groundwater, surface water and air with hazardous and toxic chemicals causes significant problems for human health and the general environment [1].

Heavy metals constitute one of the most harmful groups of contaminants in drinking water. A few common heavy metals, recognized for their toxicity towards humans are As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Sn, V [2]. Hexavalent chromium is considered as one of the top sixteen toxic pollutants because of its carcinogenic characteristics for humans. Exposure to Cr(VI) causes irritation to skin and vital organs. Short duration exposure to Cr(VI) can cause ulcer and irritation of the nasal and the gastrointestinal tracks. It has adverse effects on kidney and liver. Inhalation of Cr(VI) may affect the immune system. United States Environmental Protection Agency (US EPA) has prescribed a permissible level of 0.05mg/L for Cr (VI) in drinking water [3].

One of the versatile and effective techniques for the removal of heavy metals from water is by adsorption on an appropriate solid material. Despite of the advantages of adsorption, the major obstacle for its industrial application is the very high price of the adsorbents (usually activated carbon). However some natural and renewable materials which are present abundantly in the environment along with some industrial and agricultural waste products are also studied as adsorbents [4].

The present work investigates the possible use of Kala Jamun *(Syzygium cumini L.)* bark powder, KBP as a biosorbent for the removal of Cr(VI) from spiked water.

2. MATERIALS AND METHODS

A stock solution containing 1000 mg/L of Cr(VI) was prepared using $K_2Cr_2O_7$ in double-distilled water. All other chemicals used were of analytical grade. Successive dilutions of stock solutions were carried out to set up standard solutions, ranging from 5-50 mg/L. All the reagents were used without further purification. All aqueous solutions were prepared in double-distilled water.

Kala Jamun Barks were collected locally. Initially the barks were washed with filtered water in several times to avoid dust and other soluble impurities. The barks were dried in the Sun at 303-308 K and later put it in an air oven at 323-333 K for 6-7 hours till they became crisp and were ground in a mechanical grinder to a fine powder. The powder was sieved and the 240-320 mesh fractions were chosen as the biosorbent.

3. RESULTS AND DISCUSSION

Specific surface Area

The specific surface area of the adsorbent, KBP, was determined by dye adsorption method using Methylene Blue to adsorb on the adsorbent [5, 6]. The specific surface area of KBP was found to be 28.34 m^2/g. Specific surface areas of 21.7 and 33.2 m^2/g have been reported for commercial cellulose powder and cellulose-based anion exchanger [7], while values of 20.31 and 17.45 m^2/g have been found for

coconut husk and teak tree bark respectively [8]. The value obtained for KBP in this work is similar to these values.

Surface Topography

The surface topography of KBP was studied with Scanning Electron Microscopy (SEM) analysis at the Sophisticated Instruments Facility (SIF), North Eastern Hill University, Shillong, India (JEOL JSM-6360). The SEM micrographs of KBP particles are shown in Fig. 1. The SEM micrographs of KBP particles have clearly showed that the adsorbent consists of particles of different sizes and shapes. The particles have irregular surfaces with a large number of wavy edges. Further, the KBP surface contains some heterogeneous pores and small openings, which help to give a porous look to the surface, and indicate a lager surface area and a high adsorption capacity of the adsorbent.
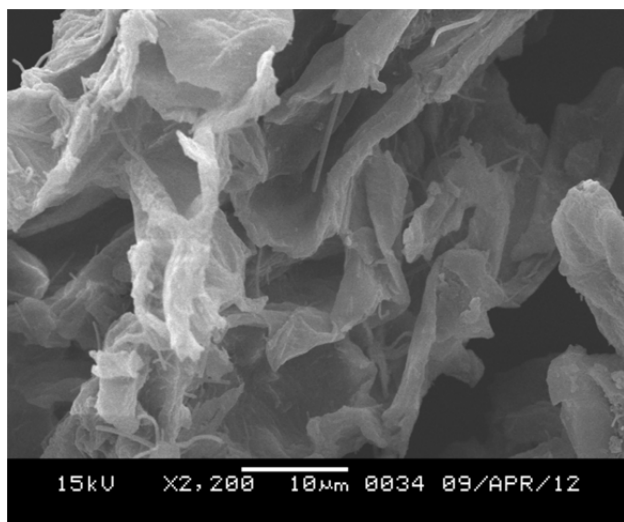

Fig. 1: SEM image of KBP particles

Cation Exchange Capacity (CEC)

The cation exchange capacity (CEC) of KBP was determined by Copper(II)-bisethylene-diamine complex method [9].

The CEC of KBP is measured to be 2.20 meq/100g, showing that the biosorbent has considerable CEC due to the presence of polar functional groups like -OH, -C≡N, >C=O, etc., on the surface. The high value of CEC indicates that KBP particles have the capacity to hold considerable amount of cations by ion exchange mechanism.

Anion Exchange Capacity (AEC)

The anion exchange capacity (AEC) of KBP was determined using conductometric method [7]. The anion exchange capacity of KBP was measured to be 1.34 meq g^{-1}. It may be noted that values of 0.69 and 1.81 meq g^{-1} have been reported for commercial cellulose powder and cellulose-based anion exchanger [7]. It is observed that KBP has a value in the same range.

Identification of Surface Functional Groups

The surface functional groups of the biosorbent, KBP, were identified with FTIR spectroscopy (Shimadzu, IR Affinity-1, CE; range 4000 – 400 cm^{-1}) by KBr pellet technique. It is found that KBP contains a number of important functional groups like -OH (3426 cm^{-1}), -CH$_3$ (1373 cm^{-1}), -C≡N (1031 cm^{-1}), -C≡C- (2925 cm^{-1}), >C=O (1620 cm^{-1}), and C-X (667 cm^{-1}). These functional groups definitely play a role in the adsorption process by interacting with Cr(VI) anions in water.

Effects of pH on adsorption of Cr(VI)

Adsorption of Cr(VI) on KBP was studied at different acidity/alkalinity of the spiked water by adjusting the pH of the aqueous solution from 1.0 to 9.0 by adding either 0.1 N NaOH and 0.1 N HCl dropwise. The pH of Cr(VI) aqueous solution, as prepared, was 4.9, indicating the acidic nature of the solution. The effects of pH on Cr(VI) adsorption by KBP was investigated by carrying out the interactions for 60 min at 303 K with KBP amount of 2 g L^{-1} and 50 ml of Cr(VI) solution of concentration, 50 mg L^{-1}. The results are shown in Fig. 2. A decreasing trend was seen in the values of q_e (the amount adsorbed per g at equilibrium) with increasing pH.
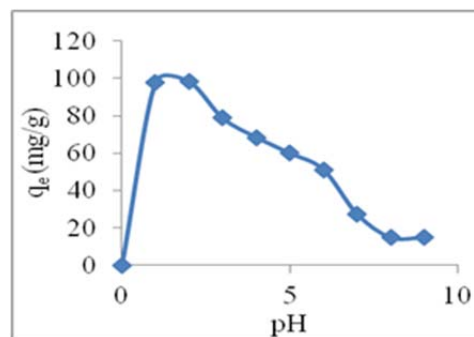

Fig. 2: Effects of pH on Cr(VI) adsorption

Maximum adsorption of 97.75 % was obtained at pH = 2. It has been reported that 86.0, 99.0, 97.0, and 87.0 % Cr(VI) adsorption could be achieved with an initial Cr(VI) concentration of 50 mg L^{-1} on nitric acid treated coconut shell charcoal, silver impregnated ground nut husk, unimpregnated ground nut husk, and eucalyptus bark, respectively [10 – 11, 13]. The results obtained in the present work are comparable to these.

Effects of contact time and adsorption kinetics

Changing contact time on Cr(VI) adsorption (Time 05, 15, 30, 45, 60, 90, 120, 180, 240, 300 min, Cr(VI) concentration 10 to 50 mg L^{-1}, KBP biomass 2 g L^{-1}, temperature 303 K) by KBP showed that Cr(VI) uptake increased with the increase in contact time up to 30 min and then slowly attained equilibrium at 60 min. There was not any further increase after 60 min. A similar equilibrium time of 60 min was reported for adsorption of Cr(VI) on gooseberry seeds [14].

In the present work, the adsorbate-adsorbent interaction data were fitted into three kinetic models, viz., the pseudo first order, the second order and the intra-particle diffusion models to find out the exact mechanism of the interactions.

The rate processes are worked out from the series of experiments done with different concentrations of Cr(VI) solution (10 to 50 mg L^{-1}) and a constant amount of KBP (2 g L^{-1}) at temperature 303 K and pH as prepared. The pseudo first order kinetic plots obtained by plotting log ($q_e – q_t$) vs. t, for different Cr (VI) concentrations according to the equation [15]:

$$\log (q_e−q_t) = \log q_e − k_1/2.303.t \qquad (1)$$

where q_e and q_t are the amounts adsorbed per g of KBP at equilibrium and at time t respectively, and k_1 is the first order rate coefficient.

As the first order kinetics did not yield the correct values of the amount adsorbed at equilibrium, second order kinetics was tested with the rate equation:

$$dq_t/dt= k_2(q_e− q_t)^2 \qquad (2)$$

where k_2 is the second order rate coefficient (g mg^{-1} min^{-1}). The rate coefficient is obtained from the plots of t/q_t vs. t for different initial Cr(VI) concentrations. The second order kinetic model yielded linear relationship (mean linear regression coefficient of 0.99) allowing calculation of q_e and k_2. The values of q_e obtained from the second order plots agreed with the experimental values of q_e with small deviations. This indicates that the Cr(VI) adsorption follows a second order mechanism. The second order rate coefficient, k_2, was found to have a mean value of 1.03×10^{-3} g mg^{-1} min^{-1}. Similar results have also been obtained by other workers for Cr(VI) adsorption [14, 16].

Adsorption isotherm

The adsorption capacities of KBP with respect to Cr(VI) were determined by using the well-known Langmuir adsorption equation [17]:

$$C_e/q_e= (1/bq_m) + (1/q_m)C_e \qquad (3)$$

where b is k_a/k_d (the respective rate coefficients for adsorption and desorption), q_m is the quantity of adsorbate required to form a single monolayer on unit mass of the solid and q_e is the amount adsorbed on unit mass of the solid when the equilibrium concentration is C_e.

The Langmuir isotherm plots of C_{eq}/q vs. C_{eq} at different Cr(VI) concentrations and KBP amounts were used to find values of q_m and b from the slopes and the intercepts of the linear plots. It is seen that the adsorption capacity, q_m, of KBP for Cr(VI) remained between 11.1 to 21.2 mg/g for different Cr(VI) concentrations indicating that the adsorbent could take up a considerable amount of Cr(VI) from water. Similar results of q_m of 21.5 mg/g were found for Cr(VI) sorption by using pine needles as adsorbent [18]. Values of q_m= 16.13 and q_m= 19.23 mg/g were also found for Cr (VI) sorption [14, 19].

4. CONCLUSION

The present work shows that Kala Jamun Bark powder, KBP, has successful application as an adsorbent and it shows high efficiency for the removal of Cr(VI) from aqueous solution. FTIR spectral analysis showed that the functional groups like carbonyl and hydroxyl ions played an important role in the biosorption of Cr(VI). The adsorption process is pH-dependent with maximum adsorption at pH 2.0 and equilibrium is attained quickly in 60 min. Cr (VI) adsorption is m0ost favoured at pH 2.0 and can be considered as an ion exchange reaction between $HCrO_4^-$ and KBP surface. The kinetics of the biosorption process was found to follow second-order rate law. Langmuir isotherm showed that KBP can take up a substantial amount of Cr(VI) on its surface. Biosorption of Cr (VI) is also dependent on contact time, adsorbent amount and initial Cr(VI) concentration. Kala Jamun Bark Powder is easily available and its utility as a biosorbent will be economical and can replace the expensive adsorbents like activated carbon in the adsorption process.

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