Physisorption of Chromium from Aqueous Solutions Using Agro and Horticultural Wastes as Adsorbent

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Abstract

Batch experiments were conducted at room temperature to evaluate the performance and feasibility of various agro and horticultural waste sorbents such as Petha (Benincasa hispida) waste (PW), discarded potato (Solanum tuberosum) waste from cold storages (DPWC) and almond seed (Prunus dulcis) shell waste (ASSW) to remove chromium (VI) from the aqueous solutions. Impacts of pH, adsorbent dose, initial adsorbate concentration, temperature, contact time, adsorbent grain size and start up agitation speed on chromium removal efficiency were investigated. The highest adsorption was found at pH 4.5-5.0 with initial chromium concentration of 50 mg/L, at startup agitation speed 80 rpm, with adsorbent grain size 1.18 mm with adsorbent doses 10 g/L for PW and ASSW and 20 g/L for DPWC in first 45 - 135 minutes of contact time. Equilibrium adsorption isotherms and kinetics were analyzed. The adsorption isotherm data were fitted to Langmuir, Freundlich and Tempkin isotherms. The Langmuir maximum monolayer coverage capacities have been observed as 2.75 mg/g, 2.00 mg/g and 11.11mg/g for PW, DPWC and ASSW respectively with separation factors (R_L) as 0.0299, 0.0151 and 0.0985 showing favorable adsorption influenced by pH of metal solution. From Freundlich isotherm model the sorption intensity (n) less than unity also revealed the normal adsorption. The heat of sorption (B) was also determined from Tempkin isotherm model as 0.282, 0.161 and 0.179 respectively, vividly proving a favorable physical sorption. The positive Gibbs free energy was found maximum for PW as 0.3295 KJ/mole. Out of the above combination of adsorbents of this study petha waste was comparatively the best economic and suitable adsorbent for the removal of hexavalent chromium from aqueous solutions.
INTRODUCTION

Chromium causes Nausea, vomiting, epiesgestric pain, severe diarrhea, hemorrhage, dermatitis by skin contact, nasal mucous membrane, ulcer (Satyanarayan et al, 1995), lung cancer and tissue necrosis in humans, reduction in fish production at high concentrations, chromium accumulates in fish tissues and reaches to consumers. Gold fish and trout are killed at a concentration of 180 mg/l (Sohail, 1997, Xavier, et al 2013, Attia, et al 2010).

The Indian industrial estate is full of a variety of small, medium and large scale industries like electroplating, metal finishing, cooling towers, dyes, paints, anodizing and leather tanning industries, where chromium is frequently used and is found as traces in effluents finding their way to natural drains or rivers or some other water bodies causing hazardous toxicity to the health of humans, animals and aquatic lives directly or indirectly. Various methods for the removal of chromium reported in literature being expensive and not very easy to operate so a study of physiosorption by agro and horticultural wastes has been tried which is quite simple, inexpensive and effective method (Ayub, et al, 1998, 1999, 2001, 2002, 2014, Mulu Berhe Desta, 2013).

Agra is worldwide famous for leather production, leather foot wear manufacturing, potato farming, petha sweet with high consumption of dry fruits as a result, a lot of discarded potato waste from cold storages, petha solid waste, almond seed shell waste is generated which either causes solid waste disposal problem and somehow it finds way to Yamuna river resulting high BOD and posing a serious threat to the aquatic environment. Keeping this in view adsorption studies were made using petha solid waste, discarded potato waste from cold storages and almond seed shell waste as low cost adsorbent for Chromium removal was dual beneficial i.e., an ideal solution to overcome the local disposal problem of these plenty solid wastes of Agra and removal of chromium from tannery effluents and thereby saving aquatic life from chromium contamination in Yamuna river (Baskaran, P.K. et al 2010, Gupta and Mote, 2014, Sharma, et al, 2010, 2013, 2015, 2016, 2016).

SAMPLE COLLECTION:

Many wastewater samples were tested for pH, chloride, alkalinity, suspended solids, hardness, total dissolved solids and chromium content. Mostly the surface water was within the chromium safe limit except a few cases where the water was found not very good for direct disposal in river. However, the chromium content in the surface water was found above the prescribed EPA safe limit 0.1 mg/L.

The surface water samples from various locations were collected and analyzed for the various parameters and results have been listed in Table:1.
Table 1: Quality Parameters of Surface Water of Agra City

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Location</th>
<th>pH</th>
<th>Chloride mg/l</th>
<th>Alkalinity mg/l as CaCO₃</th>
<th>Suspended Solids mg/l</th>
<th>Hardness mg/l as CaCO₃</th>
<th>Total Solids mg/l</th>
<th>Chromium (VI) mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Tundala Road</td>
<td>7.4</td>
<td>78.4</td>
<td>54.5</td>
<td>282</td>
<td>398.5</td>
<td>960.0</td>
<td>13.2</td>
</tr>
<tr>
<td>2</td>
<td>NH-2 Runkta-Sikandra</td>
<td>6.5</td>
<td>120.6</td>
<td>60.2</td>
<td>432</td>
<td>660.6</td>
<td>1580</td>
<td>54.6</td>
</tr>
<tr>
<td>3</td>
<td>Industrial area, Shastripuram</td>
<td>6.4</td>
<td>110.4</td>
<td>52.4</td>
<td>250</td>
<td>400.5</td>
<td>700</td>
<td>52.4</td>
</tr>
<tr>
<td>4</td>
<td>Foundry Nagar, Hathras Road</td>
<td>6.8</td>
<td>145</td>
<td>53.4</td>
<td>360</td>
<td>340.2</td>
<td>1100</td>
<td>39.6</td>
</tr>
<tr>
<td>5</td>
<td>Bharat Pur Road</td>
<td>7.0</td>
<td>155.3</td>
<td>70.2</td>
<td>364</td>
<td>745.6</td>
<td>1540</td>
<td>3.6</td>
</tr>
<tr>
<td>6</td>
<td>Gawalior Road</td>
<td>7.8</td>
<td>160</td>
<td>75.8</td>
<td>400</td>
<td>258.4</td>
<td>2000</td>
<td>2.4</td>
</tr>
<tr>
<td>7</td>
<td>Yamuna at Taj</td>
<td>6.7</td>
<td>180</td>
<td>82.4</td>
<td>660</td>
<td>300.5</td>
<td>2440</td>
<td>49.8</td>
</tr>
</tbody>
</table>

MATERIALS AND METHODS

To investigate the hexavalent chromium adsorption capacity of Petha solid waste, discarded potato waste from cold storages and almond seed shell waste, batch experiments were carried out using synthetic wastewater with known concentrations of Cr (VI) kept in glass stoppered conical flasks to mix known quantities of the adsorbent. The system was equilibrated by shaking the contents of the flask at room temperature so that adequate contact time between adsorbent and the metal ion was achieved. The suspension was filtered through Whatman No.1 filter paper and the filtrate was analyzed to evaluate the remaining concentration of Cr (VI) metal in the treated wastewater as per Standard Methods (Standard Methods, 1989) using Atomic Absorption Spectrometer (Perkin Elmer, Atomic Absorption Spectrometer, Pin AAcle 900F, Civil Engineering Department, Aligarh Muslim University).

SITE DESCRIPTION, COLLECTION AND PREPARATION OF ADSORBENTS

Petha Waste from Petha Industries

For sampling, we visited Noori Gate, Agra and found many large heaps of petha waste along the road side where from we collected it in a plastic carry bag and after sun drying for 15 days oven drying for 5 hours per day for 3 days ground it to powder form.

Discarded Potato Waste from Cold storages

The discarded potato from local cold storages at Khandauli town (Agra) was collected, meshed and sun dried for 10 days. After removing all dirt and peel dust the
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Dry meshed potato was grinded to the powder form and then oven dried for two days at 90°C five hours daily.

**Almond Seed Shell Waste**

After using almond seeds as dry fruits, a healthier diet with high protein, the outer hard almond shell waste which was almost dry, even after sun and oven drying for two days at 90°C five hours daily during laboratory working hours. The beauty of this adsorbent was that it was almost free from lignin so there was no fear of increased BOD left after tannery wastewater treatment.

After grinding all the above adsorbents collected the dry powders were sieved through a 225 mesh (Indian Standard Sieve) to get an average and uniform sized particle. Then we washed these powders several times with distilled water to get rid of lighter materials, color releasing substances, dirt and other impurities. The adsorbent was dipped in 0.1N NaOH for a period of 9 hrs and washed several times with distilled water to remove the lignin and then dried again. The adsorbent was again rinsed separately with double distilled water two times and dipped into 0.1N H2SO4 for the period of 9 hrs again to remove traces of alkalinity. The acid treated adsorbent was washed thoroughly with double distilled water. Then the dry powders so prepared were exposed to sun and stored in a desiccator. Before using the powders as adsorbent a size range was also achieved by sieving through a sieve set 1.7 mm, 1.18mm, 600µm, 425µm, 300µm, 150µm, 75µm and pan i.e. less than 75µm (Indian Standard Sieve) so as to optimize the size of the adsorbent.

**Experimental Procedure**

To understand the adsorption behavior a series of batch experiments were conducted as per the Standard Methods to investigate the effects of various parameters such as pH, adsorbent dose, initial concentration of the chromium metal, contact time, temperature, adsorbent particle size and agitation speeds etc. For all these studies, synthetic wastewater of various concentrations of hexavalent chromium was prepared from the stock solution and kept separately in glass stoppered conical flasks. Then suitable doses of adsorbents had been added to these wastewaters kept in conical flasks each of capacity 250 ml. The contents of the system were shaked for equilibration at room temperature on a mechanical shaker (Indian Scientific Instruments Factory, Ambala Cantt, India) so as to achieve all-round contact and adequate contact time between adsorbent and the metal ions. After maintaining proper time of quiescent adsorption, the suspension was filtered through Whatman (No. 1) filter paper and then the filtrate was analyzed for the concentration of hexavalent chromium metal in the treated wastewater by using Atomic Absorption Spectrometer (Perkin Elmer, Atomic Absorption Spectrometer, PinAAcle 900F). Adsorption studies were made for various times and as a result optimum time of adsorption was also determined. During the study the room temperature was 20 to 25°C in winter and 35
to 40°C in summer. To study the effect of temperature variation the temperature was maintained using heaters in a closed chamber.

RESULTS AND DISCUSSIONS

While investigating the effect of pH, adsorbent dose, contact time, temperature, adsorbent grain size and startup investigating agitation speed; the initial chromium (VI) was kept 50 mg/l, as found in tannery waste water and also reported chromium concentration from chrome plating wastewater varying from 3-50 mg/l (ISI 7453-1977).

Effect of pH on Fraction Removed.
The adsorption of other ions is severely influenced due to strong adsorption of hydrogen from the solution and hydroxyl ions on the adsorbents. The pH of the solution also influences the degree of ionization which ultimately affects the adsorption process (Khan, et al 2001). In the present study various pH values maintained by 1M sulphuric acid and 1M sodium hydroxide ranging from 1.0 to 6.0 have been studied with an initial chromium concentration of 50 mg/l. An adsorbent dose of 10 g/l was added to 50 ml of synthetic wastewater for the evaluation of hexavalent chromium removal by adsorbents such as Petha solid waste (PW), discarded potato waste from cold storages (DPWC) and almond seed shell waste (ASSW). The most suitable pH for the above set of parameters was found to be in the range 4.5 to 5. as shown in Figure 1

![Figure 1: Effect of pH on Chromium Cr (VI) Sorption](image)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>25°C</td>
</tr>
<tr>
<td>Initial Conc.</td>
<td>50 mg/l</td>
</tr>
<tr>
<td>Adsorbent dose</td>
<td>10 g/l</td>
</tr>
<tr>
<td>Contact time</td>
<td>1 hr</td>
</tr>
<tr>
<td>Size of adsorbent</td>
<td>300-600 μm (average size)</td>
</tr>
<tr>
<td>Agitation speed</td>
<td>80 rpm</td>
</tr>
</tbody>
</table>

Effect of Adsorbent Dose on Fraction Removed.
Maintaining pH 4.5 to 5.0 at room temperature 25°C all the samples with amount 50 ml having initial chromium concentration 50 mg/l were tested for 1 hour time of...
contact for various doses of adsorbents right from 10 to 50 g/l with average sizes of adsorbent particles at rate of 80 rpm agitation speed and the observations for various adsorbents were analyzed. It has been observed that adsorption capacity of the adsorbents petha waste (PW) decreases on increasing the doses from 10 g/l whereas in the case of discarded potato waste from cold storages (DPWC) and almond seed shell waste (ASSW); the same thing occurs after an optimum value of 20 g/l i.e. the optimum values of adsorbent doses may differ for various adsorbents as shown in Figure -2.

![Figure 2: Effect of sorbent dose on Sorption](image)

Here in the present study the optimum range of adsorbent dose was found to be 10 to 20 g/l and there after the adsorption capacity remains almost the same i.e. meaning to say that beyond a proper dose additional doses are ineffective, so there is no use of wasting extra adsorbents which could be used further. Perhaps this might be due to the saturation in adsorption capacities or a very few amount of adsorbate remaining in the solution further to be adsorbed (Sharma, et al, 2016).

**Effect of initial chromium concentration on Fraction Removed**

Synthetic wastewater samples each 50 ml, having different concentrations of hexavalent chromium ranging 10 to 60 mg/l were taken separately in glass stoppered conical flasks, and then already decided best average doses of adsorbents 25 g/l were added to each flask. At initial stages the contact time was 1 hour for all average sized adsorbents at room temperature $25^\circ\text{C} \pm 1^\circ\text{C}$ at pH 4.5. The common pattern of adsorption in case of discarded potato waste from cold storages (DPWC) and almond seed shell waste (ASSW) was found that as we increase the initial chromium concentration the adsorption capacity of the adsorbents decreases; the optimized initial chromium concentration for these two adsorbents was found 10 mg/l, whereas for the petha waste (PW) its optimum value was observed 30-50 mg/l and this is why the petha waste is best suited adsorbent for the adsorption of chromium locally in Agra region with view point of its plenty availability as well as the amount of chromium observed
in tannery wastewater in the same range here at Agra local. The reason of decrease in adsorption with increased amount of initial chromium concentration may be because of all sites of adsorbents get saturated there remains no further scope of adsorption (Sharma, et al, 2015, 2016, 2016) as shown in Figure 3.

Effect of Contact Time on Fraction Removed.
Contact time plays a very crucial role in adsorption. Uptaking of adsorbate species is found quite rapid in the initial stages of the contact period between adsorbent and adsorbate combinations but gradually become slower as soon as equilibrium reaches (Ayub, et al, 2014, Sharma,P.K., et al, 2015, 2016, 2016). Various synthetic samples in optimum pH 4.5, with average size, adsorbent dose 25 g/l, initial chromium concentration of 50 mg/l, at room temperature 25ºC ±1ºC having agitation speed 80 rpm at start, were tested for different periods of contacts right from 45 minutes to 270 minutes for various adsorbents and a common pattern of adsorption was observed and optimized contact time was 1hr. Almost 65% of adsorption occurs in first 45 minutes after which adsorption continues but slowly. For an optimization of contact time it was ideal to keep the contact time 1 hour so as to save time and get maximum adsorption possible. Only in case of DPWC, the optimum value of contact time was observed 135 minutes and in first 45 minutes the adsorption recorded was more than 50%. Therefore, in rest of experiments the contact time was taken to be in the optimized range i.e.45 minutes to 1hour. The study analysis for various amounts combinations of adsorbate and adsorbents have been depicted in Fig-4 and very near to previous researchers.
Effect of Adsorbent Particle size on Fraction Removed

Indian Standard Sieved seven particle sizes < 75, 75, 150, 300, 425, 600, 1180 µm of various adsorbents at pH 4.5, with 25 g/l doses, with initial chromium concentration 50 mg/l, at room temperature 25°C±1°C with contact time 1 hour, at rate of 80 rpm starter agitation speed, were tested taking 50 ml samples in flasks. The study reveals that very small size also not very effective for adsorption, also it takes longer time and extra labour to grind it to micron size, making the adsorbent costlier. The optimum size that is why has been taken in the range 300 µm-600 µm as an average size (Sharma, et al., 2016, 2015, 2016). The study graphs shown in Figure 5.

Effect of Temperature on Fraction Removed.

Maintaining pH range 4.5, initial adsorbate concentration 50 mg/l (as existing in local tannery wastes) optimized average sized adsorbent dose of 25 g/l, with contact time 1 hour, starter agitation speed 80 rpm in all experimental set ups, the effect of
temperature variation, taking 50 ml of each sample was studied for varying temperatures like $10^\circ$C, $20^\circ$C, $30^\circ$C, $40^\circ$C and $50^\circ$C by keeping them in temperature controlled oven (Indian Scientific Instruments factory, Ambala Cant, India), were studied and after a series of observations literated temperature was verified as optimum temperature to obtain the optimum adsorption. The residual concentrations of chromium were subsequently determined. The optimum adsorption was found in all the cases of adsorption $25^\circ$C to $30^\circ$C. At higher temperatures desorption starts taking place (Ayub, et al, 2014). The study results shown in Figure 6.

![Temperature vs Sorption](image)

**Figure 6: Effect of Temperature on Sorption**

**Effect of startup Agitation Speed on Fraction Removed.**

Maintaining pH range 4.5, initial adsorbate concentration 50 mg/l, optimized average adsorbent grain sized from 300 µm to 600 µm, adsorbent dose of 25 g/l, with contact time 1 hour, various agitation speeds such as 80 rpm, 100 rpm, 120 rpm and 140 rpm, were tried in different samples each of 50 ml in flasks kept over different rpm set shaker. The observation revealed that more the agitation speed more greater was the adsorption but beyond a certain range of starter agitation speed i.e. 70 rpm to 90 rpm (optimum 80 rpm); the results were not very well, more over the higher speed was time, energy and maintenance consuming, resulting tear and wear and higher costs involved (Sharma, et al 2015, 2016, 2016). The study results so obtained are shown in Figure 7.
Taking best values of affecting parameters the batch study was made to obtain maximum adsorption of hexavalent chromium from wastewater using petha waste (PW), discarded potato from cold storages (DPWC) and almond seed shell waste (ASSW); as adsorbent and the results so obtained have been depicted in Figure 8.

**Figure 7:** Effect of Agitation Speed on Chromium Cr (VI) Sorption

**Figure 8:** Adsorption at fittest parameters for various sorbents
Column Study

Though the information obtained from the results of batch experimental set ups for the application of adsorption to the removal of wastes constituents study were very useful, yet the column study provides the practical application in wastewater treatment technology for the design of continuous adsorption columns. When wastewater enters the top of adsorbent clean bed, most of adsorbate is initially removed in a rather thin layer of top of the column which is referred as the adsorption zone and this way the top layer gets saturated with adsorbate. As the adsorption continues, the adsorption zone increases downward through the bed resulting the whole packing adsorbent material to be the adsorption zone up to the bottom of the column and eventually, saturated and the adsorbate concentration effluent thereby increases.

A plot effluent adsorbate concentration versus time usually shows an S-shaped curve which is known as break through curve and the point where adsorbate concentration in effluent reaches its maximum allowable value is known as break through (Sharma, P.K., et al, 2016).

A burette of internal diameter 1.0 cm was used for the column study at room temperature. The optimized dose of adsorbent as obtained from batch study was suspended in distilled water on magnetic stirrer for 15 minutes dispersing the particles by shaking it at agitation speed of 80 rpm so as to avoid conglomeration and then transferred in to the burette. The cotton was placed at top and bottom ends of the adsorbent in the column to avoid the loss with the liquid flow or floating. The flow rate was controlled by regulator used in outflow pipe maintaining 6.0 l/d. Concentrations of the influent stream to the burette and exit stream from the burette were determined using Atomic Absorption Spectrometer (Perkin Elmer, AAS, Pin AAcle 900K).

Comparison of Batch and Column Study for Fittest Parameters Using Tannery Wastewater

To compare the results of batch (synthetic) and column studies for fittest parameters (real tannery wastewater) with adjusted initial chromium concentrations 50 mg/l, at pH adjusted 5, temperature 25°C, agitation speed 80 rpm with average size adsorbent doses 10 g/l with contact time 3.75, 2.25 and 0.75 hour, of petha waste, discarded potato waste from cold storage and almond seed shell waste adsorbents respectively were tried and considerable reduction in chromium adsorption was found as shown in Figure 9.
The reduction in adsorption with real tannery wastewater may be due to other interfering ions present in tannery wastewater that acquire the available surface for adsorption on adsorbent. Some other contaminants present in tannery wastewater may also get adsorbed on the available surface reducing the adsorption surface for chromium (Sharma, et al, 2015, 2016, 2016).

**Desorption and Hydrolysis Tests**

Desorption test was also conducted for the best adsorbent after comparison petha, discarded potato from cold storage and almond seed shell waste used as adsorbent to remove the chromium i.e. petha waste. About 10 g of saturated adsorbent was kept in 300 ml capacity BOD bottle full of distilled water and shaken for two hours and then filtered. The filtering analyzed for the chromium residue and no desorption was observed.

**Rate Kinetics**

**Thermodynamic Parameters**

For each adsorbent “Gibb’s free energy versus Temperature in Kelvin” graphs as shown in Figure 10 (a), Fig-10 (b) and Fig-10 (c) for petha waste (PW), discarded potato waste from cold storage (DPWC) and almond seed shell waste (ASSW) respectively, were plotted and then using linear equation \( \Delta G = (-\Delta S) x + \Delta H \), the values of various thermo dynamic constants were determined and tabulated in Table-2 in later section (Sharma, et al; 2012 a & b, 2016, 2015, 2016).
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Figure 10 (a) PW

Figure 10 (b) DPWC

Fig-10 (c) ASSW
Table-2: Summary of Thermodynamic Parameters and Isotherms Constants for all adsorbents used in the study.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>(Max. monolayer coverage capacity, mg/g)</th>
<th>(Langmuir Constant) KL</th>
<th>Freundlich Constants</th>
<th>Temkin Constants</th>
<th>Thermodynamic Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>qmax</td>
<td>1/q0</td>
<td>RL</td>
<td>k</td>
<td>1/n</td>
</tr>
<tr>
<td>PW</td>
<td>2.75</td>
<td>0.36</td>
<td>0.6269</td>
<td>0.0299</td>
<td>1.244</td>
</tr>
<tr>
<td>DPWC</td>
<td>2.00</td>
<td>0.50</td>
<td>1.282</td>
<td>0.0151</td>
<td>1.179</td>
</tr>
<tr>
<td>ASSW</td>
<td>11.11</td>
<td>0.09</td>
<td>0.1627</td>
<td>0.0985</td>
<td>1.202</td>
</tr>
</tbody>
</table>

Keeping fixed initial chromium concentration 50 mg/l and varying doses of adsorbents in batch adsorption study, the data were fitted to the linearized Freundlich adsorption isotherm as

\[
\log (q_e) = \log K_f + \frac{1}{n} \log C_e \quad (\text{Dada, A.O; 2012})
\]

Where, \( q_e = \frac{x}{m} \) = the amount of hexavalent chromium adsorbed per unit mass of adsorbent (mg/mg). \( C_e \) = the equilibrium concentration of aqueous solution.

Kf = Constant of adsorption capacity. 1/n = Constant of adsorption intensity

The values of the thermodynamic constants using Freundlich isotherm as drawn in Figure 11 (a), (b) and (c) were calculated using best linearized equations

\[
Y = -0.139 x + 0.218, \quad y = -0.128 x + 0.165 \quad \text{and} \quad y = -0.120 x + 0.184
\]

As Freundlich Isotherm Constants (Kf) = 1.244, 1.179 and 1.202 along with 1/n = -0.139, -0.128 and -0.120 respectively for the adsorbents petha waste (PW), discarded potato waste from cold storages (DPWC) and almond seed shell waste (ASSW). Since 1/n values are <1, which indicates the favourable adsorption (Shrichand, 1994, Dada, A.O; 2012).
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**Figure 11 (a):** Plot of Freundlich Isotherm for (PW)

**Figure 11(b):** Plot of Freundlich Isotherm for (DPWC)

**Figure 11 (c):** Plot of Freundlich Isotherm for (ASSW)
4.3 Using Langmuir Isotherms

Langmuir equation \( q_e = (Q_o \, K_L \, C_e) / (1 + K_L \, C_e) \) transforming to linear form as

\[
1/q_e = 1/q_o + (1/q_o \, K_L) \, (1/C_e)
\]

\( KL = \) Langmuir Isotherm Constant (L/mg)

The values of \( q_{\text{max}} \) and \( K_L \) were computed from the slope and intercept of the Langmuir plot \( 1/q_e \) versus \( 1/C_e \).

The separation factor or equilibrium parameter \( R_L \), which is a dimensionless quantity and its value indicates the nature of adsorption means if \( R_L > 1 \) unfavorable, linear if \( R_L = 1 \), \( 0 < R_L < 1 \) favourable and irreversible if \( R_L = 0 \) (Dada, A.O; 2012).

\[
R_L = 1/[1+(1+K_L\,C_o)]
\]

Where,

\( C_o = \) initial concentration of adsorbate = 50 mg

\( K_L = \) Langmuir constant related to the energy of adsorption

All the above Langmuir constants were determined for all the adsorbents of which plots have been shown in Figure 12 (a), (b) and (c).

![Thermodynamic parameters (using Langmuir Isotherm)](image)

**Figure 12(a):** Plot of Langmuir Isotherm for (PW)
Using Temkin Isotherm

In Temkin isotherm “Qe versus ln Ce” is linearized to the form $Q_e = B \ln AT + B \ln Ce$.

(Dada, A.O; 2012)

For petha waste study, $B \ln AT = 1.810$, $B = 0.282$ j/mol (according to line equation), $AT = 615.54 = $ Temkin isotherm equilibrium binding constant (L/mg), $B = RT/bT = $ Constant related to heat of sorption (J/mol), $R = 8.314$ j/mol/K, $T=298K$, $bT = 8785.71 = $ Temkin isotherm constant, as shown in Fig-13(a). Negative sign indicates the physical sorption.
For discarded potato waste from cold storage (DPWC), using Temkin equation: 
\[ Q_e = B \ln AT + B \ln C_e \]

\[ B \ln AT = 1.187, \quad B = 0.161 \text{ j/mol (according to line equation),} \quad AT = 1599.313 = \text{Temkin isotherm equilibrium binding constant (L/mg),} \]
\[ R = 8.314 \text{ j/mol/K, T = 298 K,} \]
\[ bT = 15388.65 = \text{Temkin isotherm constant, as shown in Figure 13 (b).} \]

**Fig-13 (a)** Temkin Isotherm for PW

**Fig-13 (b)** Temkin Isotherm for DPWC
Scanning Electron Microscopy (SEM):

Scanning Electron Microscopy (SEM) was done to observe the surface characteristics of the adsorbents well before (RAW) and after adsorption (USED). The scanning electron microscopy of all adsorbents at various resolutions and magnifications was conducted in University Sophisticated Instrument Facilitation Centre, Aligarh Muslim University, Aligarh (INDIA) Scanning Electron Microscope JSM 6510 LV, Make. JEOL (Japan) under the technical help of Mr. Maaz Khan, the Technical Assistant at USIF Center, AMU, Aligarh, INDIA.

From these figures, it is investigated and evident that the structure of the used adsorbents has comparatively reduced percentage of honey combing structures in petha waste (PW), discarded potato waste from cold storage (DPWC) and pores in almond seed shell waste (ASSW) after the adsorption, indicating suitability for adsorption of chromium ions. A large surface area due to honey combing and pores is also evident from these photographs enhancing adsorption capacity. SEM photographs also reveal that the honey combing type porous structure found in adsorbent surface collapses to some extent which may be due to the fact that adsorbent being a natural biological material changing its characteristic (Sharma, P.K., et al 2016, 2015, 2016).
Figure 14: Scanning Electron microscopy for Raw (unused) Petha Waste

Figure 15: Scanning Electron microscopy for Used Petha Waste

Figure 16: Scanning Electron microscopy for Raw (unused) DPWC
Figure 17: Scanning Electron microscopy for Used DPWC

Figure 18: Scanning Electron Microscopy for Raw (unused) ASSW

Figure 19: Scanning Electron Microscopy for Used ASSW
CONCLUSIONS

The study can be concluded in the following points.

- Adsorption depends on the nature of adsorbent and all the agro and horticultural waste adsorbents would not behave in similar fashion.

- The chromium adsorption capacity of all the agro and horticultural adsorbents used in the study, is highly dependent on pH which is best suited in the range 4.5-5.0 and most of the tannery waste waters pH is found above 5.0 so generally pH adjustment is not needed.

- Percentage removal of chromium increases with decrease in initial chromium concentration. The optimized initial chromium concentration for waste potato from cold storage and almond seed shell adsorbents was found 10 mg/l, whereas for the petha waste (PW) its optimum value was observed 30-50 mg/l i.e. reverse in case of petha waste and hence petha waste was the superior to other adsorbents to adsorb chromium from aqueous solutions. Though chromium concentration can not be fixed in real tannery wastewater yet the study was made to compare the three adsorbents suitability as said.

- In the first hour chromium removal is very fast but slows down later as the saturation limit reached. Though the best sorption is found at 270 minutes of contact time but within 45 minutes of contact time almost 70 % sorption of hexavalent chromium is adsorbed so the contact time of 1 hour was taken as convenient so as to reduce the HRT and the size of tank in column studies.

- The optimum temperature was found to be in the range of 25-30ºC but because the room temperature those days was 28ºC, so all the experiments were conducted at the room temperature of 25-28º C. Further increase in temperature causes decrease in adsorption.

- The mixing or Agitation speed after optimization was found to be in the range of 80 to 100 rpm. Beyond this range on both sides adsorption efficiency was observed lower.

- The positive values of the change in apparent enthalpy (∆H) confirm the endothermic nature of the sorption process and suggest strong binding possibility between sorbate and sorbent and the positive value of (∆G) for all the adsorbents shows the random feasibility and non spontaneous process of adsorption.

- Adsorption at a solid solution interface generally shows an increase in entropy (∆S) showing faster interaction during the forward adsorption. Association, fixation of adsorbate on the interface between two phases result in loss of the degree of freedom there by, showing a negative entropy effect for all the adsorbents except potato waste from cold storages used in this study and that is very near and similar to earlier researches. The positive value of (∆S) for discarded potato waste from cold storage reflects the affinity of the adsorbent material.
• For all the used adsorbents, desorption or leaching test was also conducted and no chromium detected in the water indicating no desorption.

• The agro and horticultural waste adsorbents used did not hydrolyze and BOD of leachate remained unchanged indicating the adsorbents are stable materials under the process conditions but in case of discarded potato waste from cold storages BOD leachate was observed to increase and that is why the discarded potato use as adsorbent of chromium was not encouraged after study.

• As compared to that of batch process the exhaustive capacity of adsorbent was higher in column study and that may be due to continuous large concentration at the interface of the sorption zones as sorbate passes through the column.

• Regeneration of used adsorbents need not to be studied keeping the low cost in view and can be disposed off and burnt after drying safely, as no of rural technologies for disposal are getting evolved. Although safe disposal of adsorbents containing small quantities of hexavalent chromium can be disposed off on low –lying areas.

• The reduction in adsorption trend in all adsorbents observed with real tannery wastewater may be due to other interfering ions present in tannery wastewater that acquire the available surface for adsorption on adsorbent. Some other contaminants present in tannery wastewater may also get adsorbed on the available surface reducing the adsorption surface for chromium.

• 10 to 20 g/l adsorbent dose is enough to remove 50% hexavalent chromium from wastewater with an initial chromium concentration of 50 mg/l. The study results may be quite helpful for full-scale adsorber for tannery wastewater treatment.

• Petha waste and discarded potato waste from cold storages both the adsorbents show high chromium removal so these can be best utilized in industrial wastewater treatment containing chromium.

REFERENCES


