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Adsorption of Dye by Using the Solid Waste from Leather Industry as an Adsorbent

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ABSTRACT: *The batch adsorption experiment was carried out for the removal of dye by using the leather waste from the leather industry as an adsorbent. The efficiency of the adsorbent was studied by varying the parameters contact time, initial concentration, adsorbent dose, pH and Temperatures. The isotherm was studied by shaking 250 mg of adsorbent in 50 ml of dye solution of concentration range of 50-125 mg/l. The equilibrium was achieved after 180 minutes for this study. The experimental equilibrium data for this system has been analyzed using the linearized forms of Langmuir and Freundlich isotherms. The Langmuir isotherm was found to provide the best theoretical correlation of the experimental data. The maximum capacity of adsorbent was determined by analyzing the experimental equilibrium data. This study showing the utilization of solid waste to treat the liquid waste and also satisfying the applicability and suitability of this adsorbent for dye containing wastewater treatment.*

Keywords —*Adsorption, CCLW, dye, Langmuir, Freundlich isotherm.*

I. INTRODUCTION

Dyes are widely used in many industries such as textile, rubber, paper, plastic, cosmetic etc. Among them, textile ranks first in usage of dyes (Saiful Azhar et al., 2005). Presently, more than 10,000 of different commercial dyes and pigments are available (Eren and Acar, 2006; Ozer et al., 2006), and more than 7×10^5 tons per year are produced world wide (Crini, 2006; Saiful Azhar et al., 2005). Two percent of dyes that are produced are discharged directly in aqueous effluents (Crini, 2006). These colored compounds are not only aesthetically displeasing, but they also impede light penetration, retard photosynthetic activity and inhibit the growth of biota. Therefore it is necessary to eliminate dyes from wastewater before it is discharged.

The utilization of alternative low-cost materials with high adsorption activity to solve environmental problems for example, clays (Oliveira et.al, 2002), cane waste (Nassar and Magdy, 1997), wood (Asfour et.al, 1991), and fish scales (Villanueva-Espinosa et.al, 2001) and mineral carbon (Nicolet and Rott, 1999) have been tested as adsorbent on remediation of contamined water. The solid waste from the tanning industry as adsorbent to other contaminants is an interesting alternative to (i) eliminate their harmful effect on the environment and (ii) provide a profitable use of these materials. Previous work by leather waste as adsorbent (Sreeram et.al, 2004 and Fathima et.al, 2005).

This study was aimed to investigate the adsorption capacities of Chrome containing leather waste (CCLW) based activated carbon for the removal of dye from wastewater. Also to investigate the influence of various parameters like initial concentration, Adsorbent dose, pH, time and temperature on adsorption of acid red 131 dye.

II. MATERIALS AND METHODS

a. ADSORBENT

The chromium contained leather waste (CCLW) was obtained from a nearby Leather industry were cut into the small pieces, washed with distilled water and dried at 120°C for 3 hour and finally kept in muffle furnace for 4 hours at 450°C for carbonization. The carbonized material was ground and again washed with distilled water for leach out the Cr^{+6} present in it, dry the wet powder at 120°C for further 2 hour and finally stored in a desiccators until use. Hence the carbon formed by leather waste containing chromium i.e. Chrome contained leather waste activated carbon (CCLW-AC) was used as activated carbon for this adsorption study.

b. PREPARATION OF AQUEOUS SOLUTION

The tannery wastewater obtained from the waste streams containing Acid red 131 (AR 131) dye and preparing the aqueous solution by diluting it with distilled water accordingly to obtain the solution of desired concentration in the range of 25-150 mg/L of acid red 131 dye. The pH adjustment was carried out by using dil. H_2SO_4 and NaOH.

c. BATCH ADSORPTION EXPERIMENT

Batch adsorption experiments were carried out by treating 50 ml of AR 131 dye solution of different concentrations (25–150 mg/l) with 0.250 g of the CCLW-AC in conical flask and shake in water bath shaker for the pre-determined period to reach equilibrium. At the end of predefined time interval the CCLW-AC was removed from aqueous solutions by centrifugation. The progress of adsorption was determined by determining the concentration of AR 131 dyes by a UV-Visible Spectrophotometer (Shimadzu, Japan).

Adsorption isotherm study was carried out with different initial concentrations of dye ranging from 50-125 mg/l while maintaining the adsorbent dose of 0.25 g/50 ml. The effect of pH was studied by maintaining the initial dye concentration of 100 mg/l and the dose 0.50 g/50 ml of solution, the pH adjustment was done by dil.H_2SO_4 and NaOH. The influence of time on dye adsorption was studied at 30°C with initial concentration ranging from 50-125 mg/l with an adsorbent dosage of 0.250 g/50 ml. The effect of adsorbent dosage was studied by varying the CCLW-AC amount as 0.25 g, 0.50 g, 0.75 g, 1.00 g, 1.25 g and 1.50 g with dye concentration of 150 mg/l. Also, the effect of temperature on removal of 150 mg/l dye with 0.50 g of adsorbent was studied at 30°C, 35°C, 40°C, 45°C and 50°C.

The amount of adsorption at equilibrium, q_e (mg/g), was computed as follows:

$$q_e = \frac{(C_o - C_e)V}{m_s} \qquad (1)$$

Where, *C_o & C_e are the initial and equilibrium AR 131 dye solution concentrations (mg/L), respectively, V is the volume of the solution (L) and m_s the weight of CCLW-AC used (g).*

d. ADSORPTION ISOTHERM STUDIES

i. Langmuir Isotherm

The widely used Langmuir isotherm has found successfully application in many real sorption processes and also helps to estimate the maximum adsorption capacity of adsorbents can be expressed as (Ravikumar et.al, 2007 and Langmuir, 2007):

$$\theta = \frac{q_e}{Q_m} = \frac{bC_e}{1+bC_e} \qquad (2)$$

The linear form of the above expression is:

$$\frac{C_e}{q_e} = \frac{1}{bQ_m} + \left(\frac{1}{Q_m}\right)C_e \qquad (3)$$

A further analysis of the Langmuir equation can be made estimating an equilibrium parameter, R_L (Hall et.al. 1966), known as the separation factor, given by equation (4):

$$R_L = \frac{1}{1+bC_e} \qquad (4)$$

$0<R_L<1$, favorable adsorption,
$R_L = 1$, linear adsorption,
$R_L = 0$, irreversible adsorption,
$R_L > 1$, an unfavorable adsorption,
Where, *q_e (mg/g) is the amount of dye adsorbed per unit weight of CCLW-AC, Q_m (mg/g) is monolayer adsorption capacity and Ce (mg/l) is the equilibrium concentration of AR 131 dye in solution*.

ii. Freundlich Isotherm

The well known Freundlich isotherm is often used for heterogeneous surface energy systems (Shouman et.al, 2012). The Freundlich equation is given as:

$$q_e = K_F C_e^{1/n} \tag{5}$$

A linear form of this expression is:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{6}$$

Where, *K_F (l/mg)is the Freundlich constant* and *n* the *Freundlich exponent.* K_F and n can be determined from the linear plot of log q_e versus log C_e as shown in equation (6).

III. RESULTS AND DISCUSSIONS

a. EFFECT OF CONTACT TIME

During this study as shows in figure 1, the removal of AR 131 dye was faster, gradual increment pattern and then become constant after equilibrium stage. Therefore, the time profile is single, smooth and continuous curve leading to saturation indicating monolayer coverage of dye on adsorbent surface. The adsorption of AR 131 dye increases sharply with time and attains equilibrium at after 180 minutes for all concentrations studied.

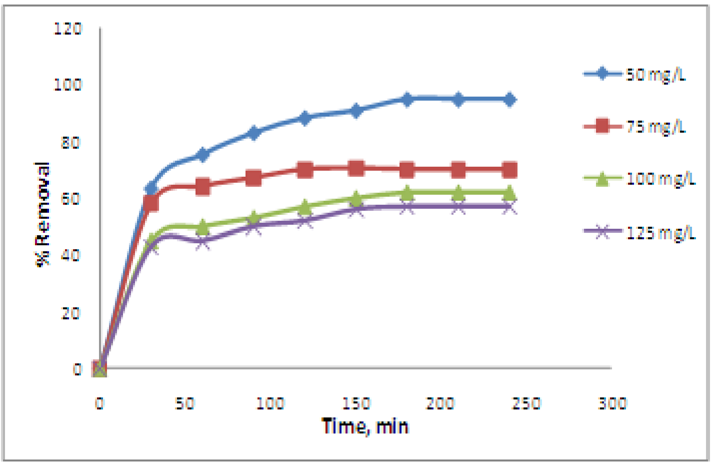

Fig. 1 Effect of contact time for the adsorption of AR 131 dye onto CCLW-AC.
***Condition:* 0.25 g/ 50 ml, pH 4.5 at 30°C.**

b. EFFECT OF INITIAL CONCENTRATION

The Initial concentrations of AR 131 dye in the solution were varied between 25 to 150 mg/l for adsorption by maintaining the quantity of CCLW-AC of 0.250 g/50 ml as shown in figure 2. The maximum removal 99.8 % was achieved at concentration 25 mg/l and then, the removal efficiency was decreased to 58 % at 150 mg/l. This trend is because as larger the concentration of dye for specific surface area of CCLW-AC less will be the adsorption.

Also, the adsorption capacity was depend on initial concentration as shown in figure 3, the maximum capacity, 14.40 mg/g was achieved at high concentration at 150 mg/l and the minimum capacity 4.99 mg/g was at 25 mg/l. This was because as higher the initial concentration more will be the equilibrium concentration and hence the capacity was increased from concentration 25 mg/l to 125 mg/l and then, become constant at high concentration.

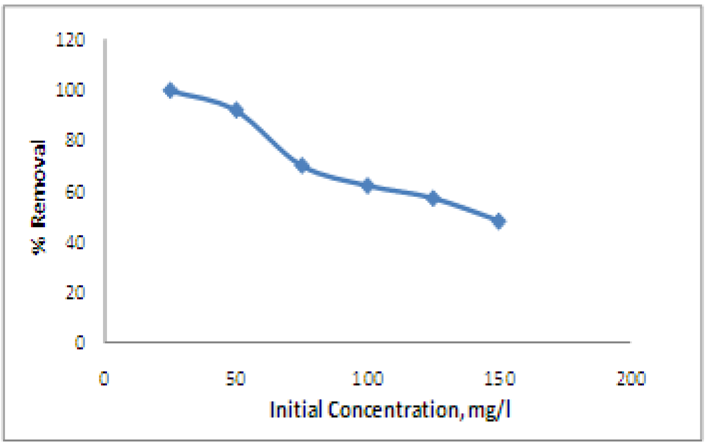

Fig. 2 Effect of initial concentration for the adsorption of AR 131 dye onto CCLW-AC.
Condition: **After 180 minutes, 0.250 g/ 50 ml, pH 4.5 at 30°C.**

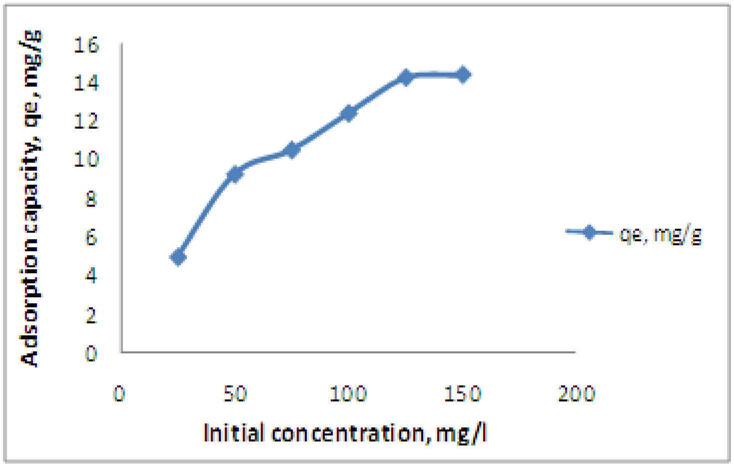

Fig. 3 Effect on adsorption capacity (mg/g) for the adsorption of AR 131 dye onto CCLW-AC.
Condition: **After 180 minutes, 0.25 g/ 50 ml and pH 4.5 at 30°C.**

c. EFFECT OF AMOUNT OF ADSORBENT

The effect of CCLW-AC amount on dye adsorption by varying the amount from 0.25 g to 1.50 g / 50 ml of 150 mg/L dye solution as shown in figure 4. The % removal was increased from 50.80 % to 90.20 % with an increase in amount of adsorbent from 0.25 g to 1.50 g respectively. The maximum removal was 90.20 % at dose 1.50 g/ 50 ml of AR 131 dye solution. This trend was due to increase in surface area and adsorption sites available for adsorption.

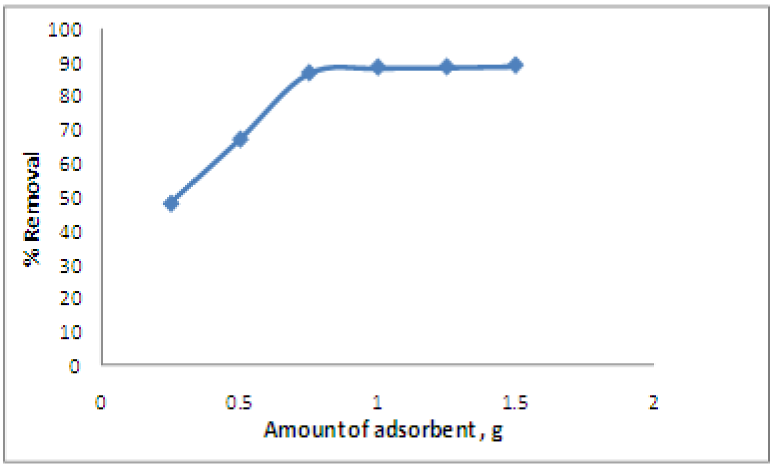

Fig. 4 Effect of CCLW-AC amount for the adsorption of AR 131 dye onto CCLW-AC.
Condition: **After 180 minutes, 150 mg/L, pH 4.5 at 30°C.**

d. EFFECT OF pH

The effect of pH was studied by maintaining the adsorbent amount 0.50 g/50 ml of 100 mg/L dye solution at various pH values in the range of 2.5 to 10.5 by maintaining with dil. H_2SO_4 & NaOH.

As shown figure 5, the adsorption was high at pH 2.5 i.e. 99 % removal. As pH value increased from 2.5 to 8.5 the adsorption was decreased from 99 % to 98.01 %. Further increased in pH from 8.5 to 12.5, the % removal of AR 131 dye decreased to 58 %. Hence, the maximum adsorption was achieved at lower range of pH. The optimum pH was 4.5 at which the adsorption was found effectively.

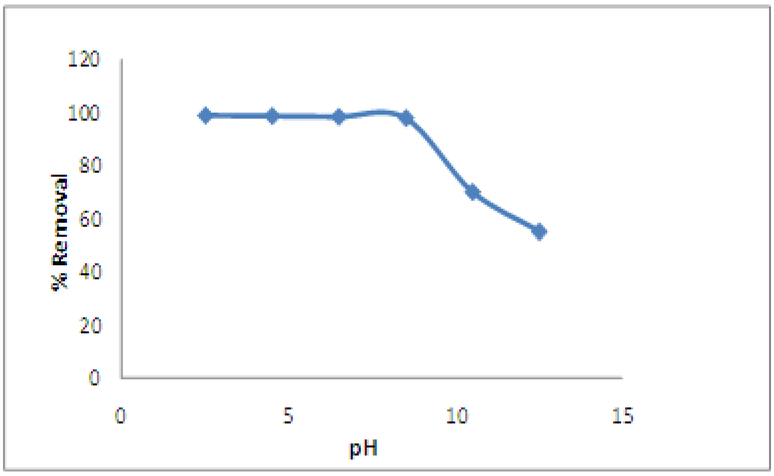

Fig. 5 Effect of pH for the adsorption of AR 131 dye onto CCLW-AC.
***Condition:* After 180 minutes, 0.50 g/50 ml, 100 mg/L at 30°C.**

e. EFFECT OF TEMPERATURE

The effect of temperatures was studied in the range 30°C to 50°C. It has been shown from the figure 6 that by maintaining the CCLW-AC amount 0.50 g/50 ml of 150 mg/L of AR 131 dye solution, the % removal of dye was increased from 67.07 % to 94.7 % from temperature 30°C to 35°C respectively. As temperature increased from 35°C to 50°C, the % removal of dye decreased from 93.50 % to 83.15 %. Therefore, the maximum removal of AR 131 dye was achieved at 35°C i.e. 93.50 %.

This trend was achieved because as temperature increase from 30°C to 35°C, slightly increase in surface area of CCLW-AC for adsorption but further increase in temperature expansion is occur & the loss of active surface area resulting from the prolonged exposures to high temperatures. Hence, the adsorption was slow at high temperatures. The optimum temperature was 35°C at which the adsorption was very effective. Hence, the present study shows the exothermic behavior in nature.

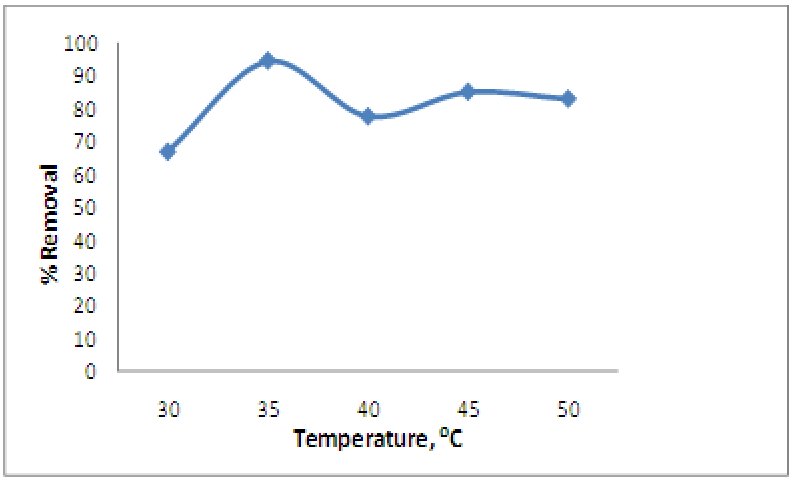

Fig. 6 Effect of Temperature for the adsorption of AR 131 dye onto CCLW-AC.
***Condition:* 0.50 g/50 ml, 150 mg/L, and pH 4.5**

f. ADSORPTION ISOTHERM STUDIES

i. LANGMUIR ISOTHERM

The isotherm data has been linearized using the Langmuir equation and was plotted between C_e/q_e versus C_e as shown in equation (3). The results obtained from the Langmuir model for the removal of dyes onto CCLW-AC are shown in Table I. The correlation coefficients reported in Table I showed strong positive evidence on the adsorption of dyes onto CCLW-AC follows the Langmuir isotherm. The applicability of the linear form of Langmuir model to CCLW-AC was proved by the high correlation coefficients $R^2 = 0.986$. also, the maximum adsorption capacity for CCLW-AC also estimated in Table 1 and the adsorption was favorable as proved by calculating the separation factor, R_L, which is a measure of adsorption favorability ($0 < R_L < 1$).

ii. Freundlich isotherm

The applicability of the Freundlich isotherm was analyzed based on adsorption on heterogeneous surface using the same equilibrium data of dye adsorption. Freundlich constants, K_F and n are obtained by plotting the graph between log q_e versus log C_e as shown in equation (6). The results obtained are shown in Table I. The regression correlation coefficient obtained for Freundlich isotherm model was 0.972, which was lower than that for Langmuir isotherm model. Hence, the suitability of Freundlich isotherm was not proved.

Table I Calculated parameters for Langmuir isotherm and Freundlich isotherm For the adsorption of AR 131 dye onto CCLW-AC.

LANGMUIR ISOTHERM	
Adsorption capacity, Qm (mg/g)	**14.40 mg/g**
Adsorption energy, b (l/mg)	**0.257 l/mg**
The separation factor, R_L	**0.0673 and 0.493 ($0 < R_L < 1$), favorable adsorption**
R^2	**0.986**
FREUNDLICH ISOTHERM	
K_F, l/mg	**0.103**
1/n	**0.141**
R^2	**0.972**

IV. CONCLUSION

In this study the utilization of the toxic chromium-containing leather waste, from the leather processing industry, as adsorbent to remove organic contaminants from waste streams. In batch adsorption studies, data showed that chromium-containing leather waste has considerable potential on removing the acidic dye from contamined water. The CCLW-AC provides the better removal efficiency i.e. maximum 99.8 % for this kind of organic contaminants from the wastewater. The uptake of dyes by leather waste is best described by the Langmuir adsorption isotherm. The maximum adsorption capacity, Qm was found as 14.4 $mg_{\text{of AR 131}}/g_{\text{of CCLW-AC}}$. In this study, it could be concluded that the CCLW-AC can be successfully used for minimize the adverse effects of dyes in wastewater streams.

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