Research Paper

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Biosorption of Hexavalent Chromium From Aqueous Solution on Kala Jamun (*Syzygium Cumini*) Seed Powder

Chemistry

KEYWORDS : Chromium(VI); biosorption; isotherm; kinetic models.

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ABSTRACT

A plant-based biosorbent was prepared by grinding clean, dried Kala Jamun (Syzygium cumini) Seeds and the powder (KSP) was utilized as a biosorbent for the removal of hexavalent chromium Cr(VI) from aqueous solution. FTIR, SEM, Surface area, Cation Exchange Capacity and Anion Exchange Capacity measurements were used to characterize the biosorbent. The effects of pH, contact time, initial concentration and adsorbent amount on adsorption of Cr(VI) on KSP at room temperature were studied in detail. Equilibrium was attained at 180 min and the maximum adsorption was obtained at an optimum pH of 3.0. The Equilibrium data fitted both Langmuir and Freundlich isotherms. A two-step pseudo first order kinetic model agreed well with the dynamic biosorption behaviour. The optimum Cr(VI) removal from aqueous solution was 97.5% at pH 3.0 with a KSP loading of 3.0 gL-1 at 303 K. The Kala Jamun Seed powder has proven to be an efficient biosorbent for Cr(VI) in aqueous solution.

1. Introduction

Ever increasing industrial activity is the main cause behind most of the environmental problems and ecosystem damage, due mostly to accumulation of pollutants such as toxic metals (chromium, copper, lead, cadmium, zinc, nickel, etc.) [1]. 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 [2]. The presence of heavy metals in the effluents of industrial processes such as electroplating, metal finishing, metallurgical works, tanning, chemical manufacturing, mining and battery manufacturing, etc., has raised concerns throughout the world since these can be toxic and harmful even at very low concentrations if consumed by humans and other life-forms [3–5].

Several contender technologies, such as adsorption on miscellaneous adsorbents [6,7], supercritical fluid extraction [8], ion exchange [9], etc., exist for treatment and elimination of heavy metals from industrial effluents and water [10–13]. Adsorption is an effective and versatile technique for heavy metal removal, even at very low concentrations. However, the very high price of adsorbents (usually activated carbon) is considered as the major obstacle for industrial application. Thus, the focus of heavy metal adsorption studies has been focussed towards the utilization of natural and renewable materials that are available in vast amounts, as well as certain waste products from industrial and agricultural operations [14].

On the basis of metal binding capacities of various biological materials, biosorption has been found to be widely feasible to separate heavy metals from wastewater [15] and has emerged as a cost-effective and efficient alternative for application to low strength wastewaters [16]. The sorption of heavy metals onto the biomaterials is attributed to the constituents like proteins, carbohydrates and phenolic compounds that can separate the metals by binding on to carboxyl, hydroxyl, amine and other functional groups [17].

Hexavalent chromium is considered as one of the top sixteen toxic pollutants because of its carcinogenic characteristics for humans [18]. It is 500 times more toxic than the trivalent form. Hexavalent Chromium 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 also affect the immune system. Chromium is released into the environment from both natural and anthropogenic sources.

The present work investigates the possible use of Kala Jamun (*Syzygium cumini)* Seed powder (KSP) as a biosorbent for treatment of water containing Cr(VI).

2. Materials and Methods

2.1 Preparation of the biosorbent

The Kala Jamun (*Syzygium cumini L*) seeds were collected locally, washed with distilled water several times to get rid of dust and other deposits, and dried in an oven at 105°C overnight. The dried seeds were ground to a fine powder in an electric grinder to obtain the Kala Jamun seed powder (KSP) biosorbent.

2.2 Characterization of the biosorbent

The surface functional groups of the biosorbent, KSP, were studied with FTIR spectroscopy (Shimadzu, IR Affinity-1, CE) in the range of 4000 – 400 cm^{-1} by KBr pellet technique. The biosorbent sample was kept in an oven at 323 – 333 K overnight for getting rid of moisture, allowed to cool to room temperature in a desiccator and then, a little amount of it was used with spectroscopic grade KBr for the preparation of pellets.

The specific surface area of the biosorbent, KSP was determined by dye adsorption method using Methylene Blue to adsorb on the adsorbent. The amount of the dye adsorbed on unit mass of the biosorbent (q_e mg/g) at equilibrium was determined by measuring the dye remaining unadsorbed in the solution spectrophotometrically (Shimadzu U1800).

The surface topography of KSP was studied with Scanning Electron Microscopy (SEM) analysis at the Sophisticated Instruments Facility (SIF), North Eastern Hill University, Shillong, India (Scanning Electron Microscope, JEOL JSM-6360).

The cation exchange capacity (CEC) of KSP was determined by Copper(II) bisethylene-diamine complex method (Bergaya and Vayer, 1997) [19]. In this method, 0.5 g of the biosorbent was mixed well with 5 mL of 0.05 M solution of Cu(II)-ethylenediamine complex, $[Cu(en)_2]^{2+}$ (which was prepared by mixing 50 ml of 1.0 M $CuCl_2$ solution with 102 ml of 1.0 M ethylene-diamine solution) in a 100 mL conical flask, and was diluted to 25 mL with the distilled water. The mixture was agitated for 30 min and was centrifuged. The concentration of the complex remaining in the supernatant liquid was determined by titrating iodometrically with 0.01 M thio solution. The CEC of the biosorbent was calculated from

CEC (meq/100 g) = MSV (x-y) / 1000 m
(1)

where, M is the molar mass of the complex, S the concentration of the thio solution, V the volume (mL) of the complex taken for iodometric titration, m the mass of adsorbent taken (g), *x* is the volume (mL) of thio required for blank titration and *y* is the volume (mL) of thio required for the titration (with the adsorbent).

The anion Exchange Capacity (AEC) of KSP was determined using conductometric method (Anirudhan and Jalajamony, 2010) [20]. In this method, 0.2 g of the adsorbent in 20 mL conductivity water was titrated conductometricaly against standard 0.1 M $AgNO_3$ solution. The titration was repeated for standard 0.01 M NaCl solution against the same $AgNO_3$ solution. The conductance increased only after the end point in both the cases. The conductances were plotted against the volume of $AgNO_3$ solution and from the curves, the equivalence point was determined. From the difference in volumes of $AgNO_3$ solutions in the two sets of titrations, the anion exchange capacity (AEC) was calculated using the relation,

$$AEC\ (meq/\ g) = NV/\ m \qquad (2)$$

where, N is the strength of $AgNO_3$ solution (in normality unit) and V is its volume required for m g of KSP.

2.3 Adsorption experiments

A stock solution containing 1000 mg Cr (VI) per L was prepared by dissolving 2.8289 g $K_2Cr_2O_7$ in 1000 mL distilled water. Standard solutions of Cr(VI) concentration, 10 to 50 mg/L, were prepared by appropriate dilution of the stock solution with distilled water.

Adsorption of Cr(VI) on KSP was carried out in the batch mode by agitating a known amount of the biosorbent with 50 ml of Cr (VI) solution of desired concentration in 100 mL Erlenmeyer flasks and agitating the mixture in a thermostated water bath shaker for different time intervals at a fixed temperature. After adsorption, KSP was separated by filtration using Whatman No.1 filter paper and the supernatant was analysed for unadsorbed Cr(VI) spectrophotometrically (Shimadzu U1800).

To study the effect of pH, it was adjusted between 1 to 9 by adding either 0.1 N NaOH and 0.1 N HCl dropwise for different initial Cr(VI) concentrations. The effects of biosorbent amount were studied by varying KSP from 1.0 to 6.0 gL^{-1} at various initial metal concentrations. The effects of Cr(VI) concentration was studied by varying it from 5.0 to 40.0 mg/L.

3. Results and discussion

3.1. Characteristics of the adsorbent

3.1.1. Specific surface Area

Langmuir isotherm plotted from the methylene blue adsorption data yielded a monolayer capacity, q_m. The specific surface area of KSP was found to be 13.8 $m^2 g$

Kehinde et al. (2009) have reported specific surface area of 20.31 and 17.45 $m^2 g$ for coconut husk and teak tree bark respectively [21].

3.1.2. Surface Topography

The SEM micrographs Fig. 1 of KSP particles have clearly showed that the biosorbent consists of particles of different sizes and shapes. The particles have irregular surfaces with a large number of wavy edges. Further, the KSP 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.

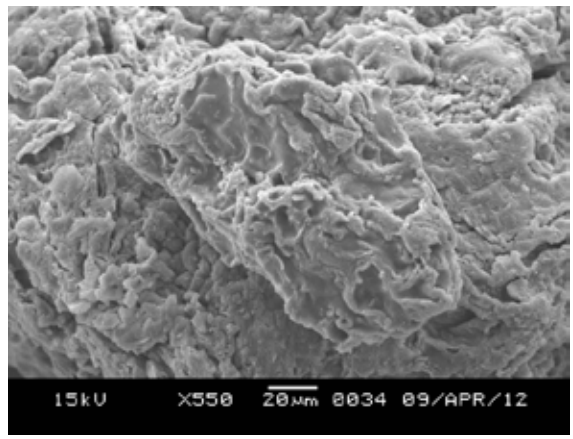

Fig. 1. SEM image of KSP particles

3.1.3. Cation Exchange Capacity (CEC)

The CEC of KSP was measured to be 1.47 meq/100g. The cation exchange capacity measurement has shown that the biosorbent, KSP, has considerable CEC value due to the presence of polar functional groups like -OH, -C≡N, >C=O, etc., on the surface.

.1.4. Anion Exchange Capacity (AEC)

The anion exchange capacity of KSP was measured to be 1.41 meq g^{-1}. It may be noted that Anirudhan and Jalajamony (2010) have reported values of 0.69 and 1.81 $meqg^{-1}$ for commercial cellulose powder and a cellulose-based anion exchanger [20].

3.1.5. Identification of Surface Functional Groups

The principal functional groups identified in KSP from the FT-IR spectra shown in Fig. 2 along with the corresponding IR bands are -OH (3842 cm^{-1}), $-CH_3$ (2992 cm^{-1}), -C≡N (2350 cm^{-1}), -C≡C- (2042 cm^{-1}), >C=O (1640 cm^{-1}), >C=S (1240 cm^{-1}), C-X (680 cm^{-1}). Similar functional group identification has been made earlier by other workers [22], [23].

3.2 Results of adsorption experiments

3.2.1. Effects of pH

The pH of Cr(VI) solution was 4.9, indicating acidic nature of the aqueous solution. The effects of pH on Cr(VI) adsorption by KSP was investigated by carrying out the interactions for 180 min at 303 K with KSP amount of 3 g L^{-1} and 50 ml of Cr (VI) solution of concentration, 50 mg L^{-1} varying the pH of the mixture from 1 to 9 are shown in Fig. 3. The results showed a decreasing trend of adsorption with increasing pH. Maximum adsorption of 97.5% was obtained at pH = 3. 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 oxidized coconut shell charcoal, silver impregnated ground nut husk, unimpregnated ground nut husk, and eucalyptus bark, respectively [24–26] The result obtained in the present work is comparable to these.

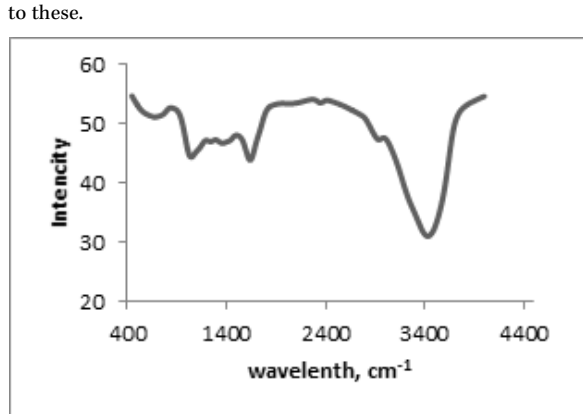

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Fig. 2. FTIR spectra of KSP

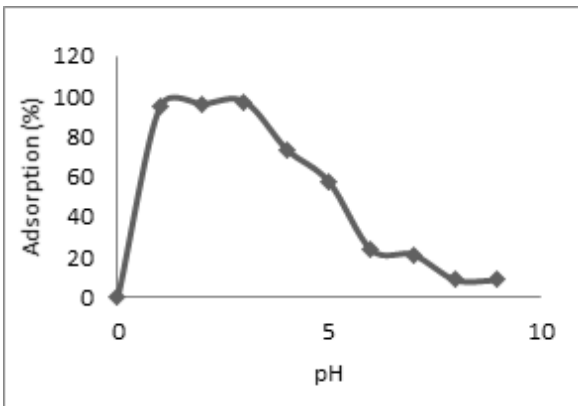

Fig. 3. Effects of pH on Cr(VI) adsorption at different initial concentrations

3.2.2. Effects of agitation time and adsorption kinetics

The effects of agitation time on Cr(VI) adsorption (Time 30, 60, 90, 120, 150, 180, 240 min, Cr(VI): 10 to 50 mg L^{-1}, KSP biomass amount 3 g L^{-1}, temperature 303 K) by KSP is shown in Fig. 4. Adsorption of Cr(VI) increased with an increase in agitation time and the equilibrium time varied for different Cr(VI) concentrations and it is seen that 180 min could be safely taken as the equilibrium time. The adsorption capacity increased significantly when the initial Cr(VI) concentration was increased from 10 to 50 mg L^{-1}. This is due to the increase in the number of ions competing for the available binding sites on the adsorbent surface. Initial concentration of Cr(VI) provides an important driving force to overcome all mass transfer resistance between the aqueous and solid phases. Hence, a higher initial concentration of Cr(VI) increases the adsorption rate [27].

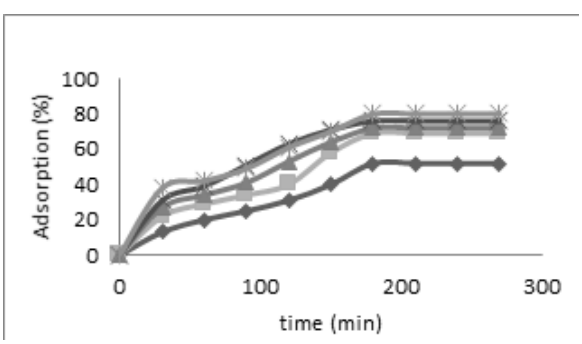

Fig. 4. Effect of agitation time and initial Cr(VI) concentration on Cr(VI) removal (adsorbent 1 g /50 ml, at normal pH).

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.

3.2.3. Pseudo first-order Kinetics

The pseudo first-order Lagergren plots were obtained by plotting log (qe – qt) vs. time according to the equation (Lagergren, 1898) (28).

$$\log(q_e - q_t) = \log q_e - k_1/2.303.t \quad (3)$$

where q_e and q_t are the amount of adsorption at equilibrium and at time t respectively, and k_1 is the rate coefficient of the pseudo first-order adsorption process. The rate processes are worked out from the series of experiments done with different concentrations of Cr(VI) (10 to 50 mg L^{-1}) and a constant amount of KSP (3 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 are shown in Fig. 5. The pseudo first order kinetics of Cr(VI) adsorption on KSP, becomes favourable when the q_e values calculated from the plots q_e (plot) are comparable with those obtained experimentally q_e (expt). Small deviations were observed between the two sets of values (Table 1), which indicates that the Cr(VI) sorption by KSP follows the first order kinetics. Similar results have been obtained by other workers [29].

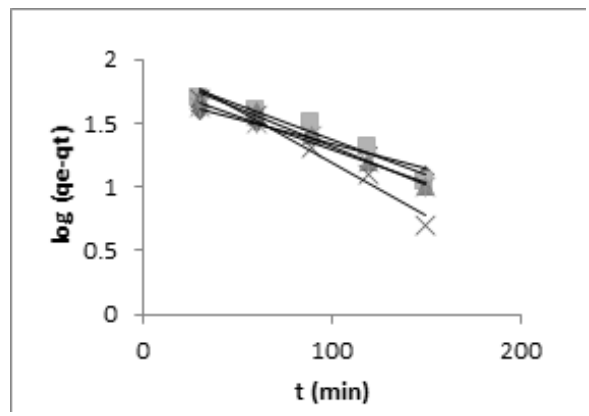

Fig. 5. Pseudo first order kinetics.

Table 1

Kinetic parameters for sorption of Cr(VI) on KSP (3g/L) at 303 K

Kinetics	Parameters	Cr(VI) (mg/L)					Mean
		10	20	30	40	50	
First order	$k_1 x10^{-3}$ min^{-1}	12	18	12	13	9	12.8
	R	0.99	0.98	0.99	0.98	0.99	0.99
	log q_e (expt) mg/g	1.9	1.9	1.86	1.84	1.72	1.84
	log q_e (cal) mg/g	1.8	2.0	1.9	1.92	1.74	1.87
Second order	$k_2 x10^{-4}$ g/ mg/min	1.3	0.2	88	45	21	31.1
	R	0.96	0.96	0.96	0.90	0.90	0.94
	q_e (expt) mg/g	80	76	72	69	52	69.8
	q_e (cal) mg/g	103	92	105	120	132	110.4
Intra particle diffusion	k_{id} mg/g/ $min^{1/2}$	4.6	4.6	4.8	5.1	4.1	4.64
	R	0.96	0.96	0.96	0.96	0.97	0.962
	Intercept	10.3	8.1	0.028	-9.2	-11.1	-1.872

3.2.4. Second order kinetics

The second order kinetics has to be tested with the rate equation:

$$dq_t/dt = k_2(q_e - q_t)^2 \quad (4)$$

where q_e and q_t are the sorption capacities (mg g^{-1}) at equilibrium and at time t, respectively and k_2 is the second order rate coefficient (g mg^{-1} min^{-1}).

The rate coefficients of the second order kinetics are obtained from the plots of t/q_t vs. t Fig. 6 for different initial Cr(VI) concentrations. The rate coefficients together with the correlation coefficient, r are listed in Table 1. 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 differ very much from the experimental values of q_e with large deviations. This indicates that the Cr (VI) adsorption is not following second order mechanism.

3.2.5. Intra particle diffusion model

The intra-particle diffusion rate coefficient (k_{id}) is given by the equation (Weber and Morris, 1962) (30).

$$q_t = k_{id} \cdot t^{1/2} \quad (5)$$

where k_{id} is the intra-particle diffusion rate coefficient. If a linear relation is observed between q_t vs $t^{1/2}$ (McKay et al., 1982) (31), k_{id} values could be determined from the slope.

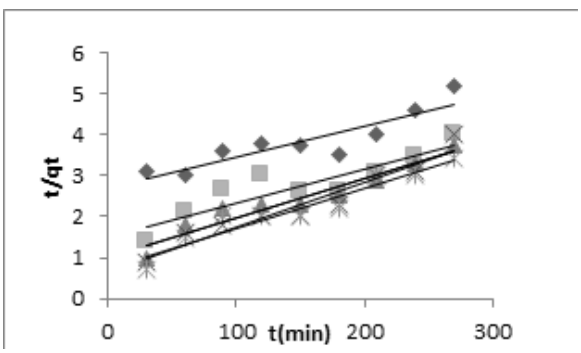

Fig. 6. Plots for second-order kinetics.

Sorption kinetic data are processed to determine whether intraparticle diffusion is rate limiting or not. The intraparticle diffusion plots are shown in Fig. 7. Since the straight lines do not pass through the origin, therefore there is limitation in proposing a major role for the intraparticle diffusion as the rate-controlling step [29] in Cr(VI) adsorption.

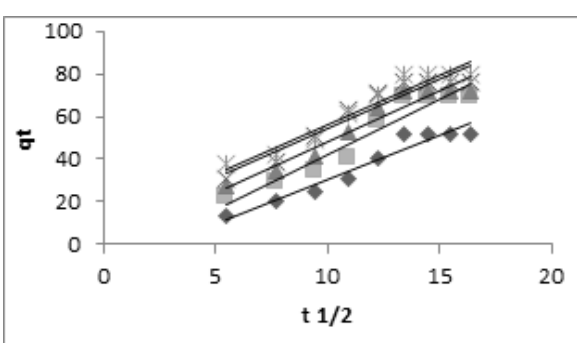

Fig. 7. Plots for Intra Particle Diffusion

3.2.6. Effects of adsorbent amount on adsorption

The adsorption of Cr(VI) was studied by increasing adsorbent amount from 1 g L^{-1} to 6 g L^{-1} with 50 ml of Cr(VI) solution (concentration 5-40 mg L^{-1}) at 303 K and interaction time of minute. The results showed in Fig. 8 indicated that the adsorption increases with increase in adsorbent amount, since contact surface of adsorbent particles is increased. Maximum removal of Cr(VI) was found to be at 3 g L^{-1} [32].

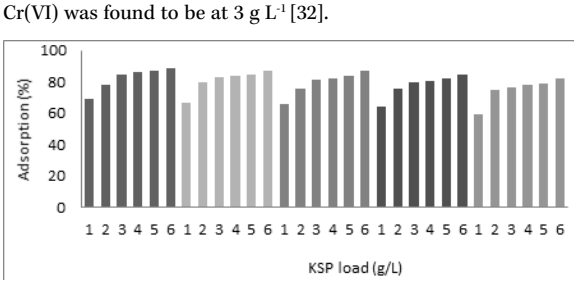

Fig. 8. Cr(VI) adsorption at room temperature at different KSP loads (1 – 6 g/L) [Cr(VI) 5, 10, 20, 30, 40 mg/L (from left to right), agitation time 180 min at normal pH].

3.2.7. Effects of increasing concentration of Cr(VI)

To investigate the effect of Concentration, 50 mL Cr(VI) solution (concentration 5, 10, 20, 30, 40, 50, 60. 70, 80 mg L^{-1}) was agitated with KSP (3 g L^{-1}) at 303 K for 180 min and are given in Fig. 9. Maximum adsorption occurred at the minimum concentration of Cr(VI). At a higher concentration, a greater number of Cr(VI) ions in the solution cause more number of collisions and thus lead to desorption of the metal ions from the binding sites of the adsorbent surface whereas with limited number of ions, the number of collisions (hence, desorption) is reduced and a higher rate of adsorption is obtained [32].

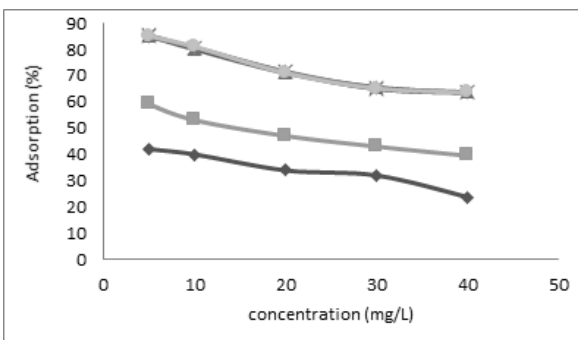

Fig. 9. Effects of Cr(VI) concentration on its adsorption on KSP (3 g L^{-1}) at 303 K

3.2.8. Adsorption Isotherms

Langmuir equation (Langmuir, 1918) (33) is of the following form

$$C_e/q_e = (1/bq_m) + (1/q_m)C_e \quad (6)$$

where b is k_a/k_d (the respective rate coefficients for adsorption and desorption) and 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 plots of C_{eq}/q vs. C_{eq} are shown in Fig. 10 for Cr (VI) adsorption on KSP. The linearity of the plots shows that adsorption follows the Langmuir model. q_{max} and b are determined from the slope and the intercept of the plots and the values are given in Table 2.

The Freundlich model (Freundlich, 1906) (22) has the following expression:

$$qe = K_f C_e^{\ n} \quad (7)$$

where C_e and q_e are the equilibrium concentrations of the metal ions in the liquid phase and in the solid phase respectively, K_f and n being Freundlich coefficients, representing adsorption capacity and adsorption intensity respectively. For favourable adsorption, n should be generally < 1. The Freundlich plots of ln C_{eq} vs ln q are shown in Fig. 11. It is observed that adsorption of Cr(VI) on KSP also follows the Freundlich isotherm model. Freundlich coefficients, K_f and n are given in Table 3.

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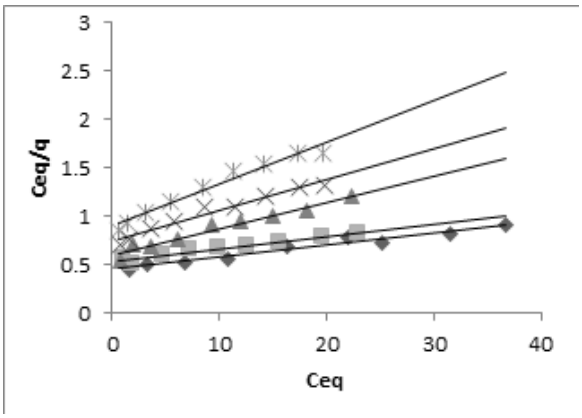

Fig. 10. Langmuir plots for Cr (VI) adsorption on KSP at 303 K (Cr(VI) 10 – 50 mg/L, KSP 3 g/L, time 180 min at normal pH)

The acceptability of Freundlich adsorption isotherm for adsorption of Cr (VI) over KSP surface also indicated that the surface is made up of small heterogeneous adsorption sites which are very much similar to each other in respect of adsorption phenomenon.

Table 2
Correlation coefficient (R^2), square root of correlation coefficient (R), Langmuir Constant (q_m, b) and R_L.

Correlation coefficient	C_e/q_e for Cr(VI) concentration (mg/L) of				
	10	20	30	40	50
R^2	0.96	0.96	0.96	0.96	0.97
R	0.98	0.98	0.98	0.98	0.98
q_m	78.0	80.0	50.0	33.0	25.0
b	0.025	0.028	0.046	0.044	0.049
R_L	0.802	0.644	0.418	0.364	0.289

The adsorption data in the present study fitted both Langmuir and Freundlich isotherms, indicating comparatively stronger interactions between Cr(VI) ions and the KSP surface. Similar results have been obtained by others [34]. The R_L values obtained for Cr (VI) adsorption on KSP are > 0 and < 1 showing favourable adsorption of Cr (VI) on KSP [34]. The values of R_L are given in Table 2.

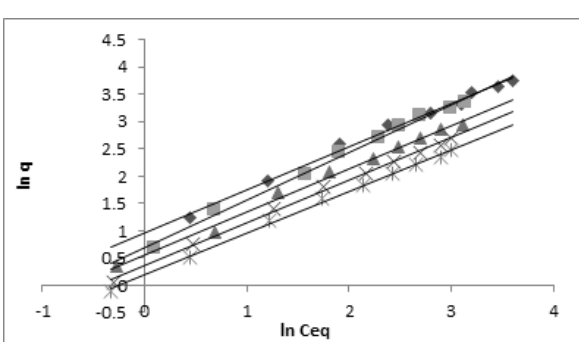

Fig. 11. Freundlich plots for Cr(VI) adsorption on KSP at 303 K (Cr(VI) 10 – 50 mg/L, KSP 3 g/L, time 180 min at normal pH)

4. Conclusion
From the present study, it can be concluded that Kala Jamun seed powder, KSP, has successful application as an adsorbent and shows its 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).

Table 3
Correlation coefficient (R^2), square root of correlation coefficient (R), Freundlich Constant (n, K_f)

Correlation coefficient	C_e/q_e for Cr(VI) concentration (mg/L) of				
	10	20	30	40	50
R^2	0.99	0.99	0.99	0.99	0.99
R	0.99	0.99	0.99	0.99	0.99
n	0.79	0.87	0.790	0.78	0.76
K_f	1.52	1.35	1.28	1.17	1.10

The Biosorption of Cr(VI) is pH-dependent with maximum adsorption at pH 3.0 and the equilibrium was attained in 180 min. Cr (VI) adsorption at pH 3.0 is considered as ion exchange reaction between $HCrO_4^-$ and KSP surface. The kinetics of the biosorption process was found to follow pseudo-first-order rate law. Both Langmuir and Freundlich isotherm equations were found to provide the close fit to the equilibrium data implying that the surface of KSP is heterogeneous and single layered. Biosorption of Cr (VI) is also dependent on contact time, adsorbent amount and initial Cr(VI) concentration .Kala Jamun seeds are easily available and their utility as biosorbent will be economical and can replace the expensive activated carbon in the adsorption process.

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