International Journal of Scientific Engineering and Technology (ISSN : 2277-1581)
Volume No.3 Issue No.5, pp : 500-506 1 May 2014

Adsorptive Removal of Toxic Metal Chromium (VI) From Aqueous Solutions by Using Sawdust

Mandeep Kumar[1*], Ankur Gupta[1], CB Majumder[2]

[1*]Department of chemical engineering, IIT roorkee, Roorkee, Uttrakhand 247667,
Corresponding Email id: mandeep23may@gmail.com
[1]Department of chemical engineering, IIT roorkee, Roorkee, Uttrakhand 247667,
Email id: guptaankur599@gmail.com
[2]Associat professor, Department of chemical engineering, IIT roorkee, Roorkee, Uttrakhand 247667

Abstract

Sawdust is obtained from naturally and easily available which is biodegradable. The bio sorption capacity of the sawdust for hexavalent chromium was studied at different solution pH values (1.5-6), initial metal concentration (50-450 mg/L), adsorbent dose (1-7 g/L). The maximum adsorption of Cr (VI) is obtained at pH 1.5, initial concentration 50 ppm and adsorbent dose 5 g/l. The adsorption of chromium attained equilibrium at about 4 h, with maximum removal percent of 99.99% at initial metal concentration of 50 mg/L at optimum pH. The equilibrium data for the adsorption of Cr (VI) on sawdust is studied with various adsorption isotherm models such as Langmuir, Freundlich, and, Temkin. The equilibrium adsorption data is better fitted to Langmuir isotherm (R^2=0.9938). Kinetic modeling is also studies for the adsorption of Cr (VI) on sawdust in which process follows the second-order kinetics and the corresponding rate constants are obtained.

Keywords: Saw dust, potassium dichromate, 1, 5-diphinylecarbazide, hydrochloric acid, acetone, Sodium chloride, Sulphuric acid, and Ultra-pure de-ionized water.

I. Introduction

The increasing environmental contamination by toxic metal comes from of urban and industrial waste waters are of great concern because of health risks on humans and animals. Among the toxic metal ions, chromium is one of common contaminants which gains importance due to its high toxic nature even at very low concentrations [1]. The most common forms of chromium are trivalent chromium [Cr (III)] and hexavalent chromium [Cr (VI)] which are commonly used in various industrial processes Chromium (VI) is most toxic and hazards because its cancer effect, skin irritation, hemorrhage, epigastria pain, severe diarrhea and can pose health risk such as liver damage. Waste water such as those generated during dyes and pigments production ,film and photography, galvanometric, metal cleaning, plating and electroplating may contain undesirable amounts of chromium(VI) anions [2].Concentration of Cr (VI) present in industrial effluent stream are in the approximation range of 50 to 400 ppm [3]. But the permission able limit of Cr (VI) in drinking water is 0.05 mg/l [4]. In order to reduce the Cr (VI) concentration to permissible limit, the effluents must be treated before its disposal into the environment. There are number of treatment methods available to remove Cr (VI) from waste water such as chemical precipitation, ion-exchange, membrane separation, electrocoagulation, solvent extraction, reduction, reverse osmosis, and adsorption. These methods are expensive and lots of disadvantages such as energy requirement, incomplete removal etc. But instead of all methods, adsorption is simple, effective and inexpensive method. To make the adsorption process less expensive, there is search for new material which has a good capacity for the Cr (VI). in the recent years, several studied have been reported on various low cost adsorbents such as wool , used tyres, sea weed , fungal biomass , green algae, sugar industry waste , distillery sludge, red mud , activated carbon derived from fertilizer waste , tea factory waste , coconut trees , rice brand , activated neem leaves ,activated tamarind seeds. Many of these adsorbents have low chromium adsorption capacity.so there is need of adsorbent which gives the high adsorption capacity.

The objectives of the present work are to investigate the use of sawdust as alternate adsorbent material for the removal of Cr (VI) from waste water. The influence of various important parameters such as pH, change in pH during adsorption, time, adsorbent amount, and initial Cr (VI) concentration is investigated. The batch adsorption kinetics study of Cr (VI) is used to estimate and compare the adsorption capacity of sawdust. The Langmuir, Freundlich and Temkin isothermal models are used to fit the experimental equilibrium isotherm data obtained in this study.

II. Material and methods

2.1 Materials

Materials used for the experiments are potassium dichromate ($K_2Cr_2O_7$) and Saw dust. Other chemicals used in the study also included 1, 5-diphinylecarbazide (DPC), sulphuric acid, hydrochloric acid, acetone and Ultra-pure de-ionized water [5].

2.2 Preparation of Saw Dust

Saw dust was collected from workshop near by Roorkee. It was washed again and again with tap water and distilled water to remove the dust particles and soluble impurities. It was kept in hot air oven for drying at a 60^0C until all the moisture was evaporate. Dried sawdust was sieved at 720 µm.

2.3 Preparation of Cr (VI) solution and experimental procedure

International Journal of Scientific Engineering and Technology (ISSN : 2277-1581)
Volume No.3 Issue No.5, pp : 500-506 1 May 2014

A stock solution of 500mg/l of Cr (VI) is prepared by dissolving 1.41 g of Potassium dichromate (K2 Cr2 O7) in 1000 ml of distilled water solution. The batch experiments is carried out in 250 ml flat bottom flask and at 50 ppm Cr(VI) solution, pH 2 and a weighted amount of saw dust in 100 ml of aqueous Cr (VI) solution. Then it is stirred for a particular time at 30 ^{0}C in incubator shaker at 150 rpm. After that solution is filtered using filter paper and adds the reagent solution 2ml which is prepared from 1, 5-diphenylcarbohydrazide by dissolving 250 mg of it, in 50 mL acetone and stored in a brown bottle.as the reagent was added, the filtered solution is change into the pinkish red colour. The absorbance is measured by using UV spectrophotometer at 540nm wave length. All the adsorption studies were repeated thrice.

The amount of Cr (VI) adsorbed is calculated by using this equation [6]

$$q_e = \frac{(C_i - C_e)V}{W}$$

C_i is initial concentration, C_e is final concentration, V is volume of aqueous solution, W in weight of dose in mg and q_e is the amount of metal adsorbed at equilibrium (mgg^{-1}).

The percent removal for chromium was calculated using the following expression-

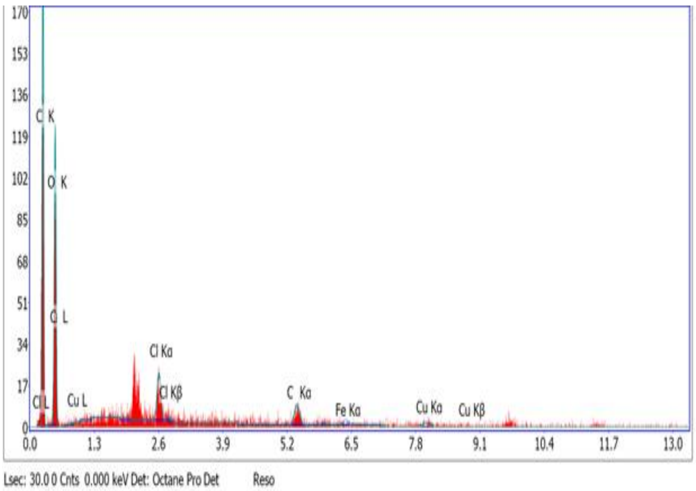
$$\%R = \frac{(C_o - C_e)\, X\, 100}{C_o}$$

III. Result and discussion

3.1 Characterization of adsorbent

Cr (VI) removal from waste water by using saw dust depends upon some factor such as pH, initial concentration, contact time, and adsorbent amount. So it is necessary to study these parameters by holding the other parameter constant.

To understand the behavior of sawdust on the adsorption of Cr (VI), physicochemical characteristics of the adsorbent was carried out. EDX spectra of sawdust were carried out before and after which is shown in figure 1 (a) and (b). It is clear from the EDX spectrum that Cr (VI) is shown in some peaks which means Cr (VI) adsorbed on the surface of sawdust shown in table 1. SEM of saw dust clearly indicates the porous structure and roughness of the surface as crests and troughs. These crests and troughs increase the surface area and consequently the adsorption capacity of the adsorbent and act as reactive adsorption centers for adsorption of Cr (VI).



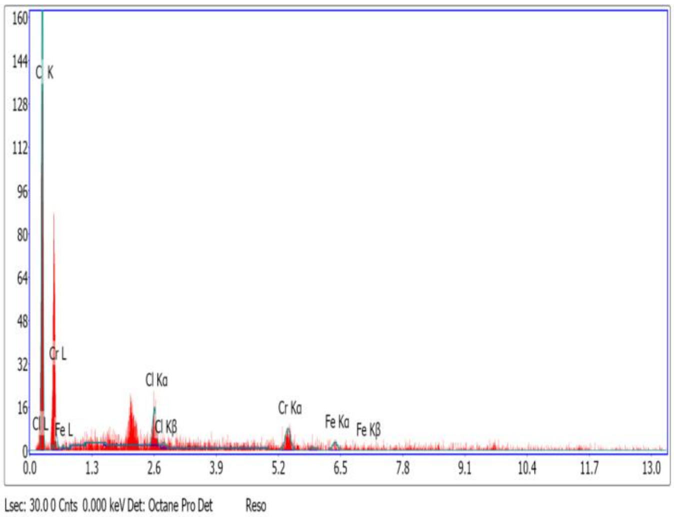


Fig -1: (a) EDX spectrum of SAWDUST before adsorption (b) after adsorption

Table 1: EDX weigh % of various constituents present on adsorbent

eZAF Smart Quant Result

Element	Weight%	%	Net Int.	Error%
C K	88.23	96.69	44.41	8.69
Cl K	3.19	1.18	8.15	17.14
Cr K	5.71	1.45	6.31	21.62
Fe K	2.87	0.68	2.26	58.22

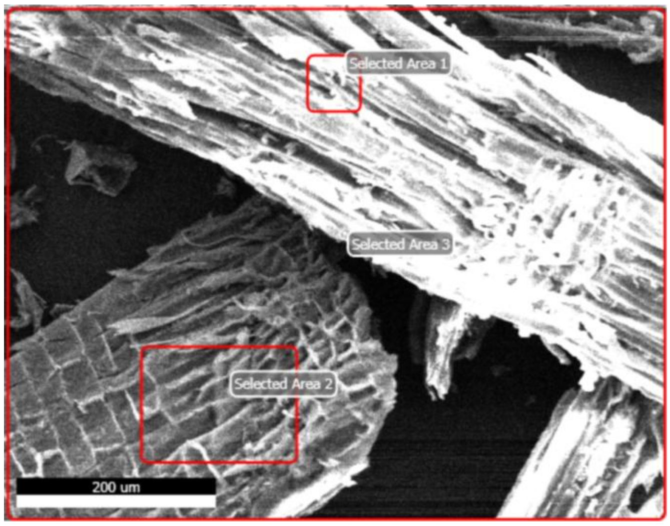
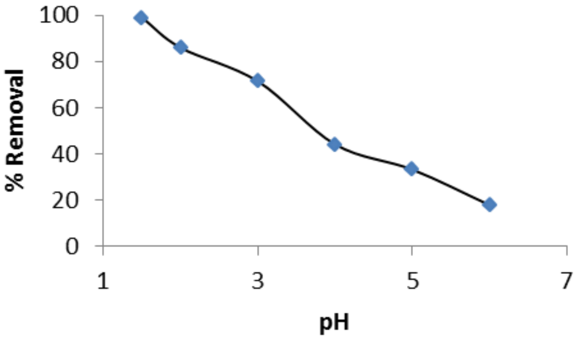


Fig - 2: Fe-SEM image of Saw dust before adsorption.

3.2 Effect of pH

pH is an important parameter for adsorption of Cr (VI) from aqueous solution because it controls the surface properties of adsorbents, the solubility of the metal ions, concentration of ions on the functional groups of the adsorbent [7]. Cr (VI) removal efficiency is strongly affected by the pH of solution. The experiments are carried out over the pH range of 1.5 - 6 by keeping all other parameter constant. pH is maintained by 0.1 N HCl and 0.1 N NaOH. From the experimental results, maximum Cr (VI) removal is observed at pH 1.5 which means adsorption is favorable at acidic condition shown in figure 3.

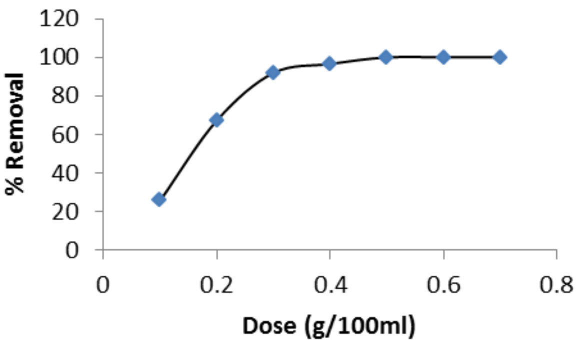
As the pH increased from 1.5 to 6, the% removal of Cr (VI) was sharply decreased 98.96- 17.78. At lower pH, the bio sorbent is positively charged due to protonation and dichromate ion exists as anion leading to an electrostatic attraction between them. By increasing the pH, it change the configuration of chromium formed the stable anions, like as $Cr_2O_7^{2-}$, $HCrO_4^{-}$, CrO_4^{2-} , and $HCr_2O_7^{-}$, and due to the weakening of electrostatic force of attraction between the oppositely charged adsorb ate and adsorbent due to that removal of Cr (VI) was decreasing. So maximum removal uptake by sawdust takes place at pH 1.5.



Fi
g - 3: Percentage removal of Cr (VI) versus pH values

3.3 Effect of Saw Dust dosage

Adsorption of Cr (VI) on saw dust dose is studied by taking the varying amount of adsorbents from 1 to 7 g/L, by keeping all the other parameters constant. [8] This is an important parameter as it determines the capacity of adsorbent. Percentage of metal Cr (VI) adsorbed increased with increase in the mass of the adsorbent. Removal of Cr (VI) increased rapidly from 25.76% to 99.99% when Sawdust dosage is increased from 1 g to 7g/l at concentration of 50 ppm. From the figure 4, The Cr (VI) adsorption capacity increased with increasing dosage to a different extent depending on the adsorbent. This is done because of number of adsorption sites for Cr (VI) is present which is proportional to the dose applied for each adsorbent. When all the Cr (VI) occupied the sites of surface, then there is no further increase in adsorption capacity. At adsorbent dose 5 g/100ml, maximum removal of 99 % is occurring. So it was the optimum adsorbent dose. Further increase in dose, equilibrium is approached in between the solution and surface.



Fi
g - 4: Percentage removal of Cr (VI) versus saw dust dose

3.4 Effect of Initial metal ion Concentration

Initial concentration is important parameter to know the lowest concentration of Cr (VI) removal at optimum dose and pH. In this work, experiments of adsorption is done to know the effect of initial Cr (VI) concentration by varying it from 50 to 400 mg/l while maintaining the sawdust amount 5 g/l and obtained results are presented in figure 5. [9] The results obtained that the increase in Cr (VI) concentration from 50 to 400 mg/l, the percentage removal decreases from 99.9% to 57.46% and capacity of adsorption increases from 14.75 to 45.97 mg/g. The decrease in percentage removal of Cr (VI) is done because of the fact that all the adsorbents had a limited number of active sites, which help to adsorb the metal ions until the saturated point, come above a certain concentration.

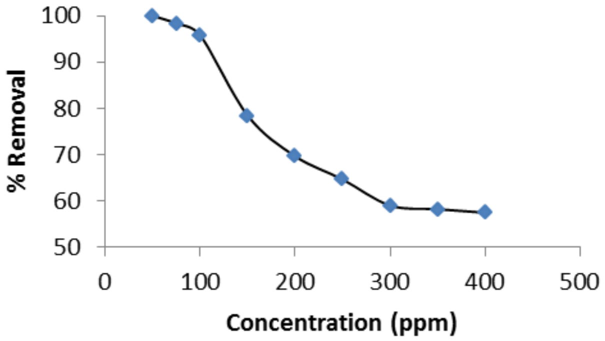


Fig - 5: Percentage removal of Cr (VI) versus concentration

3.5 Effect of Time

Figure 6 shows the effect of contact time on the extent of adsorption of Cr (VI) on sawdust at 50 ppm concentration is investigated to study the rate of Cr (VI) removal at pH 1.5 and temperature 30^0C. It is obtained from figure that time is an important parameter for the adsorption of Cr (VI) on sawdust [8]. Adsorption rate of metal ions is very high at the starting but decreasing slowly until it comes into the saturation level and reached to equilibration time. At the starting stage, number of vacates active sites are presents so large number of metal ions was bound on sawdust rapidly, so maximum removal of Cr (VI) is occur. As soon as all the vacates sites are fill by the metal ions, no further sites are available so there is formation of repulsive forces between the solid surface of chromium and the liquid phase so removal is decreasing slowly form 99.9% to 56.9% for initial Cr (VI) concentration of 50 mg/l respectively till 210 mints. Hence the equilibrium time obtained is 210 mints for the Cr (VI) adsorption on sawdust because of a further increase in the contact time has no effect on the rate of adsorption of Cr (VI).

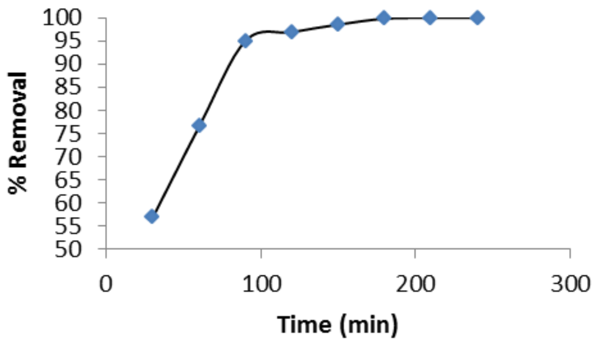


Fig - 6: Percentage removal of Cr (VI) versus contact time (min)

International Journal of Scientific Engineering and Technology (ISSN : 2277-1581)
Volume No.3 Issue No.5, pp : 500-506 1 May 2014

IV. Kinetic models

There are three kinetic model lagergren pseudo first order, pseudo second order and intra particle diffusion which are analyzed for adsorption of Cr (VI) on sawdust. [9] The effect of contact time on adsorption of Cr (VI) onto saw dust, shown in figure 7 .The adsorption capacities of saw dust increased rapidly in the initial stages of contact time and reach equilibrium at 210 mints.

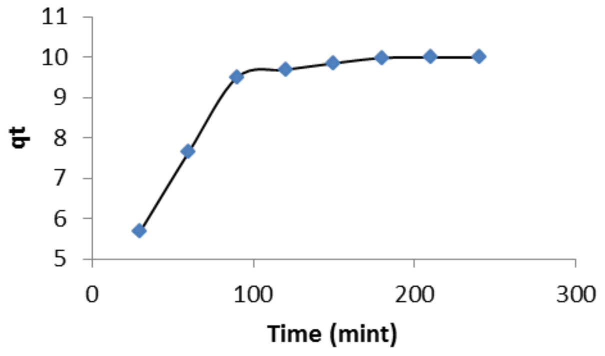


Fig -7: Adsorption kinetics of Cr (VI) onto sawdust with time

4.1. Pseudo First-Order Kinetics

The pseudo first order kinetic model expression

$\frac{dq}{dt} = k_1(q_e - q_t)$ [10]

By solving this equation

$\log(q_e - q_t) = \log q_e - \frac{k_{ad}}{2.303}t$ [11]

Where q_t is amount of chromium (VI) adsorbed (mg/g) at time t (mint), q_e is the amount of chromium adsorbed at equilibrium (mg/g), k_1 (1/min) is pseudo- first order kinetic rate constant.

The plot of log (q_e-q_t) versus t gives a straight line shown in figure 8, which represents the pseudo first-order kinetics for the removal of Cr (VI) using sawdust. The values of first-order rate constants, k_1 and q_e for the initial Cr (VI) concentration by keeping the optimum adsorbent dose are calculated from the slop and intercept and shown in Table 2. The correlation coefficient is found to be 0.9356 which seems not to be good so there is need of pseudo second-order kinetic model for the removal of Cr (VI) using sawdust.

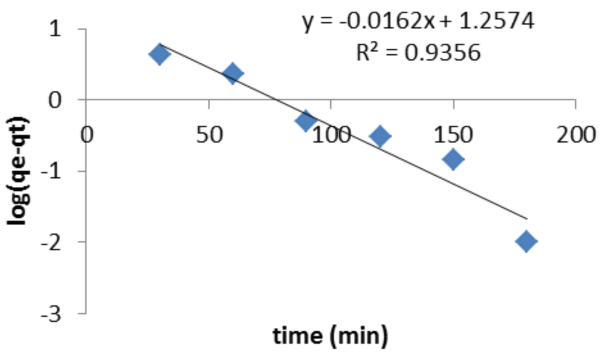


Fig - 8: Pseudo-first order kinetic plots for the adsorption of Cr (VI) on sawdust at room temperatures

4.2 Pseudo-second order kinetic mode

lThe kinetics for adsorption of Cr (VI) on sawdust is defined by pseudo-second order kinetic model when the adsorption process does not follow the first order kinetics. The second order model assumes that the adsorption process is of pseudo second order and the rate limiting step is chemisorption.The pseudo second order kinetic model expression [12]

$$\frac{dq}{dt} = k_2(q_e - q_t)^2$$

Solving this equation by integration, then it becomes

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

This equation is also known as linearized form of pseudo second order model. Where k_2 (g mg^{-1} min^{-1}) is the rate constant of pseudo-second order kinetic equation.

A graph is plotted between t/q_t vs t, yielded the second order rate constant k_2 shown in figure 9, calculated equilibrium capacity q_e and correlation coefficient for initial concentration are shown in table 2. A good agreement shown in between the calculated and experimental capacity and value of correlation coefficient is 0.9947 which indicates that pseudo second order kinetic model is best fitted for removal of Cr (VI) on sawdust.

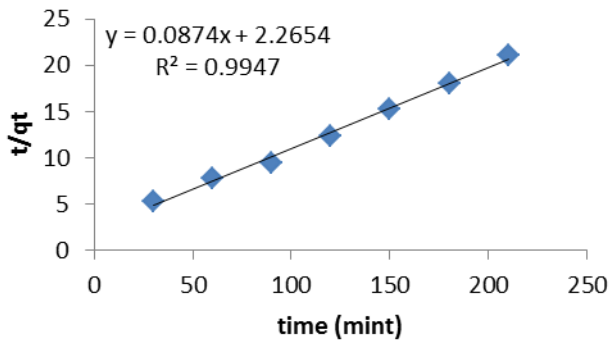


Fig-9: Pseudo-second order kinetic plots for the adsorption of Cr (VI) on Sawdust

4.3 Intra-particle diffusion model

The kinetic of adsorption on sawdust are further analyzed by the intra particle diffusion model proposed by Weber and Morris to determine. The intra-particle diffusion rate constant, k_{dif} is determined using the following equation. [13]

$q_t = k_{dif}\sqrt{t} + C$

Where k_{dif} is the intra-particular diffusion rate constant (mg g^{-1} $min^{-1/2}$)

Figure 10 shows a graph was plotting in between the q_t versus $t^{.5}$ for the adsorption of Cr (VI) which gives the result in a linear relationship, yield the value of k_{dif} and C can be calculated from the plots and shown in table 2. First step of this model is mass transfer of adsorbate molecules from the bulk to adsorbent surface; second step is intra particles diffusion in the adsorbent. And at last, the final equilibrium stage comes where intra particle diffusion started to slow down due to the extremely and low adsorbate concentrations left in the solutions.

From all the evidence shown in table that in the removal of Cr (VI), the kinetic model of pseudo second order provides a better fit than the pseudo first order and intra particles diffusion model

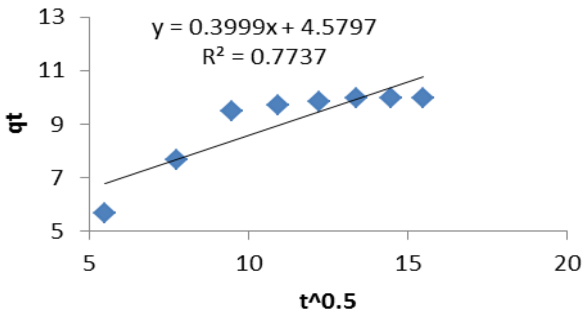


Fig - 10: Intra-particle diffusion kinetics for adsorption of Cr (VI) on sawdust

Table 2: Values of pseudo-first order, pseudo-second order and intra-particle diffusion constants for the adsorption of Cr (VI) on Sawdust

Kinetic models	q_e (exp) (mg g^{-1})	Rate constant (min^{-1})	$q_{e(cal)}$ (mg g^{-1})	R^2
Pseudo first order	9.99	0.0373	18.08	0.9356
pseudo-second order		0.0033	11.44	0.9947
intra-particle diffusion		0.3999	C = 4.5797	0.7737

V. Adsorption isotherms

To study the adsorption efficiency of Cr (VI) at the surface of the adsorbent, a mathematical relationship used to know the adsorption behavior of adsorbent adsorbate combination. An attempt is examine the relationship between the adsorbed (q_e) and aqueous concentration (C_e). There are number of isotherm models but Langmuir; Freundlich and Temkin models are most used.

Langmuir isotherm: The non-linear form of the Langmuir isotherm model for monolayer adsorption is expressed by equation [14]

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

Linear form of Langmuir equation

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

Where C_e (mg/L) is the equilibrium concentration of Cr (VI) remaining in the solution, q_e (mg/g) is the amount of adsorbate adsorbed per mass unit of adsorbent at equilibrium, q_m (mg/g) is the maximum adsorption capacity of metal ions, and k_L (L/mg) is the Langmuir isotherm coefficient.

A graph is plotted in between $1/q_e$ versus $1/C_e$ for Cr (VI) shown in figure 11, the maximum binding constant (q_m) and the adsorbent capacity (K_L) are calculated from the slope and intercept. The value of regression coefficient, K_L and q_m is shown in table 3.

There is a term in Langmuir isotherm used for analysis of Langmuir equation, R_L known as dimensionless separation factor, which is expressed as follow [15]

$$R_L = \frac{1}{1 + k_L C_o}$$

Where C_0 is the initial solute concentration (mgL^{-1}) and k_L is the Langmuir adsorption equilibrium constant (L mg^{-1})

The value of R_L indicates the type of the isotherm to be either unfavorable (R_L>1), linear (R_L=1), favorable (0<R_L<1) or irreversible (R_L=0)

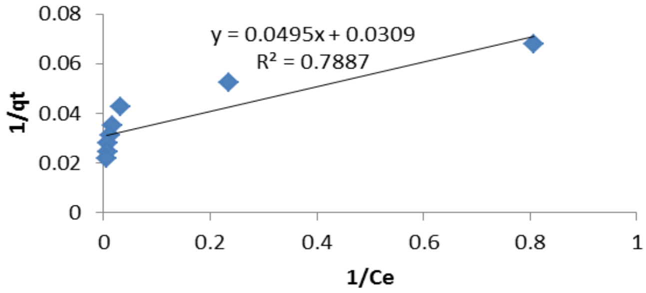


Fig - 11: Langmuir isotherm plot for adsorption of Cr (VI) on sawdust

Freundlich isotherm: Generally used in heterogeneous surface as well as multilayer adsorption. The mathematical expression for the non-linear form of the Freundlich isotherm model can be given as [16]

$$q_e = k_F C_e^{\frac{1}{n}}$$

Logarithmic form of equation is expressed as follows [17]

$$\log q_e = \log k_F + \frac{1}{n} \log C_e$$

where k_F is the Freundlich constant, which indicates the relative adsorption capacity of the adsorbent related to the bonding energy, and n is the heterogeneity factor representing the deviation from linearity of adsorption and is also known as Freundlich coefficient.

A graph is plotted in between the log q_e versus log C_e shown in figure 12, from which the values k_F and 1/n can be obtained listed in table 3. The magnitude of the exponent 1/n gives an indication of the favorability of adsorption. Values, n > 1 represent favorable adsorption condition. [19]

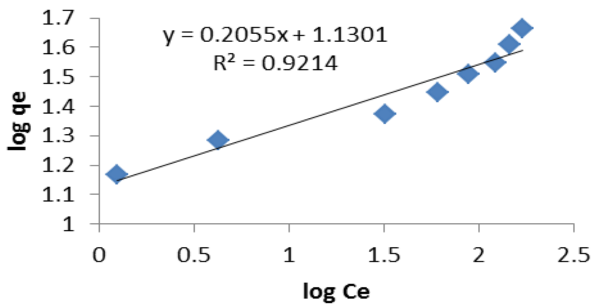


Fig -12: Freundlich isotherm plot for adsorption of Cr (VI) on Sawdust

Temkin isotherm is obtained for analysis the interaction between adsorbent and adsorbant substances, which have some assumption, like heat of adsorption in the layer which decrease linearly due to adsorbate adsorbate interaction and due to that a uniform distribution of binding energy takes place in adsorption up to some binding energy level.

Temkin equation [18]

$$q_e = \frac{RT}{b} \ln(A_T C_e)$$

The linear form of this model is

$$q_e = \frac{RT}{b}\ln A_T + \frac{RT}{b}\ln C_e$$

Where

$$B = \frac{RT}{B_T}$$

A_T is Temkin isotherm equilibrium binding constant (L/g), b_T is Temkin isotherm constant, R is universal gas constant (8.314J/mol/K), T is Temperature at 298K, B is Constant related to heat of adsorption(J/mol).

A graph is plotted in between q_e against $\ln C_e$ shown in figure 13 from there the value of constants are calculated from the slop and intercept given in table 3.

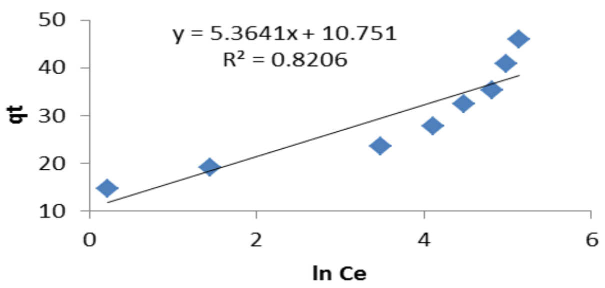


Fig - 13: Temkin Isotherm plot for adsorption of Cr (VI) on sawdust

Langmuir Isotherm	q_m (mg/g)	k_L (L/mg)	R_L	R^2
	64.102	0.4574	0.0418	0.744
Freundlich Isotherm	1/n	n	k_F (mg/g)	R^2
	0.1702	5.875	29.73	0.9746
Temkin Isotherm	A_T(L/mg)	b_T	B	R_2
	11.934	265.90	265.90	0.933

Table 3: Langmuir, Freundlich, and Temkin Isotherm constants for the adsorption of Cr (VI) ion onto sawdust

Form the Table 3; it is observed that correlation coefficient of Freundlich isotherm is higher than the correlation coefficient of Langmuir isotherm and Temkin. Therefore Freundlich isotherm is well fitted with the experimental data of the present system. The data related with Freundlich isotherm, it means the surface of the sawdust is highly heterogeneous.

VI.Conclusion

The study of removal of Cr (VI) from aqueous solutions prepared in laboratory is takes place using bio adsorbent sawdust which is found to be a better adsorbent for the removal of Cr (VI) as compared to many other low cost and commercial adsorbents. The study of the different parameter which affects the removal efficiency and adsorbent capacity are investigated. The batch experiments showed that pH, adsorbent dose, initial concentration and contact time give the more advantage to adsorption. Removal of Cr (VI) is obtained maximum at pH 1.5, contact time 210 minute, initial concentration 50 ppm and adsorbent dose 5g/l. the equilibrium Adsorption data are tested with various models for Langmuir, Freundlich and Temkin isotherm models but the result predict that Freundlich adsorption isotherm model best fitted as compared to Langmuir and Temkin model. The kinetic model for Cr (VI) are tested, the results showed that Cr (VI) adsorption on sawdust best fitted with the Lagergren pseudo second order kinetic model. The value of the adsorption capacity of 5 g/l for saw dust for removal Cr (VI) is found to be significant, which indicates that it can be successfully used for the removal of Cr (VI).

Acknowledgement

We wish to thank giving for providing sawdust. The facilities provided by IIT Roorkee and financial support provided by Ministry of Human Resources Development, Govt. of India, under grant no.MHR-187-CHD is greatly acknowledge.

References

i. Vinodhini V.; N. Das "Relevant approach to assess the performance of sawdust as adsorbent of Chromium (VI) ions from aqueous solutions, Int. J. Environ. Sci Tech., Vol. 7(1), 2010, Pp.85-92.

ii. Venkateswaran, P.; "Speciation of heavy metals in electroplating industry sludge and wastewater residue using inductively coupled plasma" Int.J.Environ.Sci.Tech, Vol. 4(4), 2007, pp.497-504.

iii. Kumar R., Bishnoi N.R.; "Bio sorption of Cr (VI) from aqueous solution and electroplating wastewater using fungal biomass," Chem. Eng. Vol. 135, 2008, pp.202-208.

iv. Selvaraj, K. Manonmani, S. "Removal of Cr (VI) using distillery sludge". Bio resources Technol. Vol. 89, 2010, pp. 207-211.

v. Y.A. Aydın, N.D. Aksoy, "Adsorption of chromium on chitosan: optimization, kinetics and thermodynamics". Chem. Eng. J. Vol. 151, 2009, pp. 188–194.

vi. B.V. Babu, S.Gupta, "Removal of toxic metal Cr (VI) from aqueous solutions using sawdust as adsorbent: equilibrium, kinetics and regeneration studies." Chem. Eng. J. Vol. 50, 2009, pp. 352–365.

vii. D.C. Montgomery, Design and Analysis of Experiments, 4th ed., John Wiley & Sons, USA, 1997.

viii. M.N. Sahmoune, N. Ouazene, "Equilibrium and kinetic modeling of Astrazon yellow adsorption by sawdust: effect of important parameters," Int. J. Chem.React. Eng. Vol. 8, 2010, pp. A151.

ix. Suresh Gupta, B.V. Babu.2009. "Removal of toxic metal Cr (VI) from aqueous solutions using sawdust as adsorbent: Equilibrium, kinetics and regeneration studies". Chemical Engineering Journal Vol. 150, 2009, pp. 352–365.

x. Malkoc, E., Nuhoglu, Y., "Potential tea factory waste for Cr (VI) removal from aqueous solutions: thermodynamic and kinetic studies". Separation and Purification Technology Vol. 54, 2007, pp. 291–298.

xi. Sharma, Y.C., Uma, Srivastava, V., Srivastava, J., Mahto, M. "Reclamation of Cr (VI) rich water and wastewater by wollastonite". Chemical Engineering Journal", Vol. 127, 2007, pp.151–156.

xii. Ho, Y.S., Mckay, G., "Pseudo-second order model for sorption processes. Process Biochemistry", Vol.34, 2009, pp. 451–465.

xiii. Weber, W.J., Morris, J.C., Sanit, J. "Engineering Division Proceedings of the Analytical Society Civil Engineers", Vol.89, 1963, pp31, 28 (SA2).

xiv. Langmuir, I. "The adsorption of gases on plane surfaces of glass, mica and platinum", Journal of American Chemical Society, Vol. 40, 1918, pp.1361–1403.

xv. Basha, S., Murthy, Z.V.P., Jha, B., "Biosorption of hexavalent chromium by chemically modified seaweed, Cystoseira". Chemical Engineering Journal, Vol. 137, 2008, pp.480–488

xvi. H. Freundlich, Adsorption solution, Z. Phys. Chemei.Vol.57, 1906, pp. 384–470

xvii. Ewecharoen, A., Thiravetyan, P., Nakbanpote, W., "Comparison of nickel adsorption from electroplating rinse water by coir pith and modified coir pith". Chemical Engineering Journal Vol. 137, 2008, pp. 181–188

xviii. M.I. Tempkin, V. Pyzhev, "Kinetics of ammonia synthesis on promoted iron catalyst", Acta Phys. Chim. USSR, Vol.12. 1940, pp. 327–356.

xix. H. Freundlich, Adsorption solution, Z. Phys. Chemei.Vol.57, 1906, pp. 384–470