Isotherms describing physical adsorption of Cr(VI) from aqueous solution using various agricultural wastes as adsorbents

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Abstract: Various agricultural wastes such as peels of pea (Pisum sativum) pod, tea (Camellia sinensis), and ginger (Zingiber officinale) and banana (Musa lacatan) waste were used to adsorb Cr(VI) from the aqueous solutions. A comparative adsorption efficiency study for all these adsorbents was done in laboratory for various pH, adsorbent doses, initial chromium concentrations, contact time, adsorbent sizes, temperature, and mixing speeds up to the optimization. The equilibrium sorption data were fitted into Langmuir, Freundlich, and Temkin isotherms and also the various thermodynamic parameters were determined. The value of $R^2$ was determined for Freundlich, Langmuir, and Temkin as 0.964, 0.963, and 0.858 (pea pod peels waste (PPP)), 0.969, 0.986, and 0.841 (tea & ginger waste (T&G)), 0.985, 0.982, and 0.886 (banana peel waste (BW)). The maximum monolayer coverage ($Q_m$) from Langmuir isotherm model for pea pod, tea & ginger and banana peels waste were found to be 4.33 mg/g, 7.29 mg/g, and 10 mg/g, respectively, with separation factors ($R_L$) 0.0331, 0.0343, and 0.0756 which are well within favorable sorption. From Freundlich isotherm model, the sorption intensity ($n$) for the same adsorbents was also less than unity showing normal sorption. The heat of sorption ($B$) was also determined from Temkin isotherm model as 0.215, 0.271, and 0.271, respectively, vividly proving a favorable physical sorption. The Gibbs free energy was found maximum for BW as 6.0679 joule/mole. Out of the above said combination, BW was found the best low-cost adsorbent with high potential for the removal of hexavalent chromium from aqueous solutions.

Subjects: Pollution; Waste & Recycling; Water Engineering

Keywords: agricultural wastes; adsorbents; aqueous solution; isotherms; thermodynamic parameters; environmental sustainability engineering

1. Introduction
There has been a worldwide public awareness for the heavy metal contamination and toxicity in aquatic environment. Many heavy metals like lead (Pb), mercury (Hg), cadmium (Cd), arsenic (As),...
chromium (Cr), zinc (Zn), and copper (Cu), etc. have widespread usage in industries and enter the environment wherever they are produced, used, or discarded. All these metals become seriously toxic as ions or compound being soluble in water and readily absorbable by living organisms. In micro amount, these are essential nutrients in human bodies but in excess cause severe physiological and health disorder. The chromium is of main concern here. Trivalent chromium as an essential trace element in the human diet enhances sugar metabolism (Katz, 1991) but hexavalent chromium is very detrimental for all living beings. Chromium intake may cause epigestric pain, nausea, vomiting, diarrhea, and hemorrhage (Browning, 1969). The chief chromium ores in nature are chromites (Cr$_2$O$_3$) or chrome ore (FeO$_x$Cr$_2$O$_3$) mostly used in the electroplating of metal to prevent corrosion, plastic coating of surfaces to prevent from water and oil adverse effects, tanning leather, finishing metal, pigmenting and wood preservative, etc. resulting hexavalent chromium bearing wastewater discharge. Hence it is now a challenge for environmental engineers to dispose off such chromium contaminated wastewaters safely. Precipitation, co-precipitation, concentration, coagulation, filtration, etc. reduce chromium from wastewater (Shen & Wang, 1995) but produce solid residues with toxic compounds disposed by landfiling involving high costs and ground water contamination which is nothing but conversion of pollutants from liquid to solid phase, which is not a proper solution to the environmental problem. The presence of organic ligands or acidic conditions in the environment might have increased Cr(III) mobility and MnO$_2$ in the soil to oxidize Cr(III) to more toxic and mobile hexavalent Cr(VI) (Heary & Ray, 1987). And that is why, the practice of landfiling and land application of chromium containing sludge is being discouraged nowadays. Chemical precipitation, reverse osmosis, and some other modern technologies become costlier for micro concentrations. The process of adsorption proved to be the potential alternative for such situations (Huang & Morehart, 1991).

In developing countries like India, the physical adsorption has been proved an effective, potential, and economic method for the removal of chromium from wastewaters offering flexibility in design and producing high-quality treated effluents of desired standards for safe disposal and moreover the adsorbents can also be regenerated by suitable desorption for reuse (Ajmal, Rao, Ahmad, & Ahmad, 2000; Ajmal, Rao, & Siddiqui, 1995; Ayub, Ali, & Khan, 1998, 1999, 2001, 2002, 2003; Huang & Wu, 1975; Raji & Anirudhan, 1998; Sharma, Ayub, & Tripathi, 2013).

Many researchers have recently explored the possibility of various agro and horticultural wastes and byproducts as potential adsorbents for the removal hexavalent chromium from aqueous solutions (Ayub, Ali, & Khan, 2006; Ayub, Sharma, & Tripathi, 2014; Ayub et al., 1998, 1999, 2001, 2002; Baskaran, Venkatraman, Hema, & Arivoli, 2010; Chand, Aggarwal, & Kumar, 1994; Cimino, Paserini, & Toscano, 2000; Deo & Ali, 1992; Drake, Lin, Rayson, & Jackson, 1996; Huang & Wu, 1975; Periasamy, Srinivasan, & Murugan, 1991; Sharma, Ayub, & Tripathi, 2015; Sharma, Dubey, & Rehman, 2010; Sharma et al., 2013; Shukhla & Sakhardane, 1991; Siddiqui & Paroo, 1994; Vaishya & Prasad, 1991; Veena Devi et al., 2012; Weber, 1996). Continuing the same, here in this study we have substituted commercial expensive activated carbon by unconventional, low-cost and locally available agricultural wastes in plenty as adsorbents.

Chromium is an odorless and tasteless metal which is naturally found in rocks, plants, soil and volcanic dust, humans, and animals. The most common forms occurring in natural waters are trivalent and hexavalent chromium.

Cr(III) is an essential human dietary element and occurs naturally in many vegetables, fruits, meats, grains, and yeast. Cr(VI) occurs naturally in the environment from the erosion of natural chromium deposits and also can be produced by industrial processes. There are demonstrated instances of chromium being released to the environment by leakage, poor storage, or inadequate industrial waste disposal practices.

As far as the chemistry of chromium is concerned it is highly active transition metal existing in a number of oxidation states and exhibiting wide range stability. Thermodynamically, the reduced
form of chromium, Cr(III), is most stable in both acidic and basic solutions as per evidence by the reduction potential ($E^0$) equations (Source: Shupack, 1991) as follows:

$$
\frac{1}{2} \text{Cr}_2\text{O}_7^{2-} + 1.3 \text{ V Cr(H}_2\text{O)}^3_6 \rightarrow -0.4 \text{ V Cr(H}_2\text{O)}^{6+} \rightarrow -0.9 \text{ V Cr}^0 \quad (1.1)
$$

(Base)

$$
\text{CrO}_4^{2-} \rightarrow -0.13 \text{ V Cr(OH)}_3 \rightarrow -1.1 \text{ V Cr (OH)}_2 \rightarrow -1.4 \text{ V Cr}^0 \quad (1.2)
$$

Reduction, oxidation, and pH conditions severely affect the stability of various species of chromium. The stable domain for various species of chromium in aqueous environment specifically depends on oxidation potential ($E^0$) and pH (Landigran & Halllowell, 1975). For industrial wastewater, the predominant species are bichromate $\text{HCrO}_4^-$, dichromate $\text{Cr}_2\text{O}_7^{2-}$, and Cr$^{3+}$ under redox conditions at pH < 3 with temperature ranging 20–30°C. One more thing interesting is that the divalent chromium ions Cr$^{2+}$, are mostly found in extremely reducing environment. The total chromium present governs the concentration distribution between $\text{HCrO}_4^-$ and $\text{Cr}_2\text{O}_7^{2-}$. The fraction $\text{Cr}_2\text{O}_7^{2-}$ remains only significant at high concentrations of total chromium (VI) (Stummm & Morgon, 1970).

Chrome tanning wastewater is typically treated in two stages, one is the conversion of hexavalent chromium to trivalent which freely bonds to hydroxide in stage-2 and finally a nontoxic precipitate: chromium hydroxide Cr(OH)$_3$. The most possible methods for reducing hexavalent chromium to trivalent chromium may be using chemical reducing agents such as sulfur dioxide (SO$_2$), sodium bisulfate (NaHSO$_3$), or sodium metabisulfite (Na$_2$S$_2$O$_5$). The following reduction reaction may take place using sulfur dioxide and maintaining pH between 2 and 3, in stage-1.

$$
3 \text{SO}_2 + 2 \text{H}_2\text{CrO}_4 + 3 \text{H}_2\text{O} = \text{Cr}_2(\text{SO}_4)_3 + 5 \text{H}_2\text{O} \quad (1.3)
$$

After the completion of stage-1 reaction as above, lime i.e. calcium hydroxide Ca(OH)$_2$ is used to maintain pH ≥ 8.0 for the precipitation of chromium hydroxide as it can be easily adsorbed, separated, or disposed by any of the usual methods and it is less toxic also. The following possible reaction of precipitation may take place in stage-2.

$$
\text{Cr}_2(\text{SO}_4)_3 + 3 \text{Ca (OH)}_2 = 2 \text{Cr(OH)}_3 + 3 \text{CaSO}_4 \quad (1.4)
$$

As far as the mechanism of adsorption is concerned, due to imbalance in surface forces, adsorbate molecules in the solution form a surface layer on adsorbent when in contact with solid surface during physical adsorption resulted from molecular condensation in the capillaries of the solid, whereas in chemical adsorption the molecular layer of adsorbate on the surface is formed through forces of residual valence of the surface molecule. Generally, high molecular weighted substances are easily adsorbed and this is why heavy metals are removed from the aqueous solutions of contaminated wastewater by the adsorption process. There is a quick establishment of an equilibrium interfacial concentration after slow diffusion into particles. The rate is inversely proportional to the square of the solute. The rate of adsorption varies directly proportional to the square root of contact period with the adsorbent. pH of the medium also affects the rate due to change in surface charges. The adsorption capacities also vary with the change of combinations of adsorbent and adsorbate. There is also a severe effect of complexity of wastewaters on adsorption capacities because of the interference between the various contaminants in the aqueous solutions.
The study compares the feasibility and potentials of agricultural waste and byproduct materials such as pea pod peels (PPP), tea and ginger waste (T&G), and banana waste (BW) to adsorb hexavalent chromium Cr(VI) from industrial wastewaters. pH, adsorbent dosage, initial chromium concentration, contact time, adsorbent grain size, temperature, and agitation speeds were optimized for sorption. The samples of the adsorbents were characterized before and after adsorption in the batch performance. Electron microscopic technique was used to characterize the surface of the adsorbent. Thermodynamic nature of the process was also studied.

2. Materials and methods

2.1. Sorbents and sample preparation

In the present study, various agricultural wastes such as peels of pea (*Pisum sativum*) pod (PPP), tea (*Camellia sinensis*) and ginger (*Zingiber officinale*) waste (T&G) and (*Musa lacatan*) BW were used to adsorb Chromium (VI) from the aqueous solution using batch adsorption processes.

2.1.1. Adsorbents

One week sun-dried BW from fruit seller and Pea pod peels from a farmhouse were first dried in oven for three days at a temperature of 90°C for 5 h daily and the T&G from a tea stall was well washed many times with water and finally with distilled water then spread for sun drying for a week, and then oven dried for three days at a temperature of 90°C for 5 h daily. After grinding, the waste powders were sieved through a 225 mesh (Indian Standard Sieve) to get an average and uniform sized particle, we washed these waste powders several times with distilled water to get rid of lighter materials and other impurities. The adsorbents were dipped in 0.1 N NaOH for a period of 9 h and washed several times with distilled water to remove the lignin and then dried again. The adsorbents were again rinsed separately with double-distilled water two times and dipped into 0.1 NH 2SO 4 for the period of 9 h again to remove traces of alkalinity. The acid-treated adsorbents were washed thoroughly with double-distilled water. Then the dry powder so prepared was exposed to sun and stored in a desiccator. Before using these powders as adsorbents a size range was also achieved by sieving through a sieve set 1.18 mm, 600 μm, 425 μm, 300 μm, 150 μm, 75 μm and pan i.e. less than 75 μm (Indian Standard Sieve) so as to optimize the sizes of these adsorbents.

2.1.2. Experimental

To understand the adsorption behavior, a number of batch studies were conducted according to the Standard Method to investigate the effect of pH, adsorbent dosage, initial chromium concentration, contact time, adsorbent grain size, temperature, and agitation speed. In the present study, synthetic wastewater of various concentrations of Cr(VI) was prepared from the “Mono-Element Standard Solution for AAS” 1,000 mg/l Chromium (Cr) in 0.5 mol/l Nitric acid (HNO 3) with a certified value 1001.2 mg/l ± 9.22 as 95% level of confidence from LOBA CHEMIE PVT. Ltd. and kept separately in glass-stoppered conical flasks. Then, varying doses of adsorbent were added to the synthetic wastewater in a conical flask of 250 ml. To achieve the adequate time of contact between adsorbent and the metal ions, the system was equilibrated by shaking the contents of the flasks at room temperature on a mechanical shaker for varying times (Indian Scientific Instruments factory, Ambala Cant, India) at Environmental Engineering Laboratory, Civil Engineering Department, Hindustan College of Science and Technology, Farah, Mathura, Uttar Pradesh (India).

The suspension was filtered through Whatman (No. 1) filter paper and the filtrate was analyzed to evaluate the concentration of Cr(VI) metal in the treated wastewater using Atomic Absorption Spectrometer (Make and Model-Perkin Elmer, AAS, Pin AAcle 900 K) installed at Civil Engineering Department, Environmental section, Z. H. College of Engineering and Technology, Aligarh Muslim University, Aligarh (India).

Adsorption studies were made for various times. Ultimate saturation time was also determined for each dose. All the studies were made at the room temperature varying from 25 to 28°C in summer. In case of low temperature study the adsorption conical flasks were put in refrigerator up to...
10°C and that for the higher temperature studies the temperature was maintained by external heaters in closed chamber up to 50°C.

2.2. Thermodynamic parameters

Thermodynamic constants of equilibrium sorption processes can be determined using Gibbs free energy equation,

\[
\Delta G = -RT \ln K
\]  (2.1)

where \(\Delta G\) = change in free energy (joule/mole), \(T\) = the process temperature in Kelvin, \(R\) = universal gas constant = 8.314.

The linear plot between \(\Delta G\) vs. \(T\) is drawn for the equilibrium temperature and then simulated using mathematical modeling Sharma, Khan, and Ayub (2012a, 2012b) to the linear equation:

\[
\Delta G = \Delta H^* - T\Delta S
\]  (2.2)

where \(\Delta H\) = changes in enthalpy and \(\Delta S\) = changes in entropy of activation (Ayub et al., 2006).

Plotting the graph between \(\Delta G\) and \(T\) as shown in Figure 9(a)–(c) for PPP, T&G and BW, respectively, we get the values of \(\Delta H\) and \(\Delta S\) for all these adsorbents used in the present study, the values so obtained are given in Table 1.

For all the adsorbents PPP, T&G, and BW Gibbs Free energy diagrams were plotted as shown in Figure 9(a)–(c), respectively, and then using best fit line and simulation thermodynamic constants such as the change in apparent enthalpy \(\Delta H\), free energy \(\Delta G\), and entropy \(\Delta S\) of sorption were calculated using thermodynamic equations and values at 301 K have been tabulated in Table 1. The negative enthalpy \(\Delta H\) values for all PPP, T&G and BW confirm the exothermic nature of the sorption process and suggested the poor binding. The positive value of free energy change \(\Delta G\) indicates the random feasibility. Adsorption at a solid solution interface generally shows an increase in entropy \(\Delta S\) 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 thereby showing a negative entropy effect (Ayub et al., 2006).

2.3. Langmuir isotherms

Langmuir adsorption parameters were determined by transforming the Langmuir equation

\[
q_e = \frac{q_o K_l C_e}{(1 + K_l C_e)}
\]  (2.3)

In to linear form as

\[
\frac{1}{q_e} = \frac{1}{q_o} + \left(\frac{1}{q_o K_l}\right) \left(\frac{1}{C_e}\right)
\]  (2.4)

where \(C_e\) = the equilibrium concentration of adsorbate in mg/l; \(q_e\) = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g); \(q_o\) = maximum monolayer coverage capacity (mg/g) \(K_l\) = Langmuir Isotherm Constant (L/mg).

The values of \(q_{max}\) and \(K_l\) were computed from the slope and intercept of the Langmuir plot \(\frac{1}{q_e}\) vs. \(\frac{1}{C_e}\).

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 \(R_l = 1\), \(0 < R_l < 1\) favorable and irreversible if \(R_l = 0\).
where \( C_0 = \text{initial concentration of adsorbate} = 30 \text{ mg} \); \( K_L \) = Langmuir constant related to the energy of adsorption (Dada, Olalekan, Olatunya, & Dada, 2012).

All the above Langmuir constants were determined for all the adsorbents of which plots have been shown in Figures 10(a) PPPL, 11(a) T&GL, and 12(a) BWL for PPP, T&G and BW, respectively, later. The values of thermodynamic constants so obtained for various adsorbents are given in Table 1.

### 2.4. Freundlich isotherms

The adsorption observations at a fixed initial concentration of Chromium in synthetic wastewater with varying adsorbent doses were fitted to linearized Freundlich adsorption isotherm as following.

\[
\log \left( \frac{x}{m} \right) = \log K + \frac{1}{n} \log C_e
\]  

where \( \frac{x}{m} \) is the amount of Chromium (VI) adsorbed per unit mass of adsorbent expressed in mg/mg and \( C_e \) is the equilibrium concentration of aqueous solution. \( K \) is a constant, which is a measure of adsorption capacity, and \( 1/n \) is the measure of adsorption intensity (Dada et al., 2012).

The value of \( K \) and \( 1/n \) are given in Table 1 and plots for Freundlich Isotherms for the adsorbents PPP, T&G, and B/W are shown in Figures 10(b), 11(b) and 12(b) respectively.

### 2.5. Temkin isotherm

This isotherm has a factor which explicitly shows the interaction between adsorbent and adsorbate. Ignoring very low and high concentrations, this model assumes that heat of adsorption of molecules in the subsequent layers decreases linearly rather than logarithmic with coverage (Aharoni & Ungarish, 1977; Tempkin & Pyzhev, 1940). As shown in equation, its derivation is characterized by uniform distribution of binding energies up to a maximum value and was obtained by plotting the amount adsorbed \( q_e \) vs. \( \ln C_e \) and the constants have been determined from slope and intercept. The model equation is as follows (Tempkin & Pyzhev, 1940)

\[
q_e = \frac{RT}{b_r} \ln (A_r C_e)
\]  

\[
q_e = \frac{RT}{b_r} \ln A_r + \left( \frac{RT}{b} \ln C_e \right)
\]
using,

\[ B = \frac{RT}{b_T} \]  

(9)

The equation becomes,

\[ q_e = B \ln A_T + B \ln C_e \]

(10)

\[ A_T = \text{Temkin isotherm equilibrium binding constant (L/g)}; \quad b_T = \text{Temkin isotherm constant}; \quad R = \text{universal gas constant (8.314 J/mol/K)}; \quad T = \text{Temperature at 301 K and } B = \text{Constant related to heat of sorption (J/mol)}. \]

From the Temkin plot shown in Figures 10(c) PPPT, 11(c) T&GT, and 12(c) BWT for all the adsorbents PPP, T&G and BW, respectively, the estimated values are given in Table 1.

2.6. Scanning electron microscopy

Scanning Electron Microscopy (SEM) by Scanning Electron Microscope Model No. JSM 6510 LV Make; JEOL (Japan), at USIF, AMU, Aligarh, was also done for all the raw and used adsorbents to study the changes in adsorbent texture before (raw) and after (used) adsorption process as shown in Figures 13(a)–(f) for raw and used PPP, T&G, and BW, respectively, below. The samples were non-conducting so before SEM these were gold coated and SEM analysis results show that the adsorbents have potential surface area and cavities to adsorb chromium within for binding.

2.7. Desorption and hydrolysis test

For leaching properties of agro-based materials so as to ensure the quality of treated effluent desorption test was also conducted for the best adsorbent after comparison among PPP, T&G, and BW used as adsorbent to adsorb chromium i.e. BW. 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 filtrate was analyzed for the chromium content desorbed of which negligible amount shows that no desorption occurred.

3. Results and discussion

Using observations of the sorption studies to optimize the pH, adsorbent dosage, initial chromium concentration, contact time, adsorbent grain size, temperature, and agitation speed various adsorption isotherms have been plotted to determine the feasibility of sorption system along with its mechanisms through kinetics. Thermodynamic parameters clearly tell the story of the feasibility of the process. The results of batch studies for various adsorbents used in the study have been compared.

3.1. Comparison of pea pod peels waste, tea & ginger waste and banana waste

As shown in Figure 1, the best results were obtained in the pH range 2.5–3.5. The better adsorption capacity at low pH values would have been due to the large number of H⁺ ions, neutralizing the hydroxyl group (OH⁻) on adsorbed surface and thus reducing hindrance to the diffusion of dichromate ions. At higher pH, low adsorption may be due to excess OH⁻ ions causing high hindrance to diffusion of positively charged chromium ions. It is well-known fact that the surface adsorbs anions favorably in low pH range due the presence of H⁺ ions, whereas the surface is active for the adsorption of cations at higher pH values due to the accumulation of OH⁻ ions (Huang & Stumm, 1973). Same results were found during the studies conducted on dihydric phenol removal on activated carbon by Mahesh, Rama, Praveen, and Usha (1999) and Sharma and Forster (1993) who used sphagnum moss peat for the removal of chromium.

As shown in Figure 2, the percentage chromium sorption is directly proportional to adsorbent dose. A dose of BW @ 10 g/l is sufficient to adsorb more than 70% Cr(VI) having 30 mg/l initial concentration of chromium within 1.0 h. On further increasing the adsorbent dose to 20 g/l more than 90% removal efficiency was observed. Similarly, 10 g/l adsorbent dose of T&G adsorbs more than
75% at pH 2.0; pea pod peels waste adsorbs 65% at pH 2.0. The same results were also reported by Ayub et al. (2001, 2002, 2014), Bansal and Sharma (1992), Kim and Joltek (1977), Mall (1992), Rao, Parwate, and Bhole (2002).

As shown in Figure 3; the removal efficiency was found dependent on the initial chromium concentration, adsorbent dose, contact time, particle size, and pH. Several researchers have reported that percent adsorption with increase in metal ion concentration considerably reduces (Panday, Prasad, & Singh, 1984). T&G is found to be best adsorbent, used BW better and pea pod peels waste equally good, with respect to the removal efficiency of the chromium metal in 10 g/l adsorbent dose and having 30 mg/l initial concentration of the solution for the average size of adsorbent ranging 600–300 μm @ 1 h contact time and pH 2.0. The removal efficiency ranges from 65 to 90% at 28°C in summer in the month of May 2015 (India).

As shown in Figure 4, in the beginning chromium Cr(VI) removal efficiency is observed to be very quick and later slows down. In first 45 min, T&G and BW adsorb more than 90% chromium, whereas PPP adsorbs 65% chromium but later by slow rate it reaches up to 80% at initial chromium concentration 30 mg/l, 10 g/l adsorbent dose, average size of adsorbent grains from 600 to 300 μm, pH 2.0. So it was observed that first hour of contact period is very important for quick adsorption which is very important for designing continuous adsorption systems in real problems.
From Figure 5 it was observed that neither too small nor too large grain size of adsorbent adsorbs the chromium but an average grain size ranging from 600 to 300 μm is most the efficient adsorbent for all the adsorbents used here in this study.

As shown in Figure 6, the optimum temperature range was from 25 to 30°C below and above this range the adsorption efficiency was observed decreasing. The initial start up agitation speed for mixing the adsorbent and adsorbate so as to achieve good contact in between these two was also studied, as a result it was observed that an average agitation speed of 80–100 rpm for first 15 min is sufficiently enough to optimum results, as shown in Figure 7. A small batch set up was also run for all the optimized affecting parameters for all the adsorbents i.e. PPP, T&W, and BW so as to get highest adsorption of chromium and the observed results have been shown in concluding Figure 8, the optimized affecting parameters have also been indicated there.

Figure 9(a)–(c) showing thermodynamic graphs where from the apparent enthalpy change (ΔH), free energy (ΔG), and entropy (ΔS) of sorption process have been calculated using thermodynamic equations and values at 28°C and shown in summary Table 1. The negative value of enthalpy change (ΔH) reveals exothermic nature of adsorbent. Negative values of ΔG reveal the process is feasible.
Figure 5. Effect of Adsorbent Size on Sorption.

Figure 6. Effect of Temperature on Sorption.

Figure 7. Effect of Agitation Speed on Chromium Cr(VI) Sorption.
and spontaneous. The negative values of free energy change for a system indicates the spontaneity of sorption process. Adsorption at a solid solution interface generally shows an increase in entropy. This shows a quicker interaction during the forward adsorption. Association, fixation, or immobilization of sorbate on the interface between two phases result in loss of the degree of freedom thereby resulting in a negative entropy effect.

The positive entropy ($\Delta S$) attributes to an increase in translational entropy due to randomness of displaced water molecules from the surface of the adsorbents. The negative values of entropy reported here show the decrease in translational entropy by regular attachment of water molecules to the surface of the adsorbent and supported by the adsorption process of hexavalent chromium on fly ash-wallastonite (Panday et al., 1984), chromium adsorption on blast furnace flue dust and COD on fly ash (Baisakh, Patnaik, & Patnaik, 1996) and adsorption on coal char (Baisakh & Patnaik, 2002).

The Langmuir, Freundlich, and Temkin isotherms have been plotted and shown in Figures 10(a) PPPL, 11(a) T&GL, 12 BWL, the Langmuir adsorption isotherms for PPP, Figures 10(b) PPPF, 11(b) T&GF, 12(b) BWF, the Freundlich isotherm curve for T&G and Figure 10(c) PPPT, 11(c) T&GT, 12(c) BWT, the Temkin isotherm curve for BW along with the summary of isotherms constants have been given in Table 1. The value of $R^2$ was determined for Freundlich, Langmuir, and Temkin as 0.964, 0.963, and 0.858 (PPP), 0.969, 0.986, and 0.841 (T&G), 0.985, 0.982, and 0.886 (BW). The maximum monolayer coverage ($Q_0$) from Langmuir isotherm model for PPP, T&G, and BW were found to be 4.33 mg/g, 7.29 mg/g, and 10 mg/g, respectively, with separation factors ($R_L$) 0.0331, 0.0343, and 0.0756 which are well within favorable sorption. From Freundlich isotherm model, the sorption intensity ($n$) for the same adsorbents was also less than unity showing normal sorption. The heat of sorption ($\Delta H$) was also determined from Temkin isotherm model as 0.215, 0.271, and 0.271, respectively, vividly proving a favorable physical sorption. The Gibbs free energy was found maximum for BW as 6.0679 joule/mole. Out of the above said combination BW was found the best low-cost adsorbent with high potential for the removal of hexavalent chromium from aqueous solutions.

Column study for a flow rate of 1.0 l/d containing initial chromium concentration of 50 mg/l at pH 1.5 was made for the best adsorbent i.e. BW until all adsorbent exhausted and the treated effluent was analyzed at different time intervals. Column capacities were greater than the batch capacities.
As per desorption test for best adsorbent i.e. BW no leaching property of adsorbent was found which showed the required quality of treated effluent.

4. Conclusions

(1) The study reveals that agricultural wastes such as pea pod peels, used T&G, and BW can be reused as potential adsorbents for the removal of hexavalent chromium from tannery and metal finishing wastewaters. It is investigated that adsorption behavior depends on the nature of adsorbent and all the agricultural waste materials do not show similar behavior.
(2) The chromium adsorption capacity of all the agricultural adsorbents is highly dependent on pH which is best suited in the range 2.0–3.0.

(3) Chromium uptake capacity follows first-order rate equation for all the adsorbents used in present study.

(4) The isotherm data obtained were best fitted to Freundlich adsorption isotherm.
The negative enthalpy ($\Delta H$) confirms exothermic nature of adsorbent and poor binding. Positive values of Gibbs free energy ($\Delta G$) indicate the non spontaneous adsorption. Negative values of $\Delta S$ indicate the less affinity of the adsorbent material.

Leaching test after sorption studies indicate traces of chromium showing poor binding between adsorbate and adsorbents but in case of BW it was found satisfactory.
Figure 12. Thermodynamic parameters for (a) BWL (using Langmuir isotherm), (b) BWF (using Freundlich isotherm), and (c) BWT (using Temkin isotherm).
(7) The agricultural waste sorbents do not hydrolyze and BOD of leachate remains unchanged which shows that the agro-based adsorbents act as stable materials under the process conditions.

(8) The exhaustive adsorption capacity of the sorbent is found satisfactory in batch process.
Figure 13. (Continued).
(9) Being relatively cheaper and locally available, the agricultural waste adsorbents are superior than activated carbon due to the evolution of more modern technologies waste disposal has also become easier in rural areas now days. All these agro and horticultural waste adsorbents require only alkali/acid treatment to increase their efficiency of sorption.

(10) SEM results show that the adsorbents have potential surface area and cavities to adsorb chromium within for binding. Better column capacities may be due to continuously large concentration at the interface of the sorption zone as the sorbate solution passes through the column, whereas in the case of batch process the concentration gradient decreases.
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