Asian Journal of Chemistry; Vol. 24, No. 11 (2012), 4991-4994

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Adsorption of Chromium Ions from Aqueous Solution Using Mixed Sorbents Prepared from Olive Stone and Date Pit

H. AKSAS*, N. BABAKHOYA, H. BABACI, R. FEGGAS and K. LOUHAB

Laboratoire de Génie alimentaire, Faculty of Engineer Science, University of Boumerdes, Boumerdes 35000, Algeria

*Corresponding author: E-mall: aksas_ha@yahoo.fr

(*Received*: 9 September 2011; *Accepted*: 6 June 2012) AJC-11544

The aim of this study is to remove chromium ions from aqueous solutions by adsorption. Mixed sorbent prepared from olive stone and date pit, an agricultural solid by-product was used as adsorbent. The adsorption experiments of Cr onto the mixture of olive stone and date pit were conducted at different parameters such as, per cent of olive stone and date pit in the mixture, temperature, initial solution pH and initial chromium concentration. Adsorption isotherms were obtained at different per cent of olive stone and date pit in the mixture. This adsorption data was fitted with the Langmuir, Freundlich and Temkin isotherms. In addition, the thermodynamic parameters, standard free energy (ΔG°), standartd enthalpy (ΔH°) and standard entropy (ΔS°) of the adsorption process were calculated. The results show that the mixture sorbent from olive stone and date pit is an alternative low-cost adsorbent for removing chromium ions.

Key Words: Sorption, Chromium, Mixed sorbent, Olive stone, Date pit.

INTRODUCTION

Chromium is an important toxic material because it does not undergo biodegradation. This pollutant is introduced into natural waters by a variety of industrial wastewaters including those from textile, leather tanning, electroplating and metal finishing industries. When accumulated at high levels, chromium can generate serious problems and, when concentration reaches 0.1 mg/g body weight, it can ultimately become lethal[1]. Currently, the most common processes for elimination chromium are adsorption, reverse osmosis and chemical reactions that involve reduction and precipitation. Among them adsorption has been shown as a feasible alternative method for removing traces of chromium from wastewater. Although many different adsorbents were tried to remove chromium from wastewaters[2].

Adsorption is by far the most effective and widely used technique for the removal of toxic heavy metals from wastewater[3]. Owing to the high cost and difficult procurement of activated carbon, efforts are being directed towards finding efficient and low cost adsorbent materials. A variety of low cost materials like fly ash[4], wood charcoal[5], bituminous coal[6], bagasse and coconut jute[7], rice husk carbon[8], peat[9], red mud[10], Used black tea leaves[11], activated carbon from sugar industrial waste[12] and sugarcane bagasse[13] have been tried.

As shown recently, research efforts have been directed towards the use of agricultural waste as an adsorbent material in an attempt to minimize processing costs and with the protection of the environment and public health.

Nevertheless, most of the recent studies have been devoted to the preparation of activated carbon from different olive stone waste and date pit waste[14]. Although the obtained activated carbon by olive stone waste and date pit waste has been reported to be a suitable sorbent material, the cost of the treatment to get the activated carbon makes this sorbent not competitive from the economical point of view[15]. Then, it would be very interesting to be find out an application to reuse the mixture of olive stone waste and date pits in their native form. In this paper, experiments have been carried out to study the sorption of chromium ion from aqueous solution using the mixture of olive stone waste and date pits waste. The factors studied include the influence of initial chromium ion concentration, percentage of olive stone waste and date pits waste in the mixture, temperature and initial solution pH on the sorption capacity. A Langmuir, Freundlich and Temkin models was developed and used to analyze the data for the sorption of chromium ions by mixture of olive stone waste and date pits.

EXPERIMENTAL

Date pits from southern Algeria and olive stones from northern Algeria were used as a starting material. They were thoroughly washed with distilled water to remove all dirt and then oven dried at 105 ºC. The dried olive stones and date pits were then mix while crushing, milled and sieved into different particle sizes. Studies were focused on a size fraction of 0.5-1.0 mm.

In order to obtain a homogenous sample of olive stone waste and date pits waste, we crush various percentages of mixture of olive stone waste and date pits (Table-1).

TABLE-1
DIFFERENT PERCENTAGE OF OLIVE STONE AND DATE PITS IN MIXTURE

Sample number	Per cent of date pits in mixture	Per cent of olive stones in mixture
1	0	100
2	100	0
4	88	12
5	80	20

The mixture of olive stones and date pits powder was impregnated with H_3PO_4 (2 g of acid per gram of mixture). The mixture was refluxed at 100 ºC during 3 h to eliminate the excess of H_3PO_4. The prepared mixture has been washed with distilled water until a neutral pH was reached. The sample was dried at 105 ºC in an oven.

Removal of chromium ion: Metal solution was prepared by dissolving appropriate amount of $K_2Cr_2O_7$ (s), in distilled water. A volume of 15 mL of $K_2Cr_2O_7$ solution with a concentration ranging from 356.0-1246.5 mg/L was placed in a 250 mL conical flask; 0.2 g of the mixture of olive stone and date pits powder was accurately weighed and added to the solution. The conical flask was then shaken at a constant speed of 350 rpm at pH 5.6 at 25 ºC. Effect of temperature on the sorption of chromium was studied using three different temperatures 10, 25 and 45 ºC with different composition of the mixture of olive stone and date pits powder. The effect of pH was observed by varying the pH of the metal solution *i.e.*, 1, 3, 5, 7 and 9 where the pH of solution was achieved at the desired value using 0.1 N HCl or 1 N NaOH. The solution was filtered and the chromium concentration of the filtrate was analyzed using SAA atomic absorption spectrophotometer. The amount of chromium sorbet by weight of dry mixture wastes was calculated as $q_t = (C_i - C_t)V/m$, where V(L) is the solution volume, C_i and C_t (mg L^{-1}) are the initial and at time t metal solution concentration, respectively and m is the dry weight of the sorbent (mixture).

RESULTS AND DISCUSSION

Equilibrium isotherm models: The nature of the adsorption reaction can be described by relating the adsorption capacity (mass of solute adsorbed per unit mass of adsorbent) to the equilibrium concentration of the solute remaining in the solution, such a relation is known as an adsorption isotherm. There are many basic isotherm models, which include: Langmuir, Freundlich and Temkin.

Temkin isotherm[16]: Temkin isotherm assumes that decrease in the heat of adsorption is linear and the adsorption is characterized by a uniform distribution of binding energies. Temkin isotherm is expressed by the following equation:

$$q_e = \left(\frac{RT}{b_T}\right) \ln(a_T C_e) \qquad (1)$$

Eqn. 1 can be rearranged to obtain eqn. 2:

$$q_e = \frac{(RT \ln a_T)}{b_T} + \left(\frac{RT}{b_T}\right) \ln(Ce) \qquad (2)$$

The plot of q_e and ln (C_e) of eqn. 2 should give a linear relationship from which b_T and a_T can be determined from the slope and intercept, respectively (Fig. 1).

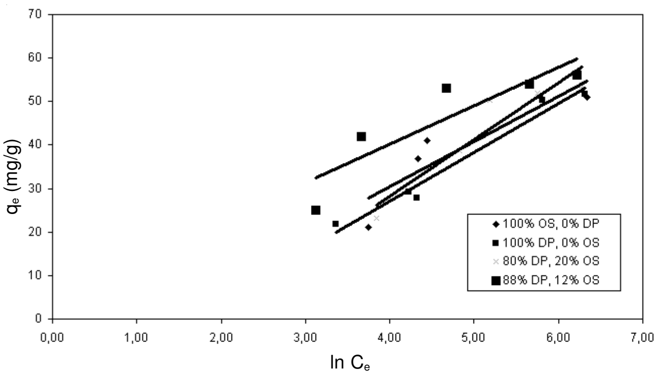

Fig. 1. Temkin transformations of equilibrium sorption isotherms

The Temkin constants a_T and b_T were appears in Table-2 and the Temkin model is unable to describe the data, as low correlation coefficients values were observed.

Freundlich isotherm: The Freundlich isotherm is originally empirical in nature, but was later interpreted as sorption to heterogeneous surfaces or surfaces supporting sites of varied affinities and has been used widely to fit experimental data.

This equation has the following form

$$q_e = K_F C_e^{1/n} \qquad (3)$$

The value of n, of this model, falling in the range of 1-10, indicates favourable adsorption[17]. In present study, we note that the values of n belong with this interval at different composition of the mixture of olive stone and date pits wastes, this indicate showing favourable sorption of chromium onto the mixture of olive stone waste and date pit waste.

TABLE-2
ISOTHERM CONSTANTS FOR CHROME SORPTION ONTO THE MIXTURE OF OLIVE STONE WASTE AND DATE PIT WASTE

Composition of the mixture OS: olive stone DP: date pit	Langmuir parameters				Temkin parameters			Freundlich parameters	
	q_{max} (mg/g)	B	R^2	R_L	a_T (L/g)	b_T (j/mol)	R^2	K_F	1/n
0 % DP, 100 % OS	56.50	0.011	0.9971	0.0802	10.292	2.36	0.8245	14.85	0.20
100 % DP, 0 % OS	56.18	0.017	0.9988	0.0543	11.229	2.88	0.9724	10.00	0.28
80 % DP, 20 % OS	78.34	0.031	0.9908	0.0315	12.984	3.16	0.887	6.85	0.35
88 % DP, 12 % OS	80.92	0.18	0.9988	0.0054	8.8342	1.57	0.7902	14.77	0.23

Langmuir isotherm: Basic assumption of Langmuir isotherm[18] is that adsorption takes place at specific homogeneous sites within the adsorbent. Langmuir isotherm can be represented as:

$$q_e = \frac{bC_e q_m}{1+bC_e} \tag{4}$$

The constants q_m and b are the characteristics of the Langmuir equation and can be determined from q linearized from of eqn. 1, represented by:

$$\frac{1}{q_e} = \frac{1}{b} C_e q_{max} + \frac{1}{q_{max}} \tag{5}$$

where C_e is the metal concentration in solution at equilibrium (mg L^{-1}), q_e is the amount of chromium sorbed per unit weight of sorbent at equilibrium (mg g^{-1}), q_{max} is q_e for a complete monolayer (mg/g); b is sorption equilibrium constant (L/mg); q_{max} and b can be determined from the plot $1/q_e$ *versus* $1/C_e$ (Fig. 2).

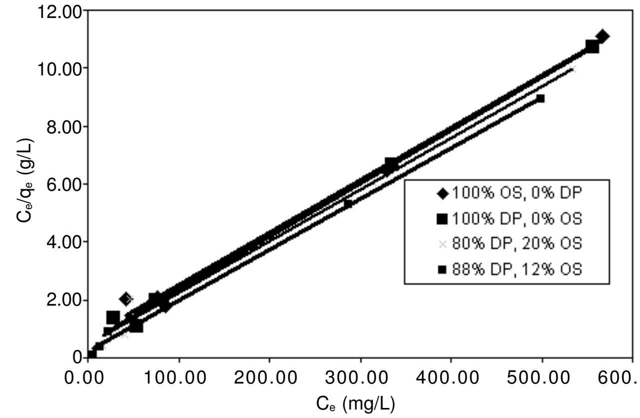

Fig. 2. Langmuir transformations of equilibrium sorption isotherms

The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter[19], it can be represented by:

$$R_L = \frac{1}{(1+bC_0)} \tag{6}$$

The value of R_L indicates the shape of the isotherms to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

R_L value ranging between 0 and 1 for the various percentages of mixtures of olive stone waste and date pit waste in the mixture. R_L value obtained using eqn. 6 for chromium sorption is greater than zero and less than unity showing favourable sorption of chromium onto the mixture of olive stone waste and date pit waste. Maximum theoretical uptake upon complete saturation of the surface of the mixture of olive stone waste and date pit waste was obtained to be 56.18 and 78.34 mg/g while per cent of olive stone waste and date pit waste in the mixture is (100 % of date pit, 0 % of olive stone) and (80 % of date pit, 20 % of olive stone), respectively.

Effect of initial pH: The effect of pH on the adsorption of Cr(VI) by the mixed sorbent (the mixture of olive stone and date pits powder) is presented in Fig. 3. The pH of the aqueous solution was clearly an important parameter that controlled the adsorption process. Adsorption of hexavalent Cr(VI) varies as a function of pH, with H_2CrO_4, $HCrO_4^-$ $Cr_2O_7^{2-}$ and CrO_4^{2-} ions present as dominant species[20], At pH 4-5, $HCrO_4^-$ was the predominant species. The surface charge of the mixture of olive stone and date pits powder should be positive at pH 4-5 and this should promote the binding of the negatively charged $HCrO_4^-$ ions. Increasing the pH will shift the concentration of $HCrO_4^-$ to other forms (CrO_4^{2-} and $Cr_2O_7^{2-}$). It can be concluded that the active form of Cr(VI) that can be adsorbed by the mixture of olive stone and date pits powder in this study is $HCrO_4^-$. After pH 7 value, for both adsorbents (different mixture), the adsorption increased highly up to pH 9. Optimum uptake of 53.42 mg g^{-1} by the mixed sorbent (88 % of date pit and 12 % of olive stone).

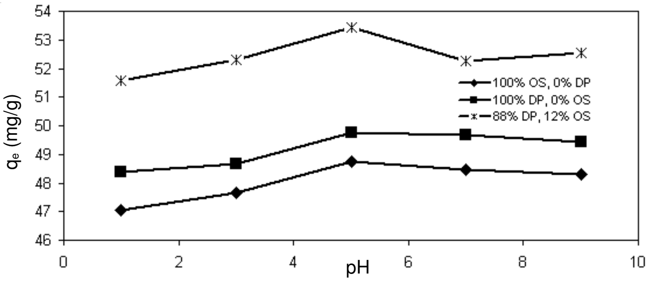

Fig. 3. Effect of pH on Cr removal (adsorbent dose = 0.2 g/15 mL, agitation speed = 350 rpm, temp. = 25 ºC, contact time = 2 h

Effect of composition of mixed sorbent: The equilibrium sorption capacity data, q_e, obtained from the study have been analyzed using Langmuir model. The correlation coefficients, R^2, maximum sorption capacity q_{max}, were calculated and presented in Table-2. The results show that the sorption capacity for chromium increases from 56.18 to 80.92 mg g^{-1} when the mixed sorbent varies from 100 % of date pits (pits date only) to 88 % of date pits in mixture. This indicates that with a mixture of sorbent, more surface area is made available and therefore the total number of sites increases[21].

Thermodynamic study: The thermodynamic parameters including change in the Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were determined by using following equations and represented in Table-3:

$$K_c = \frac{C_{qe}}{C_S} \tag{7}$$

$$\Delta G^\circ = -RT \ln K_c \tag{8}$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{9}$$

where R is the gas constant, K_c is the equilibrium constant, C_{qe} the amount of Cr adsorbed on the adsorbent from the solution at equilibrium (mg/L) and C_S is the equilibrium concentration of Cr in the solution (mg/L).

The q_e of the Languimir model was used to obtain C_{qe} and C_S. It was given the plot of ln K *versus* 1/T to eqn. 9 and Fig. 4. ΔH° and ΔS° was calculated from this plot (Van't Hoff plots).The results are given in Table-3.

TABLE-3
VALUE OF THE THERMODYNAMIC OF ADSORPTION AT VARIOUS TEMPERATURES AND AT DIFFERENT COMPOSITION OF MIXTURE (C_0 (Cr) =1007 mg L^{-1}; pH = 5.5)

Composition of the mixture OS: olive stone; DP: date pit waste	T (K)	K_c	ΔG° (Kj/mol)	ΔH° (KJ/mol)	ΔS° (Kj/mol K)
100 % OS + 0 % DP	283	0.0170	-9.63	18.230	0.0980
	298	0.0110	-9.82		
	318	0.0190	-11.83		
100 % DP + 0 % OS	283	0.0220	-9.55	18.230	0.0980
	298	0.0170	-9.48		
	318	0.0120	-11.76		
88 % DP + 12 % OS	283	0.5900	-1.31	88.290	0.9632
	298	0.1800	-4.47		
	318	0.0100	-10.38		
80 % DP + 20 % OS	283	0.0091	-7.990	31.912	0.1380
	298	0.0310	-9.220		
	318	0.0400	-11.058		

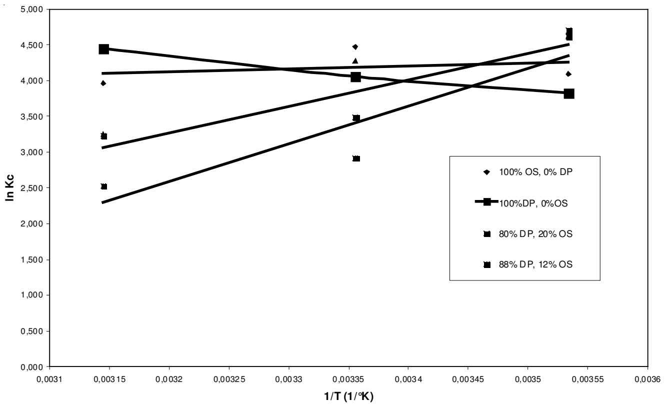

Fig. 4. Relation between equilibrium constant (K_c) and temperature (C_0 (Cr) = 1007 mg L^{-1}, pH = 5.6)

Generally, the change of free energy for physisorption is between -20 and 0 kJ/mol, however, chemisorption is a range of -80 to -400 kJ/mol[22]. The overall free energy change during the adsorption process was negative for the experimental range of temperatures at different composition of the mixed sorbent (mixture of olive stone waste and date pit waste) (Table- 3), corresponding to a spontaneous physical process of Cr adsorption. It is observed that: in the mixture, more we increase the percentage of olive stone more energy increases for various temperatures. This suggests that the adsorption was more spontaneous with a high preference of Cr on mixed sorbent when we add slowly a small amount of olive stone at date pits (100 % of date pits in mixture and 0 % of olive stone) and (20 % of olive stone and 80 % of date pits in mixture). The value of ΔH° is positive, indicating that the sorption reaction is endothermic[23]. The positive value of ΔS° reflects the affinity of the mixed sorbent for chromium ions and suggests some structural changes in chromium and mixed sorbent. In addition, positive value of ΔS° shows the increasing randomness at the solid/liquid interface during the sorption of chromium ions on mixed sorbent.

Conclusion

The equilibrium sorption capacity of Cr onto the mixture of olive stones and dates pit is studied on the basis of Langmuir, Freundlich and Temkin isotherms. The thermodynamic of chromium sorption on the mixed sorbent follows the Langmuir model. The sorption capacity for chromium increases when we add a small amount of olive stone at date pits (and a small amount of date pits at olive stone (Cr) onto the mixture of olive stones and dates pit is spontaneous and presents an endothermic nature.

REFERENCES

1. R.M. Schneider, C.F. Cavalin, M.A.S.D. Barros and C.R.G. Tavares, *Chem. Eng. J.*, **132**, 355 (2007).
2. O.D. Cooney, Adsorption Design for Waste-water Treatment II, Lewis Publishers (1999).
3. A.M. Youssef, Th. El-Nabarawy and S.E. Samra, *Colloids Surf. A*, **235**, 153 (2004).
4. M. Grover and M.S. Narayanswamy, *J. Environ. Eng.*, **63**, 36 (1982).
5. E. Pehlivan, H. Kahraman and E. Pehlivan, *Fuel Process. Technol.*, **92**, 65 (2011).
6. E.N. El-Qada, S.J. Allen and G.M. Walker, *Chem. Eng. J.*, **124**, 103 (2006).
7. A. Kh. Nassim, I. Shaliza and S. Piarapakaran, *Malaysian J. Sci.*, **23**, 43 (2004).
8. K. Srinivasan, N. Balasubramaniam and T.V. Ramakrishna, *Indian J. Environ. Health*, **30**, 376 (1988).
9. P.A. Brown and S.J. Allen, *Water Res.*, **34**, 3907 (2000).
10. V.K. Gupta, M. Gupta and S. Sharma, *Water Res.*, **35**, 1125 (2001).
11. M.A. Hossain, M. Kumita, Y. Michigami and S. Mori, *J. Chem. Eng. (Japan)*, **38**, 402 (2005).
12. N.F. Fahim, B.N. Barsoum, A.E. Eid and M.S. Khalil, *J. Hazard. Mater.*, **136**, 303 (2006).
13. S. Tandon and N. Nandini, *Asian J. Chem.*, **23**, 636 (2012).
14. F. Aioueche, H. Lounici, D. Belhocine, H. Grib, D.L. Piron and N. Mameri, *Can. Environ. Technol.*, **21**, 1215 (2000).
15. N. Fiol, I. Villaescusa, M. Martinez, N. Miralles, J. Poch and J. Serarols, *Sep. Purif. Technol.*, **50**, 132 (2006).
16. M.J. Temkin and V. Pyzhev, *Acta Physiochim. USSR*, **12**, 217 (1940).
17. Z. Aksu, *Process Biochem.*, **38**, 89 (2002).
18. I. Langmuir, *J. Am. Chem. Soc.*, **38**, 2221 (1916).
19. K.R. Hall, L.C. Eagleton, A. Acrivos and T. Vermeulen, *Ind. Eng. Chem. Fundam.*, **5**, 212 (1966).
20. I. Gaballah and G. Kibertus, *J. Geochem. Explor.*, **62**, 241 (1998).
21. Y.S. Ho and C.C. Chiang, *Adsorption*, **7**, 139 (2002).
22. P.W. Atkins, Physical Chemistry, Oxford University Press, London, edn. 4, pp. 884-890 (1990).
23. Y.-S. Ho and A.E. Ofonmaja, *Process Biochem.*, **40**, 3455 (2005).