

Original Research Article

Kinetic and Isotherm of Toxic Hexavalent Chromium Adsorption onto Natural Adsorbent

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ABSTRACT

Keywords

Natural
Adsorbent,
Hexavalent
Chromium,
Kinetic and
Isotherm

In this study the olive and egg shell used for removal of Cr (VI) ions from waste water has been investigated. The study involves investigating the effect of initial concentrations, adsorption dose, contact time and pH of solutions. The adsorption process has fit pseudo first order kinetic models. Langmuir, Freundlich adsorption isotherm were used. The maximum adsorption was found at 70 min, 0.05 gm adsorbed. Maximum adsorption capacity 82.56 and 299 for olive stone and egg shell.

Introduction

The pollution of heavy metal ions in the environment is a critical problem because of their toxicity and other adverse effects on the receiving waters and /or soils. They must be removed from wastewater before discharging them into water bodies. Water pollution by chromium is due to both, natural sources and manmade activities. Chromium is found in rocks, animals, plants, soils and in volcanic dusts and gases. Various industrial processes such as steel production, electroplating, leather tanning, nuclear power plants, textile industries, wood preservation, anodizing of aluminium, water-cooling and chromate preparation. Discharge chromium containing wastes with varied concentration between 5 and 220 mg/L

into the environment, which contaminates soil and water (Okuda, et al., 1975; Ouki, R. D. Neufeld, 2009; Altundogan, 2005). Chromite world mine production was estimated at a gross mass of 13×10^6 metric tons in 2002. In nature chromium exists in two most stable oxidation states, i.e., trivalent and hexavalent forms in aqueous systems. Although, at trace level, the trivalent form is considered as an essential nutrient (Rojas et al., 2005), hexavalent form of chromium is toxic, carcinogenic and mutagenic in nature (Zhitkovich et al., 2002; Myers et al., 2000; . Norseth, 1981; Dupont, E. Guimon, 2003; Cieslak., 1995). The hexavalent form is about 500 times more toxic than trivalent form (Kowalski, 1994). Furthermore, Cr (VI) is

highly mobile in soil and aquatic system, and also is a strong oxidant capable of being adsorbed by skin (Singh, D. R. Singh, 2002). Considering its toxicity and carcinogenic nature, the maximum levels permitted for trivalent chromium in wastewater 5 mg/L and for hexavalent chromium are 0.05 mg/L (Acar, E. Malkoe, 2004).

The most common methods of Cr (VI) ions removal from aqueous system are chemical precipitation, ion exchange, membrane processes, electro dialysis and adsorption (Tiravanti, et al., 1997; George, 1995; Dohi, et al., 1995). Hexavalent chromium usually exists in wastewater as oxyanions such as chromate CrO_4^{-2} and dichromate $\text{Cr}_2\text{O}_7^{-2}$ and does not precipitate easily using conventional precipitation methods. Ion exchange, reverse osmosis and electro dialysis are efficient for Cr (VI) ions removal but the cost is relatively high (George, 1995). Furthermore, chromium removal techniques such as co-precipitation, membrane techniques and solvent extraction are challenged by the removal of lower concentrations of metals from solution (Dohi, et al., 1995). On the other hand, adsorption has been proved to be one of the respective methods, which is simple, selective and economical process for the removal of heavy metal ions from aqueous solution.

The objectives of the present study are: 1) to study the effect of contact time of Cr^{6+} metal ions adsorption onto olive stone powder and egg husk powder; 2) to investigate the influence of pH on the adsorption of Cr^{6+} ; 3) to study the adsorption of Cr^{6+} at room temperatures to find the effect of adsorbent dose and effect PH and initial concentration on the adsorption of Cr^{6+} ; 5) to describe the

experimental data of adsorption isotherms through Langmuir and Freundlich models; 6) to investigate the adsorption properties of Cr^{6+} and to discuss its adsorption mechanism.

Materials and Methods

Preparation of char from coconut shell as Adsorbent

The olive used as an adsorbent for this research was collected from Saudi Arabia. The adsorbent was washed with distilled water to remove fines and dirt, dried in the sun, following the procedure of (Goel et al., 2005), The wet material was then dried at 110 °C for 24 h before characterization was done and used in the adsorption studies at ambient room temperature of 27 °C (± 2) after crushed and sieved to a particle size and filtering the sample with 0.5 mm membrane, and stored in discater to use in all experimental

Eggshell sample was collected from Saudi Arabia. To remove impurity and interference material such as organics and salts, the sample was rinsed several times with deionized water. Then, the sample was dried at 110°C for 24 h in the dry oven after filtering the sample with 0.5 mm membrane filters.

Adsorbate solution

The aqueous solutions (1000 mg/L) of Cr (VI) was prepared in distilled water using potassium dichromate $\text{k}_2\text{Cr}_2\text{O}_7$. The solutions of different dilutions (1–100 mg/L) required for the adsorption studies were prepared by dilution of the stock solutions.

Adsorption studies

For each experiment, the weight of the adsorbent in the adsorption studies was 0.05, 0.1, 0.5, 1 g of olive and egg husk per 150 ml of solution, depending on the time to reach equilibrium for each metal ions. concentrations of 1, 5, 10, 20, 50, 100 ppm of the actions of Cr (IV) were prepared from the following soluble salts: $K_2Cr_2O_7$, in distilled-deionized water, The pH was adjusted with hydrochloric acid (HCL 0.1 N) of analytical grade and did each metal Cr (IV) at pH 3,5,7,9 at 1ppm and 0.05g each above adsorbent.

After put in flask shaker at 200 r. p. m. and take sample 3 ml after 1,2,3,4,5,10,15,25,40, and 60 min after that filtered by using a Whatman® 0.45µm filter paper and measurement the concentration residue by atomic absorption.

Effect of sorbent dosage

The sorbent dosage was varied from 0.05,0.1,0.5 to 1.00 g using a fixed volume of 150 mL of 1 mg/L of metal Solution at the 0,1, 2, 3, 4, 5, 10, 15, 25,40,70 time for each metal.

Effect of PH

The effect of pH on metals adsorption was investigated in the initial pH range of 3,5,7,9. The initial pH of the solution was adjusted by using 0.1N HCl or 0.1N NaOH. All adsorbent (0.05 g) was added to 150mL of solution having 1 mg/L of Cr(VI) ions. After adsorption, the solutions were centrifuged and the concentrations of the solutions were determined.

Results and Discussion

Adsorption kinetics

Adsorption kinetics describe the solute uptake rate which intern control the residence time and hence the size of adsorption equipment. The experimental results for the adsorption of Cr^{6+} ions olive stone powder and egg husk powder showed rapid initial adsorption rate followed by a slower rate. Initially, the adsorption sites are open and the metal ions interact easily with the sites and hence a higher rate of adsorption is observed. Further, the driving force for adsorption (the concentration difference between the bulk solution and the solid-liquid interface) is higher initially and this leads to a higher adsorption rate. However, after the initial period, slow adsorption may be due to slower diffusion of solute into the interior of the adsorbent. Several adsorption kinetics models have been developed to understand the adsorption kinetics and rate limiting step (Vatix et al., 2005; Uzun, F. Guzel Tune, 2000; Ricordel Sep Puruf , 2001; Lagergrem Handlingar , 1898). The kinetics study for the adsorption of Cr^{6+} was conducted at optimum pH 3.0. The adsorption of Cr^{6+} was completed in 2 h for the concentration (1,5,10,50, and 100 mg/L) Cr^{6+} ions onto (0.05, 0.1, 0.5, and 1.0 g/150 mL) doses of olive stone and egg husk at 25°C.

The following models have been widely used (Ricordel Sep Puruf , 2001; Lagergrem Handlingar , 1898). Lagergren pseudo-first order model can express by Eqs. (1) and (2):

$$dq/dt = k_1(q_e - q) \quad (1)$$

$$\ln (q_e - q) = \ln q_e - k_1t \quad (2)$$

The pseudo-second order model is given by Eqs. (3) and (4):

$$dq/dt = k_2(q_e - q)^2 \quad (3)$$

$$t/q = t/q_e + 1/k_2q_e^2 \quad (4)$$

where q and q_e are the amount of Cr^{6+} metal adsorbed per unit weight of adsorbent (mg/g) at time t , and at equilibrium, respectively, and k_1 and k_2 are the adsorption rate constants.

The applicability of the above two models can be examined by each linear plot of $\ln (q_e - q)$ vs. t , and (t/q) vs. t , respectively and are represented in Figs. (1) and (2) of olive stone powder and egg husk powder. To quantify the applicability of each model, the correlation coefficient, R^2 , was calculated from these plots. The linearity of these plots indicates the applicability of the two models. However, the correlation, R^2 , showed that the pseudo-second order model, fits better the experimental data ($R^2 > 0.990$) than the pseudo-first order model (R^2 in the range of 0.888 – 0.964).

The kinetic parameters calculated are shown in Table (1). It has been found that, the equilibrium sorption capacities determined using pseudo-second order model were in agreement with the experimentally determined equilibrium sorption capacities. Also, the rate constant decreased with the solution concentration increasing.

In general, the adsorption reaction is known to proceed through the following three steps: (1) transfer of adsorbate from bulk solution to adsorbent surface, which is usually mentioned as diffusion, (2) migration of adsorbate into pores and (3) interaction of adsorbate with available sites on the interior surface of pores.

Effect of contact time

The effect of contact time on Cr (VI) ions adsorption on olive stone powder and egg husk powder was investigated to study the rate of Cr (VI) ions % removal Figs. (3, 5).

The experiment of adsorption was completed in 70 min at known initial concentrations (1, 5, 10, 50, and 100 mg/L) of Cr^{6+} ions, doses of (0.05g/150 mL) for all adsorbents. It is easily seen from the figures that the percentage removal of Cr (VI) metal ions increased with increasing the contact time. It is clear that, at the beginning % removal increased rapidly in few minutes, by increasing contact time, % removal increased lightly and slowly till reach maximum and that same in of qt in Figs. (4, 6) but adsorbed decrease with increase initial concentration value and this can be explained on the basis that, initially a large number of vacant surface sites may be available for adsorption of metal ions, and by time the surface sites become exhausted (Dorris, 2000). Increasing of contact time not only leads to increase the percentage removal of Cr^{6+} metal ions but also increase the amount of Cr^{6+} ions adsorbed per gram of adsorbent used (q_e) which is given by the following equation:

$$q_e = (C_i - C_e)/S \quad (5)$$

Figs. (3, 5) shows the relation between the amount of adsorbed Cr^{6+} ions per gram of adsorbent and contact time in the presence of different amounts of both adsorbents at 25°C. By increasing time of contact, (q_e) increases rapidly at first and by time slightly and slowly increases till reaches maximum value as explained above.

Effect of initial chromium(VI) ions concentration

The percentage removal of Cr^{6+} was studied by varying Cr^{6+} initial concentration from 1 to 100 mg/L with (0.05 g/150 mL) adsorbent doses of both adsorbents at pH (3.0), Figs. (7, 8). The results showed that, for all of palm kernel

olive stone, lupine seed, egg husk the percentage Cr^{6+} ions adsorption was decreased with increasing in initial concentration (Zeldowitsch, 1934; Sharma, C. F. Forster, 1994). But the actual amount of Cr^{6+} ions adsorbed per unit mass of the adsorbent q_e increased with increasing in Cr^{6+} ions initial concentration in the test solution, Figs. (9, 10). Compared between adsorbent at different concentration (egg husk powder and olive stone powder).

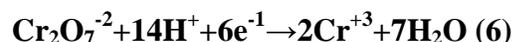
Effect of adsorbent dose

The percentage adsorption of Cr^{6+} ions onto olive stone and egg husk was studied at different adsorbent doses (0.05, 0.1, 0.5, and 1.0 g/150 mL), pH (3.0), temperature (25°C), contact time (70 min) and initial Cr^{6+} ions concentration of (1 mg/L), Figs. (11, 12). The results showed that with increasing in adsorbent dose, the percentage adsorption of Cr^{6+} increased and the maximum removal was observed with adsorbent dose 1.0 g/150 mL for both olive stone and egg husk. Increasing the percentage of adsorption with adsorbent dose may be due to the increase in adsorbent surface area and availability of more adsorption sites (Mohanty et al., 2006; Namasivayam et al., 1998). But unit adsorption was decreased with increasing in adsorbent dose, Figs. (11, 12). This is may be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles (Garg et al., 2007).

Effect of pH on the uptake of Cr^{6+}

The pH value of the solution is an important variable which controls the adsorption of the metal ions at the solid-water interface. Hence, the influence of pH on the adsorption of Cr^{6+} ions onto

olive stone and egg husk was examined in the pH range of (3-9). The experiment of adsorption as a function of pH was conducted at known initial concentration of 1 mg/L Cr^{6+} , dose of 0.05 g/150 mL for both olive stone and egg husk at 25°C. These results were represented in Figs. (13, 14), it showed that the adsorption capacities of Cr^{6+} ions onto both adsorbents increased significantly with decreasing pH value and the maximum removals of Cr^{6+} ions by both adsorbents for contact time (70 min) were carried out at pH (3.0). The improved removal of chromium(VI) at low Ph value is probably due to reduction of hexavalent chromium to trivalent chromium ions (Anon 1995), Eq. (6) :



Also at low pH, there is presence of a large number of H^+ ions, which in turn neutralize the negatively charged adsorbent surface, thereby reducing hindrance to the diffusion of dichromate ions (Sharma, C. F. Forster, 1934).

Adsorption isotherm

Several models have been used in the literature to describe the experimental data of adsorption isotherm. The Langmuir and Freundlich models (Zeldowitsch, 1934), are the most frequently employed to describe equilibrium for the adsorption of (1,5,10,50, and 100 mg/L) Cr^{6+} ions concentrations onto (0.05, 0.1, 0.5, and 1.0 g/150 mL) for olive stone powder and egg husk powder at 25°C. The Langmuir isotherm is based on the theoretical principle that only a single adsorption layer exists on an adsorbent and it represents the equilibrium distribution of metal ions between the solid and liquid phases. The basic assumption of the

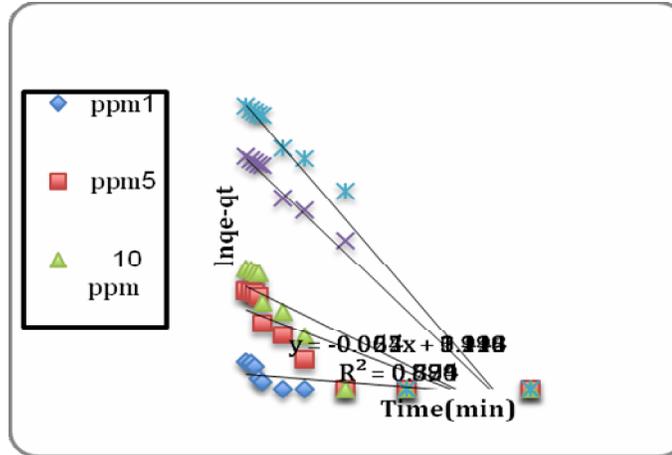


Fig.1a Pseudo- first order of olive by Cr^{+6}

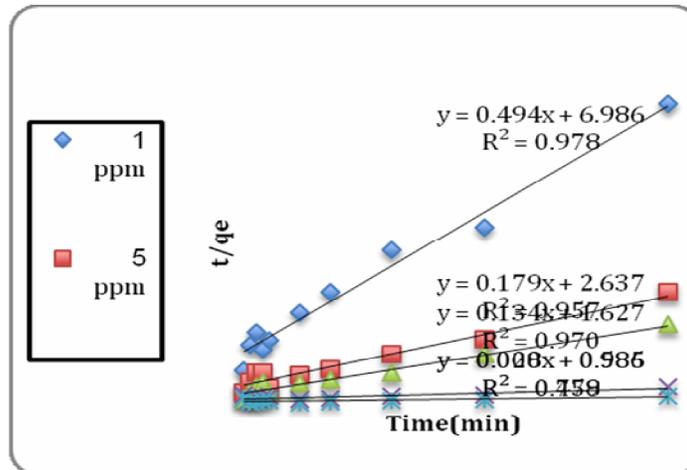


Fig.2a Pseudo- second order of olive by Cr^{+6}

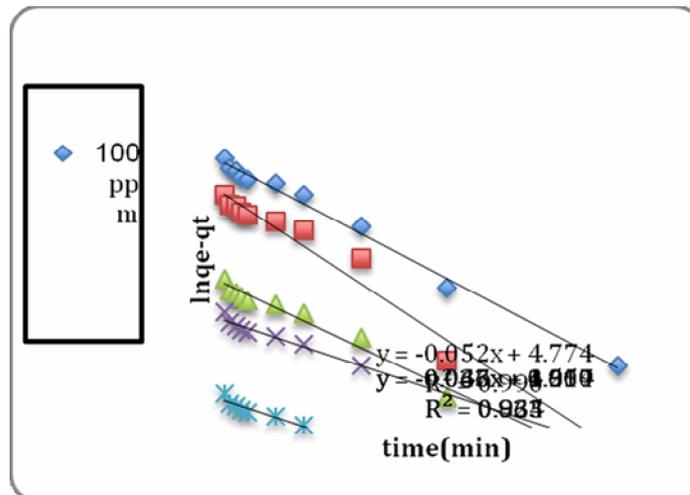


Fig.1b Pseudo- first order of egg husk by Cr^{+6}

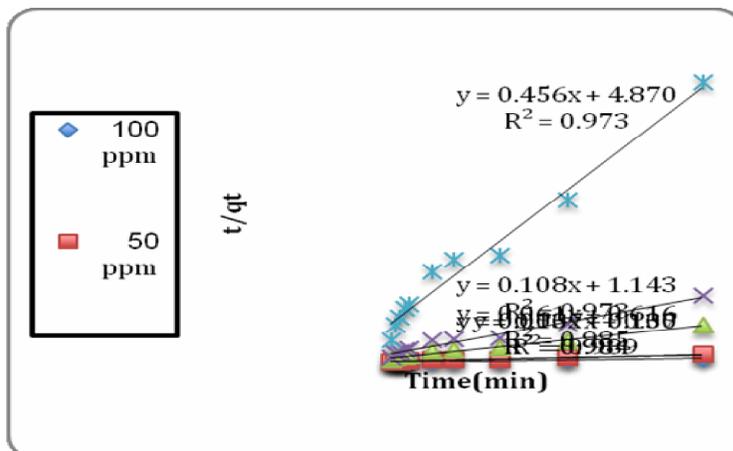


Fig.2b Pseudo- second order of egg husk by Cr⁺⁶

Adsorbent	C _i ppm	Pseudo-first order model					Pseudo-second order model			
		q _e (exp.) mg/g	K ₁ min ⁻¹	q _e (cal.) mg/g	R	±SD	K ₂ g/mg.min	q _e (cal.) mg/g	R	±SD
Olive stone	1	1.677	0.077	1.813	0.955	0.37	0.035	2.022	0.99	1.713
	5	4.47	0.09	4.93	0.972	0.36	0.012	5.56	0.98	0.893
	10	6.24	0.066	5.56	0.965	0.25	0.011	7.422	0.985	0.55
	50	26.07	0.093	34.76	0.95	0.43	0	48.64	0.872	0.273
	100	51.39	0.093	69.35	0.95	0.43	0.1	116.41	0.7	0.211
Egg shell	1	1.866	0.108	2.154	0.98	0.31	0.043	2.19	0.99	1.762
	5	7.84	0.114	9.14	0.98	0.34	0.01	9.21	0.99	0.422
	10	14.06	0.086	14.34	0.99	0.16	0.066	16.25	0.99	0.178
	50	63.33	0.131	97.92	0.98	0.34	0.001	73.8	0.99	0.04
	100	120.27	0.04	122.39	0.995	0.12	0.001	139.7	0.99	0.018

Table.1 Parameters obtained for the adsorption kinetics of Cr +6 ion for the olive stone powder and egg shell powder

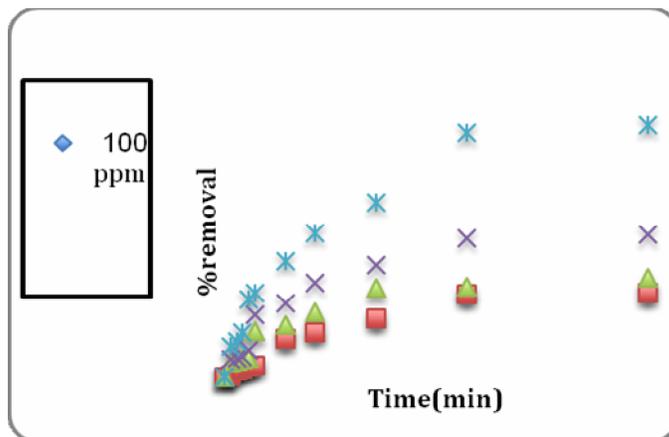


Fig. 3 % removal of chromium by 0.05 g olive in pH 3 at 200 r.p.m. with different concentrations 25° C.

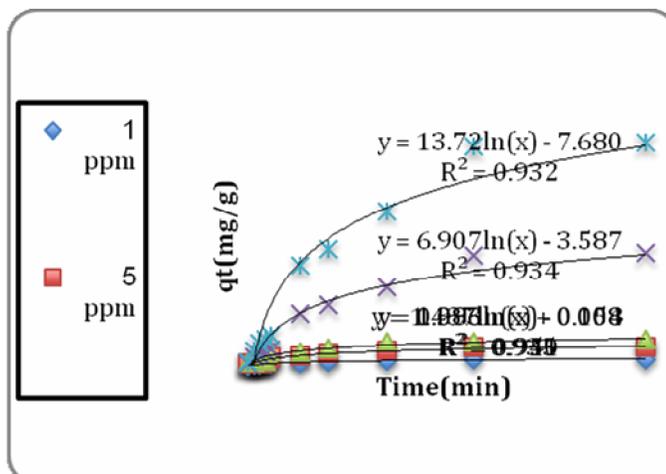


Fig.4 qt of chromium by 0.05 g olive in pH 3 at 200 r.p.m. with different concentrations 25° C

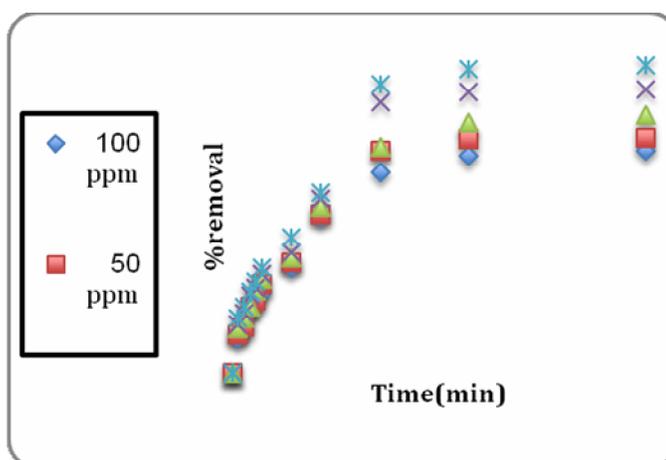


Fig.5 % removal of chromium (Cr^{+6}) by 0.05 g egg husk in pH 3 at 200 r.p.m. with different concentrations 25° C.

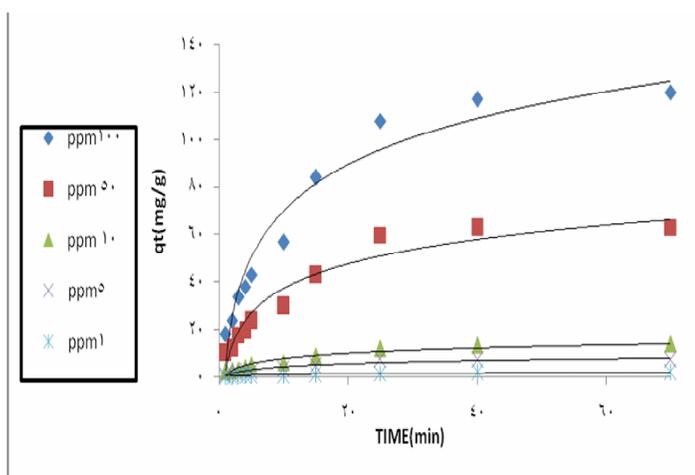


Fig.6 qt of chromium (Cr^{+6}) by 0.05 g egg husk in pH 3 at 200 r.p.m. with different concentrations 25°C

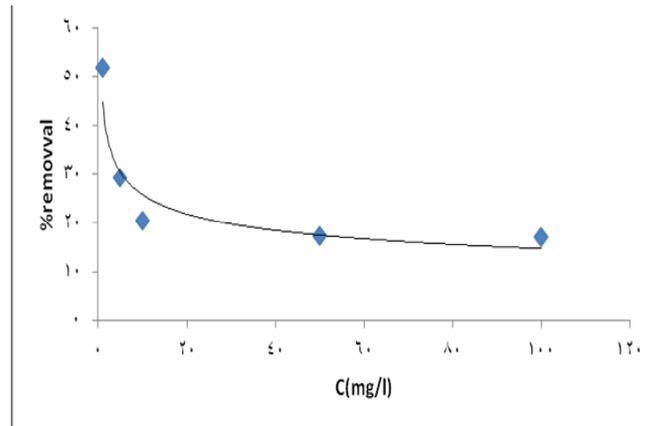


Fig.7 Effect of initial concentration on % removal using olive adsorbent.

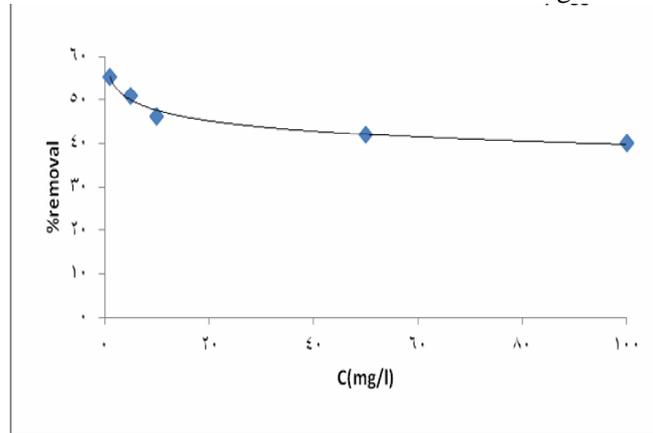


Fig.8 Effect of initial concentration on % removal using egg husk adsorbent

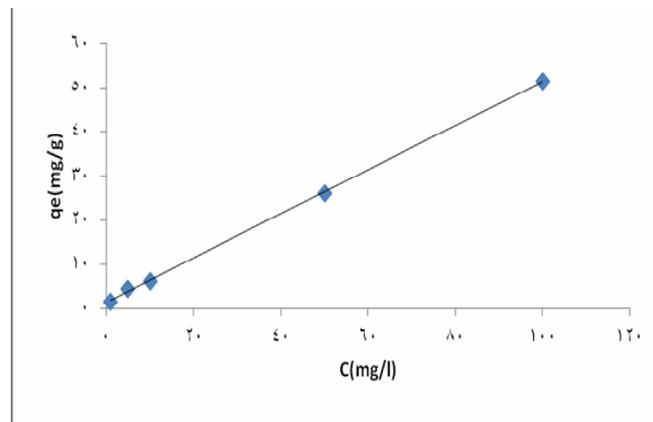


Fig.9 Effect of initial concentration on q_e using olive adsorbent.

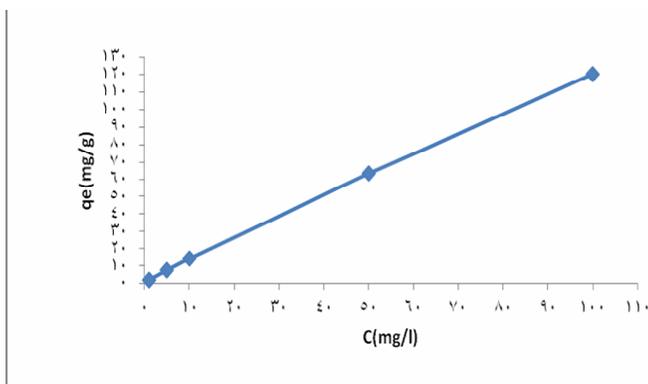


Fig.10 Effect of initial concentration on q_e using egg husk adsorbent

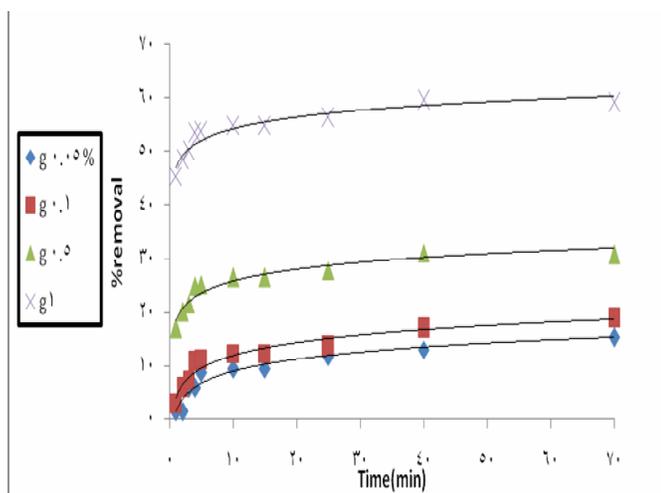


Fig.11 % removal of chromium (Cr^{+6}) adsorbed by 0.05 g olive in pH 7 at 200 r.p.m. with different dosage 25° C.

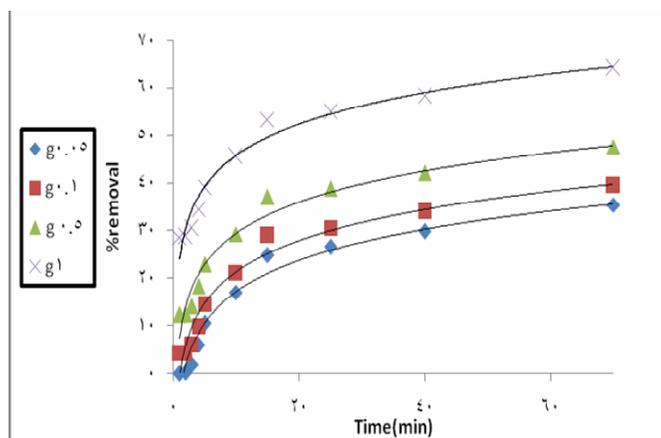


Fig.12 % removal of chromium (Cr^{+6}) adsorbed by 0.05 g egg husk in pH 7 at 200 r.p.m. with different dosage 25° C.

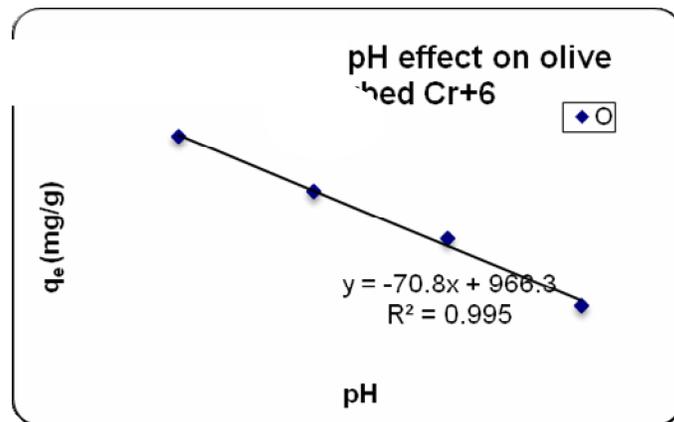


Fig.13a q_e of Effect different pH on olive by Cr^{+6}

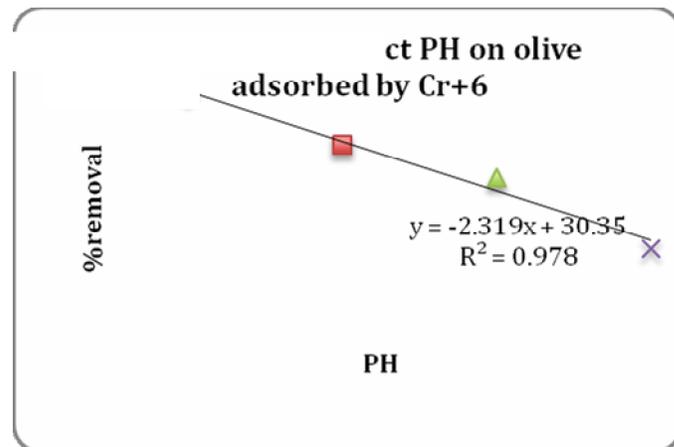


Fig.13b % removal of Effect PH on olive by Cr^{+6}

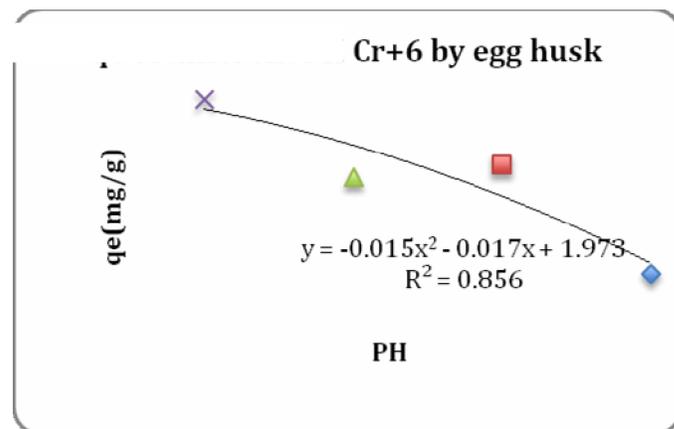


Fig.14 a q_e of Effect different pH on egg husk by Cr^{+6}

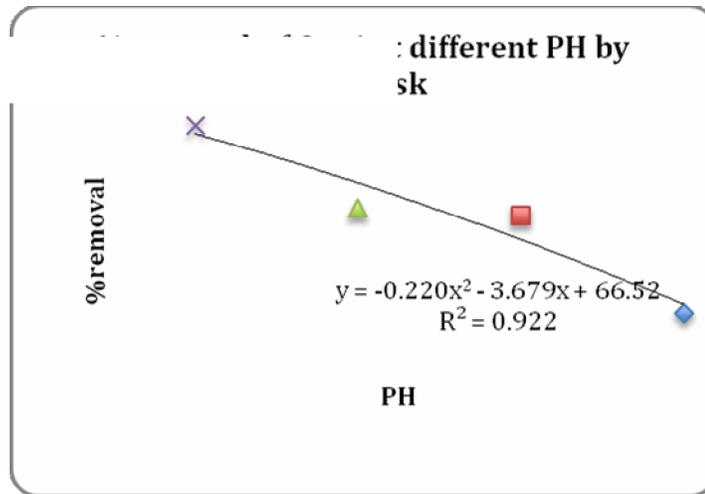


Fig.14 b % removal Effect different pH on egg husk adsorbed by Cr⁺⁶

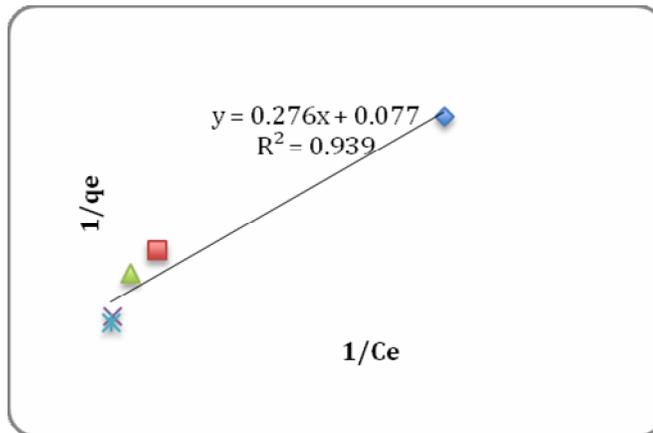


Fig.15 Langmuir adsorption isotherm in presence of Olive adsorbent.

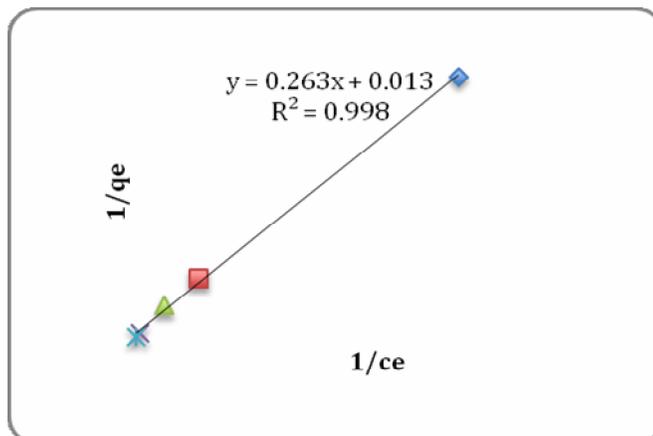


Fig.16 Langmuir adsorption isotherm in presence of egg husk adsorbent.

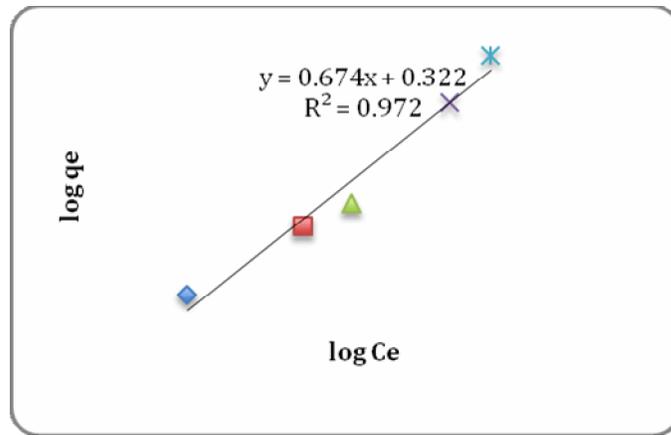


Fig.17 Freundlich adsorption isotherm in presence of olive adsorbent.

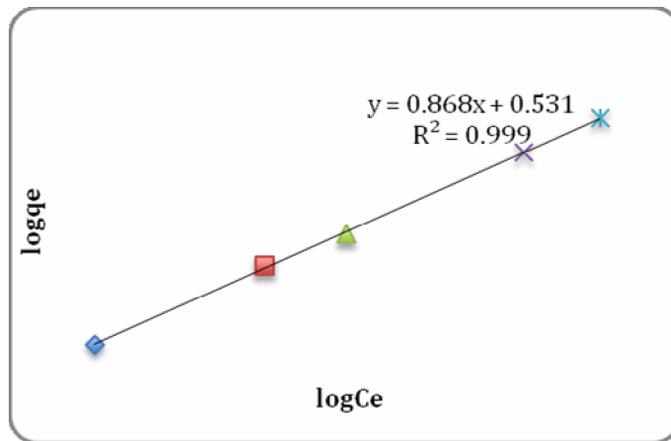


Fig.18 Freundlich adsorption isotherm in presence of egg husk adsorbent.

Freundlich parameter				Langmiurparameter				Adsorbent
± SD	R	1/n	K _f	± SD	R	b	q _m	
±0.115	0.986	0.675	2.1	±0.42	0.96	0.0152	82.51	Olive stone
±0.015	0.99	0.87	3.396	±0.049	0.9	0.0103	299.4	Egg shell

Table.2 Adsorption parameter for adsorption of Cr⁶⁺

Langmuir adsorption process is the formation of a monolayer of adsorbate on the outer surface of the adsorbent and after that no further adsorption takes place. The Langmuir-type isotherm remains to be the most widely used for practical application. The Langmuir isotherm for pure component adsorption can be obtained from Eq. (7):

$$C_e/q_e = 1/(q_{max}b) + (1/q_{max}) C_e \quad (7)$$

Where q_{max} is the maximum metal ions uptake per unit mass of adsorbent (mg/g), which is related to the adsorption capacity and b is Langmuir constant (L/mol) which is exponentially proportional to the heat of adsorption and related to the adsorption intensity, while q_e is the amount of the adsorbate adsorbed by a unit mass of adsorbent at equilibrium (mg/g adsorbent), C_e is the concentration of the adsorbate remaining in the solution at equilibrium (mg/L). Therefore, a plot of C_e/q_e versus C_e or $1/q_e$ versus $1/q_e$ gives a straight line of the slope $1/q_{max}$ and intercept $1/(q_{max} b)$ as shown in Figs. (15, 16).

Assuming an exponentially decaying function of site density with respect to heat of adsorption and obtained the classical empirical isotherm, Eq. (8):

$$\ln q_e = \ln K_F + 1/n \ln C_e \quad (8)$$

This is known as Freundlich isotherm. The Freundlich adsorption isotherm is an indicator of the extent of heterogeneity of the adsorbent surface, where the Freundlich constants K_F and n , which respectively indicating the adsorption capacity and the adsorption intensity, were calculated from the intercept and slope of the plot of $\ln q_e$ versus $\ln C_e$ as shown in Figs. (17, 18).

This Freundlich type behavior is indicative of surface heterogeneity of the adsorbents, i.e. the adsorptive sites (surface of olive

stone and egg husk) are made up of small heterogeneous adsorption patches that are homogeneous in themselves. The activation of adsorption sites takes place, leading to increased adsorption probably through the surface exchange mechanism.

The calculated results of Langmuir and Freundlich isotherm constants are given in Table (2) It can be seen that the Freundlich model yields a much better fit than the Langmuir model, when the correlation coefficient R^2 values are compared in Table (2) (R^2 values of Freundlich plot > 0.99 was close to unity, indicating isotherm data fitted well to Freundlich model). This suggests that the boundary layer thickness is increased. The Freundlich constant K_F indicates the sorption capacity of the sorbent. From Table (2), It is noted that the values of n are bigger than 1, reflecting the favourable adsorption. On the other hand, the q_{max} and the adsorption intensity values of (bentonite are higher than activated carbon. The calculated (b) values indicate the interaction forces between bentonite surface and Cr^{6+} ions are stronger than in case of activated carbon, this means that the bentonite is more powerful adsorbent than activated carbon. These results indicate that both adsorbents have a very strong adsorption capacity towards Cr^{6+} ions

References

- Acar, F. N. E. Malkoe, L. Bioresource Technology 94, 13, 2004
- Altundogan H. S., process Biochemistry, 40, 1443, 2005
- Anon. 1995. Standar Methods for Examination of Water and Waste Water 19th, Washington U.S.A. ,D C , American Public Health Association 6210 C

- Cieslak, M. Gelonka Polyhedon 15, 3667, 1995
- Dohi, S. M. Azzi and M. guardi, J. of Analytical Chemistry 363, 404, 1995
- Dorris, K. L. J. of Hazardous Material 80, 33, 2000
- Dupont, L. E. Guimon, Environmental Science and Technology 37, 4235, 2003
- Garg, U. K. M. P. Kaur, V. K. Garp and D. Sud, Hazard Mater 140, 60, 2007
- George C. C. (1995) Electroplating Waste Water Pollution Control Technology Noyes Publications Park Ridge 30-39
- Goel , J. K. Krishna, Rchiro and K. Vinod, J. Hazard Mater B 125, 211, 2005
- Kowalski, J Z.. of Hazardous Material 37, 137, 1994
- Lagergrem S. Handlingar 24, 1, 1898
- Mohanty K., M. Jha, B. C. Meikap and M. N. Biwas, Chemistry Engineering J. 117, 71, 2006
- Myers, C. R. J. M. Myers, B. P. Carsteen and W. E. Antholine, Toxic Substance Mechanisms 19, 25, 2000
- Namasivayam C., K. Kadirvelu and M. Kumuthu, Bioresource Technology 64, 77, 1998
- Norseth, T. Environmental Health Perspectives 40, 121, 1981
- Okuda, T. ISugano and T. Tsiyi, Futration and Separation 12, 475, 1975
- Ouki R. , S. K. R. D. Neufeld, J. of Chemical Technology and Brotechnology 70, 3, 2009
- Ricordel L S.. Sep Puruf Technology 24, 389, 2001
- Rojas G., J. Silva, J.A. Flores, A. Rodreguez and M. L'Maldonado 44, 31, 2005
- Sharma, D. C. C. F. Forster, Bioresource Technology 49, 31, 1994
- Singh, L. B. D. R. Singh, Environmental Technology 23, 85, 2002
- Tiravanti, D. G. Petrluzzelli and R. passin, Water Science and Technology 36, 197, 1997
- Uzun, F. Guzel Tune, J. chem.. 24, 291, 2000
- Vatix, M. W. H. Cheung and K. Zhang, J. of Hazardous Material 135, 395, 2006
- Zeldowitsch J. Acta Physiochem URSS 1, 364, 1934
- Zhitkovich, A. G, Quievryn, J. Messa and Z. Motylevich, Metal Toxicity 110, 729, 2002