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Removal of Cr(VI) Ions from Aqueous Solution by Using *Syzygium cumini* Seeds†

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The present study deals with the removal of Cr(VI) ions from aqueous solution by using *syzygium cumini* seeds. Batch adsorption studies showed that *Syzygium cumini* seeds was able to adsorb Cr(VI) ions from aqueous solutions. The maximum adsorption capacity was found to be 253.16 mg g^{-1} with 0.1 g of sorbent dosage at pH 2. The effect of pH, contact time, sorbent dosage and temperature have been studied. The adsorption of *Syzygium cumini* seeds was best fitted by the Langmuir adsorption isotherm and it follows pseudo second order kinetics.

Key Words: Adsorption, *Syzygium cumini* seeds, Cr(VI) ions, Adsorption isotherms, Kinetics.

INTRODUCTION

Heavy metal contamination is one of the most environmental problems of this century[1,2]. Chromium is the seventh most abundant element on earth crust[3]. As per the united states environmental protection agency the maximum contaminant level for Cr(VI) ions in domestic water supplies is 0.05 mg L^{-1}. Chromium is one of the most toxic metal originated from the various industries such as leather tanning, mining, dye, iron sheet cleaning, textile, dying, cement and electroplating industries. In the earth crust, among all exhibited valence states of chromium, Cr(VI) is known to be 100 fold more toxic than Cr(III) because of its high water solubility, mobility and ability to reduce itself[4].

A large number of treatment methods are available for the removal of Cr(VI) ions from aqueous solution, namely membrane separation, chemical precipitation, electrochemical treatment, solvent extraction, ion exchange, reverse osmosis and adsorption[5].

In the case of very low concentration level of chromium, most of the methods are considered as ineffective and also founded as low removal efficiency. However, adsorption is found to be an effective methodology for the efficient removal of chromium at low concentration level. Now a days, eco-friendly and low cost biomaterial (fungi, bacteria, industrial and agriculture wastes[6]) were used as biosorbents for the removal of chromium from waste water.

In the present study, *Syzygium cumini* seeds is used as a biosorbent. Jambul tree (Syzygium cumini tree) is an evergreen tropical tree in flowering plant family myrtaceae. Syzygium cumini tree is native to India, Bangladesh, Nepal, Pakistan, Srilanka and Indonesia.

The aim of the present study is to use *Syzygium cumini* seeds as a biosorbent for the removal of Cr(VI) ions from the dilute aqueous solution, evaluate the effect of various parameters such as effect of pH, sorbent dosage, contact time and temperature. Adsorption capacity of the *Syzygium cumini* seeds was evaluated by studying the equilibrium adsorption isotherms and kinetic models of Cr(VI) ions in batch experiments.

EXPERIMENTAL

All reagents used in the present study ($K_2Cr_2O_7$, 1,5-diphenyl carbazide, HCl, NaOH, H_2SO_4) were of analytical grade purchased from Merck, India.

Preparation of bio-sorbent: Syzygium cumini seeds were collected from the National Institute of Technology Warangal, Andhra Pradesh, India and were treated several times with ultra pure water to remove the impurities, dried at 70 ºC in oven for two days. After drying, the dried seeds were grounded to fine powder and sieved to get uniform particles and was used as a bio-sorbent in the present study.

Preparation and analysis of Cr(VI) solution: The stock 1000 mg L^{-1} Cr(VI) solution was prepared by dissolving the 2.804 g of potassium dichromate in one litter deionized water. All experiments were carried out by required dilution of stock solution. pH was adjusted to the desired values with 0.1 M HCl and 0.1 M NaOH solution. pH of the solution was measured

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by the pH metre, the concentration of the aqueous Cr(VI) solution (complexation with 1,5 diphenyl carbazide method) was determined by using the analytikzena specord 205 UV-visible spectrophotometre.

The adsorption experiments were performed in a Batch mode. 100 mL solution of 100 mg L^{-1} Cr(VI) ions mixed with 0.1 g of *Syzygium cumini* seeds and batch experiments were conducted in an 250 mL Erlenmeyer flask, required pH values were obtained by the addition of 0.1 M HCl and 0.1 M NaOH respectively. The resultant solution was kept in temperature controlled incubator at 100 rpm for various time intervals. After that, it was filtered and the unadsorbed concentration of Cr(VI) ions was determined. The adsorption capacity of *Syzygium cumini* seeds was calculated by employing the mass balance equation[7].

$$q = \frac{(C_i - C_e)}{W} V$$

where, q is the adsorption capacity in mg g^{-1}, C_i is the initial concentration of metal ion solution in mg L^{-1}, C_e is the equilibrium concentration of metal ion solution in mg L^{-1}, V is the volume of metal ion solution in Littre and W is the mass of the adsorbent in grams.

The adsorption capacity of *Syzygium cumini* seeds for the removal of Cr(VI) ions has been evaluated through Langmuir and Freundlisch adsorption isotherms.

RESULTS AND DISCUSSION

Characterization of the adsorbent: The FTIR spectra of native and metal loaded *Syzygium cumini* seeds adsorbents are Table-1. FTIR spectroscopy was used to determine the changes in vibration frequency in the functional groups of the adsorbents due to metal sorption. In native *Syzygium cumini* seeds an absorption peak around 3410 cm^{-1} indicates the existence of free bonded amine groups. The peaks around 1624 cm^{-1} corresponds to the C=O stretching vibration of aromatic groups. The other peaks at 762 and 858 cm^{-1} may be due to bending modes of aromatic compounds. The C=O stretching vibration absorption peak shifted to 1635 cm^{-1} when *Syzygium cumini* seeds is bind with Cr(VI) ions. Similarly the other peaks also shifted, which indicate that, the participation of these groups in metal binding. The positions of the peaks indicating Cr(VI) ions binding mostly with N-H and C=O groups. Similarly, shifts in aromatic bending modes, it indicates that metal was associated with the aromatic ring. The changes in positions of peaks confirms the complexation of Cr(VI) with functional groups present in the adsorbents.

TABLE-1

Adsorbents	ν(N-H)	ν(C=O)	Bending vibrations of aromatic compounds
SCS (native)	3410	1624	762,858
SCS-Cr(VI)	3415	1635	767,858

Effect of the pH: The adsorption of Cr(VI) ion on *Syzygium cumini* seeds as a function of pH was shown in Fig. 1. The uptake of Cr(VI) ion on to the *Syzygium cumini* seeds decreases with the increase of pH in the range of 2.0-5.0. It may be due to the existence of oxy anions ($HCrO_4^-$, $Cr_2O_7^{2-}$ and CrO_4^{2-}) of Cr(VI) ions. However, lowering of pH causes presence of strong attraction forces between Cr(VI) ions and protonated active sites present on the *Syzygium cumini* seeds in acidic medium. The maximum adsorption capacity was found to be 90 mg g^{-1} at pH 2.

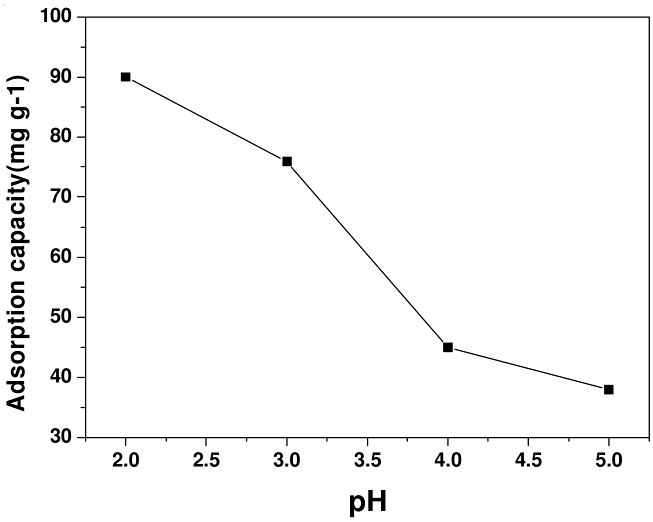


Fig. 1

Effect of contact time: The effect of contact time on removal of Cr(VI) by using *Syzygium cumini* seeds has been shown in Fig. 2. A series of 250 mL erlenmeyer flasks containing 0.1 g sorbent dosage with different initial concentrations of Cr(VI) (80, 100, 200 300 mg L^{-1}) were shaken in temperature controlled incubator at 100 rpm at different time intervals (1, 3, 6, 12, 24, 48, 96 h) at 25 ºC. It has been observed that the removal of Cr(VI) ions increases with increase of time contact up to 12 h. Further contact of Cr(VI) ions with *Syzygium cumini* seeds does not affect the removal efficiency.

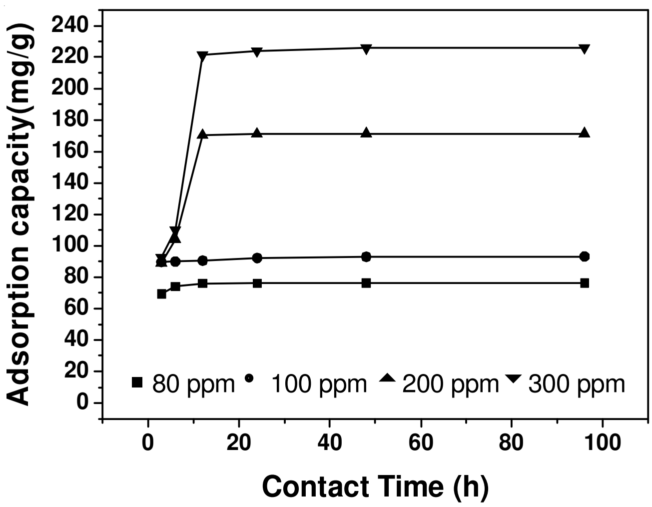


Fig. 2

Effect of sorbent dosage: The adsorption studies of Cr(VI) ions on *Syzygium cumini* seeds were done at 25 ºC by varying the adsorbent dosage from 0.05 to 0.3 g while keeping the concentration (100 mg L^{-1}) of the solution constant at pH 2.0. Fig. 3 shows influence of sorbent dosage on percentage removal of Cr(VI) ions. The percentage removal of Cr(VI) ions attain 90 % within 12 h, after that no change in percentage removal has been observed. However, 0.1 g sorbent dosage is sufficient for the maximum removal of Cr(VI) metal ion from the aqueous solution with the initial concentration of 100 mg L^{-1}. The increase in the adsorption percentage may be due to the increase in active sites on the adsorbent.

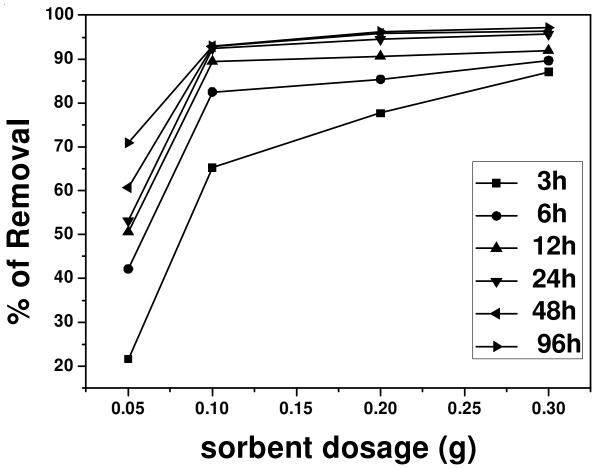
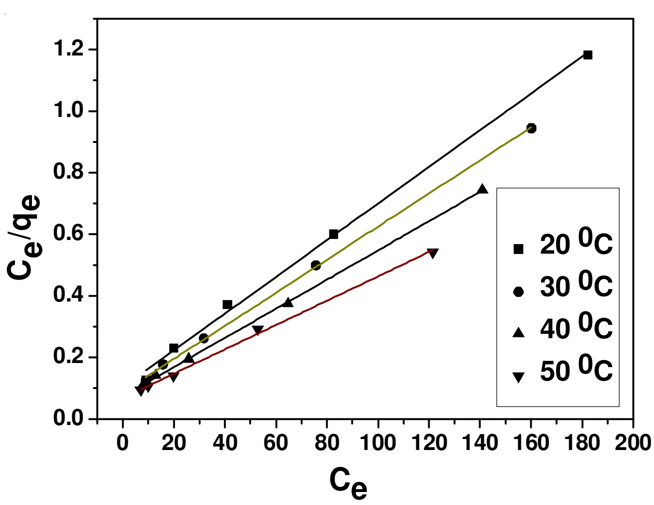


Fig. 3.

Effect of temperature: Effect of temperature on adsorption of Cr(VI) ions using *Syzygium cumini* seeds was investigated at various temperatures, keeping the constant concentration of Cr(VI) ions at pH 2.0 and 0.1 g of *Syzygium cumini* seeds. Adsorption capacity was increases with increase of temperature up to 50 ºC while maintaining 0.1g sorbent dosage in 100 mg L^{-1} of Cr(VI) ions solution. The equilibrium contact time for adsorption was attained in 12 h at 50 ºC. However, with the increase of temperature up to 50 ºC sorption increases it may be due to increase in the number of active surface sites available for sorption on the adsorbent[8].

Adsorption isotherms: Adsorption is usually described through isotherms, *i.e.*, the amount of adsorbate on the adsorbent as a function of concentration at constant temperature is shown Fig. 5. The Langmuir and Freundlisch adsorption isotherm models were used to evaluate the adsorption capacity of *Syzygium cumini* seeds for the removal of Cr(VI) ions from aqueous solution.



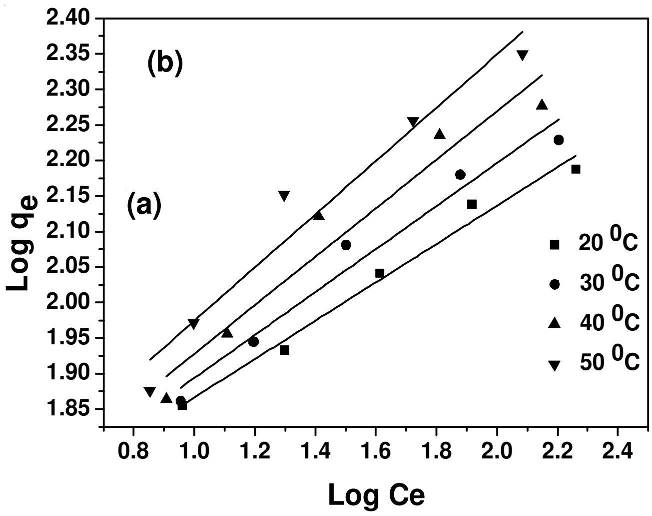


Fig. 4

TABLE-2
ADSORPTION ISOTHERM MODEL CONSTANTS AND CORRELATION COEFFICIENTS FOR THE ADSORPTION OF METAL IONS ON SCS at 20, 30, 40, 50 ºC at pH 2

Temperature (ºC)	Langmuir adsorption isotherm constants		
	K_L	Q_m	R^2
20	0.0573	167.7852	0.9967
30	0.0610	186.2197	0.9992
40	0.0634	211.4164	0.9996
50	0.0577	253.1645	0.9969
	Freundlich adsorption isotherm constants		
	K_F	n	R^2
20	1.5969	3.7061	0.9784
30	1.5919	3.3086	0.9589
40	1.5870	2.9311	0.9297
50	1.6	2.6695	0.9366

Langmuir adsorption isotherm expressed as:

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m}$$

where, C_e is the equilibrium concentration of Cr(VI) ions in solution (mg L^{-1}), q_e is the equilibrium concentration of Cr(VI) ions on the adsorbent (mg g^{-1}), Q_m is the monolayer adsorption capacity of the adsorbent (mg g^{-1}) and K_L is the Langmuir constant and related to the energy of adsorption. The values of Q_m and K_L are determined from the slope and intercept of the plots of C_e/q_e *versus* C_e at 20, 30, 40 and 50 ºC were presented in Fig. 4a.

Freundlisch adsorption isotherm expressed as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

where, q_e is the amount of Cr(VI) ions adsorbed at equilibrium (mg g^{-1}), C_e is the equilibrium concentration of Cr(VI) ions in solution (mg L^{-1}), K_F and n are Freundlich constant and intensity factors respectively. The values of n and K_F are calculated from slope and intercept of plots of log q_e *versus* log C_e at 20, 30, 40 and 50 ºC, which are shown in Fig. 4b.

The values of Langmuir and Freundlich adsorption isotherm constants and the regression correlation coefficients are given in Table-2. Based on the regression coefficient values these models were used as a fitting criteria to find out the best

TABLE-3
PSEUDO-FIRST-ORDER AND PSEUDO-SECOND-ORDER MODELS FOR THE ADSORPTION OF METAL IONS ON *Syzygium cumini* SEEDS AT 20, 30, 40, 50 °C

Temperature (ºC)	Pseudo first order kinetic model			Pseudo second order kinetic model		
	K_1 (min^{-1})	q_e (mg g^{-1})	R^2	K_2 (g mg^{-1} min^{-1})	q_e (mg g^{-1})	R^2
20	3.102×10^{-2}	74.7343	0.8132	6.941×10^{-5}	114.2857	0.9952
30	9.009×10^{-2}	74.8824	0.9869	3.831×10^{-5}	147.0588	0.9948
40	10.237×10^{-2}	58.229	0.8847	5.437×10^{-5}	148.5884	0.9962
50	9.698×10^{-2}	32.936	0.73512	12.447×10^{-5}	146.8428	0.9999

Based on correlation coefficient values, these results suggests that sorption experiments were best fitted to pseudo-second order model

fitted isotherms. It was observed that the experimental data fits Langmuir adsorption isotherm model ($R^2 = 0.99$) and also indicates the formation of monolayer adsorption.

Sorption kinetics: The kinetics of Cr(VI) sorption onto *Syzygium cumini* seeds sorbent was described by using the pseudo-first order[9] and pseudo second order[10] kinetic models. Two kinetic models have been tested in order to predict the adsorption data of Cr(VI) as a function of time using different concentrations.

Pseudo-first-order kinetic model expressed as:

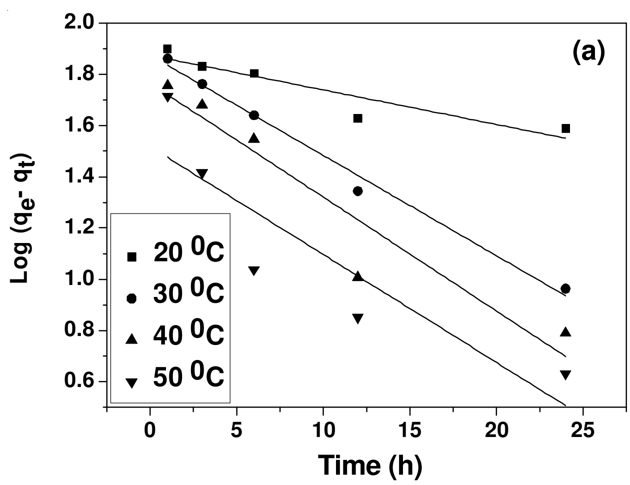
$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303}$$

where, q_e (mg g^{-1}) is the amount of Cr(VI) ions adsorbed at equilibrium, q_t (mg g^{-1}) is the amount of Cr(VI) adsorbed at any time and K_1 (min^{-1}) is the equilibrium rate constant of pseudo-first-order adsorption. The experimental values of K_1 and q_e are evaluated from the slope and intercept, the plot drawn between log (q_e-q_t) *versus t* (Fig. 5a) and are given in Table-3.

Pseudo second order kinetic model expressed as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$$

where, q_e (mg g^{-1}) is the amount of Cr(VI) adsorbed at equilibrium, q_t (mg g^{-1}) is the amount of Cr(VI) ions adsorbed at any time and K_2 (g mg^{-1} min^{-1}) is the equilibrium rate constant of pseudo-second-order kinetics. The experimental values of K_2 and q_e are evaluated from the slope and intercept, the plot drawn between t/q_t *versus* t (Fig. 5b) and are given in Table-3.



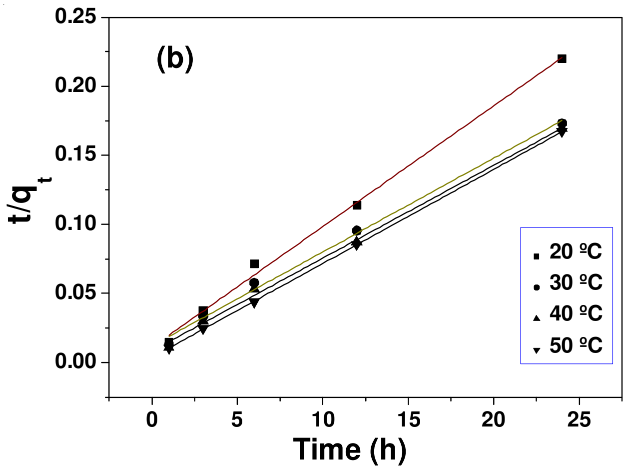


Fig. 5.

Conclusion

Syzygium cumini seeds were collected and grounded in to fine powder. The removal of Cr(VI) ions on biosorbent *Syzygium cumini* seeds was investigated through batch experiments. Experimental evidences suggests that the *Syzygium cumini* seeds to be used as efficient biosorbent for the removal of Cr(VI) ions from the aqueous solution is strongly dependence upon pH, adsorbent dosage, contact time and temperature. The maximum adsorption capacity of Cr(VI) ions on *Syzygium cumini* seeds is 253.16 mg g^{-1} was obtained at optimum pH 2.0 and temperature 50 ºC.

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