Available online at: www.basra-science- journal.org

ISSN –1817 –2695

Granite as an Adsorption Surface for the Removal of Bromo Phenol red , Bromo Cresol Green and Leishman's stain from Aqueous Solutions

L. H. Kadhim
University of Kufa , College of Education For Women, Dept. of Chemistry
Lekaa_ab07@yahoo.com
Received 19-2-2012,Accepted 1-7-2012

Abstract

Adsorption of dyes from aqueous solution on the surface of granite was accomplished under the optimized conditions of temperature ,initial concentration ,pH , contact time and weight surface. Spectroscopic technique was used for the measurement of dyes before and after adsorption. The applicability of Langmuir and Freundlich adsorption isotherm equation for the present system was also tested. Thermodynamic parameters such as change in the free energy (ΔG),the enthalpy(ΔH),the entropy (ΔS) and activation energy (Ea)were favourable ,endothermic and spontaneous . Kinetics of adsorption was studied by using Lagergreen's equation at optimum pH and the adsorption rate constant k_{ad} was calculated. The data showed that the pseudo –first -order model was best fit model.
Key words : dyes , Granite , Adsorption , Isotherms . adsorption, Kinetic

1. Introduction

The presence of very low concentrations of these effluents is highly visible and undesirable and potentially inhibiting photosynthesis. The main pollution source of colored effluents comes from textiles, leather, printing, laundry, tannery, rubber, painting, etc., processes[1].Untreated disposal of this colored water into receiving water body causes damage to aquatic life and also severe damage to the human health[2-4]. The dying effluents discharged from textile industries is one of the largest contributors to textile effluent and is comprised mainly of residual dyes and auxiliary chemicals[5].

Various physical, chemical and biological treatment techniques can be employed to remove dyes from wastewater. Many synthetic dyes do not easily decompose in biological treatments due to their toxic effects on microorganisms, adsorption is suitable under field condition due to the flexibility, easy operation and no/lesser sludge disposal problems, high efficiency and for treating a large volume of effluent especially in removing dyes from dilute solutions[6-12]. It is considered to be a potential technique for the treatment of wastewater and reclamation of water containing dyes. Most conventional adsorption plants use activated carbon[13]. However , activated carbon is costly and has regeneration problems . Recent investigations have focused on the use of low. Cost materials for the adsorption of dyes including fly ask [14] wood chips[15] , cotton[16], and diatomaceous silica[17], are rapidly gaining importance as treatment processes . However , Granite mining and process industry are one of the most promising business areas of the mining sector[18]. Regarding the adsorption of dyes using clay minerals , Kaolinite , bentonite , sepiolites and Granite have been described as adsorbents [19-21]. The relation between the amount of the adsorbate on a certain surface and the concentration of its at a constant temperature called adsorption isotherm[22] , the Giles model which is classify the adsorption isotherms into four types (S,L,H and C) [23], therefore , the objective of this work is to study the possibility to incorporate granite powder wastes with no major sacrifice of the properties of final product .

The Granite generated from sawmills or ornamental rocks comes as a great problem and it lacks undeletable solution . This problem involves the preservation of the environment and constitutes one of the subjects more critical the point of view of social beneficiation of the population[24].

2. Experimental part

2.1. Materials and Methods

2.1.1. Materials

Bromo-cresol green ,Br-phenol red and lishman's stain were supplied by B.D.H,Fluka Granite used in this work was obtained from the general company for geological survey and mining , Baghdad , Iraq[17]. The chemical analysis of granite is listed in Table. 1

Table .1: The Chemical analysis of Granite.

Constituent	Wt%
SiO_2	52.40
Al_2O_3	14.54
Fe_2O_3	12.49
MnO	0.17
MgO	2.91
CaO	7.51
Na_2O	3.08
K_2O	1.69
TiO_2	3.17
P_2O_5	0.50

2.2. preparation of dyes solutions

Standard stock solution of 200ppm of dyes was prepared by dissolving 0.02g of dyes in a minimum amount of distilled water in a 100ml volumetric flask and volume were made up to the mark with distilled water. The Solution of different concentration were prepared by serial dilutions for dyes between 2-20ppm. Absorbance Values of these solutions were measured at the selected λ_{max} values Table .2. The calibration curves in the concentration range that falls in the region of applicability of Beer-Lambert's law were employed.

Table. 2 : λ_{max} values of dyes on granite

Dyes	λ_{max}/nm	
	Observed	Literature
Bromo cresol green	425	423
Bromo phenol red	560	557
lishman's stain	648	642

2.3. Preparation of clay powder

The clay was washed with excessive amounts of distilled water , it was suspended in HCl solution pH=3 to remove carbonate then washed with an excess amount of distilled water to remove the soluble materials[25]. It was dried at 150°C for three hours. The clay was ground and sieved to a particle size of 600µm.

2.4. Methods

To determine the equilibrium time that is needed for the adsorption system to reach equilibrium at a given temperature , the 0.2gm of granite was added to from 15ml of dye 20ppm in glass bottle and shaked .The absorbance was measured at different time intervals, until the septum reached the equilibrium. The initial concentration were determined .

The quantities of dyes adsorbed were calculated according to the following equation [26] .

$Q_e = (C_o – C_e)\ V/ m$

Q_e : the amount of dyes adsorbed (mg/g)

C_o and C_e : the initial and equilibrium concentrations (ppm) of the adsorbate in solution , respectively,

V : the volume of solution (L) ; (m) the mass of adsorbent(g)

3. Result and Discussion

3.1. Effect of contact time

The nature of the adsorption of dyes on granite as a function of time at a fixed initial concentration 20ppm was studied Fig. 1, for each dyes at different times between 15,30,45,60,75,90,105,120,135,150,165 and 180min.From the experimental data, it was observed that the amount of adsorption increasing ,with time and optimum contact times were 60,75 min of Bromophenol red , Bromocresol Green and Leishman's stain respectively .The amount of adsorbed dyes was ranged between 0.766-1.112 mg/g .

Adsorption Isotherms

The adsorption isotherms for all the dyes in aqueous solution on granite , when the system at equilibrium , are shown in the Fig.2 . All the adsorption isotherms were found regularly positive and converge . The isotherm showed a sharp rise in the initial stages and then became parallel to the concentration axis , indicating that the saturate values have been reached.The contact time up to 60,75min of Bromophenol red , Bromocresol Green and Leishman's stain for adsorption respectively.

3.2. Adsorption Model

The Langmiur and Freundlich models were used to quantify the adsorption of dyes from aqueous solution onto the granite . Freundlich proposed the following model [27]

$Q_e = K[C_e]^{1/n}$

A more convenient form of the above equation is[28]

$\log Q_e = \log k + 1/n \log C_e$

Where k and n are Freundlich constants ,Q_e is the amount adsorbed in (mg.g^{-1}) and C_e is the concentration of solute in the solution(mg/l) . Thus , a plot of log Q_e Vs log C_e will yield a straight line Fig.3 , the slope 1/n and intercept of log k.

According to Langmuir model[29]

$C_e/q_e = 1/K_Lq_m + C_e/q_m$

Where q_e (mg g^{-1}) is the amount adsorbed per unit mass of adsorbent corresponding to complete coverage of sites , C_e (mgL^{-1}) is the equilibrium concentration of dye in solution , q_m (mg g^{-1}) is the monolayer adsorption capacity of the adsorbent and the Langmuir constant K_L .A linear plot of C_e/q_e Vs C_e shows the applicability of Langmuir isotherm Fig. 4. The correlation coefficient obtained with both kinds of regressions are shown in table 3. Based on these parameters the date seems to be best fitted to the Freundlich model rather than the Langmuir model , the reverse situation was also reported[30-31]

3.3. Effect of temperature

The temperature dependence of dyes onto granite sand was studied over the range of 30,40 and 50°C. The considerable decrease in the amounts of dyes adsorbed with temperature confirms the exothermic nature of the process any adsorption only , into surface. The enhancement of adsorption capacity of granite , with temperature is attributed to the possible decrease in the temperature of active sites a available for adsorption on the surface [32] in the shown is (Fig. 5-7) .

Thermodynamic parameters such as change in free energy (ΔG) $KJ.mo^{-1}$, enthalpy (ΔH)K_J. $mo^{-1}$and entropy (ΔS) $K_J.mo^{-1}$ were determined using the following equations [33-34]

$K_C = C_{Ae}/C_e$

$\Delta G = -RT \ln K_C$

$\text{Log } K_C = -\Delta S/2.303R + \Delta H/2.303RT$

Where K_C is the equilibrium constant , C_{Ae} is the concentration at equilibrium (mg/l), C_e is the concentration in solution (mg/l) , R is gas constant. The values of ΔH and ΔS are determined from the slope and the intercept of the plots of log K_C versus 1/T in the shown Fig. 8 .Thermodynamic parameters obtained from equations for the adsorption of dyes on granite are given in Table 4. As shown in the Table , the positive value of ΔG confirms the feasibility of the process and the unspontaneous nature of sorption. The values of ΔH were positive , indicating that the sorption reaction is endothermic. The positive value of ΔS shows an increase randomness at the adsorption .

3.4. Effect of pH

The pH value of the solution is an important parameters controlling uptake of dyes from aqueous solution. Fig.9. Shows the amount adsorbed of the four dyes onto granite as a function of pH at dyes concentrations 20 ppm and a granite 0.2g . The initial pH values of the dye solution affect the surface charge of the adsorbent and thus the adsorption of the charged dye groups on it. In general the acidic pH system showed good adsorption behaviour for the dyes solutions, the removal of dyes increased with a decrease of the pH from 14 to 2. As the pH of the system decreases , the protonated surface groups facilitate the adsorption of the negatively charged dye. The number of positively charged sites increases resulting binding sites for anionic dye molecules [35]. A lower percentage of the removal of dyes in al kaline pH, it can be expected that the granite surface becomes more negatively charged due to the presence of excess of OH- ions , thus more electrostatic repulsion forces appears between the dye anions and negatively charged sites which caused the decreased uptake of dyes [36] .

Effect of initial concentration

The study showed that for the powdered granite the values C_o-C_e/C_o of dyes were very high, 85% for all initial dye concentration with contact time. The effect of the initial concentration of the dyes solution on the adsorption process was studied using a group of different initial concentration in the range (6,12,16ppm) at optimum pH and different contact time at 30°C. It was found that the concentration at equilibrium state increases with increasing of the initial concentration. The amount of adsorbed increase is with an increase of initial concentration in the showns Fig. 10-12.

3.5. Effect of weight surface

The effect of the weight surface of the granite on the adsorption process was studied using different weights between (0.05-0.2gm). It was found that the amount of adsorption increasing with 0.2gm from granite by the application of C_o-C_e/C_o Vs contact time , it was found that the optimum adsorption in 0.2g from granite for adsorption of dye. Fig.13-15.

3.6. Kinetic study

The rate constant $k_{ads.}$ is determined from the following pseudo first –order expression given by Lagergren [37].

$Log(q_e-q_t)= log\ q_e- k_{ads.}t/2.303$

Where q_e and $q_t(mg.g^{-1})$ are the amounts adsorbed at time (min) and at equilibrium respectively . A linear relationship was obtained by plotting log (q_e-q_t) V_s time(Fig 16), gives the slop $-k_{ad.}$ /2.303 and intercept ln q_e . Similar result was reported in the adsorption of dyes on granite , this kinetic indicates that system variable , should be more extensively and that several kinetic model and correlation coefficients should be used to the experimental sorption date if a mechanism can't be confirmed . The variables should include agitation speed , solute concentration , sorbent mass . Our experiment date is carried out by depending on the Lagergreen equation[38] .

The adsorption rate contact is expressed as a solution function of temperature by the following relationship[39]

$log\ K_{ads.} = log\ A-Ea/2.303RT$

Where $k_{ads.}$ is the rate constant (min^{-1}) , A is a Arrhenius constant , Ea. is the activation energy $(K_J.mol^{-1})$ and T is temperature (k), for an increase in temperature range 30 to 50⁰C are calculated . These values are found to decrease log $K_{ads.}$ Values with an increase of temperature, give the slope . Ea/2.303R and intercept log A. in the shown Fig.17.

Conclusion

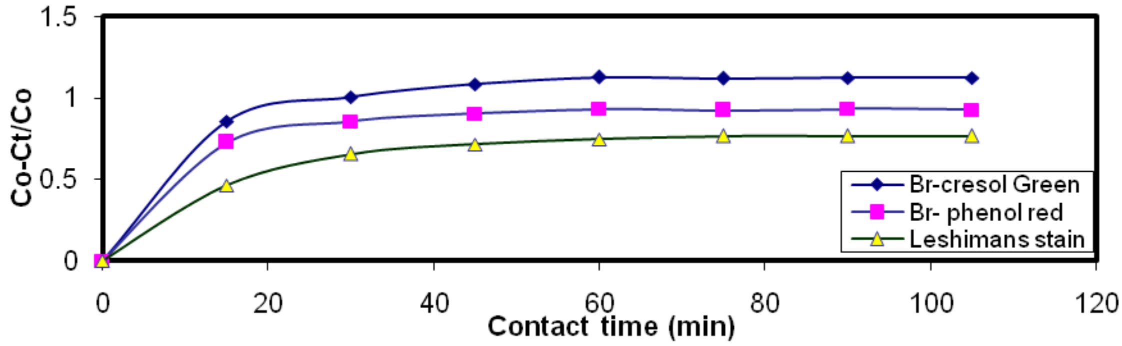
1- The present study that the batch adsorption process for removal of dyes onto granite is dependent on initial concentrations ,solution PH,adsorbent dosge ,contact time and temperature .
2- The equilibrium study was made for the adsorption of dyes onto granite ,the Langmuir and Freundlich isotherms models were used .
3- The adsorption of dyes onto granite follows pseudo –first –order kinetics model .
4- The Positive values of ΔG confirmed the unspontaneous nature of adsorption process, the positive value of ΔH and Ea indicated the adsorption process was endothermic and the positive values of ΔS showed the increased randomness at the solid-solution interface during adsorption .

Table.3 The Langmuir , Freundlich constants for the adsorption of dyes solutions on granite at 30°C

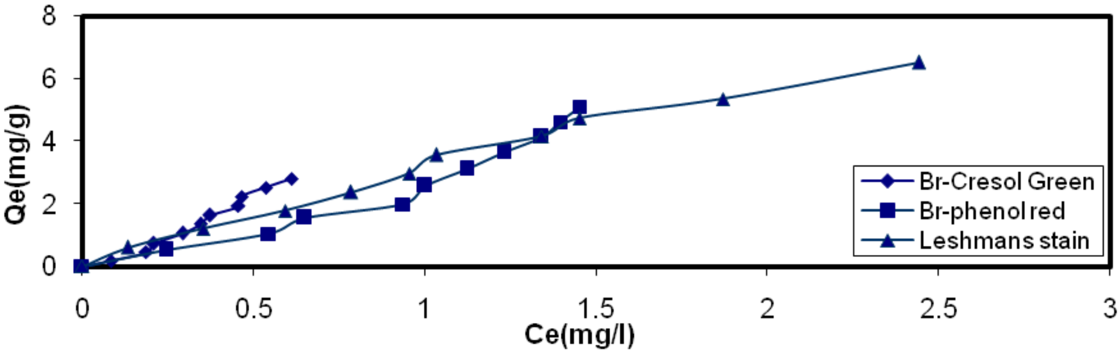
Dyes	K_f	n	R^2	K_L	q_m	R^2
Bromocresol green	1.442	67.11	0.8253	2.223	2.116	0.7371
Bromophenol red	5.274	0.861	0.9912	1.767	5.540	0.7633
Lieshman's stain	2.503	1.334	0.9941	3.765	22.72	0.5816

Table .4 Thermodynamic parameters for the adsorption of dyes onto granite

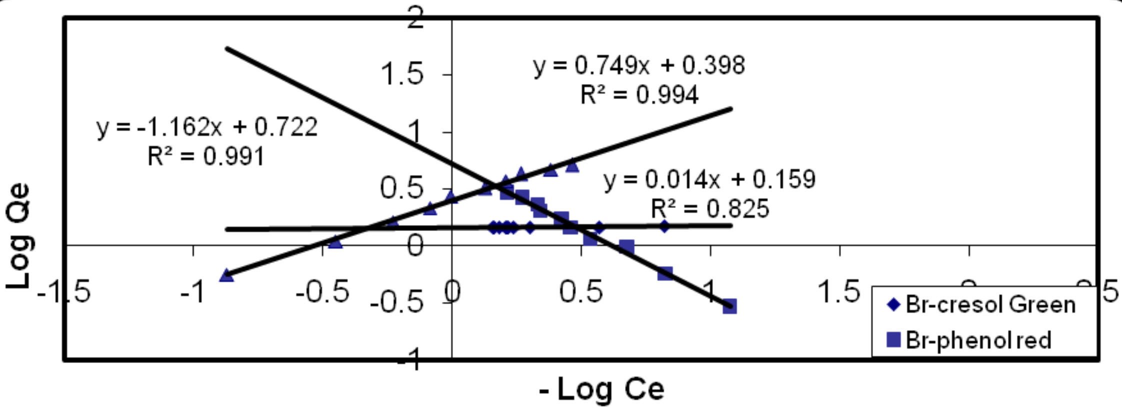
Dyes	$\Delta H(KJ.mol^{-1})$	$\Delta G(KJ.mol^{-1}.k^{-1})$	$\Delta S(J.mol^{-1})$	$Ea(KJ.mol^{-1})$
Bromocresol green	19.43	4.66	48.76	75.63
Bromophenol red	29.19	4.24	82.35	47.06
Lieshman's stain	25.37	3.60	71.52	72.75



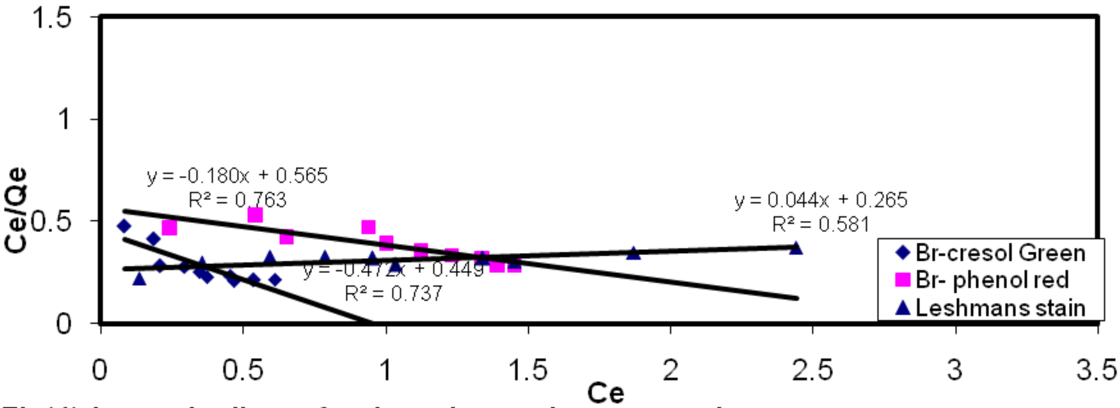
Fig(1):Effect of contact time for adsorption dyes on granite



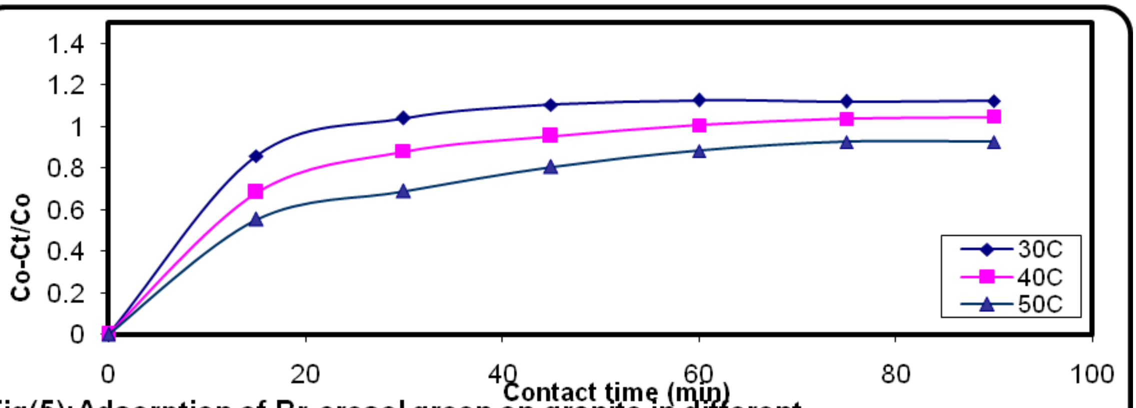
Fig(2):Adsorption isotherms for dyes on granite



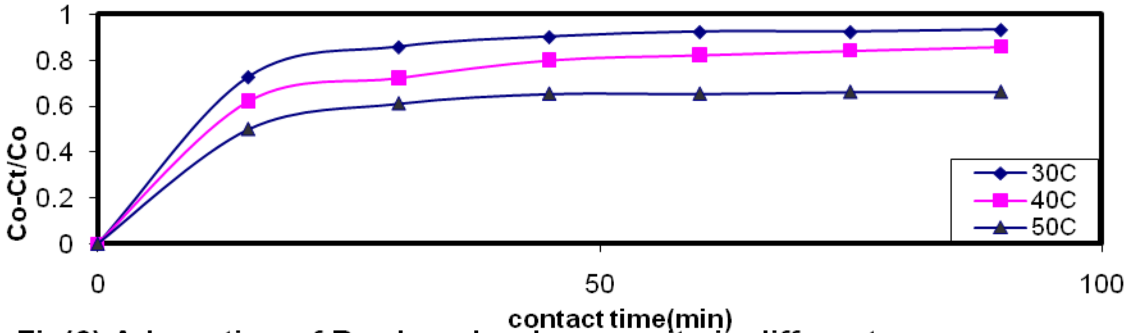
Fig(3):Freundlich linear for adsorption dyes on granite



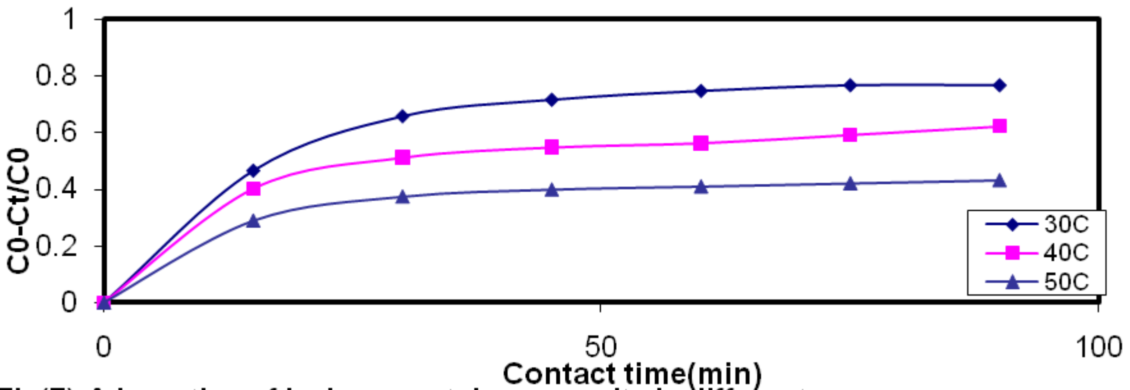
Fig(4):Langmiur linear for dyes dasorption on granite



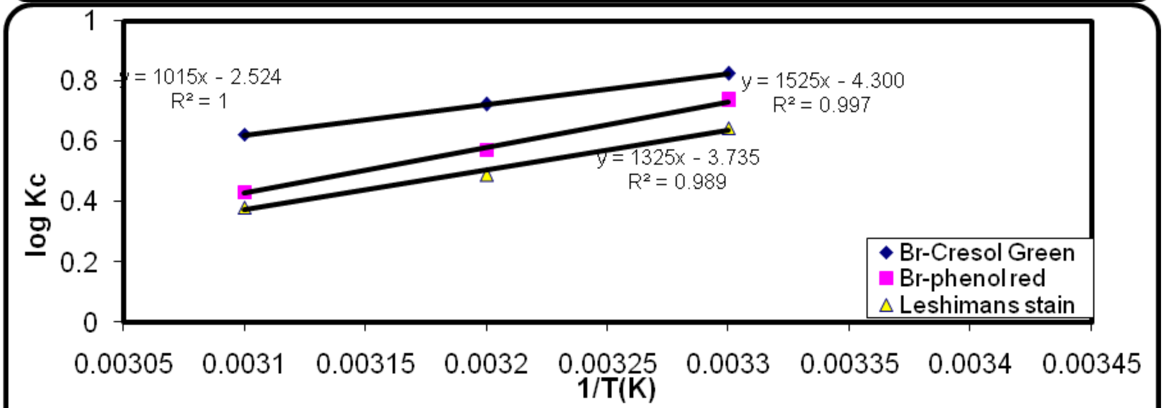
Fig(5):Adsorption of Br-cresol green on granite in different temperature



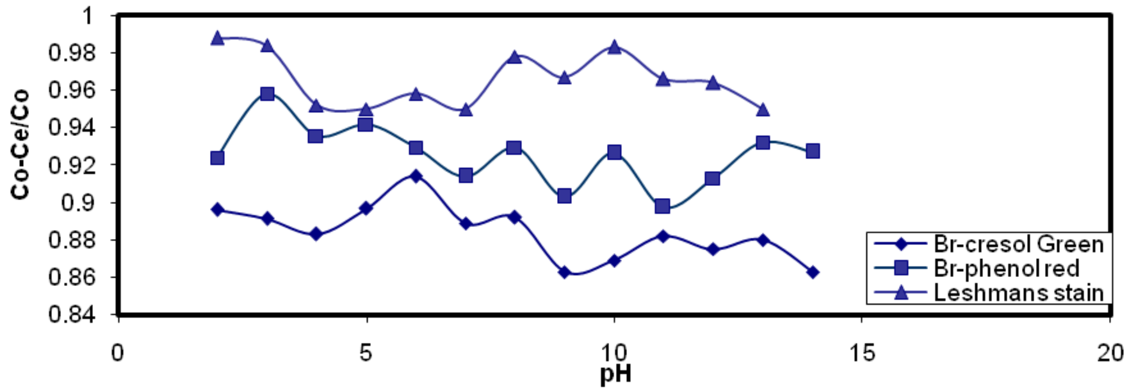
Fig(6):Adsorption of Br-phenol red on granite in different temperature



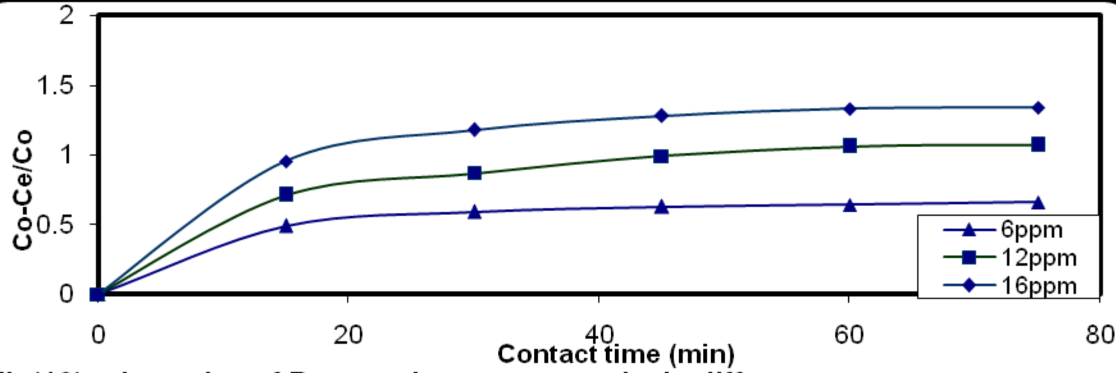
Fig(7):Adsorption of leshmans stain on granite in different temperature



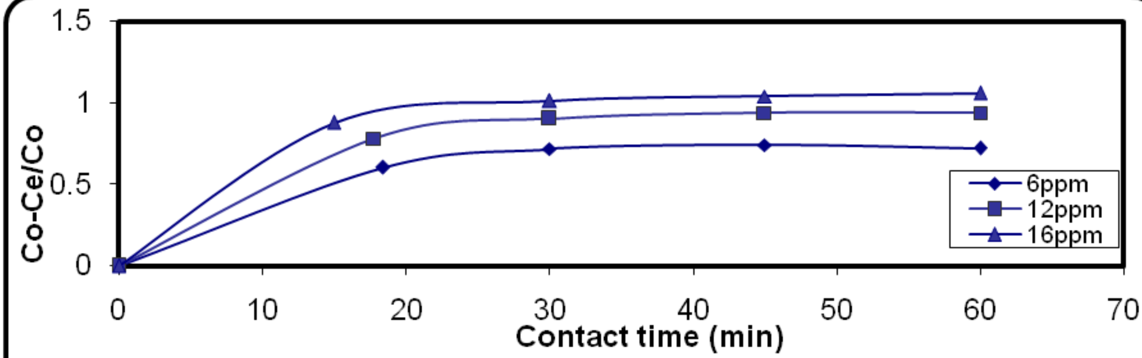
Fig(8):Relation between log Kc and 1/T for adsorption dyes



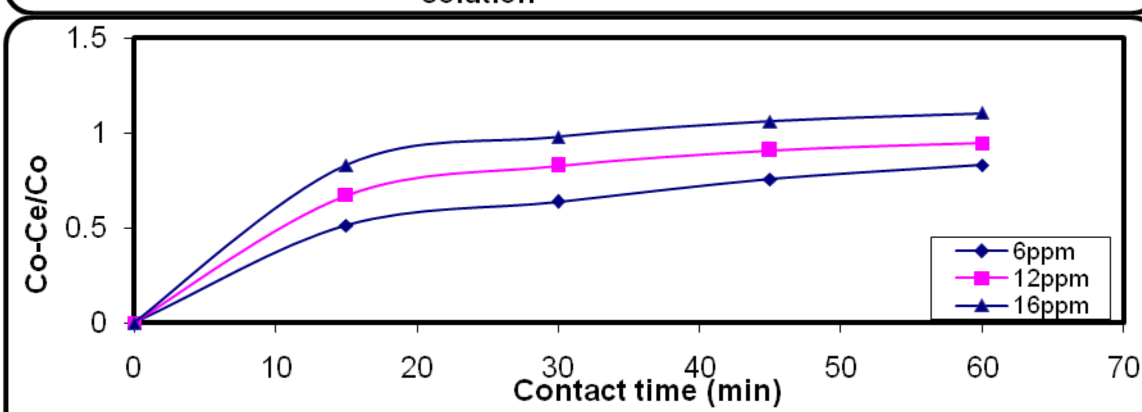
Fig(9):Effect of PH for adsorption dyes on granite



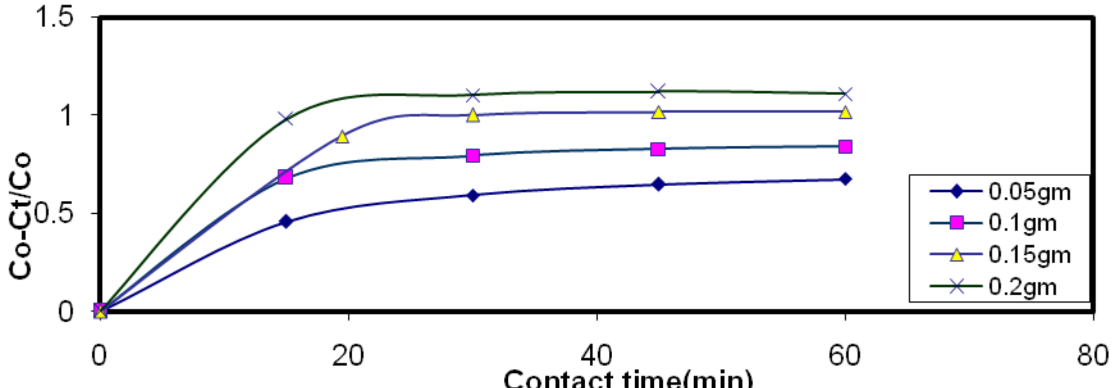
Fig(10):adsorption of Br-cresol green on granite in different initail solution



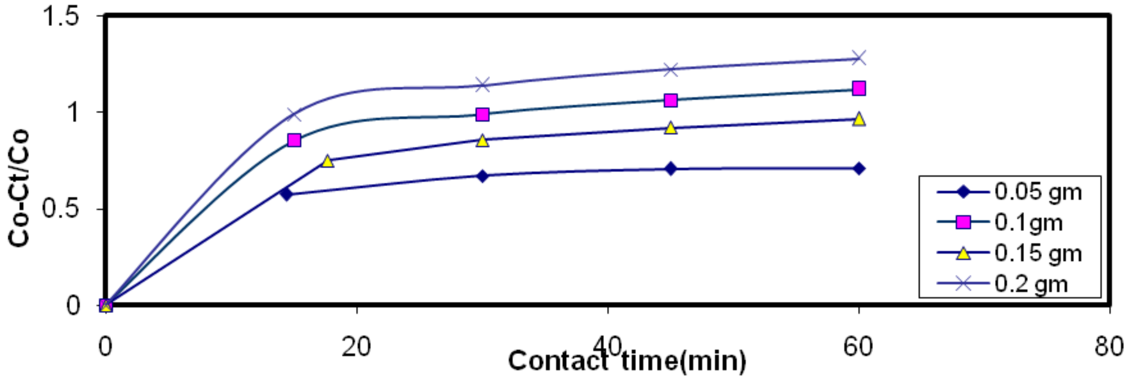
Fig(11):adsorption of Br-phenol red on granite in different initial solution



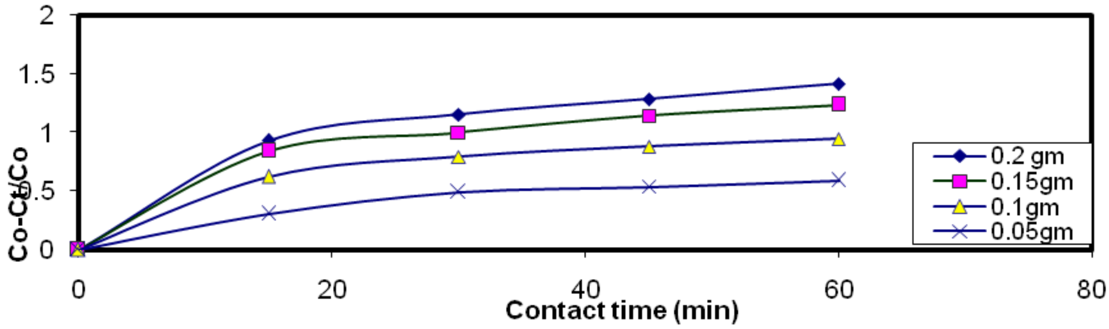
Fig(12):adsorption of leshmans stain on granite in different initail solution



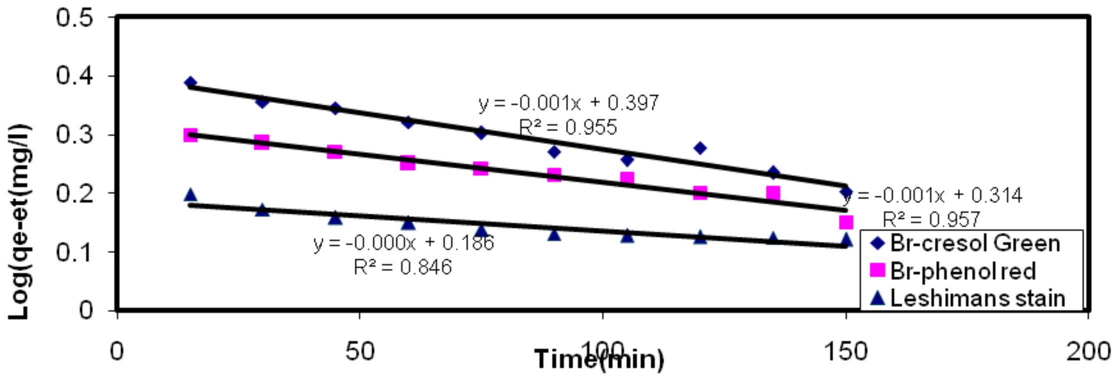
Fig(13):adsorption of Br-cresol green on granite in different weight surface



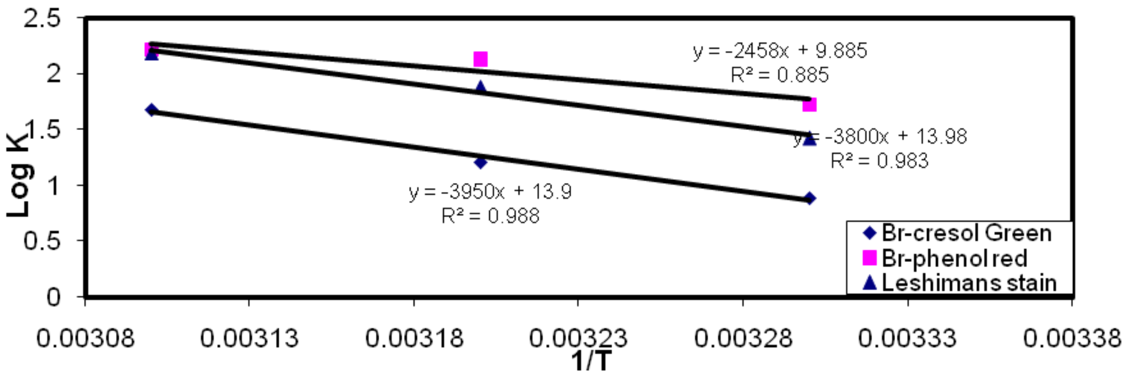
Fig(14):adsorption of Br-phenol red on granite in different weight surface



Fig(15):adsorption of leshmans stain on granite in different weight surface



Fig(16):Lagergen equation for dasorption dyes on granite



Fig(17):Relation between log K and 1/T for adsorption dyes

References

[1] Ren J.m., Wu S.w., Jin W., World Academy of Science, Engineering and Technology 2010,65

[2] Baskaralinggam P, Pulikesi M, Elango D, Ramamurthi V, Sivanesan S. , J.Hazard. Mater, 2006,128:138-144.

[3] Özcan A, Öncü E M, Özcan A S, Colloid Surf. A: Physicochem. Eng. Aspects, 2006,277: 90-97.

[4]Özcan A, Öncü E M, Özcan A S.,J. Hazard. Mater, 2006, 129: 244-252.

[5] Ghaedi M.Ramazani S. and Roosta M.,Indian J. of Sci and Tech.,2011,4,10 .

[6] Ravikumar K, Deebika K, Balu K., J. Hazard.Mater, 2005, 122: 75-83

[7] Ravikumar K, Pakshirajan K, Swaminathan T, Balu K. Chem. Eng. J, 2005, 105: 131-138

[8]Gupta V K, Ali I, Suhas, Mohan D.. J. Colloid Interf. Sci., 2003, 265: 257-264

[9] Gupta V K, Mittal A, Krishnan L, Gajbe V. Purif. Technol, 2004, 40: 87-96

[10] Mittal A, Kurup Krishnan L, Gupta V K. J. Hazard. Mater, 2005, 117: 171-178

[11] Mittal A. J. Hazard. Mater,2006, 128: 233-239

[12]Bhattacharyya KG, Sharma A. J. Environ. Manage, 2004, 71: 217-229

[13]Saja S.J. , J. of chem. 2008 ,31,466-475,.

[14]Banergee K. , cheremisin off ,P.N. and cheng L.S. , water RES. , 1997,31,249,.

[15]Wang K., Furney T.D. and Halway M.C. , chem.. Eng. Sci., 1995,50,2883.

[16]Oakes J. and Dixon S. , color techuol , 2003,119,140.

[17]Al-Qodah Z., J. Env. Tech. , 1998,17,128,.

[18]Swaminathan D.B.G. and thirunavukkarasu R., J. of Earth and Envi. And sci, 2009,4,2,146-160

[19]Gosh D. and Bhattacharyya K.G. , Appl. Clay sci, 2002,20,295.

[20]Rytwo G., Nir S. and Margulies L., J. colloid interface sci, 1996,181,551.

[21]El.mouzdahir Y. , El.mchaouei A. , Mahboub R., Gil A. and Korilli S.A. , J. chem. Eng. Date, 2007, 52,1621.

[22]Ahmeed K.A. , J. of chemistry, 2008, 30,306-322.

[23]Ribeiro R.C.C. , correia J.C.G., seidl P.R., contro de techologio mineral , 2008.

[24]Al-Gohary O., Lyull J. and Mrray J.B., pharm. Acta. Helv, 1987,62(30),66.

[25]Mohammed Y. , M.Sc. thesis , college of Ibn Al-Haitham edu. , Bag., unive., 2004.

[26]Babatunde A.I., Abiola O.K., Osideko O.A. and oyelola O.I. ,J. of Biotechnology, 2009,8(14), 3364-3368.

[27]Nasiruddin M.K. and Zareen U. , J. of the Iranian chem.. Soc., 2004,1,2,152-158,.

[28]Erdem E., J. of colloid and inter., Sci, 2004,280,309-314.

[29]Medhat A.S.,American J. of App. Sci, 2007,4(8), 605-612.

[30]Zeki A., turk .J. chem. , 2001,25,311.

[31]Purakayastha P.D. , Bandyopadhay M.I., Envi., Sci, and Health, 2001,37,925.

[32]Anoop. K.K, Ind. J. Chem. Tech. , 2002,9,32.

[33]Megat M.A.K., Yaha M.Z.A. , Zakaria H. and Ibrahim S.C., J. of Applies Sci. 2007,7(4),489-493.

[34]Sudha R., Kalpana K., Rajachandrasekar T., and Arivoli S., E.J. of chemistry , 2007,4,2,238-254.

[35]Bekkouche S., J. of science . chem. , 2004,166,355-362.

[36]Namasivayam C., Dinesh M.K., selvi K.B. , Ashruffunissa R. vanathi T. and Yamuna R.T., Biomass Bioenergy , 2001,21,477-483.

[37]Aditya P., Sangeela S. and pt serk P.R. , India J. of chem. Tech. , 2008,15,146- 154,

[38]Al-Ameene A., M.S.C. thesis , Ibn Al-Haitham coll., 1996

[39]Nasiruddin K.M. and Zareen U., J. of the Iranian , chem. Soc., 2004,1,2,152- 158.