

Characteristics of azo-dye onto surfactant modified chromium contained leather waste

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Abstract : A modified low-cost material, chromium contained leather waste (MO CCLW) has been used for study the adsorption behavior of anionic dye orange II dye. The modification carried out by treated the CCLW with cetyl trimethyl ammonium bromide (CTAB) as cationic surfactant. Equilibrium isotherm models applied showed Freundlich isotherm model with the best regression coefficient R^2 , followed by Temkin, Dubinin – Radushkevich D-R isotherm and the least value was obtained with the Langmuir isotherm. The Langmuir isotherm constant (K_L) and the Freundlich constant (n) indicated a high affinity of MO CCLW for orange II dye. The separation factors R_L values lies between 0 and 1 indicated a favorable adsorption process. Physisorption was indicated by the values of the apparent energy of adsorption obtained from the Dubinin – Radushkevich isotherm. The Kinetic models pseudo-first order, Pseudo-second order, Elovich and intraparticle diffusion model were used. The data were in good agreement with Pseudo-second order rate model with intra particle diffusion being the rate controlling step. The thermodynamic measurements suggest that all process are endothermic accompanied with negative ΔG^0 and positive ΔS^0 , ΔH^0 .

Keywords: Adsorption isotherm, orange II, MO CCLW, Elovich kinetic.

I. Introduction

Environmental pollution control has been a concerned issue in many countries. One of major environmental pollution is wastewater. The polluted water comes from the domestic and from the industries. These contaminants such as heavy metal, cyanide, phenols, turbidity and color from the industries are become a great concern to the environment and public health. Decolorization of wastewater has become one of the major issues in wastewater. This is because many industries used dyes to color their products, such as textiles, rubber, paper, plastics, leather, cosmetics, food, and mineral processing industries [1]. These dyes are invariably left in the industrial wastes. Since they have a synthetic origin and complex aromatic molecular structures, which make them inert and difficult to biodegrade when discharged into waste streams, people overlook their undesirable nature. Dye molecules have two major components, the chromophore groups, responsible for making the color such as $-C=C-$ and $-N=N-$, and the auxochrome groups, as for example $-NH_2$, $-OH$, $-COOH$ and $-SO_3H$, which render the solubility of the molecules and give affinity for the fibers [2]. Azo dyes are the most common and constitute, 20 to 40% of all dyes used for coloring. These dyes have hetero-cyclical structure and one or more azo rings ($-N=N-$) [3]. Due to their toxicity to humans and aquatic life as well as poor degradability, the fate of the dye compounds is a subject of the considerable interest and the destruction of these pollutants has become an important issue in recent year. It is difficult to remove the dyes from effluent, because dyes are not easily degradable and are generally not removed from wastewater by conventional wastewater systems [4]. Many physical and chemical processes for color removal have been applied including coagulation, flocculation, biosorption, photo-decomposition and ultrafiltration, oxidizing agents and electrochemical. Adsorption process has been found to be an efficient and economic process to remove dyes, pigments and other colorants [5]. It is also has been found to be superior to other technique for wastewater treatment in terms of initial costs, simplicity of design, ease of operation and insensitivity to toxic substances, many kinds of adsorbents have been developed for various applications such as zeolite [6], sepiolite [7], Kaolin [8], activated carbon [9], clinoptilolite [10] and raw red mud [11].

The leather 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. Orange II azo dye has been chosen as it is inexpensive and widely used for variety of materials of nylon, silk, wool, leather. Table (1) regroups the results obtained in some recent works where the adsorption of orange II on to various adsorbent has been studied [12-18]. In recent years extensive research has been going on in the field of surfactant based separation process such as a micellar chromatograph, micellar enhanced ultrafiltration [19] and surfactant modification adsorbents. Modification of adsorbents such as clays has done by using tetrabutyl ammonium chloride [20], this organo clay have been effective used for treatment of phenols [21]. A second type of modification of adsorbent has been done by treated the adsorbent with known concentration of surfactant in order to improved the adsorption ability for adsorbent. This work concentrates on the study of azo dye (orange II) sorption on to modified CCLW. The modification occurred by treated the

CCLW with cationic surfactant cetyl trimethyl ammonium bromide .Different isotherms model were used to fit the equilibrium isotherm .The adsorption rates were determined quantitatively and compared by the first order, second order, Elovich and intra-particle diffusion model . Thermodynamic parameters of orange II adsorption on to modified CCLW were reported.

II. Experimental

2.1 Materials

2.1.1 Adsorbate : Orange II was procured from Fluka analytical without any purification . Orange II is an anionic azo dye . The structure of dye is given in Fig.(1) . Its IUPAC name is 4-[(2-hydroxy -1-naphthyl)azo] benzene sulfonic acid , sodium salt . Its molecular mass 350.32 , with molecular formula $C_{16}H_{11}N_2 NaO_4S$.It is orange-colored power soluble in water .Its C.I. number is 15510 . This dye shows λ_{max} at 483 nm .A stock solution of orange II dye (1000 mg L^{-1}) was prepared in distilled water .

2.1.2 Adsorbent : The chromium contained leather waste (CCLW) was obtained from AI-waffe company for leathers tanning , were cut into a small pieces , washed with distilled water and dried at 120 °C for 3 hour and finally kept in desiccator .The cetyl trimethyl ammonium bromide (CTAB) , cationic surfactant with molecular mass 364.46 using as modified agent was provided by Fluka .A stock solution of CTAB (1000 mg L^{-1}) was prepared in distilled water. Modified CCLW (MO CCLW) was prepared by mixing 100 ml of 2 mM surfactant solution with 10 gm of CCLW . The mixture is stirring for 3 hour at room temperature , the solution was filtered . Modified CCLW dried at 120 °C for 3 hour then kept in desiccator.

2.2 Method

Adsorption experiments were conducted in which aliquots of dyes solution of known initial concentration (25-125 mg L^{-1}) introduced into around bottom flask containing accurately weighted amount (0.25 gm) of the adsorbent . The flasks were shaken for a prescribed length of time and at temperature range (283-323 k) to obtain equilibrium. The adsorbent was then removed by filtration. The equilibrium of dyes concentrations were determined using the uv-visible spectrometer (Shimadzu Japan) at the maximum absorption ($\lambda_{max} = 483$ nm) . The amount of dye absorbed onto the modified CCLW q_e (mg/g), was calculated by amass balance relationship.

$$q_e = (C_o - C_e) V/W \quad (1)$$

Where C_o and C_e are the initial and equilibrium liquid-phase concentrations of dyes respectively (mg L^{-1}) , V the volume of the solution (L) and W the weight of adsorbent used (g) .The procedures of kinetic experiments were basically identical to those of equilibrium tests .The aqueous samples were taken at present time intervals , and the concentration of dyes were similarly measured .The structural characterization of the MO-CCLW was carried out using a Shimadzu FTIR-8400 Fourier Transform Infrared Spectrometer .The experiment was done in the range between 4000 and 400 cm^{-1} using transmission KBr pellet technique 1.00 gm of MO-CCLW is mixed with 11.00 gm of anhydrous KBr to make apellet .

III. Results and Discussion

3.1 FTIR characterization

The FTIR spectra of MO CCLW Fig.(2) suggest that the protein structure of the leather is maintained after the chromium based extraction. The protein structure is evidenced by the signal at 1627.81 cm^{-1} due to carbonyl group C=O and at 1542.95 cm^{-1} due to N-H [22] .

3.2 Adsorption isotherms

The adsorption isotherm experimental data collected at different dye concentrations and various temperatures. Four adsorption models Langmuir, Freundlich , Temken and Dubinin – Radushkevish (D-R) isotherms were used to describe the equilibrium between adsorbed dye on the mixture and dye in solution C_e at a constant temperature .

3.2.1 Langmuir isotherm

The Langmuir isotherm assumes that the surface of any adsorbent material contains a number of active sites where the adsorbate attaches itself. This attachment can either be physical or chemical. When the attachment is via van der waals interactions. It is known as physisorption where as when it is via covalent bond , it is known as chemisorption .There is also not much interaction between the adsorbed molecules and once a saturation value has been reached , no further adsorption would take place (23) .The linear form of Langmuir equation can be write in the following form :

$$C_e / q_e = 1 / K_L + (a / K_L) C_e \quad (2)$$

Where q_e is the amount of orange II adsorbed (mg.g $^{-1}$) , C_e is the equilibrium concentration of the adsorbate (mg / L) , a is the maximum adsorption capacity for monolayer coverage , K_L is Langmuir constant related to

the affinity of binding sites (L/g). Fig.(3) shows a linear plot of C_e / q_e versus C_e at 293 k obtained from Langmuir isotherm data for the adsorption of orange II by modified CCLW. The values of Langmuir constants and R^2 presented in Table (2). The important characteristic of the Langmuir isotherm can be expressed by means of dimensionless constant separation factor, which is calculated using the following equation

$$R_L = 1 / (1 + K_L C_0) \quad (3)$$

Where C_0 is the initial dye concentration ($\text{g} \cdot \text{L}^{-1}$) and K_L is the Langmuir constant. R_L values indicate the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$) [24]. Our results show that the adsorption of orange II dye on the modified CCLW is favorable and has an R_L value between 0 and 1 Table (3).

3.2.2 Freundlich isotherm

The well known Freundlich isotherm is based on the assumption that adsorption occurs on a heterogeneous adsorption surface having unequally available sites with different energies of adsorption [25]. The Freundlich equation is given as:

$$\ln q_e = \ln K_f + 1/n \ln C_e \quad (4)$$

Where K_f (L / mg) and n are constants incorporating factors affecting the adsorption capacity and intensity of adsorption or the relationship between adsorbent and adsorbate. Fig.(4) illustrates the plot obtained for the Freundlich isotherm at 293 K. The values of Freundlich constant and R^2 are presented in Table (2). The Freundlich isotherm describes reversible adsorption and is not restricted to the formation of monolayer. It has been found that the adsorption of orange II onto modified CCLW is favorable and has an n value between 1 and 10, which represents a beneficial adsorption process and high affinity for the modified CCLW to the dye molecular [26].

3.2.3 Temkin isotherm

The Temkin isotherm model was also applied to the experimental data, unlike the Langmuir and Freundlich isotherm models, this isotherm takes into account the interactions between adsorbents and the dye molecular. The isotherm can be represented by the following linear form [27]:

$$q_e = RT / b_t [\ln (a_t C_e)] \quad (5)$$

where b_t is Temkin constant related to the heat of sorption (J mol^{-1}) and a_t is Temkin isotherm constant. The values of a_t , b_t were estimated from the slope and intercept of the plot of q_e against $\ln C_e$ Fig.(5). The values of a_t , b_t and R are presented in Table (2). The value of a_t lies close to 1.00 at all temperatures and b_t decreases with increase of temperature suggesting endothermic nature of the adsorption.

3.2.4 Dubinin-Radushkevich isotherm (D-R)

The Dubinin – Radushkevich isotherm (D-R) model is more general than the Langmuir isotherm since it does not assume a homogeneous surface or constant sorption potential. The D-R equation is:

$$\ln Q_e = \ln K_{D-R} - B_D \epsilon^2 \quad (6)$$

$$\text{Where } \epsilon = RT \ln (1 + 1 / C_e) \quad (7)$$

Q_e is the amount of dye adsorbed per unit weight of MO-CCLW ($\text{mg} \cdot \text{g}^{-1}$), C_e is the equilibrium concentration ($\text{mg} \cdot \text{L}^{-1}$). The constant K_{D-R} is the D-R constant representing the theoretical saturation capacity ($\text{mg} \cdot \text{g}^{-1}$) and B_D ($\text{mol}^2 / \text{J}^2$) is a constant related to the mean free energy of adsorption per mol of the adsorbate. The value of the sorption energy (apparent energy of adsorption) E can be correlated with B_D :

$$E = 1 / (-2 B_D)^{0.5} \quad (8)$$

The value of $\ln Q_e$ against ϵ^2 at 298 K is shown in Fig. (6), the constant K_{D-R} and B_D were calculated from the intercept and slope respectively. The D-R isotherm parameters and regression parameter R^2 are given in Table (2). If the value of E lies between 8 & 16 KJ mol^{-1} the sorption process is a chemisorption one, while values of below 8 KJ mol^{-1} indicates a physical adsorption [28]. Values of the apparent energy of adsorption obtained, indicated physical adsorption between MO-CCLW and the dye molecular. Comparing the quality of fitting the four models of isotherms in terms of correlation coefficient, R^2 , it can be seen that the Freundlich isotherm fits the data better than the D-R isotherm that followed by the Temkin isotherm and then the least fit was obtained with the Langmuir isotherm.

3.3 Dynamic modeling

The kinetics of adsorption is important from the point of view that it controls the process efficiency. To examine the rate limiting step of the adsorption process various kinetics models have been used such as pseudo-first order and pseudo-second order kinetic models, Elovich and the intraparticle diffusion one.

3.3.1 The pseudo-first order and pseudo-second kinetics

The Lagergrens rate equation is the most widely one used for the adsorption of a solute from a liquid solution. Thus this first order equation. [29]

$$\text{Log} (q_1 - q_t) = \text{Log} q_1 - K_1 / 2.303 t \quad (9)$$

Where q_1 and q_t are the amounts (mg. g⁻¹) of solute bound at the interface at the equilibrium and after time t (min) respectively, K_1 is the rate constant of pseudo first order adsorption (min⁻¹). The pseudo – second order kinetic model is:

$$t/q_t = 1/K_2 q_2^2 + t/q_e \quad (10)$$

Where K_2 is the pseudo second order rate constant (mg⁻¹. g .min⁻¹). The plot validating the pseudo first order model [Log ($q_1 - q_t$) versus t] and the pseudo second order model (t / q_t versus t) for 100 mg.L⁻¹ initial concentration of the orange II at 293 K are given in Figs.(7) and (8) respectively. The parameters of pseudo first order and pseudo second order model are listed in Table (4). The pseudo second order kinetic model fitted better than Lagergreen model. The correlation constant was higher than first order model.

3.3.2 Elovich kinetic model [30]

The Elovich model equation is generally expressed as

$$q_t = 1/B (\alpha B) + 1/B \ln t \quad (11)$$

Where α is the initial adsorption rate (mg. g⁻¹. min⁻¹), B is the adsorption constant (g .mg⁻¹) during any one experiment. The plot of q_t versus $\ln t$ should yield a linear relationship for the applicability of the simple Elovich Kinetic Fig. (9). The kinetics constants obtained from the Elovich equation are listed in Table (4). The regression coefficient was found to be 0.9458.

3.3 Intra particle diffusion

The dye adsorption process from aqueous solution onto porous solids involves several steps (i) transport in the solution (ii) diffusion through the liquid film surrounding the solid particle, known by external diffusion or boundary layer diffusion (iii) diffusion within the liquid included in the pore, known by internal diffusion or intra particle diffusion, (iv) adsorption or desorption on the face of the interior [31]. The first step has no rate limitation effect as the experiments were performed at rapid shaking conditions. In addition Previous studies showed that the last step is a very fast process for the adsorption of organic molecules onto porous adsorbent [32]. The most commonly used technique for identifying the mechanism involved in the sorption process is by fitting the experimental data in an intra particle diffusion plot. The plot of q_t versus $t^{0.5}$ represent multi linearity, which characterizes the two or more steps. The rate parameter for the intra particles diffusion model is determined using the following equation [33].

$$q_t = k_{id} t^{0.5} + C \quad (12)$$

Thus the intra particle diffusion constant k_{id} (mg/g.min^{0.5}), and C values obtained from the slope and intercept of the plot of q_t (mg/g) versus time^{0.5} (min), Fig.(10), for initial dye concentration 100 mg.l⁻¹ at 293 k. The k_{id} , C and R^2 values are listed in Table (4). Fig.(10) showed that the plot are not liner over the whole time range, however, they exhibit a tri - linearity revealing the extence of three successive adsorption steps. The first stage being faster than the second is attributed to the external surface adsorption correlated to the boundary larger diffusion. Consequently, the second linear part attributed to the intra particle diffusion states that this latter is highly involved in the rate control of this mechanism. The third linearity attributed to the equilibrium stage. It is worth to note the fact that the second linear plots did not pass by the origin which indicates that the intra – particle diffusion is involved in the adsorption process but it is not the only rate controlling step.

3.4 Thermodynamic Parameters

The thermodynamic parameters of the adsorption process such as change in free energy (ΔG^0) (J.mol⁻¹), enthalpy (ΔH^0) (K Jmol⁻¹) and entropy (ΔS^0) (J mol⁻¹) were determined using the following equations [34].

$$K_d = C_{solid} / C_{liquid} \quad (13)$$

$$\Delta G^0 = -RT \cdot \ln K_d \quad (14)$$

$$\Delta G^0 = \Delta H - T \Delta S^0 \quad (15)$$

$$\ln K_d = \Delta S^0 / R - \Delta H^0 / R \cdot 1/T \quad (16)$$

Where K_d is the equilibrium constant, C_{solid} is solid phase concentration at equilibrium (mg L⁻¹), T (K) is the temperature, R (8.314 J mol⁻¹ K⁻¹) is the gas constant. The values of ΔS^0 , ΔH^0 were determined from the slopes and intercepts of the vant Hoff plots $\ln K_d$ Vs. $1/T$ Fig. (11). The calculated thermodynamic parameters based on the above function were listed in Table (5). The values ΔH^0 are positive in the range from 22.92 to 45.89 K J mol⁻¹ indicates the physisorption. As the adsorption process is pore diffusion controlled, an increase in molecular diffusion occurs at higher temperatures leading to endothermic enthalpy of

adsorption .The low ΔH^0 value depicts dye is physisorbed onto the modified CCLW . Furthermore , negative values of Gibbs free energy ΔG^0 shows the adsorption process is highly favorable and spontaneous at all the temperatures. However , the negative value of ΔG^0 decreased with an increase in temperature ,indicating that the spontaneous nature of adsorption is inversely proportional to the temperature . The positive values of ΔS^0 show the increased disorder and randomness at the solid /solution interface during the adsorption of orange II into the adsorbent ,while the adsorption there are some structural changes in the dye and the adsorbent occur . The adsorbed water molecules , which are displaced by the adsorbate species , gain more translational energy than is lost by the adsorbate ions , thus allowing the prevalence of randomness in the system . The enhancement of adsorption at higher temperature may be attributed to the enlargement of pore size and /or activation of the adsorbent surface [35].

IV. Tables and Figures

Table (1) Comparison of the maximum monolayer adsorption capacities of orange II onto various adsorbents.

Adsorbent	Max .monolayer adsorption capacities mg.g ⁻¹	references
Commercial activated carbon fibers –generated from pitch ACFC	209-438 (10-60) C ⁰	12
Commercial activated carbon fibers-made with polyacrylonitrile ACFT	25-185 (10-60) C ⁰	12
Sludge adsorbent	83-270 (10-60) C ⁰	12
Bottom ash	12.50 (30) C ⁰	13
Phosphoric acid modified clam shell powder	1017.13 (25) C ⁰	14
Surfactant – modified zeolite	3.62 (35) C ⁰	15
Modified bentonite (organophilic fluidgel)	11.15 (25) C ⁰	16
Titania aerogel	402.32 (30) C ⁰	17
HDTMA bentonite	52.36 (25) C ⁰	18

Table (2) Equilibrium isotherm parameters

Temp. K	Langmuir isotherm model			Freundlich isotherm model		
	K _L	a	R ²	K _f	n	R ²
283	0.21607	0.0361	0.8273	0.8623	2.843	0.9473
293	0.6067	0.1013	0.8016	1.2187	1.4166	0.981
303	0.9111	0.0718	0.9449	1.3272	1.7736	0.9892
313	1.4605	0.10459	0.8576	1.8952	1.82983	0.9762
Temp. K	Temkin isotherm					
	B (J/mol)	A _t (L/g)	b _t (L/g)	R ²		
283	1.3	0.6807	1809.9	0.92		
293	1.69	0.306	1414.4	0.9554		
303	2.6936	0.8927	1020.72	0.9503		
313	2.743	0.7811	713.54	0.907		
Temp. K	D –R Isotherm					
	B _d mol ² / J ²	K _{D-R} mol/g	R ²	E KJ/mol		
283	0.8369	4.349	0.936	0.7738		
293	0.0128	9.0259	0.9472	6.250		
303	0.007	8.7146	0.925	8.045		
313	0.005	7.1029	0.8776	10		

Table (3) Langmuir R_L Values for adsorption of orange II onto modified CCLW at different temperatures.

C ₀ mg . L ⁻¹	R _L Value			
	283 K	293 K	303 K	313 K
10	0.3487	0.1427	0.1127	0.079
25	0.1689	0.058	0.047	0.0285
50	0.0907	0.031	0.0236	0.0148
75	0.0602	0.01952	0.0152	0.0094

100	0.0451	0.0147	0.0112	0.0069
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Table (4) Comparison of kinetic constants for the adsorption of orange II on modified CCLW at 293 K for 100 mg. L⁻¹ dye concentration

First - order kinetic model			Second - order kinetic model		
q _i (mg/g)	K ₁ (min) ⁻¹	R ² ₁	q ₂ (mg/g)	K ₂ .10 ⁻² (g/mg .min)	R ² ₂
7.94	0.021	0.9501	11.2108	0.254	0.9802
Elovich model			Intraparticle Diffusion		
B (g.mg ⁻¹)	α (mg.g ⁻¹ .min ⁻¹)	R ²	K _{ipd} (mg.g ⁻¹ .min) ^{-0.5}	C (mg.g ⁻¹)	R ² ₂
0.4159	0.5153	0.9115	0.6567	1.4342	0.8931

Table (5) Values of thermodynamic parameters for the adsorption of orange II at various temperature

C ₀ mg.L ⁻¹	-Δ G (J .mol ⁻¹)				ΔH ⁰ KJ.mol ⁻¹	ΔS ⁰ J.mol ⁻¹
	283 K	393 K	303 K	313 K		
25	3490.5	5221.6	6992.6	8738.02	45.89	174.45
50	2487.9	3515.88	4543.18	5570.78	26.59	102.76
75	3116.2	3577.7	4338.03	5404.48	18.59	76.66
100	990.7	2080.37	3170.1	4259.8	29.85	108.97
125	1807.78	2680	3567.1	442.7	22.92	87.36

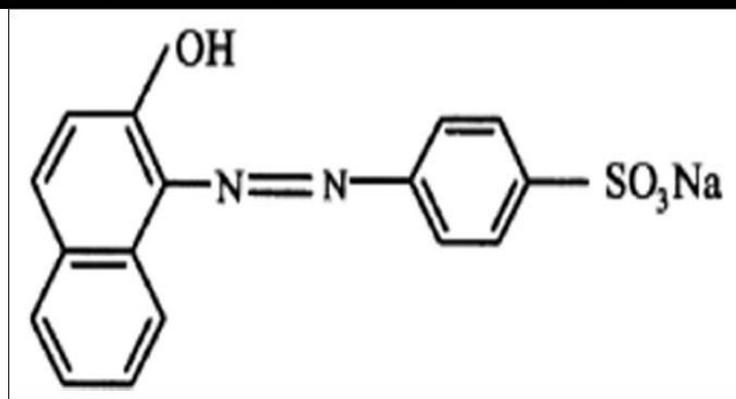


Fig (1) Chemical structure of orange II.

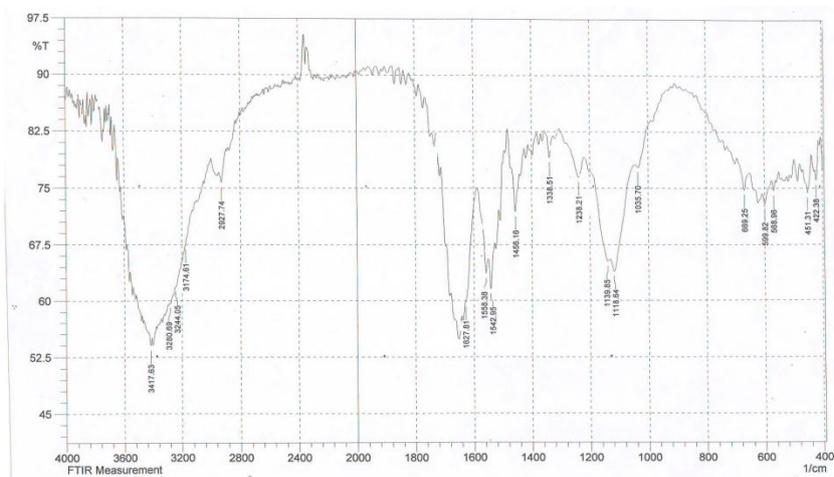


Fig (2) FTIR of MO –CCLW .

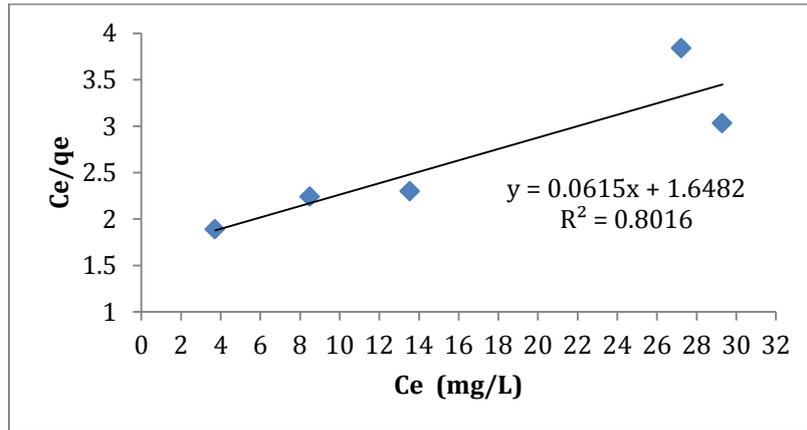


Fig (3) Langmuir isotherm plot for adsorption of orange II onto MO-CCLW at 293 K.

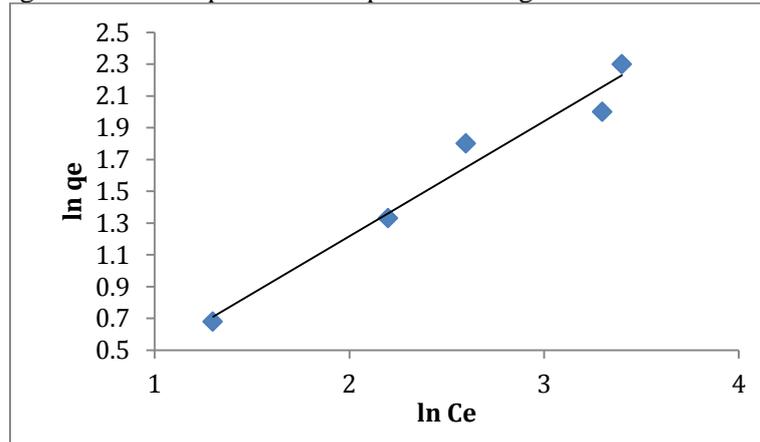


Fig (4) Freundlich isotherm plot for adsorption of orange II onto MO-CCLW at 293K .

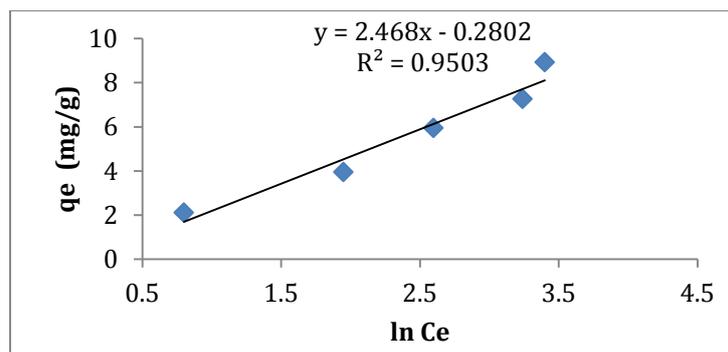


Fig (5) Temkin isotherm plot for adsorption of orange II onto MO-CCLW at 303K .

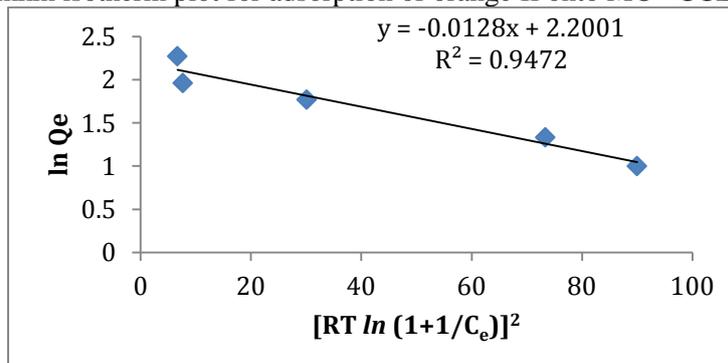


Fig (6) Dubinin-Radushkevich isotherm model for adsorption of orange II onto MO-CCLW at 293K.

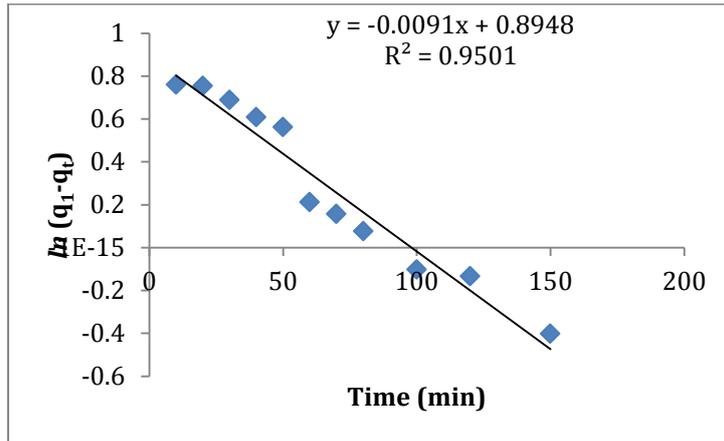


Fig (7) First order plot for adsorption of orange II onto MO-CCLW at 293 K for ($C_0=100\text{mg} \cdot \text{L}^{-1}$).

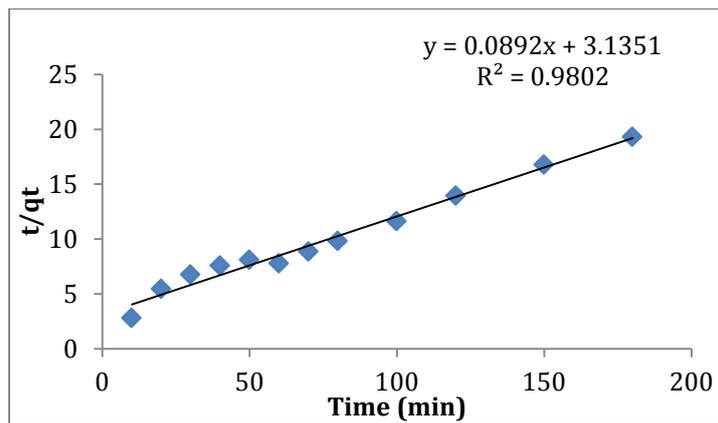


Fig (8) Second order plot for adsorption of orange II onto MO-CCLW at 293K for ($C_0=100\text{mg} \cdot \text{L}^{-1}$)

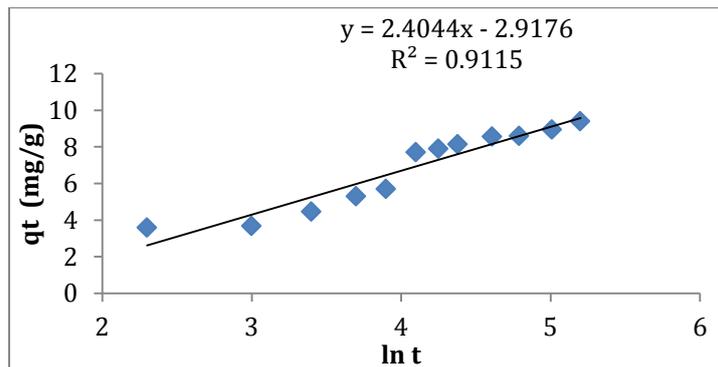


Fig (9) Elovich plot for adsorption of orange II onto MO-CCLW at 293K for ($C_0 = 100\text{mg} \cdot \text{L}^{-1}$)

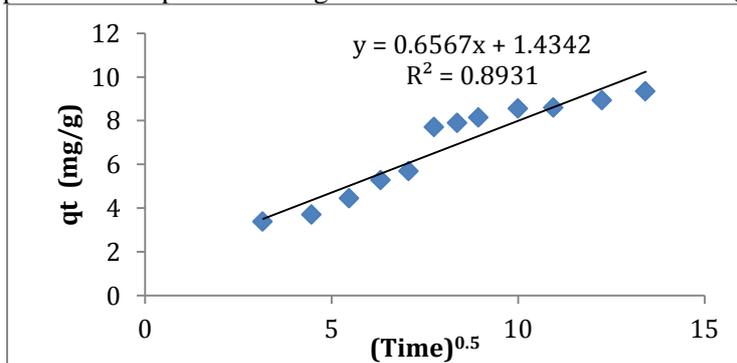


Fig (10) Intra particle plot for adsorption of orange II onto MO-CCLW at 293K for ($C_0 = 100\text{mg} \cdot \text{L}^{-1}$)

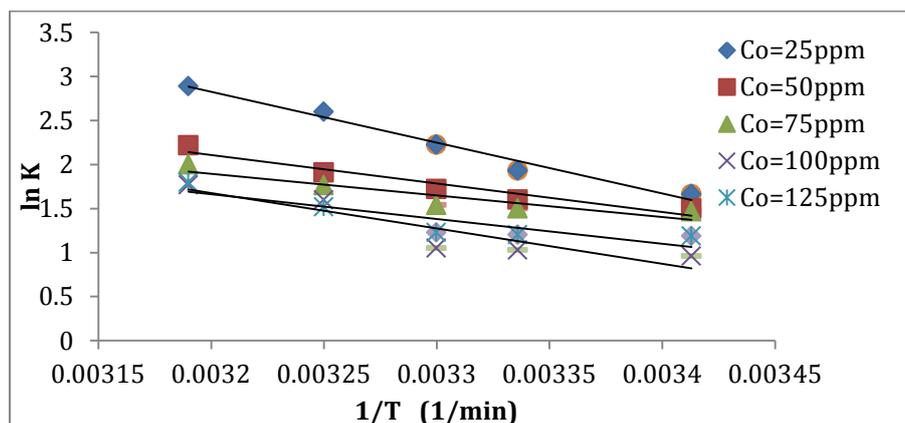


Fig (11) Plot of $1/T$ Vs. $\ln K$ for the adsorption of orange II onto MO-CCLW .

V. Conclusion

The present work deals with the using modified chromium containing leather waste with cationic surfactant as a low –cost adsorbent to remove anionic dye from aqueous solution . Among various models of adsorption isotherm applied the freundlich model agreed well with experimental data –moreover the results indicate that the adsorption process onto the MO –CCLW follows the pseudo second order rate model with intraparticle diffusion being the rate controlling step .The Thermodynamic study revealed an endothermic and spontaneous process .This study showed the MO-CCLW to be highly efficient adsorbing material .

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