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Application of *Citrullus lanatus* rind as biosorbent (CrossMark for removal of trivalent chromium from aqueous

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KEYWORDS

Watermelon rind; Chromium; Adsorption; Kinetics; Isotherms **Abstract** Watermelon rind (WR) an agro waste was evaluated as an adsorbent for the removal of Cr^{3+} ions from aqueous solution. Batch mode adsorption studies were performed by varying parameters such as pH, contact time, adsorbent dose and initial metal ion concentration. Maximum loading capacity of WR was found to be 172.6 mg g⁻¹ for Cr³⁺ ions at pH 3. Kinetic studies show that removal of Cr³⁺ ions is rapid and follows a pseudosecond order model. Equilibrium data fit better with the Langmuir isotherm than the Freundlich isotherm. Thermodynamic parameters such as ΔG° , ΔH° and ΔS° were derived for the current system. The negative values of ΔG° show that the nature of sorption process is spontaneous. FTIR studies reveal that hydroxyl and carboxyl groups were responsible for uptake of metal ions. Successive desorption of Cr³⁺ ions reveals that WR can be an economical sorbent for the removal of heavy metals from aqueous solution. The results conclude that watermelon rind an agro waste can effectively be used for the removal of chromium ions from aqueous solution.

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1. Introduction

Chromium is considered as one of the toxic heavy metal ions which has adverse effects on human and aquatic life. Many treatment processes such as precipitation, ion exchange, filtration, membrane filtration, electrochemical treatment and reverse osmosis are available [1,2]. However these conventional techniques have many disadvantages such as less efficiency, high treatment and disposal costs [3]. Adsorption is a

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more efficient and cost effective technique for the removal of heavy metals from wastewater. Many agricultural wastes have been used as effective and low cost adsorbents for the removal of heavy metals from wastewater. Many of the fruit peels and seeds such as banana peel [4,5], mango [6], orange peel [7,8], citrus peel [9], jackfruit peel [10], pomegranate peel [11], and pine fruit coat [12] are used as effective sorbents for the removal of heavy metals from aqueous solution.

Watermelon (*Citrullus lanatus*) being the largest and heaviest fruit is one of the most abundant and cheap fruits available in India with an average production of 3 million tons per year. Watermelon constitutes 6–7% of overall fruit production and

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is high during summer. In watermelon red flesh present inside is sweet, edible and used for juices and salads but the outer rind is considered as waste which has no commercial value [13]. Watermelon rind consists of pectin, citrulline, cellulose, proteins and carotenoids [14-16]. These polymers are rich in functional groups such as hydroxyl (cellulose) and carboxyl (pectin) and can easily bind metal ions. In our earlier reports, we have investigated watermelon rind as economical sorbent for the removal of cationic dyes, Cd, Ni and Co from aqueous solution [17–19]. The present study investigates the potential use of watermelon rind as a cost effective adsorbent for the removal of Chromium (III) ions from aqueous solution through batch mode adsorption studies. Batch mode adsorption studies were conducted by varying the parameters such as pH, contact time, adsorbent dosage and initial metal ion concentration. The equilibrium adsorption data were fitted to the Langmuir and Freundlich isotherms. Kinetic data were fitted to pseudofirst order, pseudosecond order kinetic models and intra-particle diffusion model. Desorption studies were employed in order to assess the practical utility of WR.

2. Materials and methods

2.1. Preparation of adsorbent

Watermelon rinds (WR) were obtained from a local fruit market and washed under tap water several times followed by double distilled water. After thorough washing it was cut into small pieces and dried under sun light for 7 days to remove all moisture present. Later the dried pieces were washed with hot water (70 °C) to remove any soluble matter present and dried in an oven at 85 °C for 48 h. The oven dried WR was powdered using conventional mixer and sieved through 100 mesh range. The sieved powder was stored in desiccators and used for batch experiments.

2.2. Preparation of synthetic stock solutions

The stock solution of Cr^{3+} was prepared by dissolving chromium nitrate salts in deionised water. pH adjustments were done using 0.1 M HCl and 0.1 M NaOH solutions. All reagents were of AR grade and deionised water was used for dilutions. Each experiment was repeated twice and average values have been reported.

2.3. Batch mode adsorption studies

Batch experiments were conducted at room temperature in orbital shaker at 150 rpm using 100 ml conical flasks. Effect of pH was evaluated by varying pH from 2–8 using 0.1 M HCl and 0.1 M NaOH for adjustments. The contact time was varied between 10 and 120 min to study the effect of time on sorption and adsorbent dosage was varied from 0.5 g L⁻¹ to 5 g L⁻¹ for 30 min to learn the effect of dosage while rest of the parameters were kept constant for each parameter studies. Sorption capacity of WR was determined by contacting 1.5 g L⁻¹ with 20 ml of known concentration of metal solution (50–300 ppm). The solid phase was separated using 0.45 µm filter paper and the residual metal concentration spectro-photometer (AAS).

2.4. Instrumentation

Flame atomic absorption spectrophotometer (Varian, AA240) equipped with air/acetylene burner was used to determine the residual concentration of Cr^{3+} ions. FTIR spectroscopy (Thermo Nicolet, AVATAR 330) was used to identify the functional groups present in the WR. FTIR spectra of WR alone and metal loaded WR was recorded in mid IR region in the range of 4000 to 400 cm⁻¹ by KBr pellet method. Scanning electron microscope (Phillips XL30, Netherlands) equipped with electron dispersive X-ray was used to confirm the adsorption of Cr ions onto WR. pH meter (Seven easy pH, Metller Toledo) was used to monitor and adjust the pH of the solutions.

2.5. Desorption studies

To investigate the possibilities of repeated use of the adsorbent, desorption and regeneration experiments were also conducted. Metal loaded WR sorbent (0.1 g) was shaken with 20 ml of 0.1 M HCl, 0.1 M NaOH and water as the desorbing agents in 100 ml conical flask at 150 rpm for 30 min at room temperature. The centrifuged supernatant was analyzed for metal ion detection and metal desorbed WR was used as a regenerated sorbent in four repeated cycles to determine the reusability potential of adsorbent.

3. Results and discussions

3.1. Preliminary adsorption studies

3.1.1. Effect of pH

The solution pH is considered as a very important parameter in adsorption process. The functional groups responsible for binding of metals ions in the adsorbent are affected by pH. It also affects the competition of metal ion that get adsorb to the active sites of adsorbent. The pH optimization was done by varying the pH in the range of 2–8 for Cr³⁺ ions. It was found that maximum removal of Cr3+ ions was established in the range of pH 2-3 and further increase in pH beyond pH 6 resulted in the formation of precipitation. After the completion of each batch process, there was a slender decrease in the final pH (pH 2.8) of the solution. This can be attributed to exchange and release of H⁺ ions from functional groups such as hydroxyl and carboxyl groups of WR. It is extensively reported in the literature that Cr³⁺ ions exist predominantly up to pH 3 beyond which several hydroxides start precipitating based on the acidity. Hence, further batch experiments were operated at pH 3 with the help of 0.1 M HCl solution.

3.1.2. Effect of adsorbent dosage

Adsorbent dosage is one of the important parameters studied while conducting batch mode studies. The effect of adsorbent dosage on the removal of Cr^{3+} ions was studied by varying dosage from 0.5 g L⁻¹ to 5 g L⁻¹. From our results it was found that adsorption was highly dependent on adsorbent concentration and it increased with increase in adsorbent dosage. Maximum removal efficiency of 90.8% for Cr^{3+} ions (50 ppm) was observed at 1.5 g L^{-1} of dose respectively. Further increase in dose resulted in decrease in loading capacity and

removal efficiency was found to be same. Increase in adsorption by an increase in adsorbent dose is due to the availability of more number of active sites on surface and the decrease in efficiency at a higher concentration of an adsorbent is due to the decrease in surface active sites by consequence of partial aggregation of adsorbent.

3.2. Adsorption kinetics studies

Contact time plays an important role in affecting efficiency of adsorption. In order to optimize the contact times for the maximum uptake of metal ions, contact time was varied from 10 to 120 min. Results show that adsorption of Cr^{3+} ions onto WR is rapid and equilibrium is established within 30 min. Hence, a contact time of 30 min was fixed for further experiments.

The experimental data were fitted into two well known kinetic models such as pseudofirst order and pseudosecond order kinetic equations to understand the mechanism of adsorption. The pseudofirst order rate equation of Lagergren is represented as

$$ln(q_e - q_t) = lnq_e - k_1 t \tag{1}$$

where q_e is the amount of metal adsorbed at equilibrium (mg g⁻¹), q_t is the amount of metal adsorbed at time t and k_1 is the first order reaction rate constant. A straight line of ln (q_e-q_t) versus t suggests the applicability of this kinetic model and values of k_1 and q_e were determined from the plot. Based on the sorption equilibrium capacity pseudosecond order equation can be expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{2}$$

where k_2 (g mg⁻¹ min⁻¹) is the rate constant of pseudosecond order adsorption. The plot of t/qt versus t is shown in Fig. 1 and values of k_2 and q_e can be calculated from the plot. The values and correlation coefficients calculated from pseudofirst order and pseudosecond order are represented in Table 1.

From Table 1 it is seen that correlation coefficient of pseudofirst order kinetic model is low and the theoretical q_e values are also not close to the experimental values. It was observed that experimental data fit better to pseudosecond order kinetic model. The better fit is supported by its correla-



Figure 1 Plot of pseudo second order kinetic model for the removal of Cr ions from aqueous solution by WR.

tion coefficients. The theoretical q_e values were also close to the experimental values. These observations suggest that removal of Cr^{3+} ions onto WR from aqueous solution follows pseudo-second order reaction suggesting that the process controlling the rate may be a chemical sorption involving valences forces through sharing or exchanging of electrons between sorbate and sorbent.

Kinetic data were further analyzed using intraparticle diffusion model in order to study the steps of diffusion mechanisms. The intraparticle diffusion equation can be written as

$$q_t = k_{\rm int} t^{1/2} + C \tag{3}$$

where k_{int} is the intraparticle diffusion rate constant and C is the intercept related to the thickness of the boundary layer. According to Eq. (3) a plot of q_t versus $t^{1/2}$ should give a straight line if the adsorption mechanism follows intraparticle diffusion process only and if the plots show multi linear plots, it indicates that two or more steps take place. It is clear from the figure (Fig. 2) that there are two separate zones present. The first linear plot is due to the immediate utilization of ample active sites on the adsorbent surface and the second linear plot attributed to very slow diffusion of the adsorbate from the surface site into the inner pores [20]. Thus initial adsorption of Cr^{3+} by WR may be governed by intraparticle transport of surface diffusion and later part controlled by pore diffusion [21]. However the intercept of the line fails to pass through the origin which may attribute to the difference in the rate of mass transfer in the initial and final stages of adsorption [22].

3.3. Adsorption isotherms

At equilibrium, sorbent was allowed to contact with varying concentrations (50–300 ppm) of Cr^{3+} ions to evaluate the maximum loading capacity of WR. It was observed that metal loading capacity increased with increase in initial metal ion concentration. In order to examine the relationship between concentration of metal ion at equilibrium (C_e) and metal loading capacity (q_e) equilibrium data were analyzed with Freundlich and the Langmuir isotherms. The linear form of Freundlich adsorption isotherm is given as

$$logq_e = logK_f + \frac{1}{n}logC_e \tag{4}$$

where K_f and *n* are Freundlich constants denoting distribution coefficient and intensity, respectively. If Eq. (6) applies, a plot of log q_e versus log C_e will give a straight line.

The linear form of Langmuir equation after rearrangement is given as

$$\frac{C_e}{q_e} = \frac{1}{bV_m} + \frac{C_e}{V_m} \tag{5}$$

where C_e is the concentration of metal solution at equilibrium (mg^{-1}) , qe is the amount of metal adsorbed per mass unit of adsorbent $(mg g^{-1})$, V_m is the amount of adsorbate at complete monolayer coverage $(mg g^{-1})$, and b is a constant that relates to the heat of adsorption $(L mg^{-1})$. If the biosorption follows Langmuir isotherm then a plot of C_e/q_e should be a straight line with slope $1/V_m$ and intercept $1/bV_m$.

The results of Freundlich and Langmuir isotherm constants are given in Table 2. The equilibrium data for adsorption of

Table 1 Kinetic parameters of pseudofirst order and pseudosecond order expressions (pH 3, dose 1.5 g L^{-1} , initial metal ion concentration 50 mg L⁻¹ and temperature 303 K).

Metal ions	Experimental $q_e \ (\text{mg g}^{-1})$	Pseudofirst order constants			Pseudosecond order constants		
		$q_e (\mathrm{mg \ g}^{-1})$	$k_1 ({\rm min}^{-1})$	R^2	$q_e \ (\mathrm{mg \ g}^{-1})$	$k_2 (g mg^{-1} min^{-1})$	R^2
Cr ³⁺	28.406	3.451	-0.0039	0.914	28.57	0.306	0.999



Figure 2 Weber and Morris plot for the removal of Cr ions from aqueous solution by WR.

 Cr^{3+} ions onto WR fit better to Langmuir isotherm than the Freundlich model (Fig. 3). The correlation coefficient of Freundlich isotherm is found to be low, which suggests that the Freundlich isotherm might not be applicable to present system. The correlation coefficient of Langmuir isotherm was very close to one which suggests that Langmuir model fits better for adsorption of Cr^{3+} ions onto WR. The theoretical monolayer coverage (V_m) of Cr^{3+} ions onto WR was calculated as 175.4 mg g⁻¹, respectively against 172.63 mg g⁻¹ found experimentally. Based on the Langmuir monolayer coverage the loading capacity of WR was found to be higher than many other agricultural wastes reported in the literature (Table 3).

The essential feature of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor; R_L that is used to predict whether an adsorption system is "favorable" or "unfavorable" and is defined as

$$R_L = \frac{1}{1 + bC_e} \tag{6}$$

where C_e (mg L⁻¹) is the equilibrium concentration of metal ions and *b* (mL mg⁻¹) is the Langmuir isotherm constant. The adsorption process as a function of R_L may be described as $R_L > 1$; unfavorable, and $0 < R_L < 1$; favorable, linear



Figure 3 Plot of Langmuir isotherm model for the removal of Cr from aqueous solution by WR.

Table 3 R_L values for the removal of Cr ionsfrom aqueous solution.				
Initial concentration of Cr ion	R_L values			
50	0.782			
100	0.657			
150	0.531			
200	0.485			
250	0.460			
300	0.398			

and irreversible for $R_L = 1$ and 0 respectively, The values of R_L calculated for different initial concentrations of Cr^{3+} ions are given in Table 4. R_L is in the range of 0–1 for Cr^{3+} ions at different initial concentrations confirm the favorable uptake sorption process.

3.4. Thermodynamics of adsorption

In order to describe the thermodynamic behavior of sorption of Cr^{3+} ions onto WR, at equilibrium, temperature was varied from 303 K to 323 K. Thermodynamic parameters including change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were derived from the following equations:

Table 2 Freundlich and Langmuir isotherm constants obtained for the removal of Cr ions from aqueous solution by WR (pH 3, dose 1.5 g L^{-1} , time 30 min and temperature 303 K).

Metal ions	Freundlich isotherm model			Langmuir isotherm model		
	K _f	1/ <i>n</i>	R^2	$V_M (\mathrm{mg}\mathrm{g}^{-1})$	$b (L mg^{-1})$	R^2
Cr ³⁺	22.54	0.11	0.9894	175.4	0.037	0.9989

Table 4 Comparison of loading capacity (q_e) of WR with other agro sorbents.

Biosorbent	Loading capacity (q_e)	Refs.	
Neem sawdust	58.82	[23]	
Gular fruit	23.1	[24]	
Waste crab shell	22.9	[25]	
Banana peel	131.56	[5]	
Tea factory waste	54.65	[26]	
Tamarind hull	70	[27]	
Corn cob waste	84.54	[28]	
Orange peel	9.43	[29]	
Watermelon rind	172.6	This study	

Table 5 Thermodynamic parameters derived from removal of Cr^{3+} ions from aqueous solution by WR. (pH 3, dose 1.5 g L⁻¹, time 30 min and initial metal ion concentration 50 mg L⁻¹).

Temperature	ΔG°	ΔH°	ΔS°
(K)	$(kJ mol^{-1})$	(kJ mol ⁻¹)	$(J mol^{-1} K^{-1})$
303	-3330.3	-3741.5	-582.4
313	-2234.3		
323	-2165.5		

$$K_D = \frac{q_e}{C_e} \tag{7}$$

$$\Delta G^{\circ} = -RT \ln K_D \tag{8}$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} \tag{9}$$

where K_D is the equilibrium constant related to the Langmuir constant 'b', R is the universal gas constant (8.314 J Mol⁻¹ K⁻¹) and T is temperature in Kelvin.

The thermodynamic parameters calculated for the present systems are presented in Table 5. The calculated ΔG° values of Cr^{3+} ions were found to be negative which indicates the spontaneous nature of adsorption onto WR. The decrease in negative values of ΔG° with increase in temperature expresses that the removal process is less spontaneous at high temperature. The negative values of ΔH° indicate exothermic process and negative ΔS° values indicate the decrease in the randomness of solid–liquid interface during the sorption.

3.5. Possible adsorption mechanisms

3.5.1. FTIR analysis

The pattern of adsorption of metals onto plant materials is attributable to the active groups and bonds present on them [30]. In order to identify the major functional groups present in WR preliminary quantitative analysis was done with FTIR spectroscopy. FTIR spectra (Fig. 4) of WR displayed a number of peaks pertaining to different functional groups. The broad and intense peak around 3371 cm^{-1} corresponds to -OH stretching vibrations of cellulose, pectin and lignin and peaks at 2917 cm⁻¹ attributes to -CH stretching vibrations of methyl and methoxy groups [6]. A peak at 1734 cm⁻¹ corresponds to -C=O stretching of carboxylic acid or esters and

asymmetric and symmetric vibrations of ionic carboxylic groups (-COO-) respectively appeared at 1633, and 1423 cm^{-1} . The peak at 1383 cm⁻¹ may be assigned to symmetric stretching of -COO- of pectin. The peaks from 1300 to 1000 cm⁻¹ can be assigned to stretching vibrations of carboxylic acids and alcohols. It is well indicated from FTIR spectrum of WR that carboxylic and hydroxyl groups are present in abundance and as biopolymers these groups act as proton donors. Hence deprotonated carboxyl and hydroxyl groups may be involved in coordination with metal ions.

FTIR spectra of metal (Cr^{3+})-sorbed WR showed slight or marginal peak shifts respectively from 3371, 2917, 1734, 1633, 1423, 1323 and 1062 cm⁻¹ to 3407, 2917, 1736, 1621, 1417, 1327 and 1066 cm⁻¹ due to Cr^{3+} ions sorption. These shifts may be attributed to changes in counter ions associated with carboxylate and hydroxylate ions suggesting that acidic groups, carboxyl and hydroxyl groups are predominant contributors in metal uptake.

3.5.2. EDX

Elemental analysis of metal laden WR was carried out in order to confirm the sorption of Cr onto WR. Electron dispersive X-ray analysis of WR before and after Cr sorption is shown in Fig. 5. The EDX pattern of WR before sorption shows the presence of K^+ and Mg^{2+} ions while after sorption the disappearance of K^+ and Mg^{2+} signals and presence of Cr^{3+} signals are evidenced. This can be attributed to ionexchange mechanism for sorption of Cr^{3+} ions onto WR. The vacant sites generated due to desorption of K^+ and Mg^{2+} ions are occupied by Cr^{3+} ions.

3.6. Desorption and regeneration of WR

Desorption and regeneration of the biosorbent is of crucial importance in assessing its potential for commercial applications. In order to make the sorption process most economical, desorption and regeneration potential of WR was investigated four times using 0.1 M HCl, 0.1 M NaOH and water as desorbing agents for 30 min. The desorbed acidic solution was subjected to Atomic Absorption Spectrometer to determine the metal concentration. It was observed that 0.1 M NaOH shows higher desorption percentage compared to that of 0.1 M HCl and water. Desorption of Cr³⁺ ions from the metal loaded WR resulted in 98.7% metal recovery for first cycle by 0.1 M NaOH. The efficiency remained almost unchanged during four repeated adsorption-desorption cycles. These results reveal that WR can be potential adsorbent for the removal of Cr³⁺ ions from aqueous solution in multiple cycles.

3.7. Treatment of tannery effluents by WR

The applicability of watermelon rind for the removal of Cr^{3+} ions from tannery effluents collected from SIPCOT industrial area, Ranipet, Tamil nadu, India was investigated. The effluents were passed through whatman filters (grade-I) to remove the solid sediments present in the solution and the physical-chemical properties of effluent are presented in Table 6. The effluent was diluted to 10 times with distilled water and pH of the solution was adjusted to pH 3. To different aliquots of 50 ml effluent solutions, WR dose was varied and agitated



Figure 4 FTIR of a) native watermelon rind and b) Cr metal ion loaded watermelon rind.



Figure 5 EDX profile of Cr loaded WR.

 Table 6
 The physical-chemical properties of tannery effluent used in the present study.

Parameter	Characteristics
pН	6.7
COD	109 mg L^{-1}
BOD	$12 \text{ mg } \text{L}^{-1}$
Turbidity	160 NTU
TDS	9521 mg L^{-1}
Chloride	$1642 \text{ mg } \text{L}^{-1}$
Sulfate	76 mg L^{-1}
Nitrate	$85 \text{ mg } \text{L}^{-1}$
Sodium	4452 mg L^{-1}
Potassium	562 mg L^{-1}
Chromium	38 mg L^{-1}

in orbital shaker for 30 min and resulting supernatant solution was subjected to AAS for residual concentration of Cr^{3+} ions. It was observed that removal efficiency increased with increase in adsorbent dose (0.5–5 g L⁻¹) and maximum removal efficiency was observed at 1.5 g L⁻¹ of dose. However the removal efficiency of WR for Cr^{3+} from tannery effluent was found to be 77% compared to that of 90.8% from synthetic solutions.

Table 7 Effect of presence of co cations on sorption of Cr^{3+} ions from aqueous solution by WR (at dose 1.5 g L⁻¹; time 30 min; initial metal concentration 50 mg L⁻¹; temperature 303 K).

pН	% Remov	% Removal of metal ions					
	Cr ³⁺	Cd^{2+}	Ni ²⁺	Cu^{2+}	Fe ²⁺		
2	89.2	22.7	5.6	4.1	20.3		
3	89.9	40.2	10.6	12.5	21.5		
4	64.2	70.5	41.4	39.5	24.2		
5	43.8	87.6	56.3	51.7	40.6		
6	23.1	85.5	56.9	53.4	37.6		
7	21.5	83.9	51.7	51.2	34.6		

The decrease in efficiency is due to the presence of other cocations and complex forming anions in the effluents. Further multimetal sorption studies were performed to access the capability of WR to adsorb Cr^{3+} ions in the presence of other cations. It was observed that sorption of Cr^{3+} ions was superior at pH 3 and then decrease with increase in pH from 2–7 (Table 7). At pH 3, Cr^{3+} ions were found to be the predominant adsorbate compared to other co-cations. This can be attributed to metal speciation occurring with respect to solution pH. These results reveal the capability of WR for sorption of Cr^{3+} ions from effluents in the presence of other co-cations.

4. Conclusions

Watermelon rind was evaluated as economical sorbent for the removal of Cr^{3+} from aqueous solutions. The removal was found to be rapid and equilibrium been reached within 30 min and follows pseudosecond order kinetic model. The equilibrium data fit better with Langmuir isotherm model. EDX analysis confirms the adsorption of chromium onto WR. Desorption studies reveal that WR can be used for coupled of cycles without any decrease in efficiency. Hence, these observations suggest that watermelon rind can be used as a non hazardous agro material for the removal of Cr^{3+} ions from aqueous solutions.

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