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Adsorption of Chrome Cr (VI) from Aqueous Solution by Olive Leaves Powder

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Abstract: The pollution caused by the heavy metals presents in industrial effluents has increased in the last decades, thus raising the concern of the industries to treat their waste correctly as well as the search for low cost techniques. Adsorption of Cr (VI) from aqueous solutions by olive leaves powder was investigated in batch experiments. Olive leaves were selected because of its porous morphology and rich in carboxyl, hydroxyl, and carbonyl among other functional groups which responsible for adsorption. The effect of pH, powder dosage, contact time, initial Cr (VI) concentration, mixing speed and particles size on removal efficiencies of olive leaves was studied. The adsorption percent was found to be 91.5% from the initial Cr (VI) metal ion concentration of 50 mg/L with 18 g/L adsorbent dose of leaves powder (150 – 200 µm) at pH = 4 after contact time of 90 min with agitation speed of 200 rpm. The adsorption data were found to be fitted well with Langmuir adsorption isotherm model. Olive leaves were shown to be a promising biosorbent for Cr (VI) removal from aqueous solutions and can be used as an alternative to the processes of wastewater treatment.

Key words: *Biosorption, Adsorption, Chrome Cr (VI), olive leaves.*

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Introduction

Aquatic environment contamination by toxic heavy metals is one of many serious problems. Many industries discharge untreated effluents into the neighboring drains or fields. These effluents have toxic metals like Cr, Cu, Cd, Ni, Pb that may stimulate growth of many crops and retard germination (1-3). Chromium is one these metals that gain a big attention in the last years, since it is used in so many industries such as plating, metallurgy, tanning and metal finishing. Chromium can exit in two stable forms as it introduced into the environment, Trivalent Cr (III) and hexavalent Cr (VI). From a health stand point Cr (III) is intrinsically less toxic than Cr (VI). Chromium hexavalent is mutagenic in nature, carcinogenic and of high mobile in soil and aquatic system (4-7). So it is essential that industrial effluent should be treated to reduce level of chromium to the acceptable level before it is discharged in the natural environment. As recommended by the World Health Organization (WHO), the maximum acceptable concentration of chromium Cr (VI) is 0.05 ppm in drinking water and 50 -200 ppm in industrial effluent streams (8). Therefore it is necessary to treat the industrial effluent in order to reduce the concentration of chromium concentration to the acceptable level before it is discharged in the natural environment.

As described in the literature, many methods have been used to remove Cr (VI) from industrial effluent (9- 12). These methods include membrane filtration, electrochemical precipitation and ion exchange treatment. These methods are costly and not applicable in local conditions. Therefore, it is necessary to develop inexpensive, easily available, and effective methods for waste water treatment. Adsorption is proved to be an adaptable and cost effective method for heavy metals removal. Olive trees are abundantly found and easily available (13-16). The aim of this study is to find the best conditions (pH, contact time, Dosage of leaves powder adsorbent and initial chromium concentration) for removal of Cr (VI) from aqueous solutions.

Materials and Methods

Preparation of Adsorbent

Olive leaves were collected from the campus of Baghdad University. The collected leaves were then washed several times with distilled water to remove surface adhered particles and water soluble impurities. The washed materials were dried in an oven at 80^{o}C for 24 h. Dry olive leaves were crushed by a ball mill and sieved to different particle sizes: (150- 200), (200- 250), (250- 300), and (300-400) μm. Leaves powder was activated by treating with diluted H_2SO_4 (5 wt %). Finally, the powder was dried and stored in glass bottle for experimental use.

Preparation of Cr (VI) Solutions

A stock solution of Cr (VI) of 1000 ppm was prepared by dissolving 2.832g of analytical grade $K_2Cr_2O_7$ in one liter of twice distilled water. Different solutions of initial Cr (VI) concentrations were used in this study ranging from 50 – 300 ppm. The desired concentration of solution was obtained by further diluting the stock solution (1000 ppm) with appropriate amount of twice distilled water (16).

Characterization of Adsorbent

Fourier transforms infrared spectroscopy FTIR was used to characterize olive leaves powder adsorbent. As shown in figure 1, the spectra display a number of absorption peaks. The FT-IR spectroscopy analysis shows bands at 3420 cm^{-1}, which indicated the bonded –OH groups. Also bands observed at 2930 cm^{-1} which assigned to the aliphatic –C-H group. The peak around at 1620 cm^{-1} assigned to C=O group. The peaks displayed at 1485 cm^{-1} and 1460 cm^{-1} assigned to C=C stretching. The peak around 1050 cm^{-1} shows O-C group.

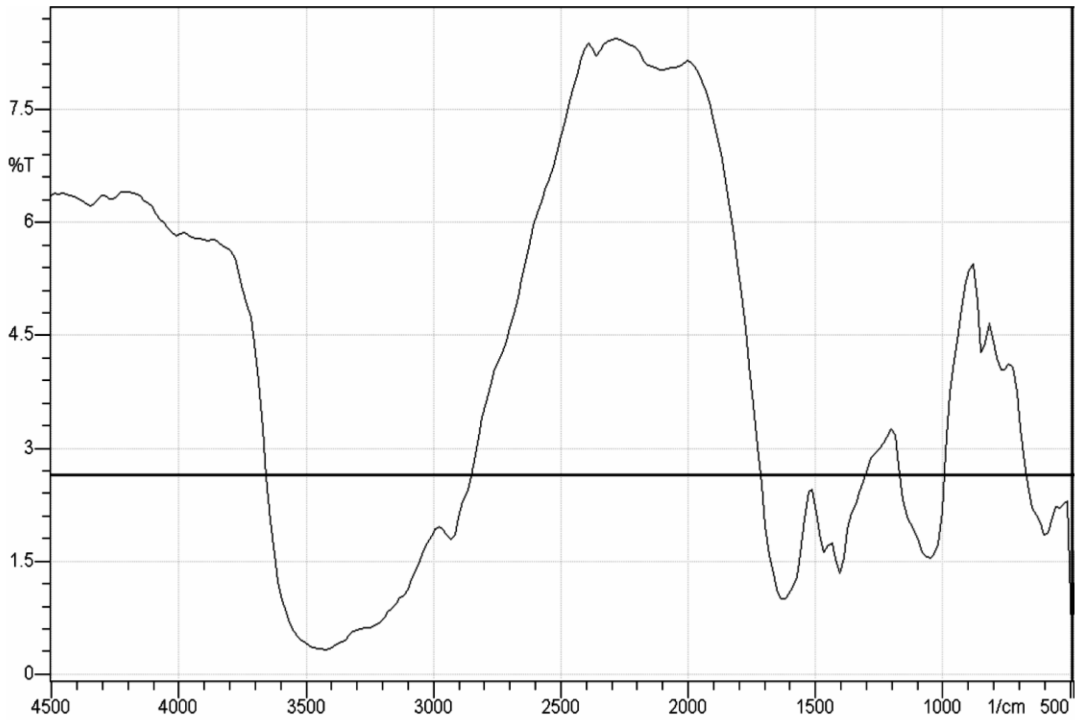

Figure 1: FTIR spectra of olive leaves powders

Batch Adsorption Experiments

Experiments were studied at room temperature in batch experiments. The parameters studied were pH, adsorbent dose, contact time, shaking speed, particle size and initial concentration of Cr (VI) solution. Table (1) shows the values of these parameters which used in this study. After each experiment the residual was separated by filtration with Whatman paper (No.42). Ten milliliter of each sample was collected for Cr (VI) analysis. Atomic adsorption spectrophotometer (with air acetylene flame) was used to measure the concentration of Cr (VI) after adsorption.

The percentage adsorption of the metal by adsorbent is determined by the following equation:

$$\% \text{ Adsorption} = \frac{C_o - C_e}{C_o} \text{ x } 100\% \quad \ldots\ldots\ldots\ldots\text{.. (1)}$$

Where Co is initial concentration of Cr (VI) and Ce is Cr (VI) concentration after shaking.

Table 1: Experimental parameters values

parameter	pH	AC (g/L)	r(rpm)	S(µm)	t(min)	Co(ppm)
pH	2-8	18	200	150-200	90	50
Adsorbent conc., AC (g/L)	4	3-18	200	150-200	90	50
Shaking speed, r(rpm)	4	18	100-300	150-200	90	50
Particle Size. S(µm)	4	18	200	150-200 to 300-400	90	50
Contact time, t(min)	4	18	200	150-200	20-150	50
Initial Cr(VI) Conc., Co(ppm)	4	18	200	150-200	90	50-400

Results and Discussion

Effect of pH

Figure 2 showed the effect of pH on adsorption percent of Cr (VI) from aqueous solution. All other parameters were kept constants (adsorbent doses 1.8 g in 100ml Cr (VI) solution, contact time 90 min., particle size range 150-200 µm, Cr (VI) concentration 50 mg/L and mixing speed is 200 rpm). From (Figure 2) we deduced that the maximum Cr (VI) removal occur at pH=4 for olive leaves. This finding is in agreement with result of Khezami *et al*.(17) who found that the best absorption of Cr(VI) by activated carbon occur at range of pH= 4 - 4.5.

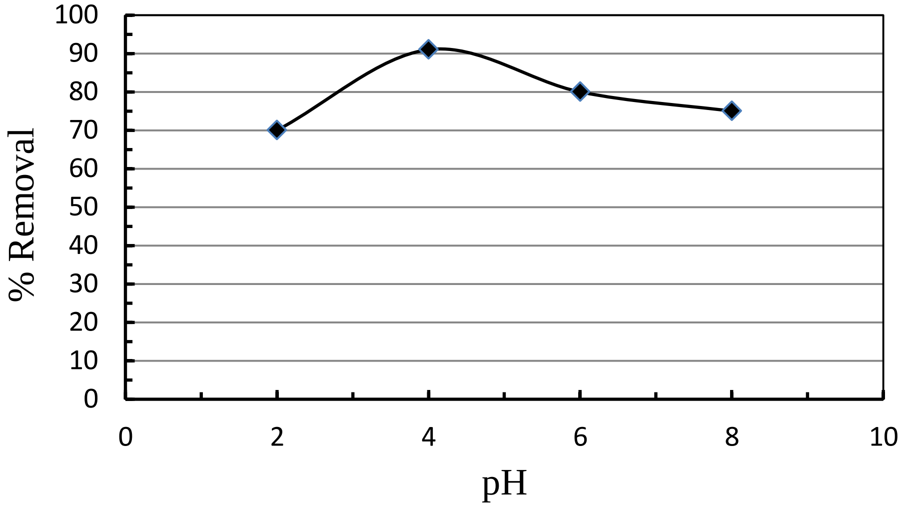

Figure 2: Effect of pH on adsorption of Cr(VI) by olive leaves powder

Effect of Adsorbent Mass

To show the effect of adsorbent dose on removal efficiency of Cr (VI), different dosages of olive leaves powder were tested as adsorbent. The values were 3, 6, 9, 12, 18 g/L of Cr (VI) solution. Figure 3 shows that the removal efficiency increases as the adsorbent does increases and the maximum removal of chromium ions was occur when using 1.8 g/100 ml. This is because the number of adsorption sites in the adsorbent (leaves powder) increases by increasing adsorbent doses which will lead to improve the removal efficiency of the Cr (VI) from the aqueous solution.

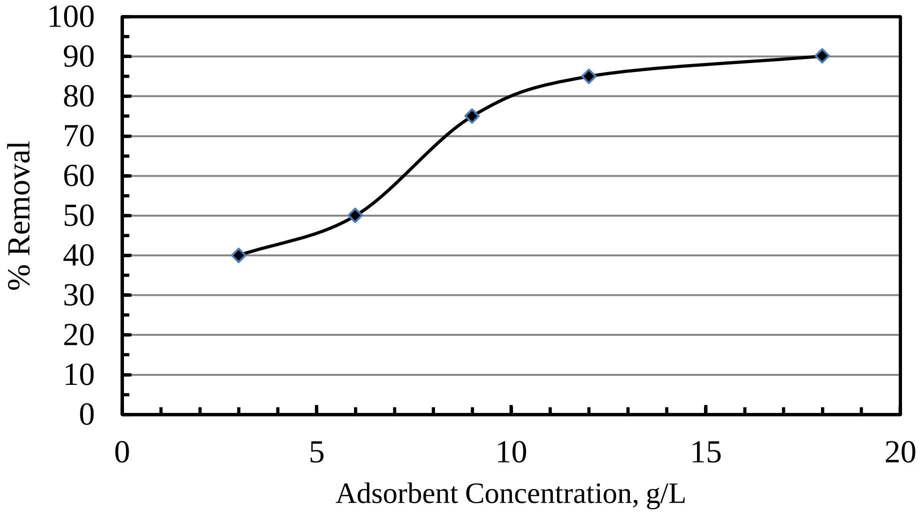

Figure 3: Effect of adsorbent concentration on the adsorption of Cr (VI) by olive leaves powder

Effect of Shaking Speed

Removal of chromium ions from aqueous solution is much affected by shaking speed. To show this effect experiments were conducted with deferent shaking speed; 100, 150, 200, 250 and 300 rpm. Figure 4 shows a best value for shaking speed obtained at nearly 200 rpm. At higher values of shaking speed the percent removal begin to decrease by about 5%. This can be interpreted as increasing the shaking speed will liberate energy which is used in the formation of bonds metal ions and adsorbent. But at speed greater than 200 rpm, the percent removal efficiency will decrease due to liberation of extra energy which will be used in breaking the bonds between metal ions and adsorbent. Mohanty, *et al.* (18) found that the best rpm is 250 when they studied the adsorption of Cr (VI) by activated carbon.

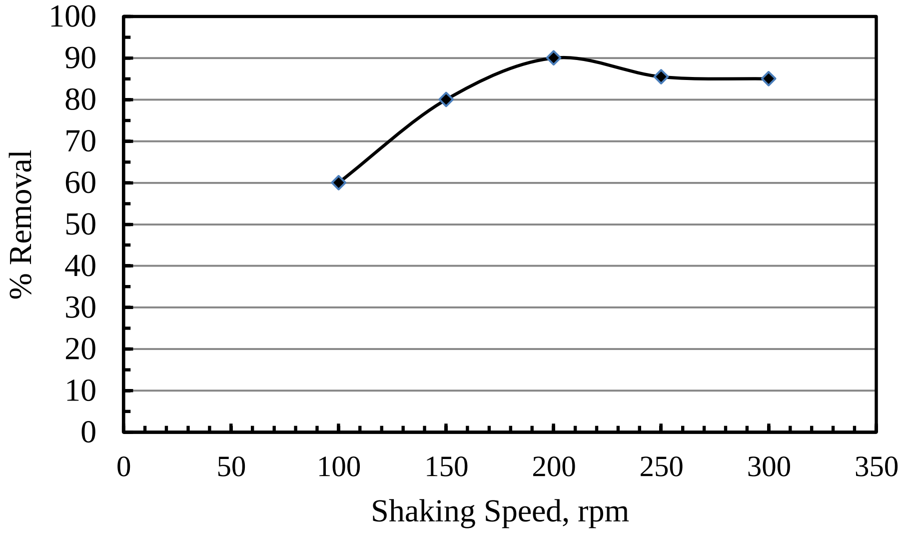

Figure 4: Effect of shaking speed on the adsorption of Cr (VI) by olive leaves powder

Effect of Particle Size

Four different particle sizes were used to show the effect of particle size on removal efficiency. These sizes were (150- 200), (200- 250), (250- 300) and (300-400) µm. Figure 5 shows that the removal efficiency is increased as the particle size decreases. This is due to high surface area that provided by smaller particles size.

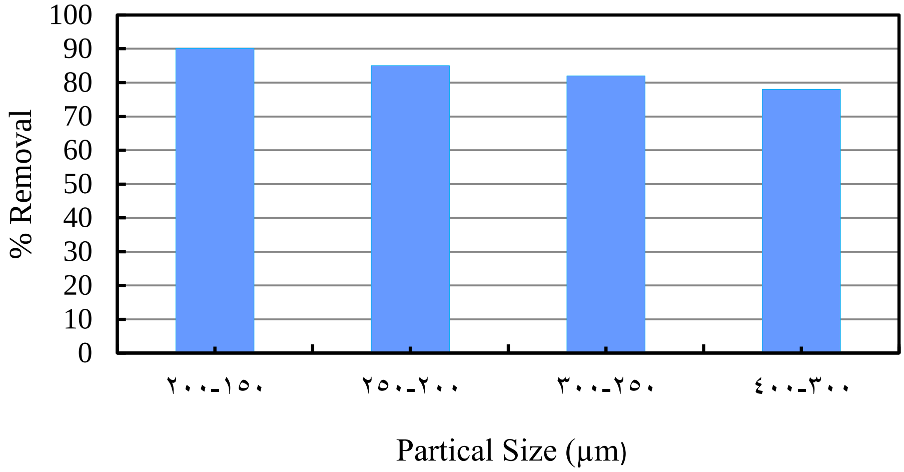

Figure 5: Effect of particle size of olive leaves powder on adsorption of Cr (VI)

Effect of Contact Time

The effect of contact time on percent removal was shown in (figure 6) which shows that maximum removal efficiency of adsorbent was found 90 min. Increasing the contact time after 90 min will not affect the percent removal of Cr (VI) from aqueous solutions. This is due to reaching equilibrium after 90 min and all the active sites were occupied by chromium ions.

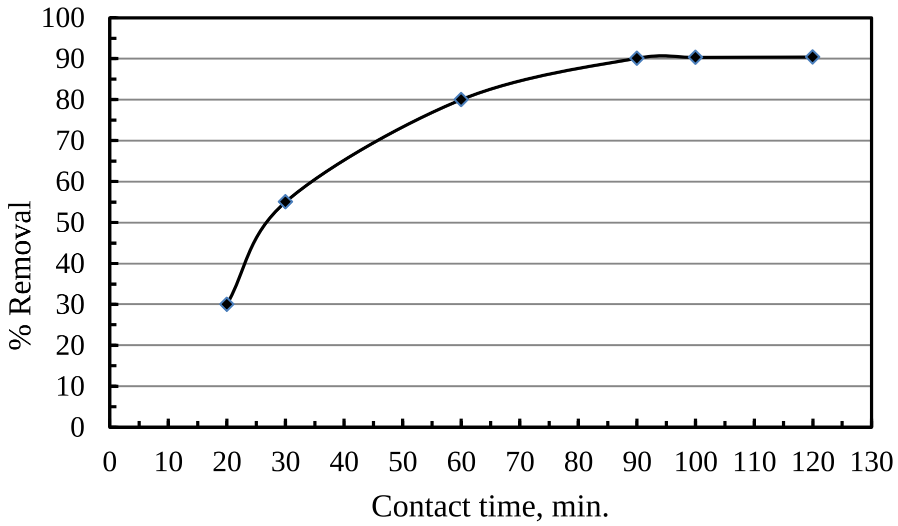

Figure 6 : Effect of contact time on the adsorption of Cr (VI) by olive leaves powder

Effect of Initial Metal Ion Concentration

In order to show the effect on initial concentration of Cr (VI) on removal efficiency of olive leaves powder, four initial concentrations were used (50, 100, 200 and 400) ppm. (Figure 7) indicates that increasing initial concentration of metal ions will decrease the removal efficiency of adsorbent. This is due to the fact that increasing the initial metal ions will lead to the increasing the competitions between these ions on the active sites of the adsorbent surface. These competitions will decrease the percent removal efficiency since much more ions will be left in the aqueous solution without adsorption. These results are in agreement with that found by Mor *et al*. (19) who studied chromium absorption by activated alumina. They deduced that the best initial concentration of Cr (VI) was about 50 ppm.

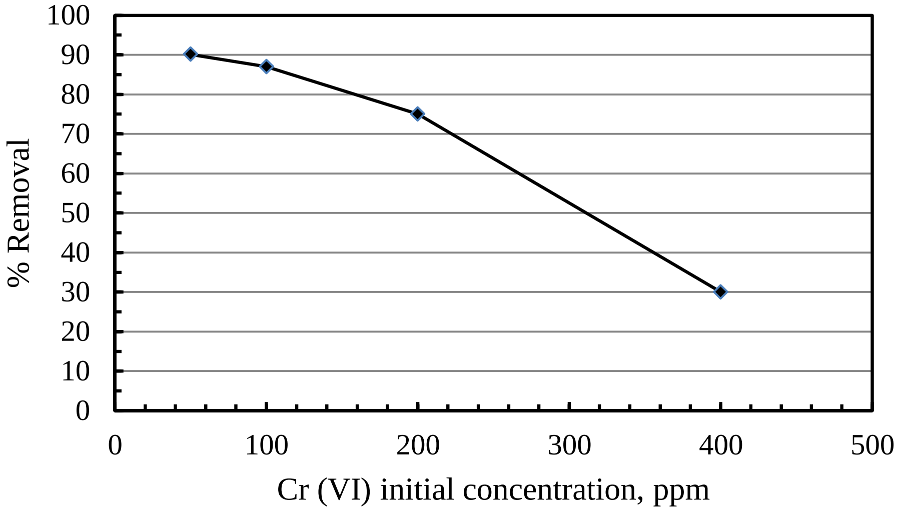

Figure 7: Effect of initial adsorbent concentration on the adsorption of Cr (VI) by olive leaves powder

Adsorption Equilibrium Study

Langmuir and Freundlich isotherms were used to analyze the obtained adsorption data. The Langmuir isotherm equation is given by the following equation:

$$q_e = \frac{q_{max}\ b\ C_e}{1+b\ C_e} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ (2)$$

Where qe is the adsorbate concentration in equation (mg/g), q_{max} is the maximum adsorption capacity corresponds to complete monolayer coverage on the surface (mg/g) and b is the Langmuir constant (L/mg) (20). Eq. (2) can be rearranged to following linear form:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}.b} + \frac{C_e}{q_{max}} \quad \ldots\ldots\ldots\ldots\ (3)$$

Plotting Ce/ qe versus Ce will give a straight line of slope (1/ q_{max}) and intercept (1/ qmax. b). (Figure 8) shows this plot for adsorption of Cr (VI) at different values of adsorbent concentration all other operating conditions are fixed as shown in (Figure 8).

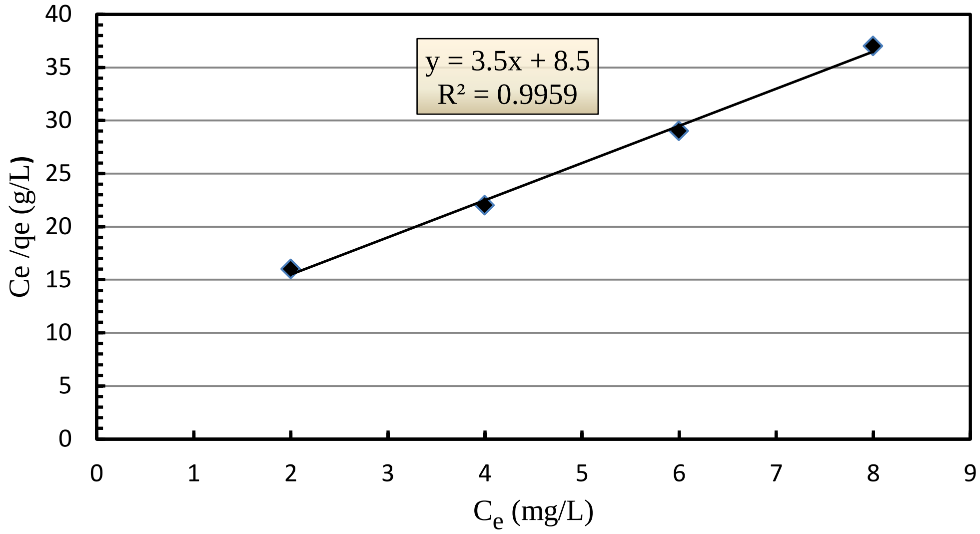

Figure 8: Langmuir isotherm for adsorption of Cr(VI) by olive leaves powder. (rpm=80, pH=4, contact time=90 min., Initial conc. Of Cr (VI) = 50 ppm, Particle size = 150 – 200 µm).

Freundlich isotherm is an empirical equation used to describe heterogeneous system given by the following equation:

$q_e = k_f\, C_e^{\frac{1}{n}}$ …………….. (4)

Where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), Ce the equilibrium concentration of adsorbate (mg/L), k_f the Freundlich constant related to the adsorption capacity and (1/n) is the heterogeneity factor (20). A linear form of the Freundlich equation is obtained by taking the logarithm of the equation (4).

$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e$ ……………. (5)

Plotting (ln q_e) versus (ln C_e) gives a straight line of slope (1/n) and intercept (ln k_f). (Figure 9) shows this plot for adsorption of Cr (VI) at different values of adsorbent concentrations.

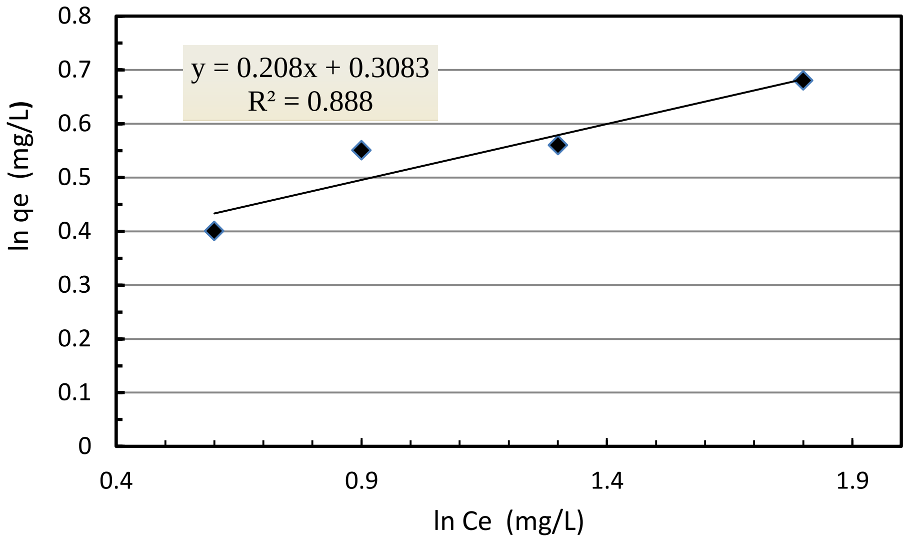

Figure 9: Freundlich isotherm for adsorption of Cr(VI) by olive leaves powder. (rpm=80, pH=4,contact time=90 min., Initial conc. Of Cr (VI)= 50 ppm, Particle size = 150 – 200 µm).

Langmuir and Freundlich equations' constants for all experimental runs are represented in table 2. The correlation coefficient (R^2) shows that the adsorption experimental data were correctly fitted by the Langmuir relation. These results are in agreement with that found by Yang *et al*. who showed that Langmuir isotherm well represent the absorption of Cr(VI) by *Sargassum sp*.(21).

Conclusion

The present study shows that the olive leaves powder is an effective adsorbent for the removal of hexavalent chromium ions Cr (VI) from aqueous solution. Experimental data show that the desorption capacity is dependent on operating variables such as pH, shaking speed ,adsorbent dosage, contact time, particle size, and initial metal ion concentration. The adsorption data fit well with Langmuir adsorption isotherm model. The best conditions of adsorption of Cr (VI) from aqueous by olive leaves powder, which gave maximum removal efficiency 91.5% , were pH = 4, contact time = 90 min., particle size range = 150 – 200 µm and initial concentration chromium concentration Cr (VI) = 50 ppm and adsorbent concentration 18 g/L.

Table 2: Isotherms parameters for adsorption of CR (VI) on olive leaves powder

Parameter	Langmuir isotherm			Freundlich isotherm		
Adsorbent Conc. (g/L)	q_{max} (mg/g)	b (L/mg)	R^2	n	k_f	R^2
3	0.1015	0.9854	0.9968	4.8071	1.3611	0.8881
9	0.1010	0.9421	0.9991	4.6012	1.2154	0.9084
12	0.289	1.1543	0.9971	4.8804	1.0988	0.8548
18	0.285	1.0134	0.9959	5.0151	2.3834	0.8685
pH	q_{max} (mg/g)	b (L/mg)	R^2	n	k_f	R^2
2	0.1506	1.0569	0.9934	4.9123	1.3876	0.7345
4	0.1476	1.1823	0.9894	5.8734	1.4679	0.85234
6	0.2349	1.0956	0.9934	5.0341	2.0945	0.8712
8	0.1945	1.0371	0.9911	4.9576	1.876	0.7756
Shaking speed rpm	q_{max} (mg/g)	b (L/mg)	R^2	n	k_f	R^2
100	0.2584	1.1932	0.9856	4.9834	1.3673	0.8871
150	0.2167	1.2098	0.8996	5.0134	1.7845	0.7483
200	0.1987	1.1698	0.9967	5.5943	1.4023	0.8165
250	0.1987	1.0982	0.9925	4.9743	1.4456	0.8456
300	0.2013	1.182	0.9451	3.9876	1.4654	0.8354
Contact time min.	q_{max} (mg/g)	b (L/mg)	R^2	n	k_f	R^2
20	0.3719	1.3864	0.7545	3.9875	2.0453	0.6345
30	0.4386	1.2956	0.8145	4.0923	2.1983	0.7845
60	0.1965	1.1402	0.9245	5.0453	1.3945	0.7934
90	0.1293	1.1938	0.9965	4.7453	1.4674	0.8295
100	0.1286	1.203	0.9919	4.6934	1.4953	0.8012
120	0.1246	1.104	0.9967	4.7034	1.4056	0.8234
Particle size µm	q_{max} (mg/g)	b (L/mg)	R^2	n	k_f	R^2
150 -200	0.1138	1.2768	0.9985	5.8765	1.4528	0.7623

200- 250	0.1275	1.1217	0.9938	5.0763	1.2650	0.6753
250 – 300	0.2187	1.2834	0.9976	4.8312	1.3245	0.7198
300 -400	0.1652	1.1765	0.9876	4.9872	1.2239	0.8765
Initial conc. Cr(VI) ppm	q_{max} (mg/g)	b (L/mg)	R^2	n	k_f	R^2
50	0.1157	1.298	0.9956	5.0967	2.1109	0.8019
100	0.1232	1.1232	0.9923	4.5612	1.9348	0.6543
200	0.1234	1.1296	0.9845	4.8723	1.4879	0.7458
400	0.1123	1.135	0.9894	4.845	1.6787	0.4387

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