SYNTHESIS OF HYDROXYAPATITE FROM AVOCADO FRUIT PEEL AND ITS APPLICATION FOR HEXAVALENT CHROMIUM REMOVAL FROM AQUEOUS SOLUTIONS - ADSORPTION ISOTHERMS AND KINETICS STUDY

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ABSTRACT

The potential of hydroxyapatite particles prepared from avocado peel (APH) for the removal of Cr (VI) ions from aqueous solutions was studied. The APH was characterized using x-ray diffraction; Fourier transforms infrared spectroscopy, and scanning electron microscopy. The adsorption of Cr (VI) ions from aqueous solutions onto APH was studied. The batch adsorption experiments were performed in 250-cm³ Erlenmeyer flasks containing 100 cm³ solution of Cr (VI) of known concentration with a known mass of adsorbent (APH) added to the solution. The flasks were agitated at 120 rpm on a rotary shaker incubator for a known time at 30°C. The impact of different parameters such as initial Cr (VI) concentration, adsorbent dosage, contact time, and pH of the solution was studied. The hexavalent chromium removal efficiency (91.27%) increased with increase in initial Cr (VI) ions concentration (50 to 200 mg/L), and adsorbent dosage (0.1 to 0.5 g/100 mL). The adsorption isotherms and kinetics of the process were also studied. The Freundlich adsorption isotherm well explained Cr (VI) adsorption onto APH. Cr (VI) adsorption onto APH very well agreed with the pseudo-second-order kinetic model as indicated by the R² value (0.99). APH is an eco-friendly and low-cost adsorbent. APH is very effective for the removal of hexavalent chromium from aqueous solutions.

Keywords: Hydroxyapatite, Avocado Peel, Isotherms, Adsorption Kinetics.

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INTRODUCTION

Pollution is one of the major challenges in the day-to-day life because of the presence of heavy metal ions, aromatic compounds, industry effluents, and dyes which has led to high toxicity in plant and animal cells. Chromium enters into water bodies from many industrial processes such as tanning, metal processing, paint manufacturing, steel fabrication, and agricultural runoff.¹ Hexavalent chromium is toxic and carcinogenic. When chromium enters the gastric system of humans, it causes epigastric pain, nausea, vomiting, severe diarrhoea and lung carcinoma.² Limits on Cr (VI) discharge in effluent streams vary between 0.05 and 10 mg.L⁻¹ for direct discharges into water bodies and 1 to 50 mg.L⁻¹ for indirect discharges into sewerage systems.³ Thus, it becomes very important to remove Cr (VI) from wastewater. Several chemical and physical methods have been developed to reduce Cr concentration in wastewater.⁴ There are a number of methods to remove Cr (VI) including electrochemical precipitation, ultra-filtration, ion exchange, reverse osmosis, solvent extraction, and membrane filtration.^{5,6} Among these, adsorption is effective and economical.⁷

In recent years, the adsorption process has been widely used for Cr (VI) removal from wastewaters and industry effluents, because of its low operation value and high removal efficiency. Several adsorbents such as distillery sludge⁸, cocoa shell⁹, sugar beet pulp¹⁰, zeolite¹¹, and sawdust¹² have been employed for Cr (VI) removal. Only a few research groups have studied the removal of Cr (VI) using hydroxyapatite as adsorbent¹³. There are many techniques available in the literature for the synthesis of hydroxyapatite

(HA), namely, thermal method or acid treatment^{14,15}, hydrothermal¹⁶, solid-state reaction¹⁷, chemical precipitation¹⁸, radiofrequency thermal plasma¹⁹, and polymer-assisted synthesis method.²⁰ The effect of adsorbent dosage, pH, initial Cr (VI) concentration, and contact time on the removal of Cr (VI) was studied by batch experiments. The adsorption isotherms and kinetics of adsorption of Cr (VI) onto APH were studied.

EXPERIMENTAL

Preparation of Adsorbent

The hydroxyapatite particles were prepared from the avocado peel. A known quantity of avocado fruit peel was boiled in water for 20 min and then filtered. 30 cm³ of this filtrate was added to 300 cm³ of 0.4 M soluble calcium nitrate tetrahydrate solution and 50 cm³ of 1:2, 25% liquor ammonia: water, mixed completely and incubated for 24 h at 30°C. The resulting solution was added to 370 cm³ of 0.156 M alkaline diammonium hydrogen phosphate salt solution and 30 cm³ of 1:1, 25% liquor ammonia: water, stirred and aged for 8 days at an ambient temperature of 30°C. The precipitate was washed many times with deionized water and oven-dried at 80°C for 24h.²¹

Characterization of Adsorbent

The prepared APH was characterized by x-ray diffraction (XRD) using Smart Lab X-ray Diffractometer (Rigaku, Japan). The Fourier transform infrared (FT-IR) spectrum was obtained using an ALPHA-T FT-IR Spectrometer (Bruker, USA) in the region 400–4000 cm⁻¹. Scanning electron microscope (SEM) analysis was done using TESCAN Vega 3 LMU (Czech Republic) to study the surface morphology of the adsorbent.

Batch Adsorption Study

All chemicals used in the present work were of analytical grade and procured in India. The adsorption of Cr (VI) onto APH was studied to determine the optimum pH, initial chromium concentration, adsorbent dosage, and contact time for maximum removal of Cr (VI). A stock solution of Cr (VI) was prepared by dissolving the required amount of K₂Cr₂O₇ in deionized water. The pH of the solution was adjusted to the required value by the drop-wise addition of 0.2 N H₂SO₄. The batch adsorption experiments were performed in 250-cm³ Erlenmeyer flasks containing 100 cm³ solution of Cr (VI) of known concentration with a known mass of the APH adsorbent added to it. The flasks were agitated at 120 rpm on a rotary shaker incubator for a known period of time at 30°C. The solution was filtered using a syringe filter (0.45 µm). 2 cm³ of 1, 5-diphenylcarbazide was added to the filtered solution till a purple complex of Cr (VI) developed. A portion of this solution was centrifuged at 5000 rpm for 20 min and the absorbance of the supernatant was determined using a UV-visible spectrophotometer (Shimadzu UV – 1800, Japan) at 540 nm.²²

The amount of Cr (VI) ions adsorbed onto APH (in milligram per gram adsorbent) was determined using the mass balance equation (Eq.-1).

$$q_e = \frac{(C_i - C_f)}{C_i} \times \frac{V}{m} \quad (1)$$

Where C_i and C_f are the initial and final Cr (VI) concentrations (mg.L⁻¹), respectively, V is the volume of adsorbate in a litre, and m is the weight of the adsorbent in grams. The percentage removal of Cr (VI) ions was calculated using Eq.-2.

$$\% \text{ Removal} = \frac{(C_i - C_f)}{C_i} \times 100 \quad (2)$$

Adsorption Isotherms

In this work, the Freundlich isotherm was used to estimate the adsorption intensity of the Cr (VI) on to APH surface based on sorption heterogeneous energetic distribution of active sites attained by interactions between adsorbed molecules. The Freundlich isotherm can be expressed by Eq.-3.

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (3)$$

Where k_f and $1/n$ are constants that describe the adsorption capacity and the adsorption intensity, respectively. The Langmuir adsorption isotherm is given by Eq.-4

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{k_L q_m} \quad (4)$$

The Langmuir constants q_m and k_L can be estimated by plotting C_e/q_e vs. C_e where q_e (mg g^{-1}) and C_e (mg.L^{-1}) are the solid phase concentration and the liquid phase concentration of the adsorbate at equilibrium, respectively. q_m (mg.g^{-1}) is the maximum adsorption capacity and k_L (L.mg^{-1}) is the energy of adsorption.²³ The values of the Langmuir separation factor, R_L obtained from Eq.-5 indicate whether the adsorption is either unfavorable when $R_L > 1$, linear when $R_L = 1$, favorable when $0 < R_L < 1$, or irreversible if $R_L = 0$.

$$R_L = \frac{1}{1 + k_a C_0} \quad (5)$$

The Dubinin-Radushkevich (D-R) isotherm was applied to express the adsorption mechanism using a quasi-Gaussian distribution with broadening at high adsorption energies.²⁴ The D-R isotherm has often successfully fitted high solute activities and the intermediate range of concentration data well and is given by Eq.-6.

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (6)$$

Where q_e is the number of chromium ions adsorbed per unit weight of adsorbent (mol/g), q_m is the theoretical isotherm saturation capacity (mol/g), β is the D-R isotherm constant ($\text{mol}^2 / \text{kJ}^2$), and ε is the D-R isotherm constant.

This approach is usually applied to distinguish the physical and chemical adsorption of metal ions with its mean free energy, E per molecule of adsorbate (for removing a molecule from its location in the sorption space to infinity) can be computed by (Eq.-7).²⁵

$$E = \frac{1}{\sqrt{-2\beta}} \quad (7)$$

The parameter ε can be calculated using Eq.-8.

$$\varepsilon = RT \ln \left[1 + \frac{1}{C_e} \right] \quad (8)$$

Where R is the gas constant ($8.314 \text{ J.mol}^{-1}.\text{K}^{-1}$), T is the absolute temperature (K), and C_e is the adsorbate equilibrium concentration (mg.L^{-1}). The slope of a plot of $\ln q_e$ versus ε^2 gives β ($\text{mol}^2.\text{kJ}^{-2}$) and the intercept yields the sorption capacity, (mol.g^{-1}).

The Temkin adsorption isotherm contains a factor that explicitly takes into account the adsorbent-adsorbate interactions. By ignoring the extremely low and large values of concentration, the model assumes that the heat of adsorption (a function of temperature) of all molecules in the layer would decrease linearly rather than logarithmically with coverage and is characterized by a uniform distribution of binding energies (up to some maximum binding energy). The model is represented by Eq. 9. The quantity sorbed q_e is plotted against $\ln C_e$ and the constants are determined from the slope and intercept.²⁵

$$q_e = B \ln (A_T C_e) \quad (9)$$

Where A_T represents the Temkin isotherm equilibrium binding constant (L.g^{-1}), b is the Temkin isotherm constant, R is the gas constant ($8.314 \text{ J.mol}^{-1}.\text{K}^{-1}$), T is the temperature, and $B = RT/b$ is a constant related to the heat of sorption (J.mol^{-1}). By plotting q_e versus $\ln C_e$, the constants A_T and B are determined.

Adsorption Kinetics

A study of the adsorption kinetics is important in determining the effectiveness of the adsorption. In this study, four different models (first-order, pseudo-second-order, Elovich, and intraparticle diffusion) were used to predict the adsorption kinetics of chromium ions onto APH.

The first-order rate equation is given by (Eq.-10)²⁶

$$\frac{1}{q_t} = \frac{1}{q_1} + \frac{k_1}{q_1 * t} \quad (10)$$

Where, q_t is the amount of adsorbed chromium per unit weight of the adsorbent, mg.g^{-1} ; t is the time, min; q_1 is the amount of chromium adsorbed per unit weight of adsorbent at equilibrium, mg.g^{-1} ; and k_1 is the first-order rate constant, min^{-1} . A straight line of $1/q_t$ versus $1/t$ suggests the applicability of this kinetic model. q_1 and k_1 are determined from the intercept and slope of the plot.

The pseudo-second-order kinetic model is given by (Eq.-11).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (11)$$

Where q_t and q_e are the amounts of Cr (VI) adsorbed (mg.g^{-1}) at time t and at equilibrium and k_2 ($\text{g.g}^{-1}.\text{min}^{-1}$) is the second-order adsorption rate constant ($\text{g.mg}^{-1}.\text{min}^{-1}$), q_e and k_2 values are obtained from the intercept and slope of a plot of t/q_t versus t .

The intraparticle diffusion-based mechanism was also studied. The intraparticle diffusion equation can be described by (Eq.-12).²⁶

$$q_t = K_{id} \sqrt{t} + C \quad (12)$$

Where q_t is the amount sorbed at time t and K_{id} is the intraparticle diffusion rate constant ($\text{mg.g}^{-1}.\text{min}^{-1}$).

The Elovich kinetic model in its nonlinear and linear forms is expressed by Eqs.-13 and 14, respectively.²⁷

$$q_t = \beta \ln (\alpha \beta t) \quad (13)$$

$$q_t = \frac{1}{\beta} \ln (\alpha \beta) + \frac{1}{\beta \ln t} \quad (14)$$

Where q_t is the quantity of adsorbate adsorbed at time t (min), α is a constant related to the chemisorption rate, and β is a constant which depicts the extent of surface coverage. These two constants can be calculated from the intercept and slope of a plot of q_t versus $\ln t$, respectively.

RESULTS AND DISCUSSION

Characterization of the Adsorbent

X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, and scanning electron microscopy (SEM) analyses were done to characterize APH.

The x-ray diffraction spectrum obtained for APH and displayed in Fig. 1 shows crystalline peaks at $2\theta = 25.9^\circ$, 32° , 33° , 35.5° , and 40° thereby confirming the formation of hydroxyapatite which matches with JCPDS No. 09-432.

The FT-IR spectrum is represented in Fig.-2 and the characteristic peaks at 3379 and 1629 cm^{-1} are due to the stretching and bending vibrational modes of the OH^- groups of the hydroxyapatite as well as the adsorbed moisture on its surface. The characteristic tetrahedral PO_4^{3-} peaks are clearly visible at 476 , 582 , 832 , 880 , and 1051 cm^{-1} .^{28, 29} The peak at 476 cm^{-1} corresponds to PO_4^{3-} (ν_2 mode) and a peak at 582 cm^{-1} corresponds to PO_4^{3-} (ν_4 mode).

Moreover, the peak at 961 cm^{-1} is for PO_4^{3-} (ν_1) and the peak at 1051 cm^{-1} is due to PO_4^{3-} (ν_3). The peak around 1415 cm^{-1} is assigned to CO_3^{2-} .^{30,31} The peaks at 1415 and 880 cm^{-1} represent the interaction of carbon dioxide with the prepared nanoparticles.³² The observation of these peaks indicates that the CO_3^{2-} group is substituted for the PO_4^{3-} group in the hydroxyapatite lattice thus confirming the existence of B-type carbonate in the prepared hydroxyapatite nanoparticles.³³

Fig.-1: XRD Spectrum for APH

Fig.-2: Fourier Transform Infrared (FT-IR) Spectrum of APH

The SEM-EDS images give an insight into the hydroxyapatite structure with respect to the morphology of the material. The EDS output indicates the presence of Ca (35.23 wt %) and P (16.03 wt %) as shown in Fig.-3b. Scanning electron microscopy - Energy dispersive spectroscopy (SEM-EDS) analysis of APH was carried out after calcination at 650°C and shown in Figs.-3a and 3b.

Fig.-3:(a) SEM Image of APH and (b) EDS Spectrum for APH

Adsorption Isotherms

The mechanism of chromium adsorption from aqueous solutions onto APH was studied using the different adsorption isotherms. The adsorption isotherms for Cr (VI) adsorption on to APH is displayed in Fig.-4.

The values of the constants and the correlation coefficient (R^2) for the linear regression fit of each adsorption isotherm were determined and shown in Table-1.

Table-1: List of Calculated Parameters from the Freundlich, Langmuir, Temkin, and D-R Adsorption Isotherms

Isotherm	Constants	Values
Freundlich isotherm	n	0.19
	K_f (mg.g^{-1})	0.048
	R^2	0.986
Langmuir isotherm	q_m (mg.g^{-1})	17.99
	K_L (L.mg^{-1})	0.185
	R_L	0.028
	R^2	0.860
D-R isotherm	β ($\text{mol}^2.\text{kg}^{-2}$)	-1.36×10^{-6}
	q_m (mg.g^{-1})	43.5×10^5
	E (kJ.mol^{-1})	0.012
	R^2	0.901
Temkin isotherm	$B = RT/b$ (J.mol^{-1})	453.7
	$B \ln A_T$	-556.78
	A_T (L.g^{-1})	0.29
	b (dimensionless)	5.55
	R^2	0.827

Fig.-4: Adsorption Isotherms for Cr (VI) Adsorption on to APH (a) Freundlich Isotherm, (b) Langmuir Isotherm, (c) D-R Isotherm, and (d) Temkin Isotherm

The isotherm constants were calculated from the slope and intercept of Fig.-4 (a to d) and listed in Table-1. The value of R^2 (0.986) for Freundlich isotherm was found to be higher than those for the other isotherms. The slope ($n = 0.19$) of the isotherm satisfies the condition of $0 < n < 1$ and is a measure of the adsorption intensity or surface heterogeneity. A value closer to zero indicates a more heterogeneous surface. A value below unity implies chemisorption where $1/n$ above one (5.26 in this case) is indicative

of cooperative adsorption³⁴. The better fit for Freundlich isotherm for the adsorption of the Cr (VI) onto the APH adsorbent implies non-ideal adsorption on heterogeneous surfaces as well as multilayer sorption.³⁵

Adsorption Kinetics

The first-order, pseudo-second-order, Elovich, and intra-particle diffusion kinetic models were employed to study the adsorption kinetics of Cr (VI) onto APH. The adsorption kinetic models are shown in Fig.-5 and the values of the calculated parameters are listed in Table-2.

The straight-line plot of t/q_e against time (t) for the pseudo-second-order kinetic model is displayed in Fig.-5(b). The linear fit to the data gave the highest correlation coefficient of 1.0 indicating that the adsorption process obeys the pseudo-second-order kinetic model. The values of q_e (4.36 mg.g^{-1}) and k_2 ($21.90 \text{ g.mg}^{-1}.\text{min}$) were calculated from the slope and intercept of the plot t/q_e versus t . The pseudo-second-order model is based on the assumption that the rate-limiting step may be chemical adsorption involving valence forces through sharing or exchange of electrons between the adsorbent and the adsorbate.³⁶

Fig.-5: Adsorption Kinetics Models: (a) First-order, (b) Pseudo-second-order, (c) Elovich, and (d) Intraparticle Diffusion Models for the Adsorption of Cr (VI) on to APH

Table -2: Calculated Parameters of the First-order, Pseudo-Second-order, Elovich, and Intra-particle Diffusion Kinetic Models for the Adsorption of Cr (VI) on to APH

Kinetic Model	Parameter	Value
First-order	R^2	0.989
	n	0.092
	k_1	0.003
Pseudo-second-order	R^2	1.000
	$q_e (\text{mg.g}^{-1})$	4.36
	$k_2 (\text{g.mg}^{-1}.\text{min})$	21.90
Elovich	R^2	0.949

Intra-particle diffusion	α (mmol.gmin ⁻¹)	12.08
	β (g.mmol ⁻¹)	0.53
	R^2	0.899
	K_{id} (mg.g ⁻¹ .min ^{1/2})	1.868
	I (mg.g ⁻¹)	28.16

CONCLUSION

Hydroxyapatite prepared from APH was successfully used as an adsorbent for the removal of Cr (VI) ions from aqueous solutions. The characterization of APH was done by XRD, FT-IR spectroscopy, and SEM-EDS to obtain information regarding the composition, bonding, and morphology of the particles. The adsorption percentage of Cr (VI) ions increased with an increase in the adsorbent dose as also the initial concentration of Cr (VI) ions. A 91.27% removal of chromium (VI) was possible at the optimal conditions of pH 7.0, initial Cr (VI) concentration of 200 mg/L, the temperature of 30°C, adsorbent dosage of 0.5 g/ 100 mL and contact time of 30 min. The adsorption process of Cr (VI) on to APH as described by the Freundlich isotherm showed a better agreement with the equilibrium data. Similarly, the pseudo-second-order kinetic model gave the best fit in this study.

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