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The Decolourization of a Chemical Industry Effluent through Adsorption over Waste Materials

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Abstract :*Adsorption of three type of industrial dyes such as direct blue DB (anionic dye) , safranin O SAF (cationic dye) ,and disperse blue DIB as (nonionic dye) on chromium contained leatherwaste CCLW as adsorbent was studied .Batch adsorption experiments were carried out for the removal of these three dyes from its aqueous solution onto CCLW . The adsorption reaches the equilibrium at 60 min. The removal percentage for these dyes decreased with increase in the initial dye concentration . The removal efficiency for anionic dye DB is higher than SAF ad DIB dye. According to Gile's classification of the adsorption isotherm L-type isotherm was observed. The Langmuir, frundlich , Dubinin –Radushkevisch (D–R) , and Temkin isotherm equations were applied to the data and values of parameters of these isotherm equations were evaluated. The R_L for the three dyes lie between 0 and 1, this suggest the applicability of CCLW for dyes removal. Based on the mean free energy calculated from D-R isotherm constant, the adsorption is chemisorption in nature.*
Keywords: *Direct blue, Safranin O, Disperse blue, Adsoprtion*

I. Introduction

Some industries have shown a significant increase in the use of synthetic complex organic dyes as coloring materials [1].Some of dyes have a potential of mutagenity, carcinogenity and toxicity [2]. The dye removal has been in considerable attention over the past decades of dye treatment in the wastewater before release to natural stream [3]. Several physical chemical methods, e.g, precipitation and coagulation, filtration,oxidation and adsorption have been used for treatment of such effluents [4]. Adsorption techniques are more economic when the cheep adsorbents such pumice stone, rice husk [5], tea water [6], a pricot waste [7], cane waste [8], wood [9],clays [10],cellulosic materials [11] were used.The tanning treatments to products the wet blue leather yield sludge containing approximately 3% (w/w) of chromium.The method commonly used for this waste disposal present high operational costs [12,13]. Re-destining this 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 [14,15]. The objective of this work was to study the removal of several organic compounds such as direct blue, safranine O, and disperse blue from aqueous solution by adsorption on chromium containing leatherwaste generated in the leather industry.In order to describe the adsorption process several isotherm models were used .

II. Material and method

Adsorbent:the chromium contained leather waste (CCLW) was obtained from AL-WAFFA company for leathers tanning ,were cut into a small pieces washed with distilled water and dried at 120 ^oC for 3 hours and finally kept in desicator.

Adsorbate: the dyes were used in this work obtain from Aldrich and used without any further purification. The characterization and structure of DB, SAF and DIB dye are given in Table (1) and Fig. (1). A stock solution of these dyes was prepared by dissolving 0.1 gm in one litter distilled water.

A

dsorption procedure: Adsorption experiments were conducted in which aliquots of dye solution,with known concentrations,(10,25,50,75 and 100 mg/l) were introduced into round bottom flasks containing accurately weighted amount 0.25 gm of the adsorbent with 25 ml solution dye. The bottles were shaken at 25^oC for one hour, the adsorbent was then removed by centrifuge at 4000rppm.The equilibrium concentrations of dyes were determined by a UV-Visible spectrometer (Shimadzu,Japan).The UV-Visible absorption spectrum For 10 mg/l of DB dye was shown in Fig.(2).The amount of adsorbed dyes were calculated with the following equation:

$q_e = (C_o – C_t) V/W$ (1)

Where C_o is the initial adsorbate concentration,C_t the equilibrium concentration is solution at time (t) ,V the solution volume(L) and (W) is the adsorbent weight (g).The percentage of dye removal from solution was calculated using the equation:

$R\% = (C_o – C_t) 100/C_o$ (2)

III. Result and Discussion

3.1 Effect of initial dye concentration: The experimental results of adsorption of three dyes at various concentrations (10, 25, 50, 75, 100 mg/l) at 298K are shown in Fig. (3). The removal percentage decreased with increase in initial dye concentration. It means that the adsorption is highly dependent on initial concentration of dye. It is because of that at lower concentration , the ratio of the initial number of dye molecules to the available surface area is low, subsequently the fraction adsorption becomes independent of initial concentration . However at high concentration the available sites of adsorption becomes fewer and hence the percentage removal of dye is dependent upon initial concentration [16]. It can be seen that the three dyes with different structures present varying removal percentage. The anionic dye DB higher than cationic dye SAF and the nonionic dye DIB has lower values that for the other dyes .This can be explained by that the adsorption at solid liquid interface is strongly influenced by the charged groups on the surface [17] .The active sites of collagen are mainly carboxyl and amino groups but most of carboxyl groups on collagen had been blocked by Cr (III) through the complex reaction after tanning. Therefore the predominant active sites of chromium containing leather waste should be amino and Cr (III) has the potential to associate with anionic groups through electrostatic interaction. So the removal efficiency for anionic dye DB is significantly high. However SAF is cationic dye and the adsorption mainly depends on it association with the limited residual carboxyl groups on collagen. Moreover, Electrostatic repulsion may exist between positively charged adsorbent and the nonionic dye disperse blue is due to affinity between the adsorbent and adsorbate.

3.2 Effect of shaking time: The time dependent behavior of dye adsorption was examined by varying the contact time between adsorbate and adsorbent in the range of 10-70 min. The concentrations of dye were kept as 0.1 mg L^{-1} while the amount of adsorbents add was 0.25 g and the temperature 298K.The amount of adsorption plotted against contact time Fig.(4).The curves show that the adsorption reaches the equilibrium at 60 min contact time.There is quickly increasing in the curves during the initial contact stages between adsorbent and solution. The fast adsorption and a short period of time to reach the equilibrium constitute the first indication that the adsorbent is suitable for removal these three dyes from wastewater.The plateau reached in all the cases shows that the adsorbent surface is saturated from this point onward and there is a limited number of active sites which become occupied with time. Furthermore the curves are distinctive, smooth and continuous indicating that the adsorbent surface is covered with a monolayer of dyes molecules [18].

3.3 Adsorption isotherm: The results concerning dye adsorption for the three dyes are presented in fig. (5-7) . It is obvious from these figers that the adsorption isotherms of these dyes on the CCLW are L-type according to the Giels Classification [19] . In this type of isotherm, the initial portion provides information about the active sites to the adsorbate and the plateau signifies the monolayer information . The initial curvature indicates that a large amount of dye is adsorbed at a lower concentration as more active sites of CCLW are available . As the concentration increases , it becomes difficult for a dye molecule to find vacant sites , and so monolayer formation occurs . The types of system which give this curve do in fact fulfil these conditions .Thus they have one of the following characteristies (i) the adsorbed molecules are most likely to be adsorbed flat or (ii) if adsorbed end-on , they suffer little solvent competition . Examples of (ii) are : (a) systems which highly polar solute and absorbent, and a non polar solvent and(b) systems with mono functional ionic substances with very strong intermolecular attraction . It is possible that in the system (b) cases the adsorbed ions may have becomes associated into very large clusters and just adsorption takes place. Where the sites are few and widely separated, the surface has large hydrophobic region [20]. The Langmuir, freundlich, Dubinin – Radushkevich and Temkins isotherm were applied in this study [21].

1- Langmuir models: The Langmuir models was originally developed to desscrible the adsorption of gas into solid surface . It suggests the formation of monolayer adsorption and also the surface is energetically homogeneous. The Langmuir isotherm can be expressed [22] as:

$q_e = q_{max} K_L C_e / 1 + K_L C_e$ (3)

Where C_e the concentration of dye remaining in solution at equilibrium (mg L^{-1}) ,q_e is the amount of dye adsorbed mg.g^{-1}, q_{max} amount of dye adsorbed per unit weight of adsorbent in forming a complete mono layer on surface mg. g^{-1} (maximum adsorption capacity) and K_L Langmuir isotherm constant (L/mg) which related to energy of adsorption. Langmuir adsorption parameters were determined by transforming the Langmuir equation (3) into linear form.

$C_e/q_e = 1/ K_L q_{max} + C_e/q_{max}$ (4)

The values of q_{max} , K_L were obtained from the slop and intercept of the plot C_e/q_eagainst C_e shown in Fig.(8) and the Langmuir isotherm parameters are given in Table(2). As it can be seen most of the adsorption isotherms fitted the Langmuir equation with correlation coefficients R>0.99 The value of monolayer coverage of CCLW by these dyes increased in the order :q_{max} for SAF>q_{max} for DB>q_{max} for DIB . The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L , which is a dimensionless constant refreed to a separation factor or equilibrium parameter .
$R_L=1/1+K_L C_o$ (5)

The value of separation factor R_L indicates the nature of the adsorption process as given below:
$R_L>1$ un favorable, $R_L= 1$ linear , $o<R_L<1$ favorable , $R_L=0$ irreversible. Table (3) shows Langmuir R_L values for the dyes. The R_L values obtained at all initial concentration for the three dyes lie between 0 and 1. This suggest the applicability of CCLW for dyes removal.

2- Freundlich Adsorption isotherm: This is commonly used to describe the adsorption characteristic for the heterogeneous surface .The freundlich equation is expressed as [23]
$q_e=K_fC_e^{1/n}$(6)

Where K_f is the measure of adsorption capacity and n is the adsorption intensity linear form of freundlich equation is:
$\text{Log } q_e = \log K_f + \frac{1}{n} \log C_e$(7)

A plot of log q_e vs log C_eFig.(9), gives a linear trace with a slope of 1/n and intercept of log K_f and the results are given in Table (4). It has been shown that n values between 1 and 10 represent beneficial adsorption. The value of n is greater than 1.0 indicating the adsorption of these dyes onto CCLW is favorable. Langmuir model is more appropriate to explain the nature of adsorption with correlation coefficient of 0.995 to 0.9969 rather freundlich shows poor fit R = 0.9782 to 0.9871.

3- Dubinin - Raduchkevich isotherm: D-R isotherm is generally applied to express the adsorption mechanism Ganssian energy distribution onto a heterogeneous surface [24].The model has often successfully fit solute activities and the intermediate range of concentrations data well.
$q_e = q_D . e^{-B}\varepsilon^2$(8)

Linear form of D- R isotherm is
$\text{Ln } q_e=\ln q_D - B\varepsilon^2$(9)

q_D is the theoretical saturation capacity (mg/g), B is a constant related to the mean free energy of adsorption per mole of the adsorbate (mol^2/J^2) and $\varepsilon$is Polanyi potential which is related to the equilibrium as follows
$\varepsilon = RT \ln (1+1/C_e)$(10)

The plots of ln qe against ε^2 are shown in Fig. (10) The parameters q_D and B obtained from the intercepts and slopes of these plots given in Table (5). The mean free energy of adsorption E, can be calculated using the relation:
$E = [\frac{1}{\sqrt{2B}}]$(11)

The determine values of E are presented in Table(4). Based on this energy of activation we can predict whether an adsorption is physisorption or chemisorption. If the energy of activation is <8 KJ / mol , the adsorption is physisorption and if the energy of adsorption is chemisorption in nature [25] . Based on the mean free energy calculated, we can predict that the adsorption of these dyes onto CCLW is chemisorption in nature.

4- The Temkin isotherm : This isotherm contains a factor that explicitly taking into the account of adsorbate interaction by ignoring the extremely and large value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the larger would decrease linearly rather than logarithmic with coverage [26] . As implied in the equation , its derivation is characterized by a uniform distribution of binding energies (up to some maximum binding energy) was carried out by plotting the quantity sorbed q_e, ln C_e and the constants were determined from the slope and intercept .

The model is given by the following equation:

$q_e = RT/b_T \ln (A_T C_e)$(12)

$q_e = RT/b_T \ln A_T + (RT/b_T) \ln Ce$(13)

Where :

$B= RT/b_T$ in (J/mol)(14)

The isotherm is represented by the following linear form:

$q_e = B \ln A_T + B \ln C_e$ (15)

b_T is the Temkin isotherm constant while A_T is the equilibrium binding constant. A plot of q_e against ln C_e in Fig. (11) and the constants are present in Table (6)

IV. Table and Figure

Table (1) Physical properties and molecular structure of the dyes

Dye name Classification Chemical formula IUPAC name Molecular weight λmax solubility	Direct blue Nonionic dye $C_{34} H_{24} N_5 Na_{40}$ 16 S4 (6E)-4- amino -6-[4[4-[N-(8-amino-1-oxo-5,7-disulfonato-2 naphthylidene) hydrazion]-3-methoxy -phenyl] -2- methoxy -phenyl] hydrozono]-5-oxo naphthalene -1,3 disulfonate 992-80404 g 589 nm Water
Dye name classification chemical formula IUPAC name Molecular weight λmax solubility	Safranin O (SAF) Cationic dye $C_{2o} H_{19} N_4^+ C1^-$ 3,7 – diamino – 2,8 – dimethyl -5- phenyl-phenazininm chloride 350-84 g. 520 nm Water
Dye name classification chemical formula IUPAC name Molecular weight λmax solubility	Disperse blue Nonionic dye 1,8 – Dihydroxy – 4-nitro -5-(N-(phenethyl alchohol) Amino) anthraqunione . 420 g 575 nm water

Table (2) Langmuir isotherms constants for the adsorption of dyes

Dye	q_{max} mg.g-1	K_L (L.mg -1)	R
DB	7.9808	0.47606	0.9969
SAF	8.0321	0.1960	0.995
DIB	0.1368	0.999	0.9952

Table (3) Langmuir R_L values for three dyes

Co/ppm	dye	10	25	50	75	100
R_L	DB	0.1736	0.0775	0.0403	0.02724	0.0205
	SAF	0.3378	0.1695	0.0926	0.064	0.0485
	DIB	0.0909	0.03896	0.0196	0.01315	0.009

Table (4) Freundlich isotherm constants for the adsorption of the dyes

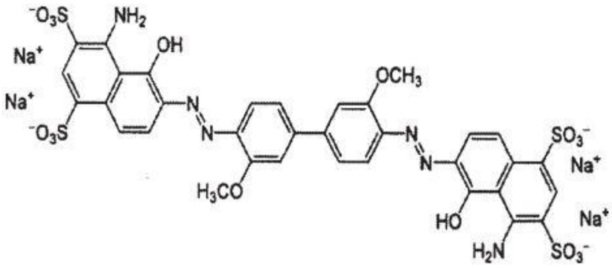
dye	1/n	n	K_f mg/g	R
DB	0.407	2.457	2.504	0.9782
SAF	2.1222	0.4712	0.39117	0.9799
DIB	3.3818	0.2957	24.589	0.9871

Table (5) D-R isotherm parameters and mean energy of adsorption of dyes

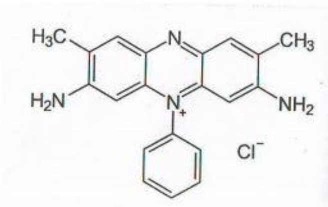
Dye	q_D (mg . g-1)	B (mol^2/ K J^2)	E (K J mol^{-1})	R
DB	5.3720	0.0031	12.7	0.8229
SAF	4.8788	0.002	15.8114	0.858
DIB	1.1959	0.007	8.4515	0.6521

Table (6) Temkin isotherm constants for the adsorption of the dyes

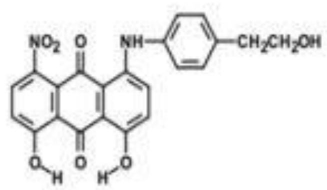
Dye	A_T(L/g)	b_T (J/mg)	B(J/mol)	R
DB	12.0480	1851	1.3383	0.983
SAF	3.1990	1687.8	1.4679	0.9622
DIB	1.5750	10588	0.2939	0.9822



(A)



(B)



(C)

Fig (1) chemical structure of the dyes (A) DB (B)SAF (C)DIB

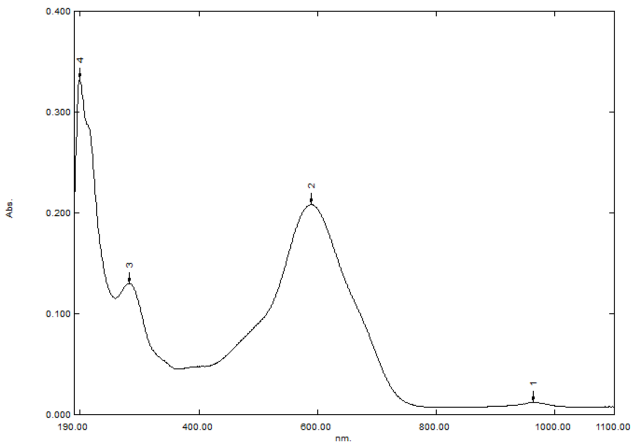


Fig (2) UV-visible absorption spectrum for 10 mg/L DB dye

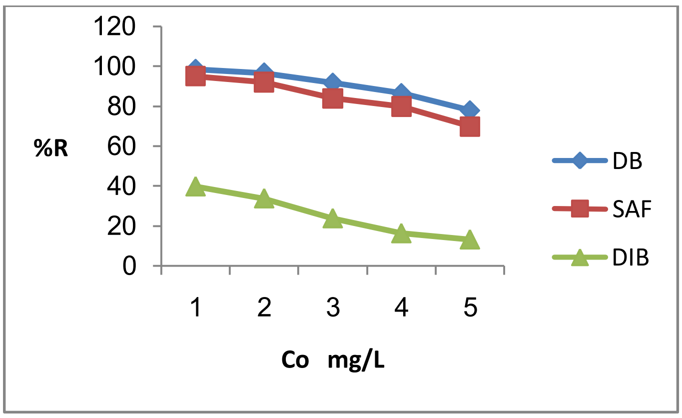


Fig (3) The effect of initial dye concentration on the desorption of the studied dyes at 298 K.

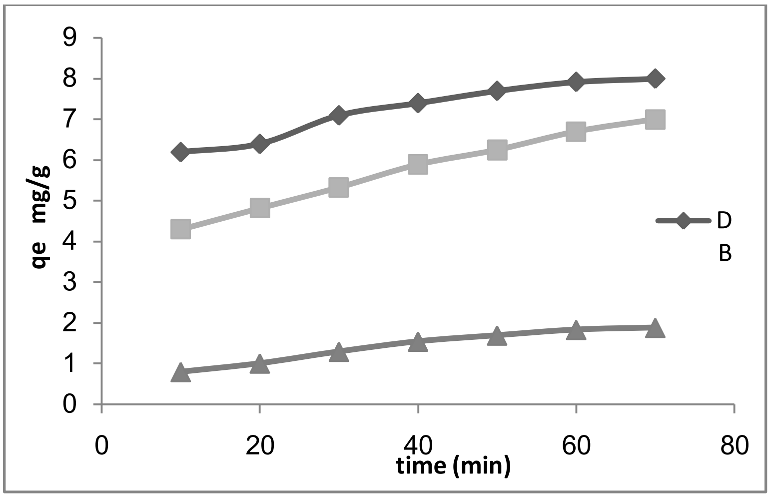


Fig (4) The effect of contact time on the adsorption of the studies dyes at 298 K and co = 100 mg $^{L-1}$.

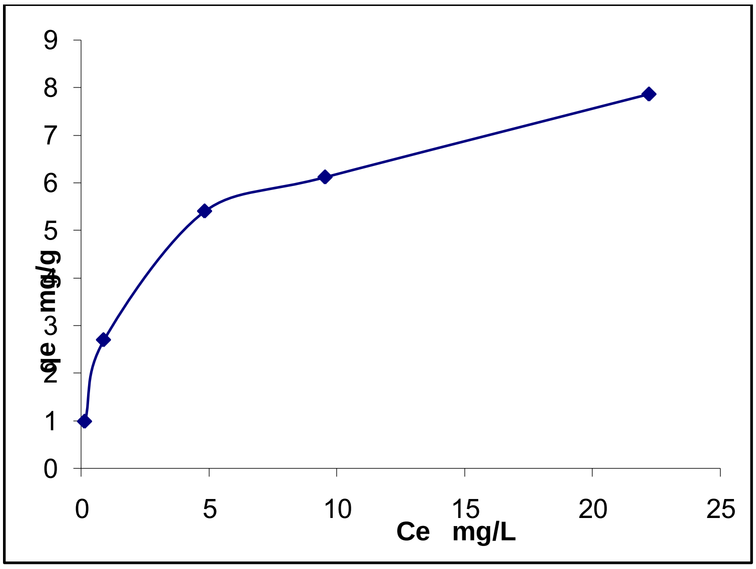


Fig (5) Adsorption isotherm for DB dyes on to CCLW at K .

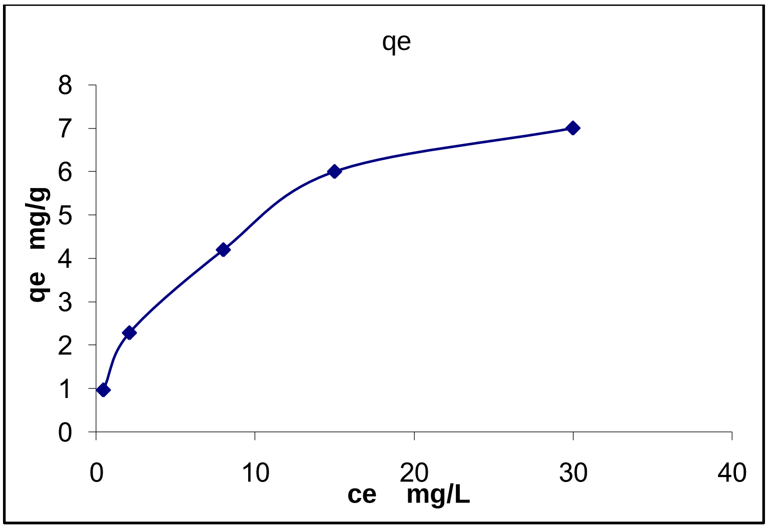


Fig (6) Adsorption isotherm for SAF dye on to CCLW at .

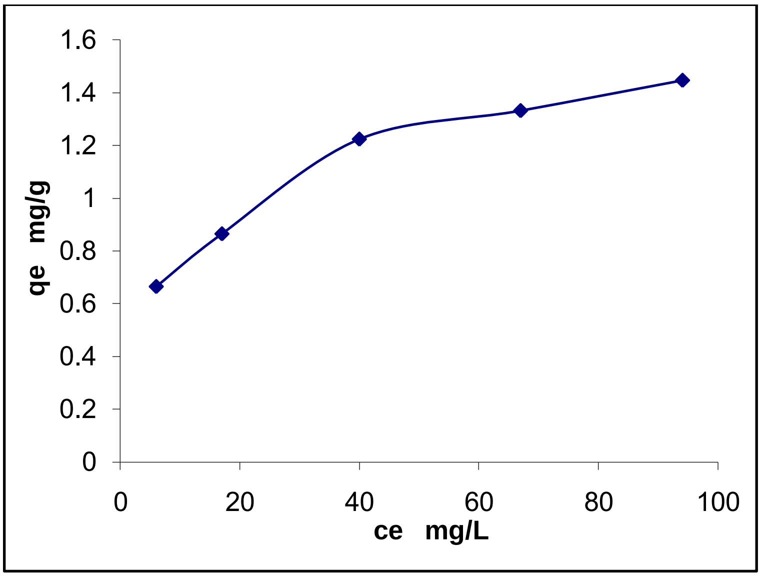
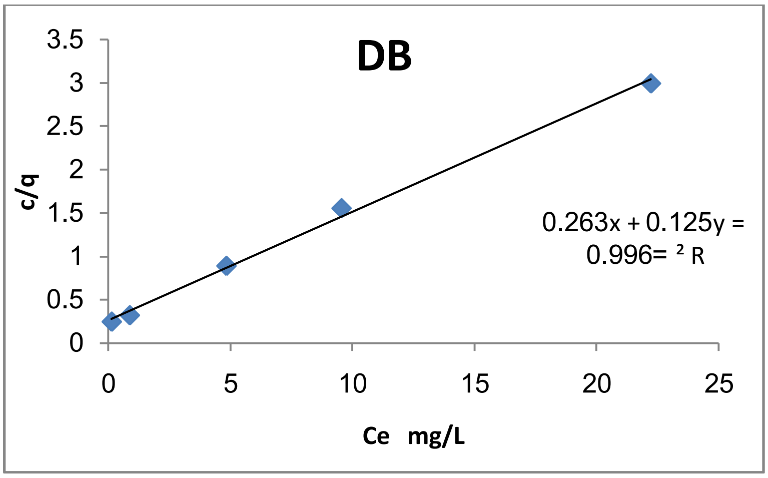
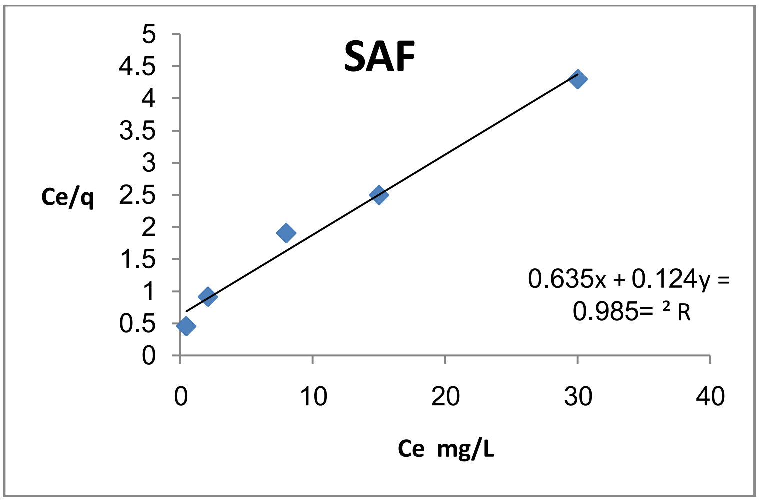


Fig (7) Adsorption isotherm for DIB dye on to CCLW at 298K .





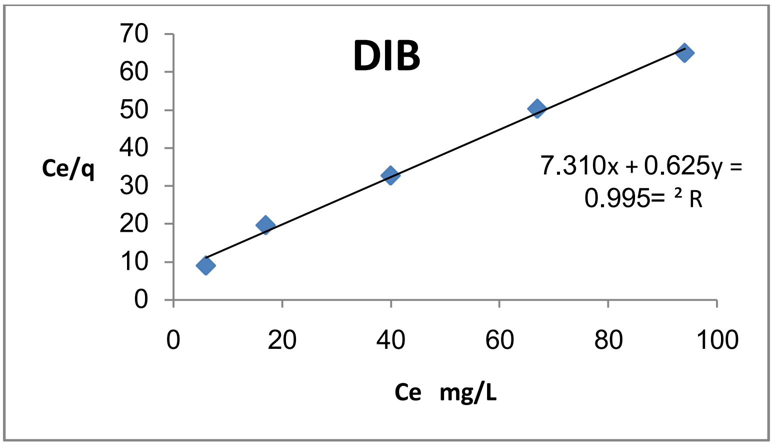


Fig (8) Langmuir plots corresponding to the adsorption of the studied dyes onto the CCLW .

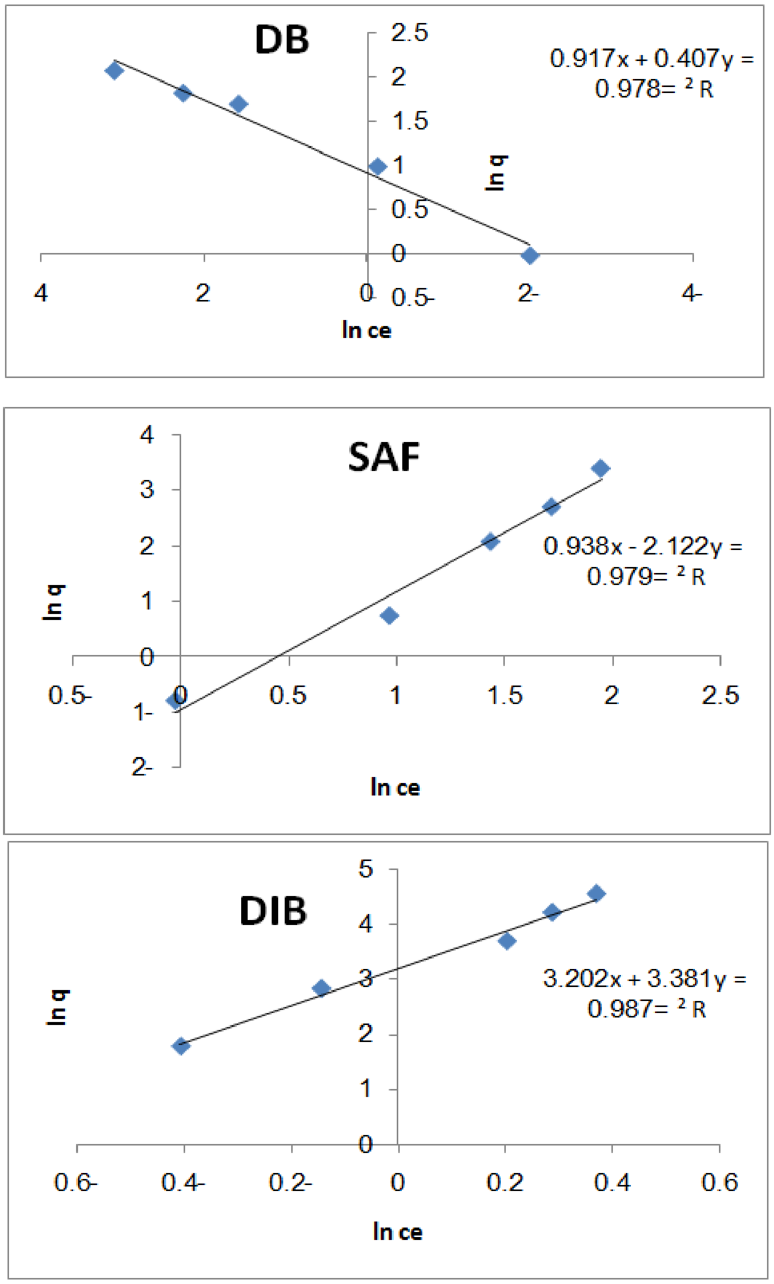


Fig (9) Freundlich plots corresponding to the adsorption of the studied dyes onto the CCLW.

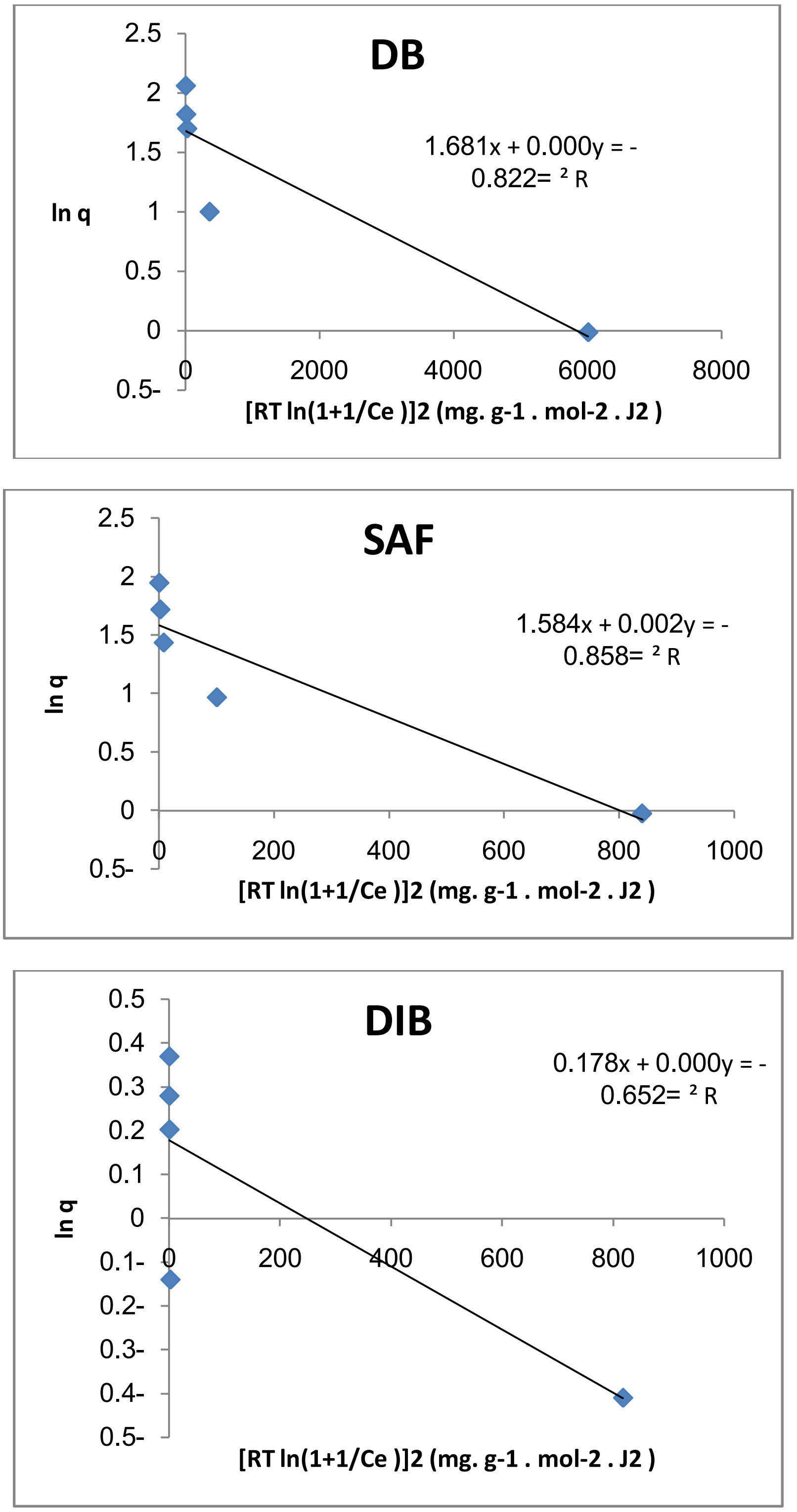


Fig (10) D-R isotherm plots corresponding to the adsorption of the studied dyes onto the CCLW .

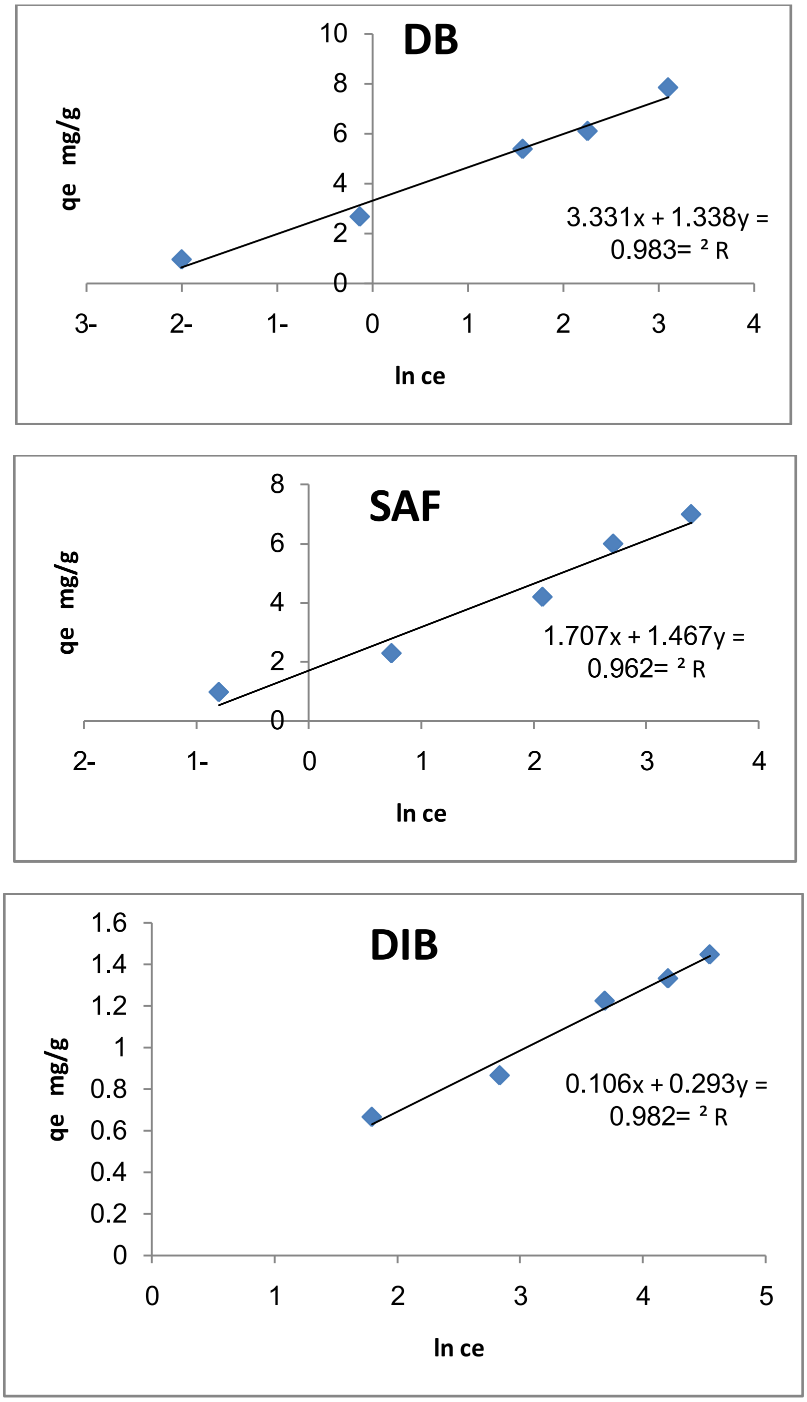


Fig (11) Temkin isotherm plots corresponding to the adsorption of the studied dyes onto the CCLW

V. Conclusion

Based upon the results of this research, the following conditions can be draw:

- The experimental results indicate that the adsorption on chromium-containing leather waste is an effective way of removing.
- The effect of initial concentration of the adsorbate and contact time on the adsorption process was found to be considerable significance.
- The adsorption isotherm of these dyes onto CCLW are L- type according to the Gile's classification.
- Amongthe four models of the adsoption isotherm used, the equilibrium sorption data are fitted with the Langmuir adsorption isotherm.
- The value of the mean free energy of adsorption calculate from the D- R isotherm constants predict that the adsorption of these dyes onto CCLW is chemisorption in nature.

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