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Chitosan Based a New Bio-Composite Adsorbent for the Removal of Cr (VI) from Aqueous Solution

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ABSTRACT

This study reports the preparation of glutaraldehyde crosslinked chitosan coated Rosehip (Rosa canina) seed shell (Cth/RS) capsules. Cth/RS was used in batch experiments to evaluate the adsorption of Cr (VI) ions. The effect of adsorbent dose, Cr (VI) concentration, time, initial solution pH on adsorption was also investigated. Adsorption equilibrium was achieved in 90 min. and maximum removal of Cr(VI) was demonstrated at pH value of 2.0. Cth/RS was characterized by FTIR analysis. The equilibrium adsorption data were described by Langmuir, Freundlich, Scatchard and D-R isotherms.Adsorption parameters (k, n, As, Kb, Xm, K, E) were calculated from these isotherms. The data were fitted to the Langmuir adsorption isotherm. The maximum capacity of Cth/RS was determined to 34.13 mg/g. Cth/RS showed high adsorption capacity for Cr (VI) ions. The pseudo-first and pseudo-second orders equation were used to evaluate the kinetic data and the constants are determined. The experimental results suggest that the Cth/RS capsules are effective for the adsorption of Cr (VI) ions.

Keywords: *chitosan, glutaraldehyde, Rosehip seed shell, chromium, isotherms, equilibrium*

INTRODUCTION

Today, environmental pollution due to human activities in industrial, mining and agricultural areas has become a global problem. Heavy metals, pesticides, organic and radioactive wastes have an important place among the water pollutants [1]. Toxic substances, even at low concentrations in water, can cause serious illnesses or even death if they cause serious harm to human health. Copper, lead, cadmium, mercury, arsenic, chromium, cobalt, etc. which are called "heavy metals" and can be found in wastewater in small amounts [2,3].

Cr (VI) in closed chemicals are a danger to people with related to the heart and blood vessels), (an organ that creates urine), liver and skin sicknesses [4]. The admissible amount for Cr (VI) in drinking water is 0.05 mg/L and 0.1 mg/L for industrial water. There are many techniques to Cr (VI) adsorption from wastewater such as chemical oxidation, ion exchange, membrane separation, reverses osmosis and adsorption [5,6]. Adsorption from these techniques is the most preferred treatment method because of its ease of use, effective purification, low cost and environment friendliness. High adsorption capacity, low cost, high adsorption rate and reusability should be considered when selecting the adsorbent. Adsorbent materials have been studied for their ability to remove heavy metals and originate from natural materials and biological waste.

In recent times, many researchers have been achieved on the sufficient elimination of Cr (VI) from wastewater applying natural biomasses such as Sterculiaguttata shell [7], gulmohar's fruit shell [8], mangrove leaf powder [9], Longan seed [10], garlic stem and horse chestnut shell [11], Juniperusprocera sawdust, avocado kernel seeds and papaya peels [12], etc. Most of these biomaterials consist of functional groups combined with polysaccharides, proteins, lignin, cellulose, and hemi cellulose as major components. Cr(VI) uptake process is united with these functional groups. The search for substituted advanced, cheap, eco-friendly, sufficient biomass to replace the economically available biomass is continuing. However, adsorption capacity of crude agricultural by-products is low in general. Chemical modification or composite forms have shown great promise in improving the adsorption capacity of agricultural by-products [13,14]. Rosehip has become a fruit that has been demanded by consumers in recent years in terms of natural antioxidants that are beneficial for human health [15]. The rate of fresh rosehip fruit is between 60-70% fruit pulp and 30-40% is composed of seeds. Rosehip fruit flesh is evaluated by processing different products, most of the time seeds are separated into waste [16].

In this research, a novel combination of composite material (Cts/RS) was synthesized and it was applied applied to remove Cr (VI) from the prepared synthetic solution by changing lot of parameters such as pH, interaction time, adsorbent dosage and the initial concentration of Cr (VI) in the solution phase.

MATERIALS AND METHODS

Materials

Chitosan flakes (degree of deacetylation, DD=75-85%) was obtained from (Sigma-Aldrich). All other chemicals were purchased from Merck Company. The pH of the solution was adjusted by mixing the appropriate amount of 0.1 M (HCl/NaOH). A stock solution of Cr (VI) with a concentration of 1000 ppm was prepared by dissolving $K_2Cr_2O_7$ in distilled water. UV-Visible Spectrophotometer (Schmadzu UV-1700) was used for the exploration of Cr(VI) amount in standard and treated solutions. pH meter (Orion 900S2) with a glass electrode and an internal reference electrode was implemented for pH measurements. Thermo stated shaker of GFL 3033 model was applied for shaking of the solutions in adsorption experiments. The FTIR spectrum was reported by a Bruker VERTEX 70 FT-IR spectrometer.

Preparation of Raw Material

The RS were obtained from the market in Konya, Turkey and they were applied for the separation of Cr (VI) as adsorbents. They were purified by using pure water numerous times to eliminate the surface impurities.

After that, the solution was dried at 60 °C for 24 h. Seeds was crushed to increase the surface area and sieved into a particle size of nearly 125 μm (called ‘RS’). The biomass was washed with distilled water and 0.1 M HCl several times, and then it was air-dried. The obtained biomass was reserved in a desiccant and then used to preparation of Cts/RS.

Preparation of Cts/RS

3 g of chitosan were mixed with 300 ml of a 2% acetic acid solution in a magnetic stirrer until the chitosan gel was gelled and after mixing with 3 g of RS, the mixture was stirred for about 1 hour using magnetic stirrer. The porous agglomerated particles were then prepared by drop-wise addition of slurry mixture into a 5% NaOH precipitation bath. The particle formation in the spheres was observed by adjusting the height of the droplets and the particle radius in the solution phase.

Then, the agglomerated beads were washed with pure water until the pH was neutral. Beads were treated with glutaraldehyde to increase the strength by forming a covalent bond with the chitosan in the structure.

Same time the number of functional groups in the structure has increased. The beads were reacted with 3 ml glutaraldehyde in an oven at 60-70 °C for 30 minutes to form a covalent bond with chitosan and the number of functional groups in the structure of adsorbent was increased and then the beadswere dried at 60 °C for 24 h then stored in a desiccator.

Adsorption Studies

The batch method was used to perform an adsorption experiment. In 100 mL Erlenmeyer flask 10 mL of Cr (VI) ion solution was taken at constant pH and 4 g/L of Cts/RS was added and allowed to shake for 1 hours at 150 rpm. After equilibrium was obtained, the filtrate was analyzed for Cr (VI) concentration using a UV-Vis. Percent adsorption of metal ions was calculated as in equation (1) below [17]:

$$\%\ Adsorption = \frac{C_i - C_f}{C_i} \times 100 \qquad (1)$$

$$Adsorption\ Capacity = \frac{C_i - C_f}{m} \times V \qquad (2)$$

where C_i and $C_f$are the initial and final Cr (VI) concentrations, respectively. The adsorption capacity per unit mass of adsorbent (q_e) was calculated using the equation (2).

The determination of functional groups present in the adsorbent was realized by A Fourier transform infrared spectrometer (FT-IR). Fig. 1 show some functional groups in RS and Cts/RSat different wave numbers. As seen in the FTIR spectrum; hydroxylgroup (-OH) appeared at 3351 and 3355 cm−1. CH2 and CH3 group aliphatic C-H stretching vibrations were appeared at 2931. -NH 1644 cm−1 and -NH2 line at 1407 cm−1 were placed due to bending band [18, 19].

This proves the evidence of the functional groups such as –NH2, –OH, and –CO–.The peak sranging from 1300 to 1000 cm−1 area scribed generally to the C–O stretching vibration in carboxylicacids and alcohols.

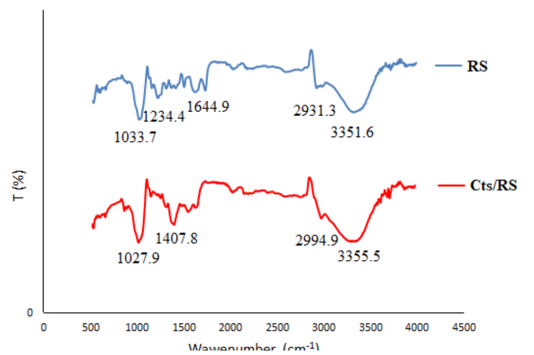

Figure1.*The FT-IR spectral characteristics ofRS andCts/RS*

RESULTS AND DISCUSSION

Equilibrium Studies

Equilibrium studies were carried out with initial chromium concentrations in the adsorption range of 5 to 150 mg/L (Fig. 2.). With an increase in the amount of starting metal ions, a rapid increase in adsorption was observed first, then at constant values (plateau line). It is obvious from the results that the maximum adsorption of Cr (VI) by Cts/RSdepends on the initial Cr (VI) concentration.

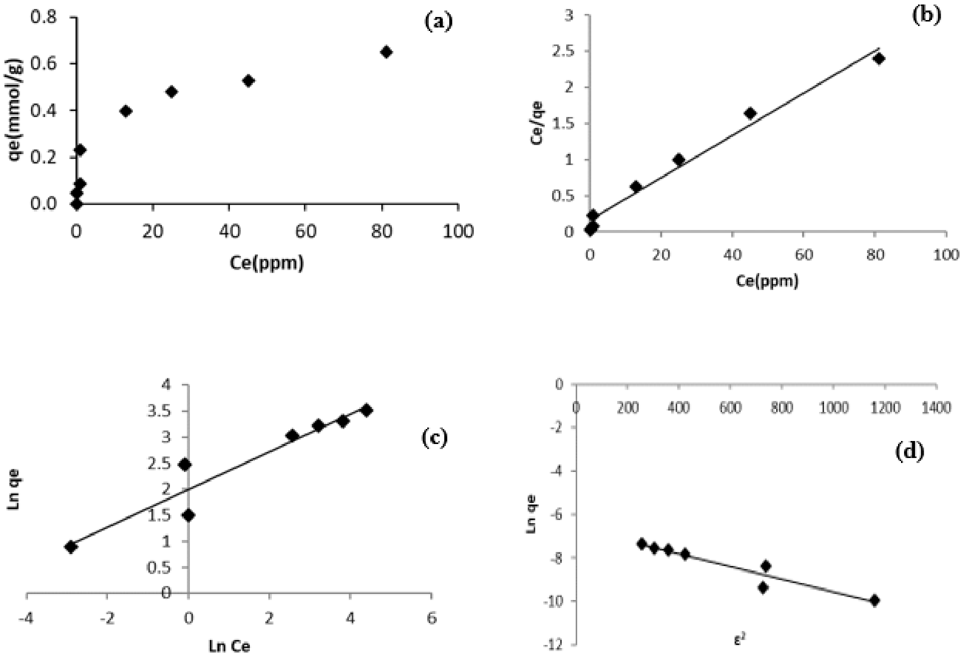

Figure 2. *Adsorption isotherms (a), Langmuir (b), Freundlich (c) and Dubinin-Radushkevich (d) isotherms plot for the adsorption of Cr (VI) onto Cts/RS.*

The Langmuir, Freundlich, and Dubinin-Radushkevich isotherms were applied in this study using Eqs. (3) (4) and (5) (Table 1). The suitability of the equilibrium curve for the Langmuir isotherm was studied and A_s and K_b were calculated from the Langmuir equation and are given in Table 3. Langmuir isotherm was more applicable for Cr (VI) adsorption compared to other isotherm data. Maximum capacity according to Langmuir isotherm was 34.13 mg/g for Cr (VI). If the value of R_L lies between 0 and 1, the adsorption process is favorable, if R_L is greater than 1, the process is unfavorable. The R_L values (0.099) received in this study lies between 0 and 1, which points to a high attraction of Cts/RS for Cr (VI) ions. The Freundlich isotherm constants are presented in Table 3. The n values were found to be 2.75, indicating that the adsorption of these values is favorable from 1 to 10.Adsorption energy (E_{ad}) value was found to be 12.91 kJ/mol which indicated a chemical ion exchange process between Cts/RS and Cr (VI) ions in solution.

Table1. *Adsorptionisothermparametersforremoval of Cr (VI)byCts/RS*

Model	Equation	Eq.	Plots	Parameters for Cr (VI)			Ref.
Freundlich	$\log q_e = \log k + \frac{1}{n} \log C_e$	(3)	Log q_e versus log C_e	k n R^2	= = =	7.32 2.75 0.911	[20]

Langmuir	$\frac{C_e}{q_e}=\frac{C_e}{A_s}+\frac{1}{K_b A_s}$	(4)	(C_e/q_e) versus C_e	A_s K_b R^2 R_L	= = = =	34.13 0.181 0.980 0.099	[21]
D-R	$\ln q_e = \ln q_m - \beta \varepsilon^2$	(5)	$\ln q_e$ versus ε^2	X_m K E R^2	= = = =	0.002 0.003 12.91 0.911	[22]

Effect of contact time

The effect of contact time on the removal of Cr (VI) is shown in Fig. 3. The time interval of the experiment is 0–360 min. As seen in this figure, the adsorption increased rapidly in the first 30 minutes. The increase in percentage of adsorption slowed down in 30-60 minutes. After 60 minutes, even if time passed, the increase in the percentage of adsorption was insignificantly small and the system seemed balanced. The equilibrium for Cr (VI) was briefly obtained and the contact duration was chosen to be 60 min.

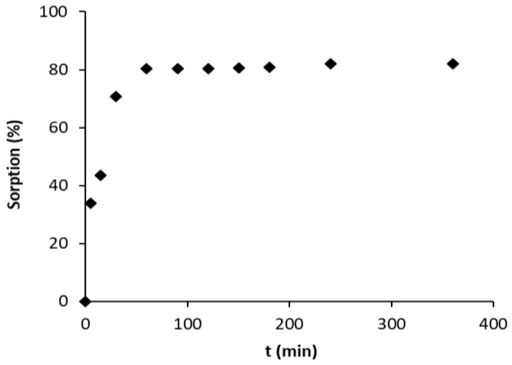

Figure 3. *Effect of contact time on removal of Cr (VI)*

Effect of pH

The pH of the solution played an important role in the entire adsorption process and affected the adsorption capacity of the adsorbent. The experiments were carried out at a pH range 1.5–6. The hydrolysis of solution, pH of the solution, redox reactions in the solution phase and the coordination as of the functional groups on the surface of the Cts/RSand the ionic state can influence the Cr(VI) decomposition and removal. Usually, at below pH 2.0, partial chromium ions in the solution exist as trivalent state, while above pH 3.0, chemical reduction of Cr (VI) to Cr(III) occurs to a lesser extent and anionic chromium species, such as $HCrO_4^-$ and $Cr_2O_7^{2-}$ are the major species [23]. The highest removal efficiency of Cr(VI) was obtained at pH 2 (nearly 85%), followed by a decrease with increasing pH (Fig. 4).Once increasing pH values from 2.0 to 6.0, the $HCrO_4^-$ gradually converts to the divalent CrO_4^{2-}. As pH increases, the surface of adsorbent become a lot of charged and therefore, the number of positively charged sites diminished. This causes increased repulsion between Cr (VI) and Cts/RS. Thus, the high removal efficiency of Cr (VI) in low pH was due to the electrostatic attraction between anionic $HCrO_4^-$and positively charged adsorbent surface.As can be seen from Fig. 4., the adsorption capacity of Cts/RS was strongly dependent on the pH value and the maximum adsorption took place at pH 2.

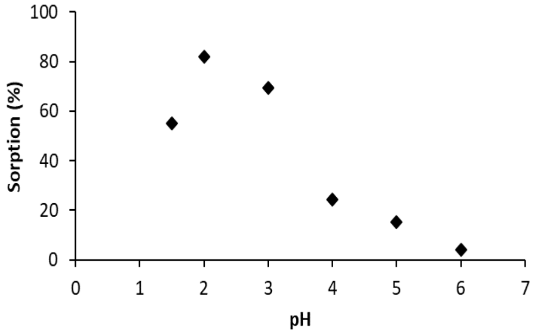

Figure 4. *Effect of pH on adsorption of Cr (VI)*

Effect of Cts/RS dosage

The adsorption amount of Cr(VI) was determined by adsorption experiments with different mass values (1.0-5.0 g/L) (Fig. 5.). The amount of Cts/RS in the solution is related to the number of surface-active sites for the adsorption process. For this reason, as the amount of Cts/RS increases, it is expected the amount of Cr (VI) increases. When the amount of Cts/RSwas increased, the percentage of adsorption is increased to plateau. The amount of adsorbent to be used in the experiments was taken as 4 g/L for Cr(VI).

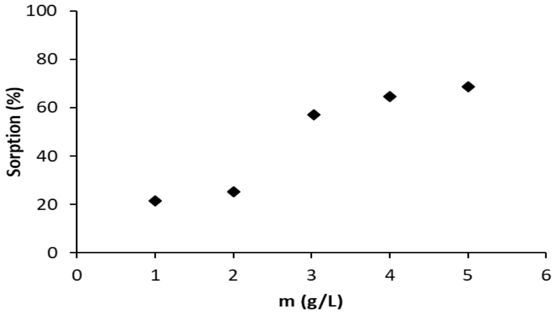

Figure 5. *Effect of adsorbent dosage on percentage removal of Cr (VI) ions.*

Thermodynamic Modelling

Adsorption of Cr (VI) onto Cts/RS was definitely carried out different temperatures (25 °C, 35 °C, 45 °C and 55 °C) for thermodynamic analysis. The thermodynamic parameters includingΔH°, ΔS° and ΔG° for the adsorption of Cr (VI) onto the Cts/RS samples are calculated from plotted data and the results were given in Table 2. The reaction is endothermic with increasing temperature and the adsorption of metal ions increases. This means that there is a tendency or a mobility of metals from solution phase to the adsorbent. ΔG° is negative and adsorption tends to be spontaneous.

Table 2. *Thermodynamic parameters*

ΔS^o	ΔH^o	ΔG^o (J/mol-1)				R^2
(J/K-1mol-1)	J/mol-1	T=298.15K	T=308.15K	T=318.15K	T=328.15K	
-53.31	-17619.53	-1725.70	-1192.62	-659.54	-126.45	0.968

CONCLUSION

In the adsorption experiment, Cts/RS was used and their performance was compared by changing such factors as the initial Cr (VI) concentration, contact time and the amount of adsorbent. It is found that the adsorption depends on pH and the optimum pH for removal is 2.0. In batch studies, the adsorption increased with an increase of contact time and Cts/RSdose. Adsorption of Cr (VI) obeys Langmuir equation. Maximum capacity according to Langmuir isotherm was (q_m); 34.13 mg/g for Cr (VI). Thermodynamic results suggested that the adsorption of Cr (VI) on the adsorbent was a spontaneous and exothermic process. Cts/RS is generated from natural sources that claim it is an environmental friendly adsorbent for application of Cr (VI) removal from a water-based medium.

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