

## COMPARISON STUDIES OF VARIOUS ADSORPTION ISOTHERMS FOR ALOEVERA ADSORBENT

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### ABSTRACT

The presence of toxic heavy metals such as chromium (VI) contaminates in aqueous streams, arising from the discharge of untreated metal contain effluent into water bodies, is one of the most important environmental problems. Adsorption is one of the effective techniques for chromium (VI) removal from wastewater. In the present studies, adsorbent is prepared from Aloe vera and studies are carried out for chromium (VI) removal. Aloe vera is activated with the use of concentrated sulfuric acids (98%w/w). Batch adsorption studies demonstrate that the adsorbent prepared from Aloe vera has a significant capacity for adsorption of chromium (VI) from aqueous solution. The parameters investigated in this study include contact time, adsorbent dosage, initial chromium (VI) concentration and pH. The adsorption of chromium (VI) is tested with Langmuir, Freundlich, Temkin and Redlich-Peterson isotherm models. Application of the Langmuir isotherm to the systems yielded maximum adsorption capacity.

### INTRODUCTION

Chromium is used in industries such as electroplating, leather tanning. Paints and pigments etc., and has the potential to contaminate drinking water sources. Chromium exists in different oxidation states in nature of chromium (VI) is the most water soluble and easily enters the living cells. In general, chromium (VI) is removed waste water from various methods such as chemical precipitation, electrochemical reduction, sulfide precipitation, cementation, ion-exchange, reverse osmosis, electro dialysis, solvent extraction and evaporation etc. These methods are, however, cost intensive and are unaffordable for large scale treatment of wastewater that is rich in Chromium(VI). Adsorption using activated carbon is an effective method for the treatment of industrial effluents contaminated with chromium (VI) and quite popular. Other commercial adsorbents are recently are generally less than those of activated carbon. In the present study, adsorbent is prepared from Aloe vera and studies are carried out for chromium (VI) removal. Aloe vera is activated

by giving heat treatment with the use of concentrated sulphuric acid (98%w/w). Batch experiment are carried out for kinetic studies on the removal of chromium (VI) from aqueous solution using the activated Aloe vera adsorbent, the effect of various parameters such as contact time, adsorbent dosage, initial chromium (VI) concentration and pH has been studied.

### EXPERIMENTAL WORK

#### Preparation of adsorbent

Aloe vera is collected and washed with distilled water and dried at 110°C for 5 hrs. The dried seeds are crushed in small particle by using jaw crusher. Then it is treated with concentrated sulphuric acids (98%w/w) in 1:1 weight ratio and is kept in oven at 150°C for 24 hrs. The carbonized material is washed with distilled water to remove the free acids and dried again at 100°C for 5hrs.

#### Effect of Adsorbent Dosage

The removal of chromium (VI) is increased with increase of adsorbent dosage.

The removal increases with 49 to 95% by increasing adsorbent dosage from 0.5 to 1 g/l. The drop in adsorption capacity is basically due to site remaining unsaturated during the adsorption process.

### Batch Experiments

The entire chemical used is of analytical grade. A stock solution of chromium (VI) is prepared by dissolving 2.8287 g of 99% potassium dichromate ( $K_2Cr_2O_7$ ) in 1000 ml of distilled water. This solution is diluted as required to obtain standard solution containing 20, 40, 50, 60, 80, 100 mg/L of Chromium (VI). 0.5 N HCl and 0.5 N NaOH solution are used for adjustments. The batch experiments are carried out in 100 ml borosil conical flasks by agitating a pre-weighed amount of the Aloe vera adsorbent with 50 ml of the aqueous chromium (VI) solution for a predetermined period at 30°C on a water bath-cum-mechanical shaker. The adsorbent is separated with filter paper. Adsorption isotherm study is carried out with different initial concentration of chromium (VI) from 20 to 100 mg/L. The concentration of free chromium (VI) ions in the effluent was determined spectrophotometrically by developing a purple-violet color with 1, 5-diphenyl carbazide in acidic solution as a complexing agent. The absorbance of the purple-violet coloured solution is obtained at 540 nm after 20 min.

## RESULT AND DISCUSSION

### Adsorption isotherms

Adsorption isotherms describe how adsorbate interacts with adsorbents and therefore are critical in optimizing the use of adsorbents. In order to optimize the design of an adsorption system. It is essential to establish the most appropriate correlation for the equilibrium curve. Several isotherm equations are available for analyzing experimental data and the important isotherms were selected in this study.

### Langmuir isotherm

The Langmuir isotherm<sup>1</sup> which is applicable for monomolecular layer adsorption has been successfully applied to obtain a maximum adsorption capacity. Langmuir isotherm assumes that maximum ion exchange depends on the saturation level of monolayer of adsorbate molecules on the adsorbent surface that the energy of ion exchange is constant, and there is no transmigration of adsorbate molecules on the surface plane<sup>2</sup>. As shown in Table 1, The Langmuir adsorption model is based on the assumption that maximum

adsorption corresponds to saturated monolayer of solute molecules on the adsorbent surface. The linear form of the Langmuir equation can be described by  $C_e/q_e = (1/Q_0b) + (1/Q_0) C_e$  where  $C_e$  (mg/L) is the equilibrium concentration of the adsorbate,  $q_e$  (mg/g) is the amount of adsorbate per unit mass of adsorbent,  $Q_0$  and  $b$  are Langmuir constants related to adsorption capacity and rate of adsorption respectively. The linear plot of specific adsorption ( $C_e/q_e$ ) against the equilibrium concentration ( $C_e$ ). (Fig.1) shows that the adsorption obeys the Langmuir model. The Langmuir constants  $Q_0$  and  $b$  were determined from the slope and intercept of the plot are presented in table.1. The  $R^2$  values (0.998) suggest that the Langmuir isotherm provides a good fit to the isotherm data

### Freundlich isotherm

Freundlich isotherm<sup>3</sup> (an empirical equation) describes adsorption onto a heterogeneous surface through a multilayer adsorption mechanism. The linear form of Freundlich isotherm is given as

$$\ln q_e = \ln K_F + 1/n \ln C_e$$

Where  $K_F$  is the Freundlich isotherm constant and  $1/n$  is the adsorption intensity. The linear plot of specific adsorption  $\log q_e$  against the equilibrium concentration  $\log C_e$  (Fig.2) shows that the adsorption obeys the Freundlich model.

Table 1 summarizes all the Freundlich parameters, together with correlation coefficients  $R^2$ . The obtained values of  $1/n$  ( $0.1 < 1/n < 1$ ) indicated a higher adsorbent ability of Cr (VI) at all temperatures studied under study. The  $R^2$  values of Freundlich isotherm were found to be lower than the values of Langmuir isotherm, indicating that the Langmuir model fitted the experimental data better than the Freundlich model.

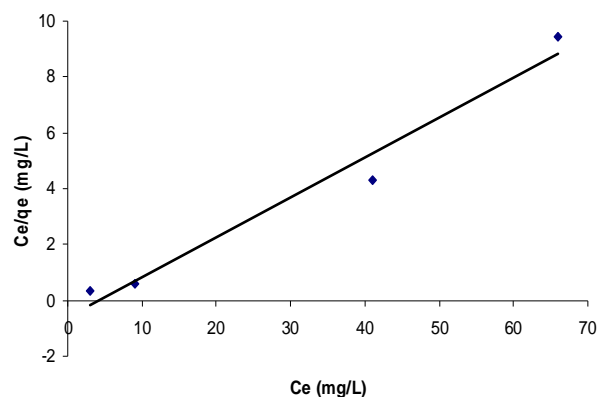


Fig.1: Langmuir isotherm for Chromium (VI) sorption onto Aloe vera

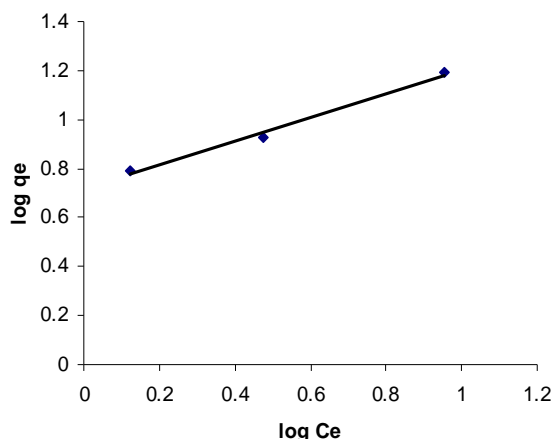


Fig. 2: Freundlich isotherm for chromium (VI) onto Aloe vera

Table 1: Langmuir and Freundlich isotherm constants and correlation coefficients for adsorption of chromium (VI) on to Aloe vera adsorbent

Langmuir isotherm	Freundlich isotherm
Qb = 0.15	$K_f = 2.039674$
b = -0.81	$n = -1.45937$
$R^2 = 0.998$	$R^2 = 0.9762$

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor  $= 1 / (1 + bC_0)$  where  $C_0$  (mg/L) is the highest initial concentration of adsorbent and  $b$  (L/mg) is Langmuir constant. The parameter  $R_L$  indicates the nature of shape of the isotherm accordingly

$R_L > 1$	unfavourable adsorption
$0 < R_L < 1$	Favourable adsorption
$R_L = 0$	Irreversible adsorption
$R_L = 1$	linear adsorption

The value of  $R_L$  in the present investigation has been found to be 0.93777 at 30°C showing that the adsorption of Cr (VI) on Aloe vera is favorable at temperature studied.

### Temkin isotherm

Temkin and pyzhev<sup>4</sup> takes into account of the adsorbent –adsorbate interactions on adsorption isotherms. It based on the assumption that due to the adsorbate-adsorbate repulsions the heat of adsorption of all the molecules in the layer decreases linearly with the coverage of molecules and the adsorption of adsorbate is uniformly distributed. The Temkin isotherm is expressed as

$$Q_e = B \ln A + B \ln C_e$$

Where  $b$  and  $A$  are the Temkin constants and can be determined by a plot of  $q_e$  versus  $\ln C_e$   $e$  Temkin parameters,  $A$  and  $B$ , together with

the correlation coefficient. The constant  $B$  related to the heat of adsorption and  $A$  is corresponding to the maximum binding energy. The  $R^2$  values of Temkin isotherm is lower than that obtained for the Langmuir isotherm and Freundlich isotherm. This indicates that Temkin isotherm model is not fit of equilibrium data as compared with the Langmuir and Freundlich isotherm models

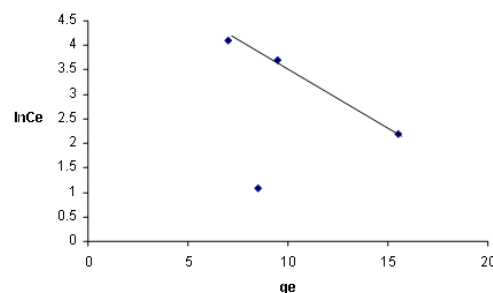


Fig. 3: Temkin isotherm for chromium (VI) onto Aloe vera

$$R^2 = .3278$$

$$S = .8708$$

$$I = 12.560$$

### Redlich-Peterson isotherms

The Redlich –peterson isotherms is an intermediate isotherm model which combines the features of both the Langmuir and Freundlich isotherms, and it often gives a more realistic representation of an adsorption system operating over wide range of concentrations, and it is a special case of Langmuir when the Redlich Peterson isotherm constant  $g$  is set equal to unity. In order to well understand the adsorption behaviors, the Redlich – Peterson equation were employed to fit the experimental data respectively (Fig is not shown)

$Q_e = AC_e / (1 + BC_e^g)$  where  $q_e$  is the adsorption capacity mg/g;  $C_e$  is the equilibrium concentration of Cr (VI) mg/l. The  $R^2$  values obtained from the Langmuir model are much closer to 1 than are those from the Freundlich model and the Redlich-Peterson model, suggesting that the Langmuir model is better than the Freundlich model and the Redlich – Peterson model to fit the adsorption isotherm of Aloe vera for Cr (VI).

### Dubin-Radushkevich

(D-R) isotherm model To determine the adsorption occurred is physical or chemical in nature, the equilibrium data were applied to D-R model. The linearizes form of the D-R model is given below

$\ln C_{ads} = \ln C_m - Y \epsilon^2$  where  $C_{ads}$  is the adsorbed metal ions on the surface of

adsorbent (mg/L),  $C_m$  is the maximum adsorption capacity (mg/g) 'Y is the activity coefficient related to mean adsorption energy ( $\text{mol}^2/\text{J}$ )<sup>2</sup> and  $\epsilon$  is the Polanyi potential ( $\text{kJ}^2\text{mol}^2$ ) Polanyi potential (32) can be calculated by using the following equation

$$\epsilon = RT \ln(1 + 1/C_e)$$

The mean adsorption energy, E (KJ/mol) is calculated with the help of the following equation

$$E = 1/2 \cdot Y$$

The adsorption potential is dependent of the temperature, but it depends upon the nature of the adsorbent and adsorbate. The mean free of the adsorption E, which is the free energy for the transfer one mole of metal ions from the infinity to the surface of the adsorbent, provide information about the nature of adsorption either chemical ion exchange or physical adsorption The values of E lie between 8 and 16 kJ/mol depict the adsorption process follows the chemical ion exchange and if  $E < 8 \text{ KJ/mol}$ , the adsorption process is of a physical nature [5,6] The mean adsorption energy  $E = 5.205, 5.161, 5.061$  and  $4.986 \text{ KJ/mol}$  was calculated for Cr(VI) ions respectively.

#### Elovich equation

Elovich equation used to describe activated adsorption can be expressed as

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln(t)$$

Where  $\alpha$  is the initial adsorption rate (mg/gmin) and the parameter  $\beta$  is the desorption constants  $\alpha$  and  $\beta$  were obtained from the intercept and slope of the plot of  $q_t$  versus  $\ln t$ , the correlation coefficients  $R^2$  were obtained in the range of 0.878-0.9856 for all the initial Cr (VI) concentration.

#### CONCLUSION

Adsorbent prepared from Aloe vera could be used for the removal of chromium (VI) from aqueous solutions. The equilibrium time for the adsorption of chromium (VI) on the adsorbent prepared from Aloe vera in the present study from aqueous solutions is found to be 180mts. The adsorption process of chromium (VI) can be described by Langmuir isotherm and Freundlich isotherm model show a good agreement with the equilibrium data.

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