

Enhanced Adsorption Of Orange II From Aqueous Solution By Chromium Contained Leather Waste Modified With Cationic Surfactant

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Abstract

Modified chromium contained leather waste (MO-CCLW) was used as adsorbent for removal of orange II as anionic dye from its aqueous solution. Cetyl trimethyl ammonium bromide (CTAB) has been taken as cationic surfactant for modification of chromium contained leather waste. The enhancement in adsorption of orange II on chromium contained leather waste treated with cationic surfactant is observed. Dye removal of CCLW after 3 hour increased from 83% in the absence of CTAB to 93.53% when CCLW treated with 2 mM of surfactant. The effect of different parameters involving, contact time, adsorbent dosage, temperature, initial dye concentration and PH solution, on the orange II dye removal was examined. According to the obtained results, the removal increased with increasing contact time and the optimum PH at which the maximum removal occurred in acidic conditions. The best removal efficiency of the dye was about 93.5% for the adsorbent dosage of 0.75 gm. With the increase of initial dye concentration in the range of 10-125 mg.L⁻¹, the removal efficiency of the dye decreased from 85 to 76.7%. By raising the temperature from 283K to 303K, the percentage removal of dye increased from 73.5 to 86%. Typical S-shaped isotherm was observed for the adsorption of orange II onto modified CCLW, according to Giles classification.

Keywords: adsorption, cationic surfactant, leather waste, orange II.

1. Introduction

The pollution of water resources with industrial effluents containing organic compounds and toxic substances is a matter of great concern (Santos et al., 2013). Azo dyes, which mostly consist of aromatic moieties linked together by N=N bonding, represent the largest class among these pollutants which are water soluble. They contribute to water toxicity and represent an increasing danger for the environment and human beings. These dyes are known to be toxic, carcinogenic, teratogenic, which leads to health and environmental risks (Abramian et al., 2009). Many industries used these dyes as food industries, leather, paper, rubber, plastics, cosmetics, pharmaceuticals and textile. Various physical-chemical processes and biological methods (coagulation, oxidation, reduction, ultrafiltration, ion exchange and combined electro-chemical adsorption techniques were used to remove dye coloration from wastewater (Ohashi et al., 2012). Among these methods, adsorption can be thought to be efficient process for the treatment of wastewater due to its low-cost and ease of operation as well as greater efficiency. A large number of adsorbing materials for soluble dyes have been studied

such as activated carbon (Valix et al., 2006), silica xerogel (Pavan et al., 2008), titania (Bourikas et al., 2005), titania silica mesoporous materials (Messina et al., 2006), waste material (Gupta et al., 2006), clay such as bentonite (Liu et al., 2007) and bentonite modified with quaternary ammonium salt used for the removal of orange II sodium salt (Sonawane et al., 2009). Surfactants or surface active agents are amphiphilic molecules possess both hydrophilic and hydrophobic parts. The hydrophilic parts called the head and the hydrophobic portion is the tail. The hydrophobic part may consist of a single chain or it may have up to four chains. The head can be a charged or uncharged polar group. According with the nature of the head groups the surfactants are classified into anionic, cationic, non-ionic and zwitterionic (Hamme et al., 2006). Surfactants are used as leveling agents in dyeing stuff (Simoneie et al., 1998). Recently the usage of surfactants in dye removal from wastewater treatment gains important (Ozdemir et al., 2009). The purpose of this work is the study of removal of orange II (anionic dye) from wastewater by adsorption on chromium contained leather waste CCLW in the presence of cetyl trimethyl ammonium bromide CTAB as anionic surfactant. The effect of surfactant, initial dye concentration, contact time, solution PH, adsorbent dose and temperature have been studied and results are discussed.

1. Materials and Methods

2.1 Materials

Adsorbate: The dye orange II sodium salt chemical formula $C_{16}H_{11}N_2 NaO_4S$, molar mass $350.33 \text{ gm.mol}^{-1}$, $\lambda_{\text{max}} = 483 \text{ nm}$ was supplied by Fluka analytical and used without further purification. The structural form of orange II sodium salt is given in Fig.(1).

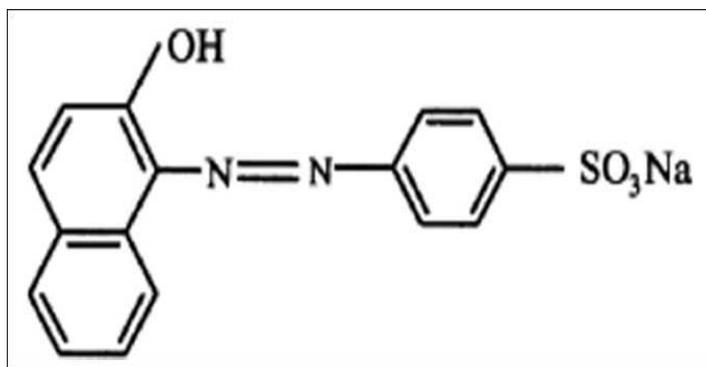


Figure 1. Structural formula of orange II.

Adsorbent: The chromium contained leather waste (CCLW) was obtained from Al-waffa company for leathers tanning, were cut into the small pieces, washed with distilled water and dried at 120° for 3 hour and ground into granules with particles size 0.1-0.2 mm, finally kept in desiccator. The cetyl trimethyl ammonium bromide (CTAB) $C_{16}H_{33}(CH_3)_3$, molar mass 364.46 selected as a modifying agent was provided by Fluka. Stock surfactant solution was prepared from surfactant, at 1.0 gl^{-1} concentration by dissolving weighted amount in distilled water. The modification carried out by mixing 50 mL of 2mM surfactant solution and 5gm of CCLW with stirring for 3 hour, then the solution was filtered, a modified CCLW was dried at 120° for 3 hour and kept in desiccators.

2.2 Methods

To examine the effect of surfactant on adsorbent removal, the flasks, containing 25 ml of 50 mg l⁻¹ dye and 0.25g of modified CCLW at PH =6, were shaking at different time from (30-180) min at 293k. The effect of PH was investigated with PH values from 1.8 to 12 by maintaining the initial dye concentration of 50 mg l⁻¹ and the dose 0.5 g/50mL of solution, the PH adjustment was done by 0.1M HCL or NaOH. For measuring the value of PH for the solution PH meter type HANNA, model 211, England, was used. In order to determine the effect of initial dye concentration, 25 ml of dye solution of known concentration from 10 to 125 mg l⁻¹, were introduced into 100 ml flasks containing accurately weighted amounts 0.25 gm of CCLW as adsorbent at 293 k. The influence of time on dye adsorption was studied at 293k with initial concentration 50 mg l⁻¹ and adsorbent dose of 0.25 g in 25 ml of dye solution. The effect of adsorbent dosage was studied by varying the MO-CCLW amount as 0.1 g, 0.25 g, 0.35 g, 0.5 g, and 0.75 g, with dye concentration of 50 mg l⁻¹ at 293k. Also the effect of temperature on removal of 50 mg l⁻¹ dye with 0.25 g of adsorbent was studied at temperature range (283 -323)K. Batch adsorption experiments were carried out by treating 25 ml of dye solution of different concentration (25 – 125 mgL⁻¹) with 0.25 gm of MO-CCLW in round bottom flask and shake the solution in shaker type Craiffin flask shaker for pre-determined period to reach equilibrium. At the end of predefined time interval the CCLW was removed from aqueous solutions by filtration. The progress of adsorption was determined by finding the concentration of orange II dyes by a UV-Visible spectrophotometer (Shimadzu, Japan). The absorbance of the color was measured at 483 nm where the maximum absorption peak exists. The FTIR of CCLW and surface derivatives was carried out using a Shimadzu FTIR-8400 Fourier Transform Infrared Spectrometer in the range of 400-4000 cm⁻¹. The adsorbent is mixed with anhydrous KBr to make a pellet and 400 scans are carried out to give the average FTIR scan.

2. Results and discussion

The adsorbed amounts of orange II were calculated from the concentrations in solutions before and after adsorption according to the equation (1).

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

Where C_o is the initial adsorbate concentration, C_e the equilibrium concentration in solution at time t, q_e is equilibrium dye concentration on adsorbent mg. g⁻¹, V is the volume of dye solution (L) and W is the adsorbent weight (g). Percentage of dye removal was calculated by equation (2).

$$\text{Dye removal (\%)} = (C_o - C_e) / C_o \times 100 \dots\dots\dots(2)$$

3.1 FTIR characterization for the adsorbent

The FTIR spectrum of CCLW Fig.(2) showed an absorbed band at 3396 cm⁻¹ for N-H stretching group and the carbonyl band appeared at 1629 cm⁻¹ while the carboxyl ate band appeared at 1550 cm⁻¹. Other evidence for the structure is the (C-N) bending at 1431 cm⁻¹.

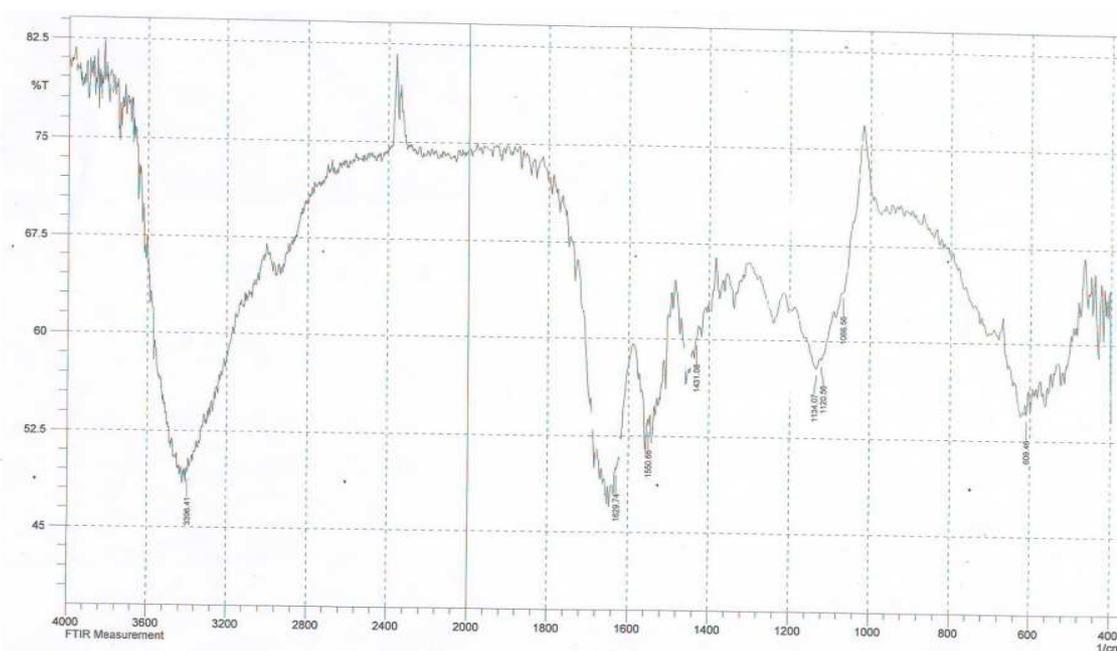


Figure 2. FTIR spectrum of the chromium contained leather waste

3.2 Effect of surfactant CTAB on adsorption

The effect of surfactant CTAB on the extent of dye removal is shown in Fig.(3). According to the data obtained that figure showed more dye adsorption activity in the presence of modified CCLW with 2mM of CTAB surfactant than in the absence of it. The dye removal after 3 hour increased from 83% without using CTAB to 93.53% in the presence of the surfactant. According to this data, using cationic surfactant enhanced the removal efficiency of the CCLW as adsorbent to orange II as anionic dye. This can be explained by the fact that the adsorption of anionic surfactant at solid-liquid interface is strongly influenced by the charged groups on the surface. 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 Predominate active sites of the CCLW should be amino groups and Cr (III) combined with collagen. At the first treatment of the CCLW with cationic surfactant. The adsorption of cationic surfactant mainly depend on its association with the residual carboxyl groups on collagen, so the adsorption of surfactant leads to increases the positively charge site in the CCLW surface. When a dye is dissolved in an aqueous solution the adsorption of it at solid-liquid interface, is strongly influenced by the charged groups on the surface of CCLW that have the potential to associate with anionic groups of dye through electrostatic interaction that cause the increase in a valid surface site on the CCLW for the adsorption of orange II. Same result showed by using dodecyl trimethyl amonium bromide as cationic surfactant for the removal of remazol blue dye by *Aspergillus versicolor* biomass (Gul et al., 2010).

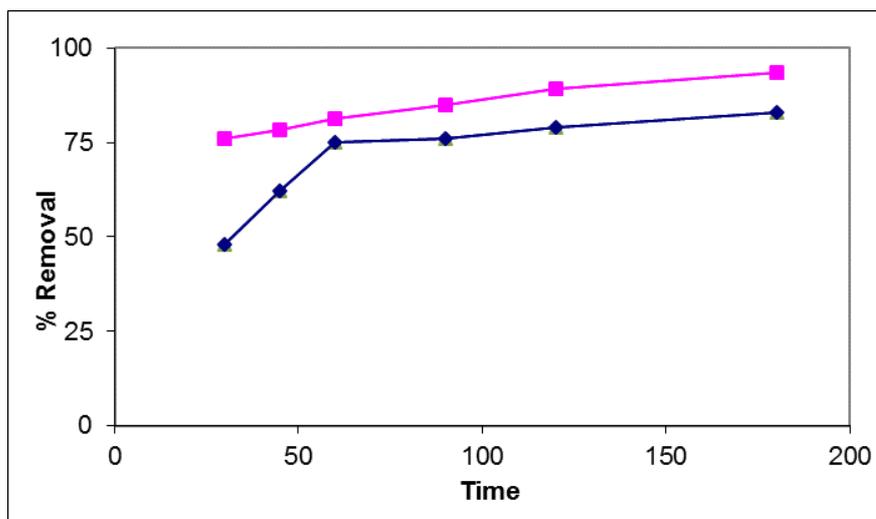


Figure 3. The effect of surfactant CTAB and contact time of the orange II adsorption onto modified CCLW.

3.3 Effect of contact time

The effect of contact time was investigated in the batch mode at dye concentration 50 mg l^{-1} . The results have been shown in Fig.(3) which suggests that adsorption of a large quantity of orange II dye onto modified CCLW after a very short contact time where the uptake of approximately 50% of molecules was noticed within the first 60 min of the experiments the adsorption of orange II dye increases sharply with time and attains equilibrium after 180 minutes. The fast removal obtained at the initial stage may be explained by an increased availability in the number of active binding sites on the adsorbent surface. The slow and insignificant adsorption observed as time progresses is due to the fact that every adsorbent has a limited number of active sites which becomes occupied with time (Badmun et al., 2007).

3.4 Effect of adsorbent dose

The effect of the MO CCLW quantity used for adsorption was tested. Fig.(4) shows the effect of adsorbent dose on the extent of removal of dye, it was found that with an increase in the dose of MO-CCLW from 0.1 to 0.75 gm, the extent of removal of orange II dye increased from 79.14% to 93.50%. This increase of removal should be due to the increase in surface area and adsorption sites available when more adsorbent is used.

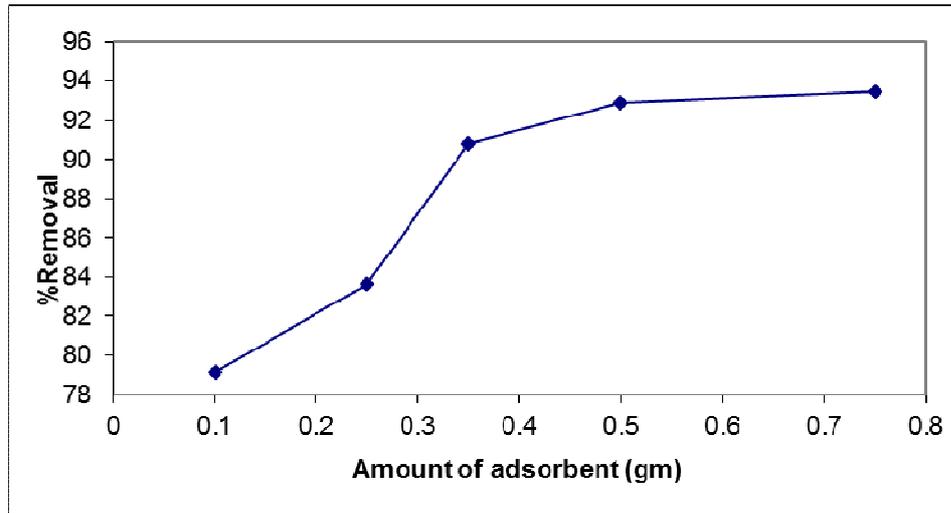


Figure 4. Effect of modified CCLW dose on the adsorption of orange I Dye

3.5 Effect of temperature

The effect of temperature on adsorption of orange II was studied by carrying the temperature controlled equilibrium experiments. It has been noticed from the Fig.(5) that by increasing the temperature from 283k to 303k, the % removal of dye was increased from 73.5% to 86%. This may be a result of increase the number of binding sites for the dye molecules on the adsorbent surface (Singh et al., 2011), also by increase of temperature the mobility of the dye molecules was increase, which means that the adsorption process is endothermic behavior in nature. As temperature raised from 303 to 323k the active sites in the surface of modified CCLW was occupied with the dye molecules causing no further increases in the dye removal percentage.

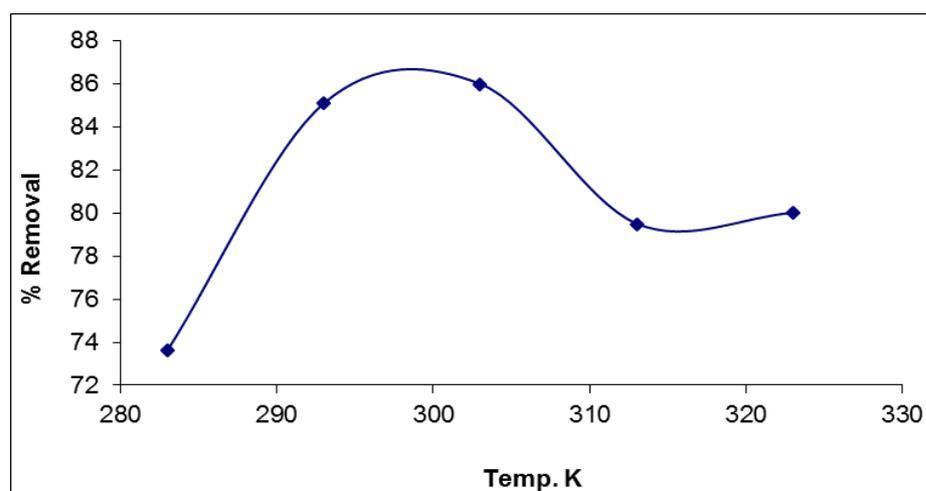


Figure 5. Effect of temperature for the adsorption of orange I onto modified CCLW.

3.6 Effect of initial dye concentration

Although dye-dye hydrophobic interactions and self association or aggregation of dye molecules are known .Orange II shows a very high solubility in aqueous solutions (116 g l^{-1} at 30 C^0) and an aggregation mean number equal to 1.00 for dye concentrations lower than 0.01 M (Bracko et al., 1997) . The effect of initial dye concentration on the adsorption was studied at different concentrations of dye at room temperature. Fig.(6) shows the effect of initial dye concentration on the dye adsorption. The % removal of orange II was greater at concentration 10 mg l^{-1} and then , the removal was decreased to 76.73 at 125 mg l^{-1} , therefore the removal efficiency of the orange II increases at dilute concentrations , where as it decreases at concerted concentrations. At low initial concentration , ratio of number of sites available per unit dye concentration was large , this enhanced the adsorption process while in high concentration of dye there is competition between ions for binding sites on the modified CCLW surface. Fig.(7) shows the effect of initial dye concentration on the amount of dye adsorbed . The amount of orange II adsorbed , in equilibrium increased from 0.7345 to 9.659 mg.g^{-1} when the initial dye concentration increased from 10 to 125 mg l^{-1} respectively. Indeed , at higher initial concentration , the resistance to mass transfer between the solid and aqueous phase is more easily overcome due to the driving forces , moreover the number of collisions between dye molecules and adsorbent is increases , increasing the adsorption (Akus et al., 2005).

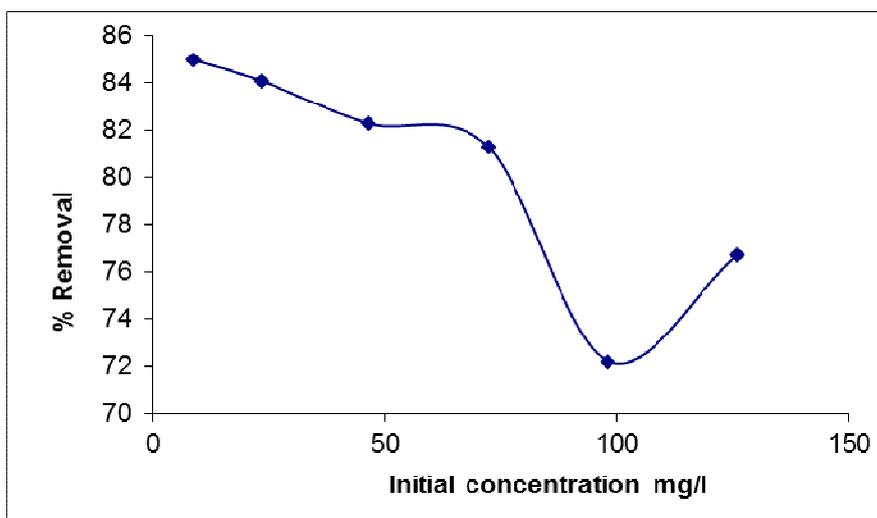


Figure 6. Effect of initial dye concentration on its adsorption by modified CCLW .

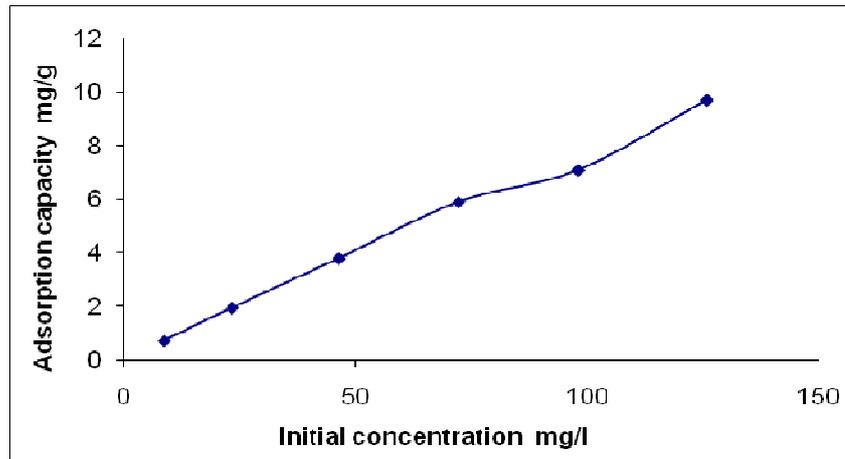


Figure 7. Effect of initial concentration (mg/l) on the adsorption capacity of orange II onto modified CCLW .

3.7 Effect of pH

The pH study has a major effect on the protonation and deprotonation of the adsorbent and adsorbate functional groups. The electrostatic attraction or repulsion between the adsorbent and adsorbate depend on the surface charges of both entities. Fig.(8) shows the effect of pH on the extent of removal of orange II dye using modified CCLW as adsorbent. The adsorption was high at pH 2.7 reaching up to 92% removal. As PH value increased the %removal decrease from 90% to 86%, further increased in pH from 7 to 12, the % removal of orange II dye decreased to 42.75 % so the adsorption of anionic dyes is more favorable under highly acidic conditions. This can explained by that at relatively lower PH more protons are available and ,as a result more amino groups and the complexed Cr (III) in the CCLW are positively charged lead to the increase of the electrostatic attraction between the surface positive charges and the negatively charged dye molecules which increases the amount of dye adsorbed (Gawade et al., 2005) .On the other hand ,the adsorption capacities at alkaline PH are lower due to the decrease of positively charged sites on adsorbent and the competition between OH^- and anionic dye from the adsorption sites . Accordingly, an electrostatic repulsion between the negatively charged dye and the surface groups took place and lead to decrease the adsorption.

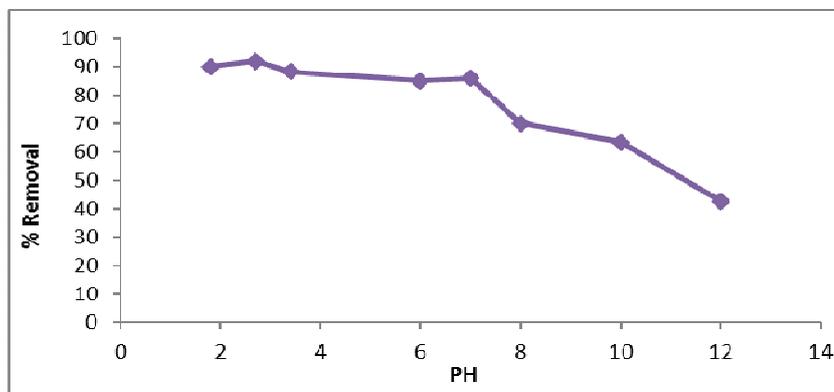


Figure8. Effect of PH on adsorption of orange II dye onto modified CCLW.

3.8 Adsorption isotherm

Equilibrium relationships between sorbent and sorbate are described by sorption isotherms, usually the relation between the quantity sorbed and that remaining in the solution at affixed temperature at equilibrium. The values of adsorption data are listed in Table (1). The adsorption isotherm of orange II dye onto CCLW and modified CCLW at 283k is presented in Fig.(9) and Fig.(10). S-shap isotherm observed from the figure according to Giles classification. The amount of dyes adsorbed increase as the concentration increases up to saturation point. Beyond this point, increasing the dye concentration will not cause further increases. This behavior is typical of solids with a limited number of accessible sites. As long as there are available sites, adsorption will increase with increasing dye concentration, but as soon as all of the sites are occupied a further increase in concentration will not increase the amount of dye on adsorbents (Tahiri et al., 2003).

Table 1: Adsorption isotherm data for the adsorption of orange II onto CCLW at 293k

C_o $mg.L^{-1}$	Unmodified CCLW		Modified CCLW	
	C_e $mg l^{-1}$	q_e $mg g^{-1}$	C_e $mg l^{-1}$	q_e $mg g^{-1}$
25	5.20	1.80	3.715	1.964
50	13.10	3.331	8.50	3.791
75	17.80	5.446	13.54	5.872
100	28	7.008	27.22	7.086
125	33.50	9.239	29.30	9.659
150	58.50	9.15	54.3	9.57

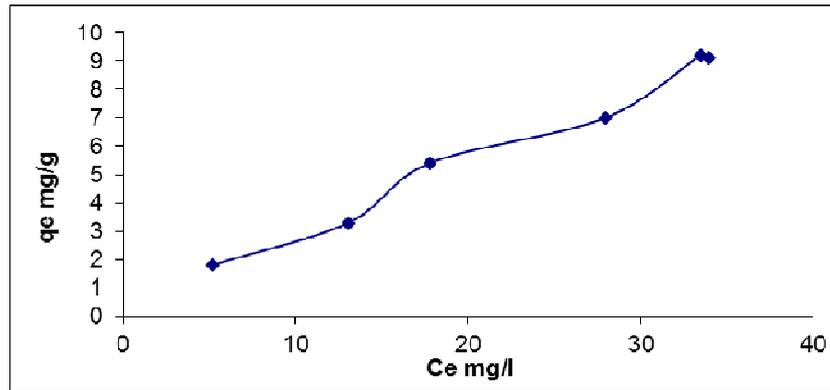


Figure 9. Adsorption isotherm of orange II unmodified CCLW at 298K.

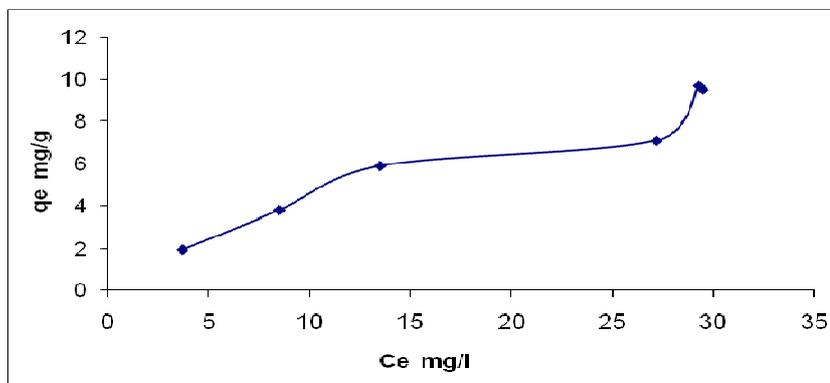


Figure 10. Adsorption isotherm of orange II on modified CCLW at 298K.

Conclusion

It could be concluded that the adsorption of anionic dye at the solid / liquid interface can be enhanced by treating the adsorbent chromium containing leather waste yielding from the tanning industry with cationic surfactant. The modified CCLW is found to have greater removal efficiency for anionic dye than unmodified CCLW. The batch experiments shows that the adsorption of orange II is dependent on contact time, adsorbent dose, temperature, initial dye concentration, and PH solution. The main characteristics of the adsorption process of the orange II on MO CCLW can be summarized as the following:

- The adsorption process reaches equilibrium in 180 min contact time.
- The removal increase with the increasing adsorbent dose.
- The best temperature for the adsorption process was 303K.
- Maximum removal occurred at acidic pH.
- The percentage of removal decreased with the increasing of the initial dye concentration.
- The adsorption isotherm is S-type according to Giles classification.
- The result indicated that modified CCLW is a promising technology adsorbent for the removal of waste dyes.

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