A Comparative Study and Kinetics for the Removal of Hexavalent Chromium from Aqueous Solution by Agricultural, Timber and Fruit Wastes

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ABSTRACT

The removal of hexavalent chromium from aqueous solutions using low cost agricultural, timber and fruits wastes is studied. The adsorbents selected were rice husk in ash and dried form, sawdust, orange peels and sugarcane bagasse. Batch mode experiments were conducted at room temperature to study the effect of pH, agitation time, initial metal ion concentration, and adsorbent dose. Equilibrium adsorption isotherms and kinetics were investigated. The adsorption isotherm data were fitted to Langmuir isotherm and the monolayer adsorption capacity has been observed to follow the order dried rice husk (16.94 mg/g) > orange peels (12.65 mg/g) > rice husk ash (11.11 mg/g) > sugarcane bagasse (5.12 mg/g) > sawdust (4.56 mg/g) at room temperature. It was found that the maximum amount absorbed metal ($q_{max}$) value is significantly influenced by liquid/solid ratio and by the pH values of the metal solutions. The kinetic data obtained at different concentrations have been analyzed using a pseudo-first-order, pseudo-second order and intraparticle diffusion equation. The experimental data fitted very well the pseudo-second-order kinetic model. On the basis of present studies, it can be concluded that dried rice husk, has a higher chromium adsorption capacities compared to other adsorbents.

KEYWORDS:
Adsorption, Hexavalent chromium, Cr (VI), non-conventional adsorbent, isotherms, heavy metal, kinetics, adsorption isotherm.

1. INTRODUCTION

Environmental pollution due to the development in technology is one of the most important problems of this century. Heavy metals like chromium, copper, lead, cadmium, etc. in wastewater are hazardous to the environment. These metals cannot be degraded or readily detoxified biologically and have tendency to accumulate in living material. Besides that, heavy metals discharge in the wastewater can be toxic to aquatic life and render natural waters unsuitable for human consumption. [7]

Hexavalent chromium has been considered as one of the top 16th toxic pollutants and because of its carcinogenic and teratogenic characteristics on the public, it has become a serious health concern. Chromium is introduced into water bodies from many industrial processes such as tanning, metal processing, paint manufacturing, steel fabrication and agricultural runoff [1]. Chromium is also used in explosive, ceramics and photography. Chromium occurs in the aquatic environment as both trivalent and hexavalent states. Hexavalent chromium, which is primarily present in the form of chromate ($CrO_4^{2-}$) and dichromate ($Cr_2O_7^{2-}$), possesses significantly higher levels of toxicity than the other valence states. Its concentration in industrial wastewater ranges from 0.5 to 270 mg/L. The tolerance limit for Cr (VI) for discharge into inland surface waters is 0.1 mg/L and in potable water is 0.05 mg/L. In order to comply with this limit, it is essential that industries treat their effluents to reduce the Cr (VI) concentration in water and waste water to acceptable levels before its transport and cycling into the natural environment.[2]

Various treatment techniques available for the removal of Cr (VI) from wastewater include reduction, precipitation, ion exchange, solvent extraction, membrane separation. The membrane system has problems like scaling, fouling, and blocking. The ion exchange system is uneconomic due to the cost of commercial ion exchange resins. Most of these methods require high investment of capital and also expensive chemicals, making them unsuitable for treating chromium-containing wastewater. These conventional methods for the removal of heavy metals have inadequate efficiencies at low metal concentrations, particularly in the range of 1–100 mg/l [3]. Adsorption is by far the most effective and widely used technique for the removal of toxic heavy metals.
from wastewater. Due to the high cost and difficult procurement of activated carbon, efforts are being directed towards finding efficient and low cost adsorbent materials.

The objective of this study was to investigate the feasibility of adsorption for the removal of Cr (VI) from aqueous solution utilizing dried rice husk, rice husk ash, sawdust, orange peels, and sugarcane bagasse as non-conventional adsorbents. Factors affecting the adsorption characteristics such as pH, agitation time, initial metal ion concentration, and adsorbent dose were studied. Rate kinetics and isotherm models were also investigated to know the adsorption behavior of the adsorbents considered for study.

2. Methods and Materials

2.1 Adsorbate

The stock solutions of Cr(VI) metal ions were prepared from 1.4143 gm of analytical grade K$_2$Cr$_2$O$_7$ in 500ml de-ionized double distilled water in 1% HNO$_3$ solution and this stock solution is diluted with de-ionized double distilled water to obtain working standard solution.

2.2 Preparation and Characterization of adsorbents

The adsorbents used are dried rice husk, rice husk ash, orange peels, sugarcane bagasse, and sawdust. The adsorbents were selected on the basis of their cost effectiveness and ready availability.

a) Dried rice Husk
The sample was collected from local rice mill, washed twice with double distilled water to remove the soluble materials present in the husk then homogenized and dried at 100°C for 3 hours. The dried sample was then cooled homogenized and ground to pass through 30 mesh screen [9], [16], [17], [18].

b) Rice husk ash
After collecting the sample from local rice mill it was washed twice with double distilled water to remove the soluble materials present in the husk then kept in furnace at 500°C for 4 hours. The ash was then cooled and ground to pass through 30 mesh screen [2], [5], [9].

c) Sugarcane bagasse
Raw sugarcane bagasse was collected, cutted into small pieces, washed several times with distilled water and kept in an oven maintained at 100°C for a period of 24 hours. Then the material was ground and sieved to get desired particle size of 30 mesh screen [9], [7], [19].

d) Orange peels
Orange peels were collected from various fruit juice centers where it was treated as waste. Collected skin of these fruits was kept for drying for more than 3 weeks by checking the moisture content of the all skins alternate days. Skin covered with a plastic paper to prevent its contamination. When all the skins get dry grinding took place. After grinding, screening is done by 30 mesh screen [9].

e) Saw dust
It was collected from local sawmill. It was mostly of teakwood origin. After collection it was washed thoroughly with double distilled water to remove muddy materials and then with 0.1N NaOH to remove lignin based color materials followed by 0.1N H$_2$SO$_4$. Finally it was again washed with double distilled water several times and dried in an oven at 100°C for a period of 6 hours and sieved to get desired particle size of 30 mesh screen. No other chemicals or physical treatments were used prior to the adsorption experiments [2], [9].

2.3. Adsorption Studies

For the adsorption experiment, the effect of adsorbent dose on the adsorption of the ions was investigated. 0.2-1.2 g of the adsorbent was weighed respectively into conical flasks. 20 ml of 5mg/L solution of each of the metal ion solution was added and the mixture shaken with a reciprocating shaker for 30 min. The mixtures were centrifuged at 2,000 rpm for 30 min, the supernatant was decanted and the metal ion content was determined using a Flame Atomic Absorption Spectrometer. The % adsorption was determined by

\[
\frac{C_0 - C_a}{C_0} \times 100
\]

Where $C_0$ = Initial concentration of solution, $C_a$ = Concentration of the solution after adsorption. In order to investigate the effect of concentration on the adsorption of metal ions, 1g of the adsorbent was added to 20 ml each of varying concentrations (between 10 - 100 mg/L) of the metal ion solutions. The mixtures were shaken, centrifuged and the concentration of the metal ions adsorbed was determined. The effect of contact time was also investigated by adding 1g of the adsorbent to 20 ml of 5 mg/L and shaking using varying contact times (between 30 – 300 min) and the percentage of adsorbed ions determined. The effect of pH on adsorption of the metals was investigated using 1g of the adsorbent and 20 ml of 5 mg/L and the pH of the solution were adjusted from 1 - 12.
The mixture was shaken for 90 min, centrifuged and the amount of ion adsorbed was determined. Metal analysis was carried out by using AAS (Atomic Absorption Spectrophotometer), Model AA-6300. The amount of adsorption at equilibrium, $q_e$ (mg/g) was calculated by equation [11], [14].

$$q_e = \frac{(C_0 - C_e)V}{W}$$  \hspace{1cm} (2)

Where, $C_0$ and $C_e$ (mg/L) are the liquid-phase concentrations of hexavalent chromium at initial and equilibrium respectively. $V$ is the volume of the solution (L) and $W$ is the mass of dry adsorbent used.

Kinetic studies of adsorption were also carried out for all adsorbents wherein the extent of adsorption was investigated as a function of time. The amount of adsorption at time $t$, $q_t$ (mg/g), was calculated by equation [11], [14].

$$q_t = \frac{(C_0 - C_t)V}{W}$$  \hspace{1cm} (3)

3. **RESULT AND DISCUSSIONS**

3.1.1 **Effect of Adsorbent Dosage on Adsorption of Cr (VI)**

The effect of adsorbent type and its concentration explained the fact that in each case, increase in the adsorption concentration resulted in an increase in percentage removal of Cr (VI) as shown in Fig 1. This may be due to the increased surface area and the availability of more adsorption sites. After certain adsorbent dose the removal efficiency is not increased so significantly due to the aggregation of adsorption sites with decrease in surface area of particles available to hexavalent chromium ions. All the curves obtained were smooth indicating formation of monolayer on the surface of adsorbent. In the initial stage the slope of the plot was around one and it decreases with time.

![Effect of mass of adsorbent on the adsorption of Cr(VI)](image)

**Fig 1**: Effect of Adsorbent Dosage on Adsorption of Cr (VI)

3.1.2 **Effect of concentration on the adsorption of the metal ions**

The increase in concentration of adsorbate decreases the chromium removal efficiency Fig 2. The maximum percentage of Cr (VI) is observed for lower initial concentration because at low metal concentration the ratio of metal ion/adsorbent ratio, metal ion adsorption involves higher energy sites. As the metal ion/adsorbent ratio increases, the available active sites get saturated, which resulted in decrease in the adsorption efficiency.
Effect of concentration on the adsorption of the metal ions

**Fig 2:** Effect of concentration on the adsorption of the metal ions

<table>
<thead>
<tr>
<th></th>
<th>Sugarcane Bagasse</th>
<th>Saw Dust</th>
<th>Orange Peels</th>
<th>Dried Rice Husk</th>
<th>Rice Husk Ash</th>
</tr>
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<tbody>
<tr>
<td>pH = 3</td>
<td></td>
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<tr>
<td>Contact time= 45min</td>
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<td>Size of adsorbent= 30 micron</td>
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<td>Adsorbent dose = 1 gm</td>
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</table>

**Initial concentration of adsorbates in solution (mg/L)**

10 20 40 60 80 100

% amount of metal ion adsorbed

**Initial concentration of adsorbates in solution (mg/L)**

10 20 40 60 80 100

% amount of metal ion adsorbed

3.1.3 Effect of pH on the adsorption of metal ions

The adsorption capacity of the adsorbents as the function of hydrogen ion concentration (pH) was determined in Fig 3. The optimum pH for removal of Cr (VI) was found to be at 3.

**Fig 3:** Effect of pH on the adsorption of metal ions

<table>
<thead>
<tr>
<th></th>
<th>Sugarcane Bagasse</th>
<th>Saw Dust</th>
<th>Orange Peels</th>
<th>Dried Rice Husk</th>
<th>Rice Husk Ash</th>
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<td>pH</td>
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<td>12</td>
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</table>

% Adsorption

Contact time= 45min

Initial Cr(VI) conc= 5ppm

Size of adsorbent= 30 micron

Adsorbent dose = 1 gm

Chromium exists mostly in two oxidation states which are Cr (VI) and Cr (III) and stability of these forms is dependent on the pH of the system. It is well known that the dominant form of Cr (VI) at higher pH is $\text{HCrO}_4^-$ . Increase in pH shifts the concentration of $\text{HCrO}_4^-$ to other forms $\text{CrO}_4^{2-}$ and $\text{Cr}_2\text{O}_7^{2-}$. At higher pH maximum adsorption indicates that it was the $\text{HCrO}_4^-$ form of Cr (VI) which was the predominant species. When the pH was further increased after 3 a decrease in percentage adsorption was observed. This might be due to the weakening of electrostatic force of attraction between the oppositely charged adsorbate and adsorbent and ultimately lead to the reduction in adsorption capacity. Beyond 6 sharp decrease is observed this is due to the competition between OH$^-$ and chromate ions ($\text{CrO}_4^{2-}$).

The net positive surface potential of the adsorbent decreased with increasing pH resulting in weakening of electrostatic force between adsorbate and adsorbent which ultimately lead to lowering of sorption capacity [2]. The high chromium(VI) removal at low pH values is probably due to reduction of chromium(VI) to chromium(III) in accordance with the following reactions taking place at low and moderate pH values.

At low pH

$$\text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ + 6 \text{e}^- = 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$$

At moderate pH

$$\text{HCrO}_4^- + 7\text{H}^+ + 3\text{e}^- = \text{Cr}^{3+} + 4\text{H}_2\text{O}$$

The predominant anionic forms at low pH values are $\text{Cr}_2\text{O}_7^{2-}$ and $\text{HCrO}_4^-$ which have the tendency to oxidize the adsorbent surface thereby getting it reduced and remains in solution as Cr (III). Therefore it is investigated that the removal of Cr(VI) is governed by both chemical reduction [Cr(VI) to Cr(III)] and physico-chemical adsorption [mainly Cr(VI)].
3.1.4 Effect of contact time on the adsorption of metal ion

The effect of contact time on adsorption was studied at different initial concentrations with various adsorption dosages in Fig 4. It is obvious that increase in contact time from 30min to 300min enhances significantly the percentage removal of Cr (VI). The initial rapid adsorption gives away a very slow approach to equilibrium. The nature of adsorbent and its available adsorption sites affected the time needed to reach the equilibrium.

![Effect of contact time on the adsorption of metal ion](image)

Fig 4: Effect of contact time on the adsorption of metal ion

3.2 Adsorption Isotherms

To examine the relationship between adsorbed \(q_e\) and the aqueous concentration \(C_e\) at equilibrium sorption isotherm models are widely employed. The isotherm results were analyzed using the Langmuir, Freundlich and Temkin isotherms. The Langmuir adsorption model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, with no lateral interaction between the adsorbed molecules. The Langmuir adsorption isotherm has been successfully used to explain the adsorption of hexavalent chromium from aqueous solutions. The expression of the Langmuir model is given [5] by Eq.(4)

\[
\frac{1}{q_e} = \frac{1}{q_a} + \frac{1}{q_a K_L C_e}
\]

(Linear form)

\[
q_e = q_a \left(1 + \frac{K_L C_e}{q_a}\right)^{-1}
\]

Where \(q_a\) is the maximum amount of adsorbed per unit mass of adsorbent at equilibrium, \(C_e\) is the equilibrium concentration of Cr (VI), \(K_L\) is the Langmuir constant, with \(q_a\) and \(K_L\) calculated from the slope and the intercept of the plot.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor \(R_L\) [5] that is given by the following Eq.(5)

\[
R_L = \frac{1}{1 + k C_0}
\]

Where \(k\) is the highest initial concentration of hexavalent chromium (mg/L) and \(C_0\) is Langmuir constant. The \(R_L\) value indicates the shape of the isotherm to be either unfavorable \((R_L > 1)\), linear \((R_L = 1)\), favorable \((0 < R_L < 1)\), or irreversible \((R_L = 0)\). The \(R_L\) values between 0 and 1 indicate favorable adsorption. The value of \(R_L\) in the present investigation was found to be favorable.

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. The Freundlich equation is expressed as [6]:

\[
q_e = K_f C_e^{1/n}
\]

Where \(K_f\) and \(n\) are Freundlich constants with \(K_f\) (mg/g (L/mg)^1/n) is the adsorption capacity of the sorbent and \(n\) giving an indication of how favorable the adsorption process. The magnitude of the exponent, 1/n, gives an indication of the favorability of adsorption. Values of \(n > 1\) represent favourable adsorption condition. To determine the constants \(K_f\) and \(n\), the linear form of the equation may be used to produce a graph of \(\ln(q_e)\) against \(\ln(C_e)\) [7].
\[
\ln q_e = \ln K_f + \left(1 - \frac{1}{n}\right) \ln C_e \quad \text{(Linear form)}
\]

Temkin isotherm model considers the effect of indirect adsorbent-adsorbate interactions on adsorption, and suggests that the heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to these interactions. This model also assumes that adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. The derivation of the Temkin isotherm assumes that the fall in the heat of adsorption is linear rather than logarithmic, as implied in the Freundlich equation \[11\], \[13\], \[14\]. The Temkin isotherm has commonly been applied in the following form:

\[
q_e = B_1 \ln K_T + B_1 \ln C_e
\]

Where \(B_1\) is the Temkin constant related to the heat of adsorption and \(K_T\) is the equilibrium binding constant (L/mg–1). The constant \(K_T\) and \(B_1\) can be determined by a plot of \(q_e\) versus \(\ln C_e\). The isotherm data obtained for Langmuir, Freundlich and Temkin adsorption isotherm is shown in Table 1, the Langmuir isotherm fits quite well with the experimental data (correlation coefficient in the range 0.96-0.99), whereas, the low correlation coefficients \(R^2 < 0.84\) show poor agreement for Freundlich and \(R^2 < 0.82\) show poor agreement for Temkin isotherms with the experimental data. The Isotherm constant for Cr (VI) on various adsorbents is tabulated in Table 2.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Langmuir</th>
<th>Freundlich</th>
<th>Temkin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Equation of graph</td>
<td>R²</td>
<td>Equation of graph</td>
</tr>
<tr>
<td>Dried Rice Husk</td>
<td>(y=0.28x+0.059)</td>
<td>0.97</td>
<td>(y=0.65x+0.508)</td>
</tr>
<tr>
<td>Rice husk ash</td>
<td>(y=798x+0.09)</td>
<td>0.99</td>
<td>(y=0.748x+0.088)</td>
</tr>
<tr>
<td>Orange peels</td>
<td>(y=1.146x+0.079)</td>
<td>0.97</td>
<td>(y=0.389x+0.296)</td>
</tr>
<tr>
<td>Sugarcane bagasse</td>
<td>(y=0.296x+0.195)</td>
<td>0.96</td>
<td>(y=0.883x+0.14)</td>
</tr>
<tr>
<td>Sawdust</td>
<td>(y=0.339x+0.219)</td>
<td>0.98</td>
<td>(y=0.311x+0.327)</td>
</tr>
</tbody>
</table>

Table 1: Adsorption Isotherm equations and regression data for the adsorption of Cr (VI)

The value of adsorption capacity \(q_a\) (maximum uptake) is highest (16.94 mg/g) for dried rice husk. Sawdust shows the lowest value of adsorption capacity \(q_a\) (4.56 mg/g). However the isotherm parameters, together with the correlation coefficient, of the Langmuir equation for the adsorption of Cr(VI) on the different adsorbents shows that the Langmuir equation gives a good fit to the adsorption isotherm. The fact that the Langmuir isotherm fits the experimental data very well may be due to homogeneous distribution of active sites onto adsorbents surface, since the Langmuir equation assumes that the surface is homogenous.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Langmuir</th>
<th>Freundlich</th>
<th>Temkin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(q_a) (mg g(^{-1}))</td>
<td>(R_L)</td>
<td>(K_L) (L/mg(^{-1}))</td>
</tr>
<tr>
<td>Dried Rice Husk</td>
<td>16.94</td>
<td>0.45</td>
<td>0.21</td>
</tr>
<tr>
<td>Rice husk ash</td>
<td>11.11</td>
<td>0.60</td>
<td>0.11</td>
</tr>
<tr>
<td>Orange peels</td>
<td>12.65</td>
<td>0.74</td>
<td>0.06</td>
</tr>
<tr>
<td>Sugarcane bagasse</td>
<td>5.128</td>
<td>0.21</td>
<td>0.65</td>
</tr>
<tr>
<td>Sawdust</td>
<td>4.56</td>
<td>0.21</td>
<td>0.64</td>
</tr>
</tbody>
</table>

Table 2: Isotherm constants for Cr (VI) on various adsorbents

3.3 Adsorption kinetics

For the examination of the controlling mechanisms of adsorption process, such as chemical reaction, diffusion control and mass transfer, several kinetic models are used to test the experimental data. For the present study, two kinetic models were applied in order to understand the mechanism of adsorption of Cr (VI) onto the adsorbent. The models are the pseudo-first order and pseudo-second-order models. A linear form of pseudo-first-order model was described by Lagergren [2] in the form:

\[
\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t
\]

where \(q_e\) and \(q_t\) represent the amounts of ions adsorbed (mg g\(^{-1}\) at equilibrium and at any time, \(t\) (min), \(k_1\) is the rate constant (min\(^{-1}\)). The values of \(q_e\) and \(k_1\) were deduced from the intercepts and slopes of the linear plots of
log \( (q_e - q_t) \) against \( t \) (not shown). For the present study however, Lagergren pseudo-first order kinetics parameters (Table 3) was not proved to be effective in representing the experimental kinetic data for the entire adsorption period and at all dye concentrations. Report of non fitting of pseudo-first order kinetic to adsorption has been published [11], [14], [15]. The pseudo-second order kinetic model can be represented with the following equation:

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e} \tag{10}
\]

where \( k_2 \) is the rate constant of pseudo-second order adsorption (gmg\(^{-1}\)min\(^{-1}\)). The adsorption process could be said to follow pseudo-second order kinetic model for adsorbents. The applicability of the pseudo-second order model suggests that chemical reaction might be responsible for adsorption of Cr (VI) onto various adsorbents. The kinetics of adsorption of Cr (VI) on various adsorbents materials have been reported to conform to pseudo-second order kinetic model. The values of \( K_2 \) and \( q_e \) were determined from the intercepts and slopes of the linear plots shown in Fig 4.

\[
t = C + k_{id} q_{1/2} \tag{11}
\]

where \( C \) is the intercept and \( k_{id} \) is the intraparticle diffusion rate constant (mg/g h\(^{1/2}\)), which can be evaluated from the slope of the linear plot of \( q_t \) versus \( t^{1/2} \) as shown in Fig 5. The intercept of the plot reflects the boundary layer effect. The larger the intercept, greater the contribution of the surface sorption in the rate controlling step. The calculated intraparticle diffusion coefficient \( k_{id} \) values are listed in Table 3. If the regression of \( q_t \) versus \( t^{1/2} \) is linear and passes through the origin, then intraparticle diffusion is the sole rate-limiting step. However, the linear plots at each concentration did not pass through the origin. This indicates that the intraparticle diffusion was not only rate controlling step.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Pseudo-first order</th>
<th>Second-order order</th>
<th>Intra-particle diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( K_1 ) (hr(^{-1})) ( R^2 )</td>
<td>( K_2 ) (g/mg h) ( R^2 )</td>
<td>( k_{id} ) (mg/gm(min(^{-1})))</td>
</tr>
<tr>
<td>Dried rice husk</td>
<td>-4.6 x 10(^{-4}) 0.930</td>
<td>3.6 x 10(^{-3}) 0.993</td>
<td>0.028</td>
</tr>
<tr>
<td>Orange peels</td>
<td>0.027 0.588</td>
<td>2.9 x 10(^{-3}) 0.966</td>
<td>0.028</td>
</tr>
<tr>
<td>Sawdust</td>
<td>0.054 0.641</td>
<td>1.88 x 10(^{-3}) 0.989</td>
<td>0.036</td>
</tr>
<tr>
<td>Sugarcane Bagasse</td>
<td>0.047 0.438</td>
<td>3.41 x 10(^{-3}) 0.992</td>
<td>0.029</td>
</tr>
<tr>
<td>Rice husk ash</td>
<td>0.058 0.631</td>
<td>1.28 x 10(^{-3}) 0.976</td>
<td>0.037</td>
</tr>
</tbody>
</table>

Table 3: Adsorption kinetic parameters for the adsorption of Cr (VI) by various adsorbents

3.4 Sorption Mechanism

In order to gain insight into the mechanisms and rate controlling steps affecting the kinetics of adsorption, the kinetic experimental results were fitted to the Weber’s intraparticle diffusion. The kinetic results were analyzed by the intraparticle diffusion model to elucidate the diffusion mechanism [14], which model is expressed as:

\[
q_t = k_{id} t^{1/2} + C
\]

where \( C \) is the intercept and \( k_{id} \) is the intraparticle diffusion rate constant (mg/g h\(^{1/2}\)), which can be evaluated from the slope of the linear plot of \( q_t \) versus \( t^{1/2} \) as shown in Fig 5. The intercept of the plot reflects the boundary layer effect. The larger the intercept, greater the contribution of the surface sorption in the rate controlling step. The calculated intraparticle diffusion coefficient \( k_{id} \) values are listed in Table 3. If the regression of \( q_t \) versus \( t^{1/2} \) is linear and passes through the origin, then intraparticle diffusion is the sole rate-limiting step. However, the linear plots at each concentration did not pass through the origin. This indicates that the intraparticle diffusion was not only rate controlling step.
Plots to Evaluate Intraparticle Diffusion rate constant

Fig.5: Plots for evaluating intraparticle diffusion rate constant

3.5 Design of Batch adsorption from Isotherm data

\[ q_0 \text{ mg of solute/g of adsorbent} \]
\[ V, L \text{ of solvent} \]
\[ C_0 \text{ mg of solute/L of Solvent} \]
\[ q_1 \text{ mg of solute/g of adsorbent} \]
\[ W, g \text{ of adsorbent} \]
\[ V, L \text{ of solvent} \]
\[ C_1 \text{ mg of solute/L of Solvent} \]

Fig 6: A single stage batch Adsorber.

A schematic diagram of a batch sorption process is shown in Fig. 6 where the adsorbate contains V(L) of solution and an initial chromium concentration \( C_0 \), which is to be reduced to \( C_1 \) in the adsorption process. During the adsorption stage \( W \) (g) various adsorbent is added separately to aqueous solution and the chromium concentration on the solid changes from \( q_0 = 0 \) (initially) to \( q_1 \). The mass balance for the chromium in the single-stage is given by

\[ V(C_0 - C_1) = W(q_0 - q_1) \]  

(12)

Under equilibrium conditions,

\[ C_1 \rightarrow C_e \text{ and } q_1 \rightarrow q_e \]

\[ VC_0 + Wq_0 = VC_e + Wq_e \]  

(13)

For the adsorption of chromium on various adsorbents, the Langmuir isotherm gives the best fit to experimental data. Consequently equation can be best substituted for \( q_1 \) in the rearrangement form of equation 13 giving adsorbent/solution ratios for the present system of various adsorbents

\[ W = \frac{(C_0 - C_1)}{q_e} = \frac{C_0 - C_e}{Q_0bC_e/(1 + bC_e)} \]  

(14)

3.6 Cost Estimation

The agricultural, timber and fruits waste has no significant industrial or commercial uses but if neglected becomes an issue and contributes to serious environmental problems. Hence, the utilization of such wastes for waste water treatment in most desirable. These wastes can be used as adsorbent which are low in cost. The cost of the adsorbents used in this study for removal of hexavalent chromium is only associated with the transport and process expenses. The process expenses include washing with de-ionized double distilled water, drying in oven, treating with chemicals or burning in furnace. The adsorbents dried rice husk, rice husk ash,
sugarcane bagasse, and orange peels, sawdust prepared in present study costs Rs. 58, 99, 222, 46, 700 per kg respectively including both transportation and processing costs. Whereas, the conventional adsorbents used for removal of hexavalent chromium are very costly. The adsorbent used in present study is renewable material, abundantly available and, therefore, low cost adsorbent. The adsorbents used in present study would be an economical alternative for the commercially available activated carbon in removal of hexavalent chromium from aqueous solution.

4. CONCLUSION

The study indicated the suitability of the adsorbents used for removal of Cr (VI) from aqueous solution. Dried rice husk- an agricultural waste was found to be the most effective one, for which the removal efficiency reached to 70% of Cr(VI) at room temperature at adsorbent dose of 1gm. The optimum pH for the removal was found to be at 3. Increase in the concentration of the adsorbent and contact time were found to increase the % removal of Cr(VI). While increasing the initial Cr(VI) concentration, removal percentage decreases for all the four adsorbents by keeping the other conditions like pH, concentration of the absorbent and temperature constant. Results obtained were modeled using three isotherm models: Langmuir, Freundlich and Temkin. Equilibrium isotherms were well described by the Langmuir equation, giving maximum adsorption capacity of 16.94 mg/g at room temperature for dried rice husk. The adsorption kinetics can be well described by the pseudo-second-order model equation. Adsorbents used in this work is freely, abundantly and locally available, the resulting sorbent is expected to be economically viable for removal of Cr (VI) from aqueous solution.

5. NOMENCLATURE

- $B_1$ = Temkin constant
- $C_e$ = Equilibrium concentration of Cr(VI), mg/L
- $C_0$ = Initial concentration of of Cr(VI), mg/L
- $K_f$ = Freundlich constant, (mg/g(L/mg) $^{1/n}$)
- $K_L$ = Langmuir constant, L/mg
- $K_T$ = Temkin constant, L/mg
- $K_a$ = Rate constant of pseudo-second-order adsorption, g mg-1min-1
- $K_1$ = Rate constant of the pseudo-first-order adsorption process, min-1
- $k_{id}$ = Intraparticle diffusion coefficient (mg/gm(min$^{-1}$))
- $m$ = amount of adsorbent added in gram
- $n$ = adsorption intensity (dimensionless constant)
- $q$ = amount adsorbed per gram of adsorbent
- $q_e$ = amount adsorbed per gm of the adsorbent at equilibrium
- $q_t$ = amount adsorbed per gram of adsorbent at time t(min)
- $q_a$ = maximum capacity of the adsorbent(mg/g)
- $R_L$ = equilibrium parameter
- $R^2$ = correlation coefficient
- $R$ = Gas constant, 8.314 J/mol/K
- $T$ = Temperature, K
- $t$ = Time, min
- $V$ = Volume of the adsorbent, L
- $W$ = Weight of the adsorbent, g

6. REFERENCES


