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-cm$^3$ Erlenmeyer flasks containing 100 cm$^3$ 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 R$^2$ 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.

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. 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. 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. 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. There are a number of methods to remove Cr (VI) including electrochemical precipitation, ultra-filtration, ion exchange, reverse osmosis, solvent extraction, and membrane filtration. Among these, adsorption is effective and economical.

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 sludge, cocoa shell, sugar beet pulp, zeolite, and sawdust have been employed for Cr (VI) removal. Only a few research groups have studied the removal of Cr (VI) using hydroxyapatite as adsorbent. There are many techniques available in the literature for the synthesis of hydroxyapatite
(HA), namely, thermal method or acid treatment\textsuperscript{14,15}, hydrothermal\textsuperscript{16}, solid-state reaction\textsuperscript{17}, chemical precipitation\textsuperscript{18}, radiofrequency thermal plasma\textsuperscript{19}, and polymer-assisted synthesis method.\textsuperscript{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 cm\(^3\) of this filtrate was added to 300 cm\(^3\) of 0.4 M soluble calcium nitrate tetrahydrate solution and 50 cm\(^3\) of 1:2, 25% liquor ammonia: water, mixed completely and incubated for 24 h at 30°C. The resulting solution was added to 370 cm\(^3\) of 0.156 M alkaline diammonium hydrogen phosphate salt solution and 30 cm\(^3\) 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.\textsuperscript{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 K\(_2\)Cr\(_2\)O\(_7\) in deionized water. The pH of the solution was adjusted to the required value by the drop-wise addition of 0.2 N H\(_2\)SO\(_4\). The batch adsorption experiments were performed in 250-cm\(^3\) Erlenmeyer flasks containing 100 cm\(^3\) 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 cm\(^3\) 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.\textsuperscript{22} The amount of Cr (VI) ions adsorbed onto APH (in milligram per gram adsorbent) was determined using the mass balance equation (Eq.-1).

\[
q_e = \frac{(C_i - C_f)}{C_i} \times \frac{V}{m} 
\]  

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.

\[
\% \text{ Removal} = \left(\frac{C_i - C_f}{C_i}\right) \times 100
\]  

**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.

\[
\ln q_e = \ln K_f + \frac{1}{n} \ln C_e
\]
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

$$\frac{C_e}{q_e} = \frac{C_m}{q_m} + \frac{1}{k_L q_m} \tag{4}$$

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. 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 $R_L = 0$.

$$R_L = \frac{1}{1+ k_L C_0} \tag{5}$$

The Dubinin-Radushkevich (D-R) isotherm was applied to express the adsorption mechanism using a quasi-Gaussian distribution with broadening at high adsorption energies. 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.

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{6}$$

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), $\beta$ is the D-R isotherm constant (mol$^2$ / kJ$^2$), and $\varepsilon$ 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).

$$E = \frac{1}{\sqrt{-2\beta}} \tag{7}$$

The parameter $\varepsilon$ can be calculated using Eq.-8.

$$\varepsilon = RT \ln [1+ \frac{1}{C_e}] \tag{8}$$

Where $R$ is the gas constant (8.314 J mol$^{-1}$ 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 $\varepsilon^2$ gives $\beta$ (mol$^2$ / 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.

$$q_e = B \ln (A_T C_e) \tag{9}$$

Where $A_T$ represents the Temkin isotherm equilibrium binding constant (L mg$^{-1}$), $b$ is the Temkin isotherm constant, $R$ is the gas constant (8.314 J mol$^{-1}$ 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.

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

\[
\frac{1}{q_t} = \frac{1}{q_1} + \frac{k_1}{q_1 t}
\]  

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).

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t
\]  

Where \(q_t\) and \(q_e\) are the amounts of Cr (VI) adsorbed (mg.g\(^{-1}\)) at time \(t\) and at equilibrium and \(k_2\) (g.g\(^{-1}\).min\(^{-1}\)) is the second-order adsorption rate constant (g.mg\(^{-1}\).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).\(^26\)

\[
q_t = K_{id}\sqrt{t} + C
\]  

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

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

\[
q_t = \beta \ln (\alpha \beta t)
\]  

\[
q_t = \frac{1}{\beta} \ln (\alpha \beta) + \frac{1}{\beta \ln t}
\]  

Where \(q_t\) is the quantity of adsorbate adsorbed at time \(t\) (min), \(\alpha\) is a constant related to the chemisorption rate, and \(\beta\) 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 \(2\theta = 25.9^\circ, 32^\circ, 33^\circ, 35.5^\circ,\) and \(40^\circ\) 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\(_4\)\(^{3-}\) (\(\nu_2\) mode) and a peak at 582 cm\(^{-1}\) corresponds to PO\(_4\)\(^{3-}\) (\(\nu_3\) mode). Moreover, the peak at 961 cm\(^{-1}\) is for PO\(_4\)\(^{3-}\) (\(\nu_1\)) and the peak at 1051 cm\(^{-1}\) is due to PO\(_4\)\(^{3-}\) (\(\nu_3\)). 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.\(^33\)
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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.

| Isotherm          | Constants          | Values       |
|-------------------|--------------------|--------------|
| **Freundlich isotherm** | \(n\)               | 0.19         |
|                   | \(K_f \text{ (mg.g}^{-1})\) | 0.048        |
|                   | \(R^2\)             | 0.986        |
| **Langmuir isotherm** | \(q_m \text{ (mg.g}^{-1})\) | 17.99        |
|                   | \(K_L \text{ (L.mg}^{-1})\) | 0.185        |
|                   | \(R_L\)             | 0.028        |
|                   | \(R^2\)             | 0.860        |
| **D-R isotherm**  | \(\beta \text{ (mol}^2.\text{kg}^{-2})\) | \(-1.36\times10^{-6}\) |
|                   | \(q_m \text{ (mg.g}^{-1})\) | 43.5\times10^5 |
|                   | \(E \text{ (kJ.mol}^{-1})\) | 0.012        |
|                   | \(R^2\)             | 0.901        |
| **Temkin isotherm** | \(B = RT/b \text{ (J.mol}^{-1})\) | 453.7        |
|                   | \(B \ln A_T\)       | -556.78      |
|                   | \(A_T \text{ (L.g}^{-1})\) | 0.29         |
|                   | \(b \text{ (dimensionless)}\) | 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 adsorption. 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.

**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 g.mg$^{-1}$.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.

![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](image)

**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  |
|                         | $q_e$ (mg.g$^{-1}$) | 4.36   |
|                         | $k_2$ (g.mg$^{-1}$.min) | 21.90  |
| Elovich                 | $R^2$           | 0.949  |

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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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α (mmol.gmin⁻¹) 12.08
β (g.mmol⁻¹) 0.53
Intra-particle diffusion
R² 0.899
K(id)(mg.g⁻¹.min⁻¹/²) 1.868
I (mg.g⁻¹) 28.16
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