Adsorptive Removal of Cr(VI) by *Acinetobacter junii* VITSUKMW3 Immobilized on Coconut Fiber in Batch and Continuous Flow Reactor

MRUDULA PULIMI, JASTIN SAMUEL, CHANDRASEKARAN NATARAJAN and AMITAVA MUKHERJEE*

Centre for Nanobiotechnology, VIT University, Vellore-632 014, India

*Corresponding author: Tel: +91 416 220 2620; E-mail: amitav@vit.ac.in; amit.mookerjee@gmail.com

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The removal of Cr(VI) by the biomass of *Acinetobacter junii* immobilized on coconut fiber in batch and continuous systems were investigated. For batch system under optimized conditions (pH 2; contact time, 480 min; 30 °C; initial Cr(VI) concentration of 50 mg/L), an adsorption capacity of 17.4 mg/g was recorded. In continuous packed bed column reactors, a capacity of 39.4 mg/g was noted with a bed height of 18 cm, a flow rate of 5 mL/min, an initial Cr(VI) concentration of 50 mg/L was employed. The batch sorption data followed the Langmuir isotherm and pseudo first order kinetics. Adsorption studies using Cr(VI) spiked freshwater, ground water and domestic wastewater in a continuous packed bed column reactors demonstrated Cr(VI) removals of 29.3, 43.6, 37.3, 25 %, respectively.

Keywords: Biomass, Coconut fiber, Sorption capacity, Cr(VI) removal.

INTRODUCTION

Hexavalent chromium toxicity has become a major concern today because of its deleterious effect on the environment and health. Anthropogenic sources of chromium(VI) are mainly industrial discharges such as tanneries, electroplating, etc. Its high solubility and permeability through biological membranes has lead to mutagenic and carcinogenic effects¹. Many processes such as precipitation, ion exchange have been in use for the removal of chromium(VI) from the effluents. However, the conventional processes are not cost effective and also generate large quantities of waste. Biosorption of chromium(VI) on low cost materials is gaining considerable popularity as an alternative method for heavy metal ion removal. Several low cost materials such as rice straw, coconut coir, tamarind seeds, wheat bran have been explored for their ability to adsorb chromium(VI)²⁻⁴. Also, cyanobacteria and bacteria have the capability, to remediate metal ions through biosorption⁵ and studies on microorganisms obtained from contaminated wastewater indicate their capability to remove chromium at a high rate^{6,7}. Chromite mine sites in the Sukinda valley, Orissa, India contain a microbial community capable of detoxifying chromium(VI) and tolerating high chromium levels⁸. The chromium(VI) remediation potential by indigenous strains obtained from the Sukinda valley, like *Acinetobacter* sp., has also been reported⁵. Composite systems such as biomass immobilized on activated carbon and zeolite have also been reported to enhance the biosorption capacity⁹⁻¹¹.

In the current study, the biosorption capacity of a composite system consisting of coconut fiber and *Acinetobacter junii* was evaluated. Batch experiments were conducted to investigate the adsorption capacity of chromium(VI) using coconut fiber with the biomass of *Acinetobacter junii*. The effects of different parameters such as the system pH, adsorbent dosage and contact time were examined. The breakthrough curves for adsorption of chromium(VI) at different concentrations, flow rates and bed depth have also been studied. Also, the efficiency of the system in removing chromium(VI) from spiked environmental water matrices was evaluated.

EXPERIMENTAL

Bacterial isolate: Chromium(VI) tolerant bacterial isolate *Acinetobacter junii* VITSUKMW2 (16S rRNA gene sequences JF346549 deposited in GenBank) was grown in molasses media. For the formation of biofilm of *A. junii*, a continuous flow reactor with sterilized coconut fiber was used. The molasses media containing *A. junii* was passed through the column at a flow rate of 2.5 mL/min for 4 days. The resultant biofilm immobilized on coconut fiber was used for batch and column studies.

Analysis of chromium: A colourimetric method was employed to analyze the concentration of chromium(VI) remaining in the solution, before and after sorption. Samples were reacted with complexation reagent, 1,5-diphenylcarbazide at low pH to obtain a purple colour¹². The measurement was carried out at a wavelength of 540 nm. Total Cr was measured at a wavelength

of 359.9 nm using a Flame Atomic Adsorption Spectrophotometer (Analyst400/HGA 900, Perkin Elmer, USA) equipped with a 35 mA chromium hollow cathode lamp.

Batch biosorption studies

Optimization of parameters: Batch studies were conducted for biosorption at an initial chromium(VI) concentration of 50 mg/L and 0.5 g sorbent in 50 mL of metal solution at 30 °C for 24 h at different pH 1.0, 2.0, 4.0, 5.0, 8.0, 10.0 by adding 0.01 N HCl. Effect of contact time was studied at an initial chromium(VI) concentration of 50 mg/L and 0.5 mg sorbent in 50 mL solution at 30 °C and optimized pH. Samples were collected for Cr(VI) at 15, 30, 60, 90, 120, 180, 240, 300, 360, 420, 480, 540, 600, 660, 720 min. Sorption studies at optimized conditions were also carried out with initial Cr(VI) concentrations in the range of 20–200 mg/L. Sorbent dosage was optimized by using sorbent amounts of 5, 10, 20, 30 and 40 g/L in 50 mL of 50 mg/L Cr(VI). The optimization studies were carried out for coconut fiber with and without biomass.

Measurement of batch adsorption capacity, isotherm and kinetics: Metal sorption efficiency of biosorbent was determined by the sorption capacity given as the amount of metal ions adsorbed per unit biosorbent (mg metal ions/g dry biosorbent). Sorption capacity and percentage of biosorption by the biosorbent were obtained by

$$q = \frac{V(C_o - C_e)}{m} \quad (1)$$

$$\text{Biosorption (\%)} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

where q is the sorption capacity in mg/g, V is the solution volume (L), C_o is the initial Cr(VI) concentration in mg/L, C_e is the Cr(VI) concentration at equilibrium and m is the weight of biosorbent (g).

The adsorption equilibrium data at 30 °C were modeled using Langmuir, Freundlich and Dubinin-Radushkevich isotherms to study the mode of interaction of Cr(VI) ions with sorbent when the metal solution phase and sorbent solid phase are in equilibrium.

Pseudo-first order and pseudo-second order models were applied to the sorption data. The model with the highest correlation coefficient value (r^2), close to unity was considered the best fit.

Continuous flow reactor studies: Continuous sorption experiments were conducted in a glass column (0.9 cm internal diameter and 30 cm height), packed with a known quantity of coconut fiber. Inoculum (150 mL) of *A. junii* was given to the column every day for 3 days at 2.5 mL/min. Molasses was pumped through the column at 2.5 mL/min for 3 days until *A. junii* isolate biomass was formed on coconut fiber. Chromium(VI) solution (50 mg/L) was pumped through the column, at desired flow rates using a peristaltic pump. Optimized parameters were used and the Cr(VI) concentration was estimated by diphenyl-carbazide method at different intervals from the sampling point¹². The packed bed reactor study was carried out at pH 2 and 30 °C. The effect of flow rate on Cr(VI) adsorption was studied at flow rates of 2.5, 5 and 10 mL/min at a bed height of 18 cm and initial Cr(VI) concentration of 50 mg/L. Effect

of bed height on sorption of Cr(VI) was evaluated at bed heights of 5, 11 and 18 cm while flow rate and inlet Cr(VI) concentration were constant at 5 mL/min and 50 mg/L, respectively. Effect of influent Cr(VI) concentration on breakthrough point and sorption capacity was studied at influent Cr(VI) concentrations of 25 and 50 mg/L, respectively, at a bed height of 18 cm and a flow rate of 5 mL/min.

Viability test: Viability of the bacteria in biomass grown on coconut fiber before and after interaction with Cr(VI) was determined by colony counts. The biomass was mixed in sterile distilled water and plated on nutrient agar. Also, to examine the release of bacteria during the adsorption process, the effluent was collected and plated on nutrient agar and incubated at 37 °C for 24 h. The clearly visualized colonies were counted¹³.

Treatment of Cr(VI)-spiked environmental water: Water samples from different locations [Ground water (GW1)-Solloor, Ground water (GW2)-Suthipattu, Lake water (LW)-VIT, Wastewater (WW)-VIT] were collected and adsorption experiments were carried out at optimized pH 2, 5 mL/min flow rate, 18 cm bed height of sorbent (Coconut fiber with biomass) and 50 mg/L of influent Cr(VI) concentration.

Statistical analysis: Each set of the experiment was carried out in triplicates (in batch sorption experiments). One-way Anova with Dunnett's post test was carried out using GraphPad Prism 5.0 software to check statistical significance of the results obtained experimentally.

RESULTS AND DISCUSSION

Batch sorption studies

Effect of pH: The pH of solution play a significant role in the sorption of Cr(VI) from the aqueous solution. The effect of pH on the removal of Chromium(VI) is in Fig. 1a. Chromium(VI) removal % of coconut fiber was maximum (90 and 89 %) at pH 1 and 2, respectively and decreased gradually till pH 10 (13.8 %). Optimized pH 2 for coconut fiber is also similar to the previous studies carried on various sorbents such as HDTMA modified coconut coir pith and coir-based adsorbent, puresorbe^{14,15}.

In case of the coconut fiber with biomass, Cr(VI) removal % at pH 1 and 2 were 98.2 and 93 %, which decreased to 33 % at pH 10. The removal % decreased as the pH increased from 2 to 10. Chromium(VI) predominantly exists in the form of monovalent HCrO_4^- at lower pH range of 1–4. Thus, at this pH range the oxyanionic species of Cr(VI) are likely to get adsorbed on the positively charged biosorbent surface¹⁶. Therefore removal of Cr(VI) from aqueous solution was maximum at pH 1–2 and all the further studies on comparative adsorption of Cr(VI) by the selected adsorbents were carried out by maintaining the solution at pH 2. Optimum pH 2 obtained for coconut fiber with biomass is well in agreement with the previous studies¹⁵.

Effect of contact time: The removal % of Cr (VI) by coconut fiber and coconut fiber with biomass increased steadily up to 94 and 100 % respectively as the contact time increased from 15 min to 660 and 480 min respectively (Fig. 1b). The sorption capacity is almost constant beyond 660 and 480 min, which indicates equilibrium conditions due to the lack of active sites left for further sorption. Further experiments were carried

out keeping the optimum contact time as 660 and 480 min for coconut fiber and coconut fiber with biomass, respectively.

Effect of sorbent dosage and initial Cr(VI) concentration: An increase removal % of Cr(VI) on coconut fiber from 65.32 to 100 % and coconut fiber with biomass from 73.6 to 100 % with an increase in sorbent concentration from 5 to 40 g/L (Fig. 1c). This is due to the availability of sorption sites for the metal ion sorption as the sorbent dosage increased¹⁷.

The Cr(VI) removal % of coconut fiber decreased with an increase in Cr(VI) concentration up to 200 mg/L for constant sorbent dosage used (10 g/L) (Fig. 1d), but the Cr(VI) removal capacity increased from 1.9 to 13.04 mg/g. Moreover, a high initial Cr(VI) concentration exerts a driving force to overcome the mass transfer resistance between the solid and the aqueous phase¹⁸.

Batch sorption studies under optimized conditions: Optimized conditions (pH: 2, contact time: 660 min, temperature: 30 °C, initial Cr(VI) concentration: 200 mg/L, sorbent

dosage: 10 g/L) were used to carry out the experiments to evaluate the sorption capacity of coconut fiber, which was measured to be of 9.56 mg/g. The Cr(VI) sorption capacity of coconut fiber with biomass under optimized conditions (pH: 2.0, contact time: 480 min, temperature: 30 °C, initial Cr(VI) concentration: 200 mg/L, sorbent dosage: 10 g/L) are 13.04 mg/g. The increase in the sorption capacity of coconut fiber with biomass compared to coconut fiber alone may be due to increase in the effective binding sites¹⁹. A statistically significant increase in sorption capacity was observed in coconut fiber with biomass compared to coconut fiber alone by One-way Anova and Dunnett's post test ($P < 0.05$). This behavior can be due to the increase of sorption sites for binding due to bacterial biomass present with coconut fiber. The biosorption capacity observed in the current study is high compared to that of the earlier studies carried out using coconut products²⁰⁻²².

Batch adsorption isotherm: Adsorption equilibrium data obtained at 30 °C was modeled using Langmuir, Freundlich

Fig. 1. (a) Effect of pH (b) contact time (c) biosorbent concentration (d) initial Cr(VI) concentration on the sorption capacity of Cr(VI) by coconut fiber and coconut fiber with biomass

and Dubinin-Radushkevich isotherms. Various isotherm parameters were compared (Table-1). The best fit of the model was obtained in the case of Langmuir model for coconut fiber and coconut fiber with biomass based on highest regression coefficient, r^2 (0.97 and 0.93) with q_0 value (10.22 and 14.49 mg/g, respectively). The theoretically quantified sorption capacity from the Langmuir plot was close to the results obtained by sorption experiments. The Langmuir model is based on the surface homogeneity. This suggests that even at the unavailability of sufficient sorption sites as in the case of coconut fiber and coconut fiber with biomass, a monolayer of sorption devoid of interaction between sorbed molecules is highly probable. Removal of Cr(VI) from aqueous solution using coconut tree sawdust activated carbon was reported to follow Langmuir isotherm²¹.

TABLE-1
COMPARISON OF $q_{\max}$ OBTAINED FROM LANGMUIR, FREUNDLICH AND DUBININ-RADUSHKEVICH ADSORPTION ISOTHERMS FOR COCONUT FIBER AND COCONUT FIBER WITH BIOMASS AT OPTIMIZED SORPTION CONDITIONS

Parameter	Coconut fiber	Coconut Fiber with biomass
Langmuir constants		
q_0 (mg/g)	10.220	14.490
b (L/mg)	0.087	0.084
r^2	0.970	0.930
Freundlich constants		
K_f (mg/g)	1.896706	2.202926
n (L/mg)	2.777778	2.398082
r^2	0.92	0.92
D-R constants		
q_D (mg/g)	1.965169	2.37684
B_D (mol ² K/J ²)	2.31E-08	2.96E-08
r^2	0.934	0.9

Batch adsorption kinetics: Pseudo first order and pseudo second order kinetics were applied to the kinetics data obtained. The rate constant values k_1 and k_2 obtained for pseudo first order and pseudo second order are given in Table-2. The correlation coefficient r^2 value suggests that the system fit best, pseudo first order for coconut fiber and coconut fiber with biomass than the second order.

Packed bed reactor sorption studies

Effect of flow rate and bed height: The effect of flow rate on removal of Cr(VI) by coconut fiber with *A. junii* biomass was studied. Fig. 2a shows the breakthrough curves for the sorption of Cr(VI) at different flow rates. It was observed that the breakthrough time decreased from 210 min at 2.5 mL/min to 30 min at 10 mL/min flow rate. The decrease in sorption capacity can be explained by the residence time of metal ion in the column. As the flow rate increases, the breakthrough time is less and the curve becomes steeper. This implies that the residence time for the metal ions inside the column has

decreased resulting in less sorption due to insufficient sorption time. Hence, lower flow rates are ideal for high sorption capacity of the column. Similar reports have been made in packed bed reactor studies using coconut coir pith for Cr(VI) adsorption from electroplating industry²³.

The breakthrough curves for Cr(VI) sorption at different bed heights were studied. The results (Fig. 2b) show that the breakthrough time and sorption capacity increased from 15 min to 100 min and 35.7 mg/g to 39.4 mg/g, respectively. This is mainly due to the higher contact time between metal ions solution and available biosorbent in the reactor and also due to more number of binding sites and ionic groups of biomass available for biosorption of metal ions^{24,25}.

Effect of initial Cr(VI) concentration: The effect of influent Cr(VI) concentration on the breakthrough curves is shown in Fig. 2c. The breakthrough time increased with increasing influent Cr(VI) concentration. Adsorption capacity increased with increasing influent Cr(VI) concentration. This can be explained by the fact that at the greater concentration gradient caused a faster transport due to an increased diffusion coefficient or mass transfer coefficient^{26,27}. The maximum adsorption capacity of coconut fiber with biomass was 39.4 mg/g at 50 mg/L influent Cr(VI) concentration, 18 cm bed height and 5 mL/min flow rate. The increase in sorption may be attributed to high influent Cr(VI) concentration providing higher driving force for the transfer process to overcome the mass transfer resistance²⁸. As the influent Cr(VI) concentration increased from 25 to 50 mg/L, the exhaustion time for coconut fiber with biomass decreased from 315 to 205 min. These results demonstrated that higher initial influent concentrations led to higher driving force for mass transfer. Hence the adsorbent achieved saturation more quickly, which resulted in a decrease of exhaustion time and adsorption zone length^{28,29}. From Fig. 2c it is that the breakthrough curves were sharper as influent Cr(VI) concentration increased, indicating a relatively smaller mass transfer zone and intraparticle diffusion controlled the sorption process²⁸. To the best of our knowledge, the maximum adsorption capacity of 39.4 mg/g at 50 mg/L influent Cr(VI) concentration is the highest reported using coconut fiber so far (Table-3)²⁰⁻²².

Breakthrough curve modeling: For all breakthrough curves, using linear regression analysis, respective values of k_{AB} and N_0 were calculated (Table-4), along with the correlation coefficients (r^2). The values of K_{AB} decreased with the decrease of flow rate and increase of bed height but increased with increasing influent Cr(VI) concentration. It shows that the overall system kinetics were dominated by external mass transfer in the initial part of adsorption in the column³⁰⁻³⁵. The Adams-Bohart model provides a simple and comprehensive approach to conduct and evaluate sorption-column test. However, its validity is to the range of conditions used³¹.

TABLE 2
COMPARISON OF PARAMETERS FOR PSEUDO FIRST ORDER AND PSEUDO SECOND ORDER KINETIC MODELS FOR COCONUT FIBER AND COCONUT FIBER WITH BIOMASS AT OPTIMIZED CONDITIONS

Biosorbent	Pseudo first order			Pseudo second order		
	k_1 (min)	(q_e)	r^2	k_2 (g/mg/min)	(q_e)	r^2
Coconut fiber	0.0009	8.9	0.99	0.00023	9.1	0.97
Coconut fiber with biomass	0.0009	17.4	0.97	0.00014	17.5	0.95

Fig. 2. Effect of (a) flow rate and (b) bed height (c) inlet Cr(VI) concentration in packed bed reactor using coconut fiber with biomass

The relative constants and coefficients were obtained using linear regression analysis (Table-4). It was shown that the Thomas model (r^2 range from 0.89 to 0.952) provided a better fitting than the Adams-Bohart model. It is that, as the flow rate increased, the value of K_{TH} increased while the value of q_0 decreased. The value of K_{TH} decreased with initial influent Cr(VI) concentration increasing. It was attributed to the driving force for adsorption in the concentration difference. Thus, the lower flow rate, higher influent concentration and higher bed depth would increase the adsorption of Cr(VI). The Thomas model was suitable for adsorption process, which indicated that the external and internal diffusions were not the limiting step^{28,32}.

Different statistical parameters of the Yoon-Nelson model were calculated (Table-4). The r^2 values higher than 0.86 indicated the validity of Yoon-Nelson model for the present system. The K_{YN} values and the 50 % breakthrough time s both decreased with increasing bed depth. The value of s decreased as the influent Cr(VI) concentration increased because the saturation of the column occurred more rapidly³³. On the other hand, with the increase in the bed height, the values of K_{YN} decreased and the values of s increased. In a comparison of values of r^2 , both the Thomas and Yoon-Nelson models can be used to predict adsorption performance for adsorption of Cr(VI) in a packed bed reactor.

Packed bed reactor studies with Cr(IV)-spiked water:

Adsorption of Cr(VI) by coconut fiber with biomass from different environmental water matrices spiked with 50 mg/L Cr(VI) were studied (Table-5). In GW1 and GW2, 43.6 and 37.3 % of Cr(VI) was removed by coconut fiber with biomass with adsorption capacity of 21.3 and 18.18 mg/g which is less than the adsorption capacity in de-ionized water matrix (39.4 mg/g). In LW and WW, 14.28 and 10.78 mg/g adsorption capacity of Cr(VI) at 29.3 and 25 % were removed by coconut fiber with biomass respectively. This suggests the application of coconut fiber with biomass for treating Cr(VI) in different environmental water matrices.

Viability test: The counts of viable cells in biomass grown on coconut fiber before and after Cr(VI) interaction were in the range of 3.4×10^9 cfu/mL and 3.1×10^9 cfu/mL respectively. This explicates that the viability decreased as 0.3×10^9 cfu/mL cells were not viable after interaction with Cr(VI) in continuous flow reactor.

Conclusion

Coconut fiber with *A. junii* biomass is an effective sorbent for chromium(VI) removal from contaminated waters. The

TABLE-3
COMPARATIVE SORPTION CAPACITIES OF COCONUT-BASED BIOSORBENTS FOR THE REMOVAL OF CHROMIUM(VI) FROM WATER. THE CURRENT STUDY SHOWS HIGHEST ADSORPTION CAPACITY ACHIEVED

S. No.	Adsorbent	Adsorbate	Adsorption Capacity (mg/g)	Reference
1	Coconut shell fibers activated carbon (ATFAC)	Cr(III)	12.2	20
2	Coconut tree sawdust	Cr(VI)	3.46	21
3	Coconut shell charcoal (CSC)	Cr(VI)	10.88	22
4	Coconut shell charcoal (CSC) oxidized with sulfuric acid	Cr(VI)	4.05	22
5	Non-treated CSC coated with chitosan	Cr(VI)	3.65	22
6	Amine-modified polyacrylamide-grafted coconut coir pith	Cr(VI)	12.43	34
7	Coconut coir	Cr(VI)	6.3-26.8	2
8	Sulphuric acid treated coconut shell activated carbon	Cr(VI)	8.42	35
9	Coconut Fiber with <i>Acinetobacter junii</i>	Cr(VI)	39.4	Current study

TABLE-4
PARAMETERS OF THOMAS, YOON-NELSON AND ADAMS-BOHART MODEL
UNDER DIFFERENT CONDITIONS USING LINEAR REGRESSION ANALYSIS

Height (cm)	Flow rate (mL/min)	C ₀ (mg/L)	Thomas model			Yoon-Nelson model			Adams-Bohart model		
			Q _e	K _{th}	R ²	K _{yn}	T	R ²	K _{ab}	N ₀	R ²
5	5.0	50	38.96	1.42	0.97	0.069	47.53	0.97	1.12	4.70	0.890
11	5.0	50	27.42	1.10	0.95	0.048	70.00	0.95	0.88	2.98	0.860
18	5.0	50	44.23	0.57	0.97	0.028	176.92	0.97	0.39	5.34	0.890
18	2.5	50	35.23	0.62	0.99	0.031	281.87	0.99	0.47	3.77	0.957
18	5.0	50	44.23	0.57	0.97	0.028	176.92	0.97	0.39	5.34	0.890
18	10.0	50	41.89	0.86	0.99	0.043	83.72	0.99	0.38	6.87	0.840
18	5.0	25	58.82	0.61	0.99	0.030	235.29	0.98	8.72	0.26	0.950

TABLE-5
CHROMIUM(VI) ADSORPTION BY COCONUT FIBER WITH BIOMASS FROM Cr(VI)
SPIKED DIFFERENT WATER MATRICES IN PACKED BED REACTOR

Sample	Flow rate (mL/min)	Mass of adsorbent (g)	Bed height (cm)	C ₀ (mg/L)	q _e (mg/g)	% Cr(VI) removal	t _b	t _c
Ground Water 1	5	1	18	50	21.3	43.6	45	135
Ground Water 2	5	1	18	50	18.18	37.3	40	110
Waste Water	5	1	18	50	10.78	25	10	70
Lake Water	5	1	18	50	14.28	29.3	25	95

Cr(VI) adsorption by coconut fiber with biomass had an advantage compared to the coconut fiber alone. The advantages of enhanced biosorption potential can be effectively exploited in packed columns for large scale continuous applications for contaminated sites.

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