

Adsorptive Removal of Chromium (VI) from Aqueous Solutions by using Sugar and Distillery Waste Material

Ankur Gupta, C B Majumder

Department of chemical engineering, IIT roorkee, Roorkee, Utrakhand 247667,

Email id: guptaankur599@gmail.com

Abstract

Raw bagasse, Bagasse fly ash and distillery sludge, the waste generated in sugar mills and distillery have been used as low-cost potential biosorbent for the removal of hexavalent chromium from an aqueous solution. The effect of hydrogen ion concentration, contact time, adsorbent dose, initial concentrations of adsorbate and adsorbent dose on the uptake of chromium were studied in batch experiments. Bagasse fly ash, Distillery sludge and sugar cane bagasse could be an economical biosorbent for the removal of hexavalent chromium from aqueous system. The order of selectivity is bagasse > bagasse fly ash > distillery sludge for Cr(VI) removal.

Keywords: Bagasse, Bagasse fly ash, distillery sludge, potassium Dichromate, Nitric acid, sodium hydroxide.

Introduction

Various Industrial activities and waste disposal practices cause the contamination of ground water and soil with chromium. Chromium (Cr) is of considerable concern as the metal is used in electroplating, leather tanning, metal finishing, and chromate preparation (L. Khezami, R. Capart, 2005). Typical concentration of chromium in various industries is listed in table 1.1. Chromium occurs in aqueous systems in trivalent Cr(III) and hexavalent Cr(VI) form but the Cr(VI) is 500 times more toxic than Cr(III) (Acar and Malkoc, 2004). Environmental Protection Agency (EPA) has set a concentration limit for total chromium in drinking water at a maximum contaminant level (MCL) of 0.1 mg/L. According to the guidelines recommended by the World Health Organization (WHO), the maximum level for Cr(VI) in drinking water is 0.05 mg L⁻¹ (Zhang et al., 2010). Chromium causes the epigastric pain, nausea, vomiting, severe diarrhoea, corrosion of skin, respiratory tract and lung carcinoma when enters the gastric system (Gladysz-Plaska et al., 2012; Shen et al., 2012).

Table 1: Concentration of Cr(VI) in waste water for various industry

Industry	Cr(VI) conc (mg/l)	Reference
Hardware factory	60.0	Xu et al., 2005
Chrome tanning plant	3.7	Gupta et al., 1999
Electroplating plant	20.7-75.4	Davis et al., 1995
Tannery plant	500-1000	Esmaili et al., 1995, Song et al., 2000

India is one of the largest growers of sugarcane with an estimated production of around 300 million tons in the year

(M. Balakrishnan et al., 2011). There are presently nearly 500 sugar factories in the country along with around 300 molasses based alcohol distilleries (Indiastat, 2010; Tewari et al., 2007). So on the basis of this waste product from this industry is taken as the adsorbent.

Adsorbent preparation

Bagasse Flyash Bagasse fly ash was obtained from a sugar refinery at Modinagar, Uttar Pradesh, India. Various reagents used were of AR grade. The bagasse fly ash was treated with hydrogen peroxide (100 volumes) at 60 °C for 24 h to oxidize the adhering organic matter. Resulting material was then washed with distilled water, dried at 100 °C and stored in a vacuum desiccator.

Bagasse Sugarcane bagasse (SCB) was collected from a sugar-cane crushing plant and the pith was separated manually. The bagasse was boiled with distilled water for 30 min in order to remove soluble sugars present in it and then dried at 120 °C in hot air oven for 24 h and then ground and finally sieved.

Distillery sludge Waste distillery sludge samples were collected from Modi sugar & distillery Modinagar, Uttar Pradesh India. All samples were dried overnight in an oven at 105 °C both before and after pretreatment which provided a biomass source of extended shelf life. Biosorbent was physically modified by heating (heated up to 50 °C in an electrical oven for 24 h), boiling (100 g biosorbent/150 ml water) and autoclaving (at 121°, 15 PSI for 1 h). The pretreated biosorbents were extensively washed with deionized distilled water (DDW) and filtered thoroughly until a pH 7±0.1 was attained.

Batch experimental study

Batch adsorption studies were carried out at desired pH, for different time, different adsorbent dose and different initial concentration to study the effect of various parameters on Cr(VI) removal. First of all, 50 ml of solution was taken in the 250 ml of round bottom flask. Then solution was maintained at desired pH by adding 0.1 N HNO₃ and 0.1 N NaOH, with desired adsorbent dose and for a definite time in a shaker cum incubator at 120 rpm maintained at temperature of 30 °C. Samples were agitated in agitator cum incubator under controlled temperature at a constant speed of 120 rpm at 30 ± 1 °C. After a certain time interval samples were withdrawn from shaker. Thereafter concentration of Cr(VI)

was measured by UV-visible spectrophotometer at 540 nm . The percentage removal of hexavalent chromium was calculated as:

$$\text{Percentage Cr(VI) removal} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

Where C_i is the initial concentration of chromium in solution (mg/l) and C_f is the final concentration of chromium in solution at equilibrium.

The adsorption capacity q_e (mg/g) was calculated as follows:

$$\text{Equilibrium adsorption capacity, } q_e \text{ (mg/g)} = \frac{(C_i - C_f)V}{w} \quad (2)$$

Where V is the volume of solution (l) and w is weight of adsorbent in (g).

Result and discussion

Effect of pH

Cr (VI) stability is dependent on the pH of the system [14]. Cr (VI) in aqueous solution can be present in different ionic forms that are closely related with the pH of the solution. The effect of pH on Cr (VI) adsorption was studied using Baggasse fly ash, raw baggasse and distillery sludge as adsorbent. The experimental results obtained which shows that the adsorption was favorable at acidic condition, maintained by 0.1 N HNO₃ and 0.1 N NaOH. The percentage removal decreased with increasing pH. The percentage of Cr (VI) adsorbed by raw bagasse, bagasse fly ash and distillery sludge decreased from 99.9 to 60.8% when the pH was increased from 2 to 7, shown in Fig.1. The maximum percent removal of Cr (VI) was obtained at pH 2; therefore pH 2 was the optimum pH of the experiment. Cr (VI) at pH 2 is present in the form of HCrO₄⁻. Adsorption of Cr(VI) below pH 2.0 suggests that the negatively charged species (chromate/dichromate in the sample solution) bind through electrostatic attraction to positively charged functional groups on the surface of activated carbon because at this pH more functional groups carrying a net negative charge, which tends to repulse the anions.

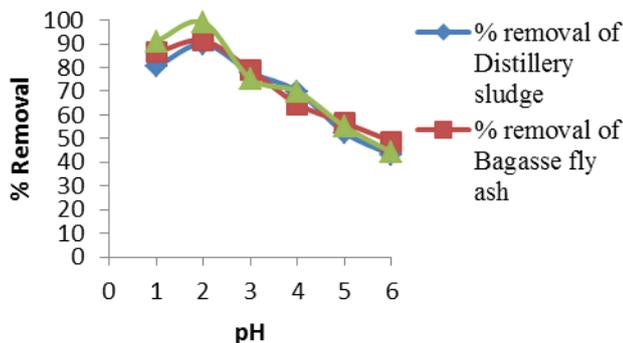


Fig-1. Percentage removal of Cr (VI) versus pH

Effect of initial concentration of metal ions

The influence of initial concentration is shown in Fig.2, which shows that removal decrease with the increase in initial

concentration (C_0). The chromium removal efficiency for distillery sludge, bagasse fly ash and bagasse decreased from 81% to 50%, 91% to 35% and 99% to 32% respectively, on increasing the initial concentration from 100 to 500 mg/l. On increasing the concentration, the solute in bulk phase increases resulting in the repulsion forces between the solute molecules which decreases efficiency for chromium removal. However, the adsorption capacity increases with increase in initial concentration (C_0), since C_0 provides the required driving force for adsorption of Chromium on adsorbents.

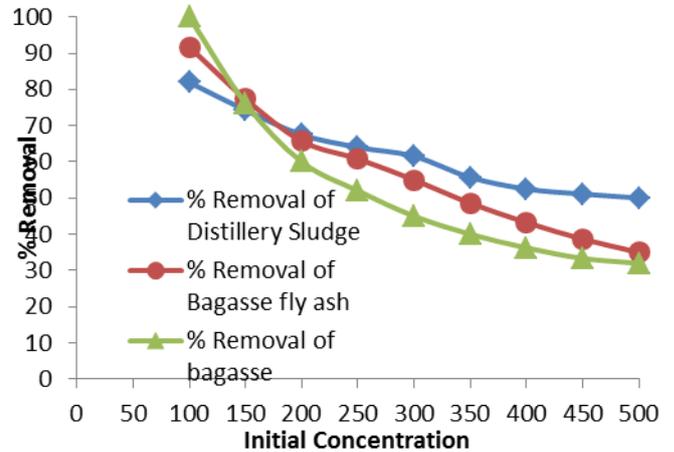


Fig-2. Percentage removal of Cr (VI) versus initial concentration of metal ions

Effect of Adsorbent dosage

Adsorbent dosage is an important parameter since it determines the ability of an adsorbent for removal of Cr(VI) at a given initial concentration and separation cost. In this paper, result shows that the removal of Cr (VI) increased rapidly from 53% to 91% when bagasse fly ash dosage was increased from 0.1 g to 0.5 g, 11% to 82% from 0.5 to 1.5 g for distillery sludge, 76% to 99% from 0.1 to 0.3 g at initial concentration of 100 ppm and 50 ml volume. Fig. 3 shows 10 g/l of bagasse fly ash doses is optimum for 91 % removal, 30 g/l for distillery sludge for 82 % removal and 6g/l for raw bagasse for 99 % removal respectively but in this paper, result shows that initially increase in doses increases the % removal of Cr (VI) as more surface area was available for adsorption. At lower dose, the adsorbent surface becomes saturated as the Cr(VI) concentration is high. Moreover, loading of metal ions and surface makes the adsorption of Cr(VI) more favorable and rapid. After optimum dose, the removal was unaffected with increases in dose of PAC because on increasing the dose further, equilibrium is approached between solution of Cr(VI) and surface of biosorbent.

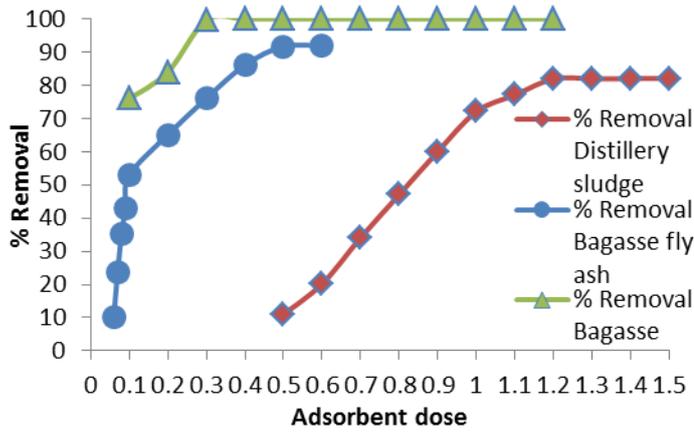


Fig-3. Percentage removal of Cr(VI) versus Adsorbent dose

Effect of contact time

The time at which the adsorption approaches a saturation limit, this time is termed as equilibrium contact time. At different intervals of time, the percentage removal of Cr(VI) for different adsorbent such as Bagasse fly ash, bagasse and distillery sludge were examined. The effect of contact time on the percentage removal of Cr(VI) and adsorption capacity for initial concentration $C_i = 100$ mg/l are shown in figure 4. This figure shows the quick adsorption by various adsorbent mentioned above in the initial small time span, and thereafter, the adsorption rate decreases gradually. It is due to the fact that large numbers of vacant sites are available during the initial period of time, and there after molecules hardly occupied the vacant sites since the adsorb Cr(VI) molecules shows the repulsive forces between each other and with the solute in bulk phase. Equilibrium time was attaining nearly at 4 h for bagasse, 12 h for distillery sludge, 20 h for bagasse fly ash respectively therefore these contact time of respective adsorbent was used to perform all the batch experiments.

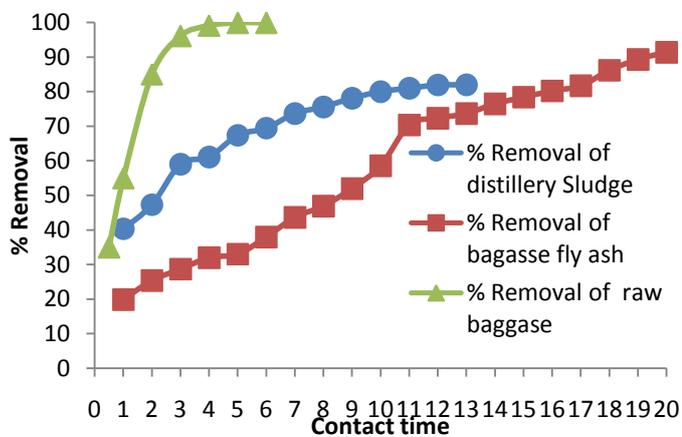


Fig- 4. Percentage removal of Cr (VI) versus contact time

Adsorption kinetics of Cr(VI)

For the purpose of determining the mechanism of adsorption, particularly the potential rate controlling step, the transient

behaviour of the chromium metal ion adsorption process was analysed using the pseudo-first order, pseudo-second order, intraparticle diffusion model. The pseudo-first-order equation can be written as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{3}$$

Where q_t is the adsorption capacity (mg/g) at particular time t , k_1 is the equilibrium rate constant (time^{-1}) and q_e (mg/g) is the adsorption capacity at equilibrium. After definite integration by applying the initial conditions = 0 at $t = 0$ and = at $t = t$, the Eq. (3) becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{4}$$

Value of adsorption rate constant (k_1) was determined by the plot of $\log(q_e - q_t)$ vs time. From the slope and the intercept the values of k_1 and q_e were calculated respectively. Equation for pseudo second-order model can be written as (Ho et al., 1999):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{5}$$

Where k_2 is pseudo-second-order rate constant [g / (mg) (min)]. The linear form of above Eq. (5) can be written as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

In many adsorption cases Weber-Morris found that, adsorbate uptakes varies proportionally with $t^{1/2}$ rather than residence time t (Alkan et al., 2007). Weber-Morris model is used to explain intra-particle diffusion. Diffusional model proposed by Weber-Morris mathematically written as (Weber et al., 1963):

$$q_t = k_{int} t^{1/2} + I \tag{7}$$

Where, k_{int} is the intra-particle diffusion rate constant (mg/(g.min)), q_t is the adsorption capacity (mg/g) and I is the intercept (mg/g). It is evident that if intra-particle diffusion is the only rate-limiting step in the adsorption process then q_t versus $t^{1/2}$ plot should go through origin. At ideal condition plot of q_t versus k_{int} gives a straight line which goes through origin.

Initial concentrations of 100 mg/l were used for Cr(VI) removal, while optimized value of pH was kept fixed. The samples were collected at specified intervals till equilibrium was achieved. The experimental data obtained was used to plot the three graphs as per Eq. (4), (6) and (7) to evaluate the predictive capabilities of pseudo first order, pseudo second order and intra-particle diffusion-limiting respectively. If intra-particle diffusion is the only rate-limiting step in the adsorption mechanism then q_t versus $t^{1/2}$ plot of Eq. (7) should go through origin, but in this research work plot does not go through origin because of other diffusion such as film diffusion may also prevailing here. Figure (5), (6), (7) shows the plot of pseudo first order, pseudo second order and intra-particle-diffusion model for Cr(VI) removal for Distillery

sludge, bagasse fly ash and bagasse respectively. The values of kinetic parameter for pseudo first order, pseudo second order and intra particle diffusion model obtained from the plot listed in Table (2), (3), (4) for bagasse, Bagasse fly ash and Distillery sludge respectively. It is observed that the experimental data fitted well with pseudo first order and pseudo second order kinetics for bagasse gave a high correlation coefficient R^2 of the order of 0.98 and pseudo second order kinetics for Distillery sludge and pseudo first order kinetics for bagasse giving high value of (R^2) correlation coefficient of the order of 0.99 and 0.97 respectively.

Table 2. Kinetic parameters of Cr(VI) for Removal of Bagasse

Kinetic Parameters	Cr(VI) removal
Pseudo-first order	
k_1	0.0175
q_e	17.31
R^2	0.9893
Pseudo-second order	
k_2	0.000695
q_e	21.27
R^2	0.9879
Intra-particle diffusion	
K_{int}	0.1293
I	-0.0936
R^2	0.9797

Table 3. Kinetic Parameters of Cr(VI) Removal for Bagasse fly ash

Kinetic Parameters	Cr(VI) removal
Pseudo-first order	
k_1	0.104326
q_e	10.3944
R^2	0.9713
Pseudo-second order	
k_2	0.043
q_e	6.5574
R^2	0.9026
Intra-particle diffusion	
K_{int}	2.2885
I	-1.1623
R^2	0.9661

Table 4. Kinetic parameters of Cr(VI) removal for Distillery sludge

Kinetic Parameters	Cr(VI) removal
Pseudo-first order	
k_1	0.11054
q_e	2.51
R^2	0.9761
Pseudo-second order	
k_2	0.13909
q_e	3.91
R^2	0.9962
Intra-particle diffusion	
K_{int}	1.176
I	-0.7323
R^2	0.9878

Kinetic Parameters	Cr(VI) removal
Pseudo-first order	
k_1	0.11054
q_e	2.51
R^2	0.9761
Pseudo-second order	
k_2	0.13909
q_e	3.91
R^2	0.9962
Intra-particle diffusion	
K_{int}	1.176
I	-0.7323
R^2	0.9878

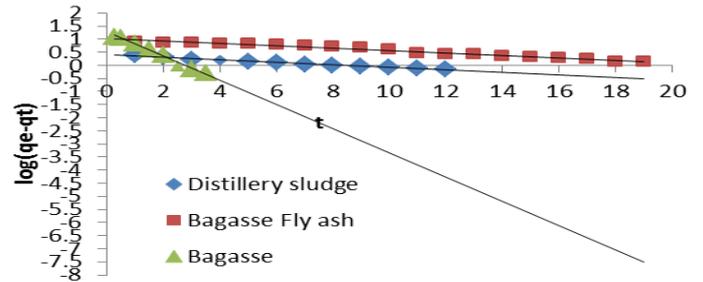


Fig.-5. Pseudo first order kinetic model

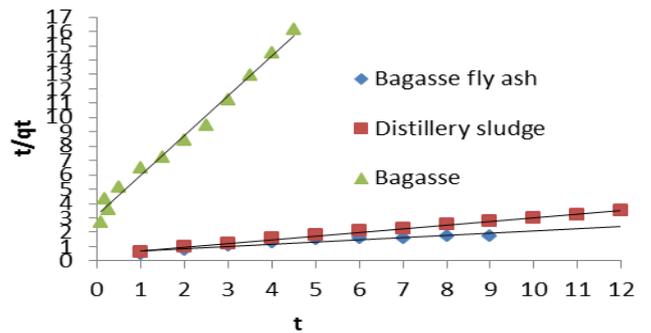


Fig-6. Pseudo second order kinetic model

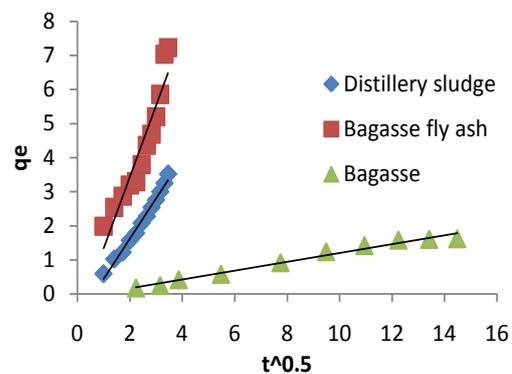


Fig-7. Intra particle diffusion model

Adsorption isotherm model

Many empirical and theoretical models have been proposed to represent the different types of adsorption isotherms. Langmuir, Redlich- Peterson (R-P), Freundlich etc. are commonly used isotherm models for reporting the dynamic equilibrium condition. Langmuir isotherm is based on assumption of monolayer adsorption (Langmuir et al). Numerically Langmuir isotherm equation can be written as:

$$q_e = \frac{Q_m K_A C_e}{1 + K_A C_e} \tag{8}$$

Where q_e is the adsorption capacity (mg/g) at equilibrium, Q_m is the adsorption capacity required for monolayer adsorption, C_e is the equilibrium concentration of solute and K_A is the constant related to enthalpy of adsorption. In many instances the heat of adsorption decreases with increasing extent of adsorption process. This decline in heat of adsorption is logarithmic which suggests that the adsorption active pores are

distributed exponentially with the heat of adsorption. Such type of behaviour was formulated by Freundlich which does not follow the limit of monolayer adsorption, can be written as (Freundlich et al)

$$q_e = K_F C_e^{1/n} \tag{9}$$

Where q_e is the mass of adsorbate adsorbed per unit mass of adsorbent at equilibrium condition, K_F is the Freundlich constant and n is the exponential constant.. Mathematical form of Tempkin can be written as

$$q_e = \frac{RT}{b} \ln(a C_e) \tag{10}$$

where C_e Equilibrium concentration, R gas constant, T absolute Temperature, a Temkin Isotherm constant, b temkin constant .

The experimental data is fitted well with langmuir, freundlich and temkin isotherm model for various adsorbent as shown in figure (8), (9) and (10) respectively. The equilibrium constants derived from above isotherm models for Cr(VI) are listed in table table (5) for bagasse, table (6) for bagasse fly ash and table (7) for distillery sludge respectively. Constants listed in table (5),(6),(7) indicates that experimental data were fitted well for Freundlich isotherm for Cr(VI) removal for bagasse and bagasse fly ash while Langmuir isotherm model for Cr(VI) removal for Distillery sludge.

Table 5. Adsorption Equilibrium Isotherm Constants for Hexavalent Chromium for Bagasse

Adsorption Isotherm Model	Model equation	Parameters for Cr(VI)
Freundlich Adsorption Isotherm	$q_e = K_F C_e^{1/n}$	$K_F = 10.353805$ $n = 6.574621$ $R^2 = 0.9939$
Langmuir Adsorption Isotherm	$q_e = \frac{Q_m K_A C_e}{1 + K_A C_e}$	$Q_m = 25.71$ $K_A = 0.063$ $R^2 = 0.9405$
Temkin Adsorption Isotherm	$q_e = \frac{RT}{b} \ln(a C_e)$	$a = 11.4427$ $b = 827.386$ $R^2 = 0.9366$

Table 6. Adsorption equilibrium isotherm constants for hexavalent chromium for Bagasse fly ash

Adsorption Isotherm Model	Model equation	Parameters for Cr(VI)
Freundlich Adsorption Isotherm	$q_e = K_F C_e^{1/n}$	$K_F = 5.766336$ $n = 4.918839$ $R^2 = 0.9565$
Langmuir Adsorption Isotherm	$q_e = \frac{Q_m K_A C_e}{1 + K_A C_e}$	$Q_m = 18.8679$ $K_A = 0.0453$ $R^2 = 0.9920$
Temkin Adsorption Isotherm	$q_e = \frac{RT}{b} \ln(a C_e)$	$a = 1.914751$ $b = 891.3846$ $R^2 = 0.9398$

Table 7. Adsorption equilibrium isotherm constants for hexavalent chromium for Distillery sludge

Adsorption Isotherm Model	Model equation	Parameters for Cr(VI)
Freundlich Adsorption Isotherm	$q_e = K_F C_e^{1/n}$	$K_F = 1.03968$ $n = 2.4248$ $R^2 = 0.9927$
Langmuir Adsorption Isotherm	$q_e = \frac{Q_m K_A C_e}{1 + K_A C_e}$	$Q_m = 12.7226$ $K_A = 0.014$ $R^2 = 0.9609$
Temkin Adsorption Isotherm	$q_e = \frac{RT}{b} \ln(a C_e)$	$a = 6.114423$ $b = 964.4125$ $R^2 = 0.9659$

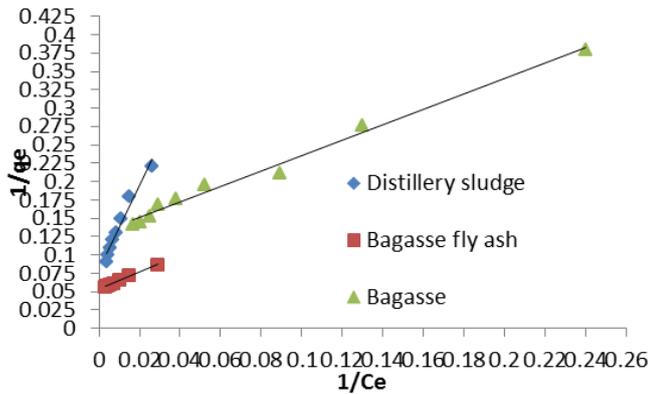


Fig.-8. Langmuir isotherm model

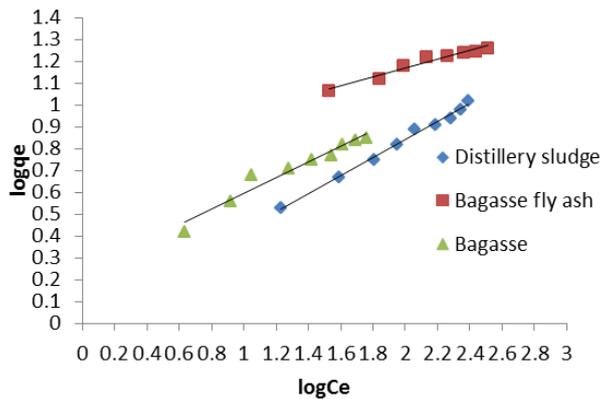


Fig. 9 Freundlich isotherm model

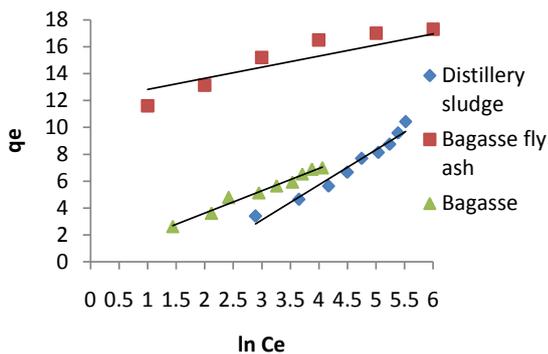


Fig.10 Temkin isotherm model

Conclusion

The present investigation was processed to study the removal of Cr (VI) from aqueous solutions using adsorption over various adsorbent such as bagasse, bagasse fly ash and distillery sludge a waste product from sugar and distillery. Experiments showed that adsorbent dose, pH and contact time contribute more to adsorption. The adsorption of Cr(VI) found to be highly dependent on solution pH, contact time and adsorbent dose. The optimum values for the adsorption of chromium from the aqueous solution was obtained at pH 2 of the Cr (VI) solution, Adsorbent dose were found to be, 10 g/l of bagasse fly ash, 30 g/l for

distillery sludge and 6g/l for raw bagasse and contact time of 4hr for bagasse, 12 h for distillery sludge, 20 h for bagasse fly ash respectively resulting in maximum adsorption of chromium. In the present study, percentage removal decreases with increase in pH value and removal increases with increase in adsorbent dose and contact time. This paper compared different kinetic and isotherm models. The results showed that Cr (VI) adsorption on bagasse followed the pseudo first order kinetic model, pseudo second order for distillery sludge, while bagasse fly ash followed both pseudo first order and pseudo second order kinetic model. The isotherm model is also studied; the Langmuir model is best fitted with the experimental data for distillery sludge and Freundlich model for bagasse and bagasse fly ash respectively. The experimental values obtained were found to agree satisfactorily result with the values predicted by the models.

The maximum removal efficiency of chromium ions was found to be 99% for bagasse, 91 % for bagasse fly ash and 82.28 % for distillery sludge respectively. Adsorbent such as bagasse, bagasse fly ash and distillery sludge is waste product of sugar and distillery industry showed good potential for chromium ion removal. These waste products are easily available in any part of India at negligible cost, which makes it the potential raw material for preparation of adsorbent. Since the removal efficiencies of Cr(VI) removal are satisfactory for various adsorbent used, it is concluded that these adsorbent is an effective and efficient alternative adsorbent for hexavalent chromium removal from waste water containing hexavalent chromium.

ACKNOWLEDGEMENT

We wish to thank for 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. Xin-jiang Hu., Jing-song Wang., Yun-guo Liu., Xin Li., Guang-ming Zeng., Zheng-lei Bao., Xiao-xia Zeng., An-wei Chen., Fei Long., "Adsorption of chromium (VI) by ethylene diamine-modified cross-linked magnetic chitosan resin: Isotherms, kinetics and thermodynamics," Journal of Hazardous Materials, Vol 185, 2011, pp. 306-314.
- ii. L. Khezami., R. Capart., J. Hazard. Mater, Vol 123, 2005, pp. 223-231.
- iii. US Department of Health and Human Services, Toxicological Profile for Chromium, Public Health Service Agency for Toxic substances and Diseases Registry, Washington, DC, 1991.
- iv. World Health Organization (WHO), Guidelines for Drinking-Water Quality, Recommendations, vol. 1, third ed., Geneva, 2004, p. 334.
- v. S.E. Bailey., T.J. Olin., R.M. Bricka, D.D. Adrian., "A review of potentially low-cost sorbents for heavy metals," Journal of Water Res. Vol. 33, 1999, pp. 2469-2479.
- vi. Y.S. Ho., G. McKay., "Pseudo-second order model for sorption processes," Process Biochemistry, Vol 34, 1999, pp. 451-465.
- vii. Weber, W.J., and Morris, J.C., "Kinetics of Adsorption on Carbon from Solution," Journal of Sanitary Engineering Division, American Society of Chemical Engineering, Vol 89, 1963, pp. 31-59.

viii. Ho, L. C., Filippenko, A. V., Sargent, W. L. W., & Peng, C. Y. 1997b, ApJS, Vol. 112, pp. 391.

ix.

x. David William O' Connell., Colin Birkinshaw., Thomas Francis O' Dwyer., "Heavy metal adsorbents prepared from the modification," The journal of bioresource technology, Vol. 99, 2008, pp. 6709–6724.

xi.

xii. Jyotikusum Acharya., J.N. Sahu., B.K. Sahoo., C.R. Mohanty., B.C. Meikap., "Removal of chromium(VI) from wastewater by activated carbon developed from *Tamarind wood* activated with zinc chloride," Chemical Engineering Journal, Vol. 150, 2009, pp. 25–39.

xiii. Vinod K. Gupta., M.R. Ganjali., Arunima Nayak., B. Bhushan., Shilpi Agarwal., "Enhanced heavy metals removal and recovery by mesoporous adsorbent prepared from waste rubber tire," Chemical Engineering Journal, Vol. 197, 2012, pp. 330–342.

xiv. A. Santhana Krishna Kumar., Timsi Gupta., Shruti Singh Kakan., S. Kalidhasan., Manasi., "Effective adsorption of hexavalent chromium through a three center (3c) co-operative interaction with an ionic liquid and biopolymer," Journal of Hazardous Materials, Vol. 239–240, 2012, pp. 213–224.

xv. Manjeet Bansal., Diwan Singh., V.K. Garg., "A comparative study for the removal of hexavalent chromium from aqueous solution by agriculture wastes' carbons," Journal of Hazardous Materials, Vol. 171, 2009, pp. 83–92.