Research Journal of Engineering Sciences ____ ISSN 2278 – 9472
Vol. **2(4),** 16-21, April **(2013)** *Res. J. Engineering Sci.*

Study the Efficiency of adsorption Leshman's Stain Dye on the surface of some metal oxides

Al-Maamori Mohammad H.[1], Al-Mosawi Ali I.[2], Khudhair Shaymaa H.[3] and Muttaleb M. K.[4]
[1]College of Materials eng, Babylon University, IRAQ
[2]Technical Institute-Babylon, Babylon, IRAQ
[3]College of Education, Babylon University, IRAQ
[4]College of Science, Babylon University, IRAQ

Available online at: www.isca.in
Received 10th September 2012, revised 22nd January 2013, accepted 4th February 2013

Abstract

The adsorption behaviors of Leshman's Stain in aqueous solution an germanium oxide and yttrium oxide as an adsorbent were studied. A series of experiments were undertaken in a batch adsorption technique to access the effect of the process variables i.e. initial dye concentration, contact time, initial pH, adsorbent dose, temperature (298K), adsorbent dosage (0.1gm) higher values of the initial pH(7.0)for $GeO_2$and Y_2O_3 respectively. The equilibrium in the solution was observed within (30min)of Leshman's Stain on GeO_2 and Y_2O_3. The equilibrium isotherm for Leshman's Stain was determined to describe the adsorption processes. The results showed that the equilibrium data were fitted by both of the Langmuir and Freundlich isotherms on GeO_2 and Y_2O_3 surfaces. Also the results obtained shows the isotherms were (S_4) on GeO_2 and (S_3) on Y_2O_3 according to Giles classification. The thermodynamic parameters at compound such as ΔH, ΔG and ΔS of adsorption were calculated.

Keywords: Adsorption behaviors, Leshman's Stain, Metal oxides.

Introduction

The organic coloring materials in water stimulate the growth of many aquatics micro-organisms[1]. Highly colored, polluted water will frequently have an associated objection able taste, but the degree to which this association is causative is known[2]. The most widely used adsorbent from industrial applications is activated carbon and metals oxides[3]. Alumina and other metals oxides is considered to be a particularly competitive and effective process for the removal of dyes at trace quantities[4,5].

The adsorption of Leshman's Stain has a long history of use as a method of surface area determination Giles[6,7] and Taylor [8,9] reported that a method based on Leshman's Stain adsorption from aqueous[10] solution gives reliable results for some (oxides, graphite, yeast, etc). In the case of clays, the adsorption of Leshman's Stain onto smectite surface has been the subject of considerable investigation due to the utility of the phenomenon in determining the presence of smectites[10] and surface area[11].

The aim of this work is to determine the efficiency of reactive Leshman's Stain form water solutions using Germanium oxide and Yttrium oxide as an adsorbents[12].

Material and Methods

Materials: Adsorbates: dye were used as adsorbates: Eiosn methylen blue (Leshman's stain) it was used as commercial salts without purification and were supplied by B.D.H. The metals oxide samples used as adsorbents were supplied form B.D.H.

Apparatus: All spectral and absorbance measurements were carried out on a shimadzu UV-Vis 1700 digital double beam recording spectrophotometer using (1)cm glass cells, Japan. A digital pH meter .720 WTW 82362 was used, Denmark.

Experimental procedure of work: Portions of Leshman's Stain solutions (30ml) of known initial concentration (2-16 p.p.m) and varied amounts of adsorbents (0.05-0.1gm) were poured into volumetric flasks. Analytical determinations of Leshman's Stain in solutions after equilibration (30 min at 25ºC) were performed by means of a Shimadzu TRUV754 spectrophotometer. Optical densities were determined at (516 nm) figure-1 for Leshman's stain, which corresponds to the maximum absorption peak of dyes .From the difference between initial and equilibrium concentrations, the amounts of Leshman's Stain adsorbed were calculated by the following relation[11]:

$$Q_e = \frac{(C_o - C_e)V_{sol}}{M} \qquad (1)$$

Where: Q_e : adsorption capacity (mg.g $^{-1}$), C_o and C_e: initial and equilibrium concentration (mg.L^{-1}) respectively, M : adsorbent dosage (g), V_{sol} : solution volume (ml).

The adsorption capacity was determined with the effects of contact time, initial concentration of Leshman's Stain and pH, temperature and agitation rate. The equilibrium concentration, adsorption capacity at equilibrium were determined to fit in the adsorption isotherm.

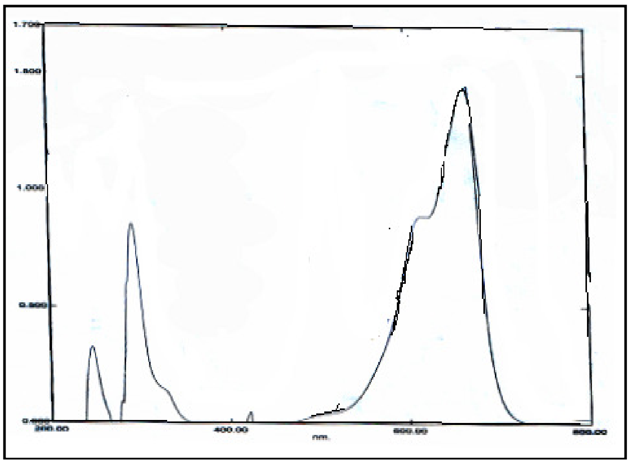

Figure-1
Spectrum of Leshman's Stain

Results and Discussion

The Freundlich and Longmuir models are the most frequently employed models. The Freundlich isotherm has been widely adopted to characterize the adsorption capacity of and dyes pollutants using different adsorbents by fitting the adsorption data figure-2.

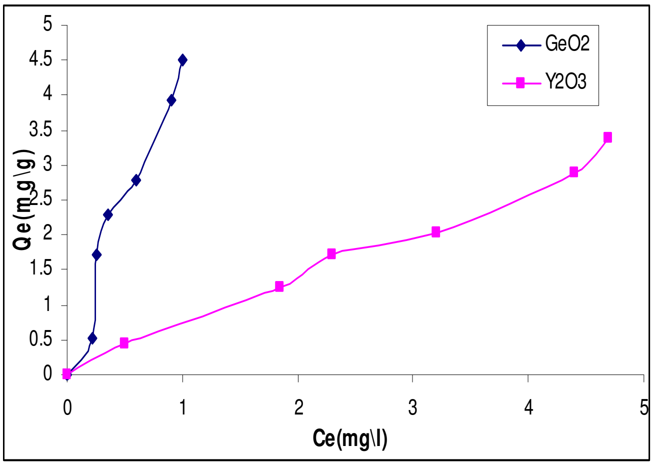

Figure-2
Adsorption isotherm of Leshman's Stain by GeO_2 and Y_2O_3 at

The linear Longmiur adsorption isotherm model can be represented by the following relation [12]:

$$C_e/q_e = 1/k_1 q_m + 1/q_m . C_e \quad (2)$$

Where: q_e : amount of dye adsorbed at equilibrium (mg.g $^{-1}$), C_e : equilibrium concentrations of Leshman's Stain, k_1 (mg.L^{-1})and q_m(mg.g^{-1}) : Longmuir constants.

$$Qe = K_f Ce^{\frac{1}{n}} \quad (3)$$

The constants q_m and k_1 can be determined from the intercept and slope of the linear plot of the experimental data of Ce/qe against Ce table-1. figure-3.

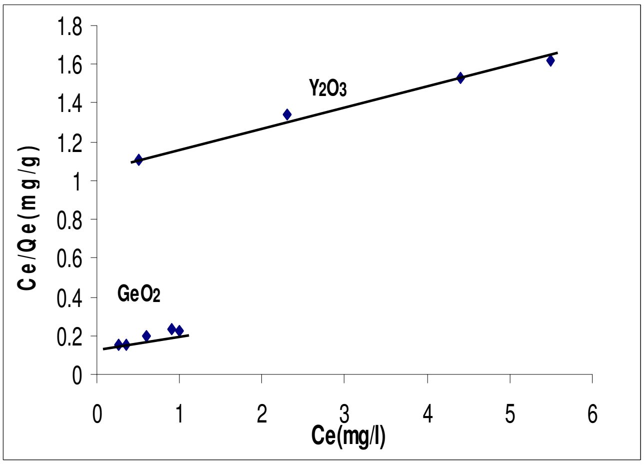

Figure-3
Longmiur adsorption isotherm of Leshman's Stain with GeO_2 and Y_2O_3 at pH=7

The Freundlich isotherm has the general from such as:
This equation can be modified as:

$$Qe = \frac{(C_o - C_e)V_{sol}}{M} = K_f Ce^{\frac{1}{n}} \quad (4)$$

Where: K_f and $1/n$: adsorption capacity and intensity of adsorption Respectively

The value of K_f and 1/n can be determined from the intercept and slope, Respectively of the logarithmic plot in eq.5 table-1. figure-4.

$$\log\ Qe = \log\ K_f + \frac{1}{n} \log\ Ce \quad (5)$$

The lienarized Freundlich and Longmiur adsorption isotherm initial Leshman's Stain concentration and pH ,16 p.p.m mg.L^{-1} and pH 7 respectively, temperature 25 °C ,calculate the adsorption capacity of GeO_2 and Y_2O_3 for Leshman's Stain. The adsorption constants evaluated from the isotherms with correlation coefficients are shown in table-1.

The values showed that the equilibrium data for Leshman's Stain fitted well to both the Freundlich and Longmuir isotherm in the studied concentration ranges .Based on the correlation coefficients (R^2). The equilibrium data was fitted in the Longmuir isotherm and Freundlich equation table-1. Many authors have used these isotherms to evaluate the adsorption capacity by different adsorbent with different dyes[13,14]. The results showed that the adsorption Leshman's Stain on to GeO_2 and Y_2O_3 was found to be effective at pH 7 .

The Freundlich and Longmuir equations were used to study data concerning the dependence of the adsorption on the Leshman's Stain at pH 7. The adsorption constants evaluated form the isotherms with correlation coefficient are shown in table-1., very high regression coefficients (0.996-0.989) were found for Leshman's Stain. The higher regression values showed that the equilibrium data for dye fitted well to both the Freundlich and Longmuir isotherms in the studied concentration ranges[14]. The percent adsorption (%) and distribution ratio (Kd) of Leshman's Stain by two adsorbents were calculated table-2.

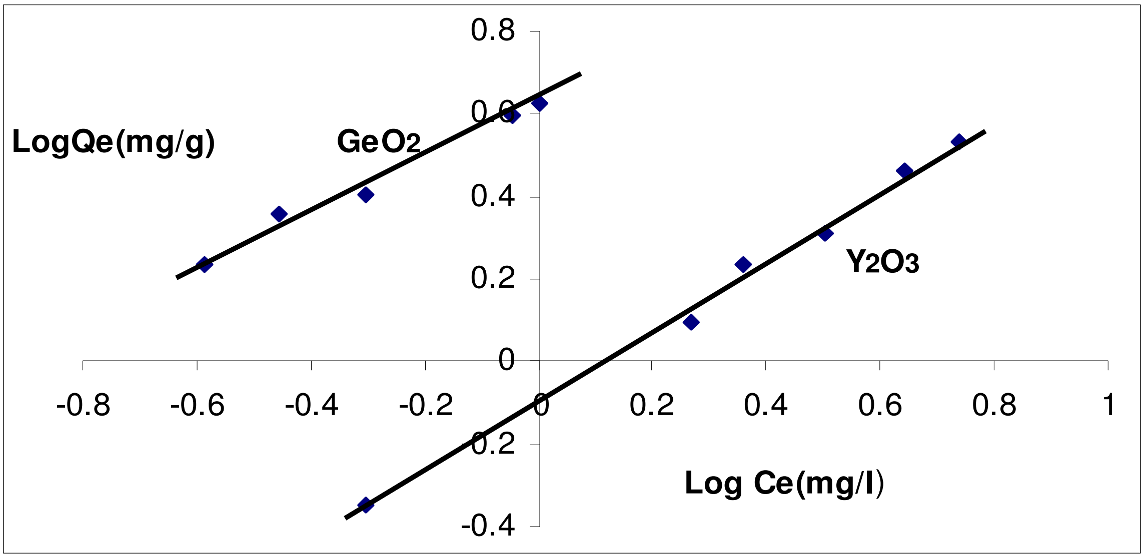

Figure-4
Freundlich adsorption isotherm of Leshman's Stain with GeO_2 than Y_2O_3 at pH=7

Table-1
Langmuir constants for Leshman's Stain in aqueous solution using GeO_2 and Y_2O_3

Adsorbent	Leshman's Stain					
	Freundlich con.			Langmuir con.		
	q_m	K_1	Rf	Log Kf	n	RL
8.258	0.921	0.986	0.6208	1.566	0.944	**GeO_2**
0.925	0.0931	0.996	0.099	1.181	0.989	**Y_2O_3**

Table-2
Kd values and % adsorption of Leshman's Stain in aqueous solution using GeO_2 and Y_2O_3 as an adsorbents

Cos.	S $J.mol^{-1}.k^{-1}\Delta$	G $KJ. mol^{-1}\Delta$	H $KJ.mol^{-1}\Delta$	Adsorbent
-0.248	-4.896	-3.726	5.185-	**GeO_2**
-0.1129	-11.2119	-0.363	-3.705	**Y_2O_3**

Table-3
Adsorbents Thermodynamic values of Leshman's Stain in aqueous solution using Ge O_2 and Y_2O_3

Leshman's Stain conc.p.p.m	GeO_2		Y_2O_3	
	%Adso.	Kd	%Adso.	Kd
75	67.5	89	79.5	2
69	62.5	95.6	86	6
71	64.9	95.6	85.6	8
68	51	94	76.5	10
68.5	61.7	93.5	84.2	14
65.6	63.5	93.7	84.4	16

Effect of pH: In order to study of hydrogen ion concentration (pH) on Leshman's Stain by two adsorbents (GeO_2 , Y_2O_3) different concentrations of Leshman's Stain were prepared based on the researches concentrations[13] in the range 2-16 p.p.m and adjusted to different pH values of 4,7 and 9 using (0.01)M of buffer solution (ammonium hydroxide, acetic acid and ammonium). The results are displayed in Figure-5.It is clear that the amount of Leshman's Stain removed varies pH, 7 pH value produces a large adsorbed quantity. This can be explained on the formation of a neutral charged surface on both adsorbents(GeO_2, Y_2O_3) .The higher adsorption capacity (4.5) was recorded in aqueous solution of Leshman's Stain by GeO_2, where as for Y_2O_3 (3.39), It may be related the surface properties of GeO_2 and Y_2O_3 are depended on pH of the solution

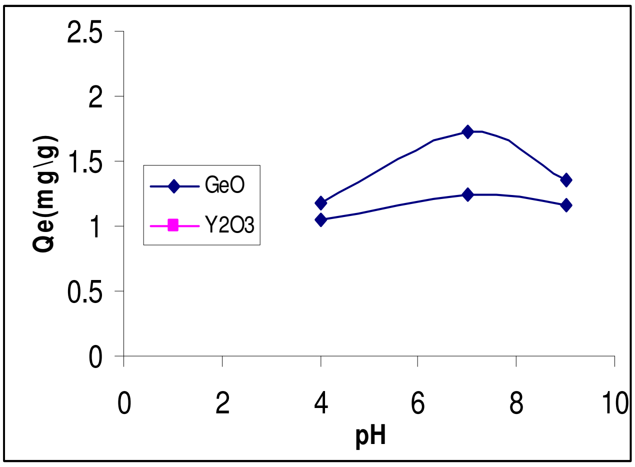

Figure-5
Removal of colour from aqueous solution of Leshman's Stain with pH of solution

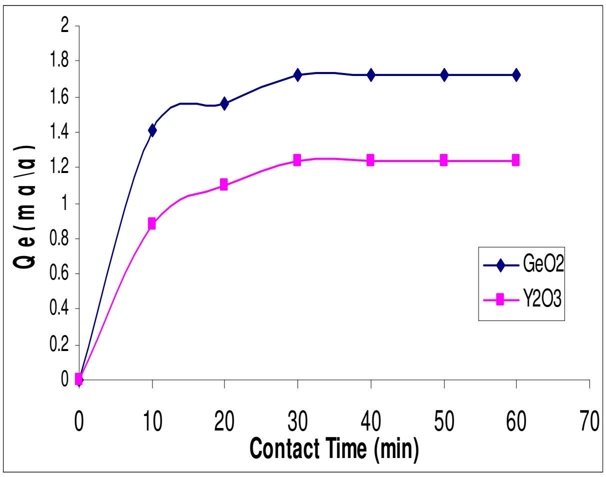

Figure-6
Adsorption capacity against contact time of Leshman's Stain with GeO_2 and Y_2O_3

The influence of the contact time on the adsorption capacity of Leshman's Stain by two adsorbents (GeO_2, Y_2O_3) was conducted through batch experiments to achieve the equilibrium as shown in figure-6. The mechanism of color removal can be described in migration of the dye molecule form the solution to the adsorbents particle and diffusion through the surface. The results showed that the equilibrium time was reached with in 30 min of operation for both adsorbents. The adsorption capacity was constant there after for case of Leshman's Stain observed.

In order to study the effect of adsorbent dosage on Leshman's Stain removal as the adsorption capacity with fixed initial concentration of Leshman's Stain and pH, temperature, agitation rate, GeO_2 and Y_2O_3were used as an adsorbents. The maximum removal of Leshman's Stain was observed with the dosage more than 0.05gm, 0.1gm used for all subsequence experiments.

Adsorption isotherms were taken for the Leshman's Stain dye in the temperature range of 298 to 328 K. The results are shown in figure-7, 8. The Longmiur isotherm and Freundlich isotherms are plotted at the temperature range from 289K.The thermodynamic parameters LnK, ΔG, ΔS and ΔH are computed from the equations below .The free energy change (ΔG) was calculated from the relation[15]:

$$\Delta G = -RT\, LnK \tag{6}$$

Enthalpy change ΔH was computed from the following (Vant Hoff-Arrheniuse equation)[16]

$$\log Xm = \frac{-\Delta H}{2.303RT} + Con. \tag{7}$$

And the entropy was calculated from the equation[17]

$$\Delta G = \Delta H - T\Delta S \tag{8}$$

The thermodynamic factors evaluated from isotherms are shown in table-3. The uptake of Leshman's Stain decreased with an increased in temperature up to 55°C .The results indicated that the adsorption process is exothermic in nature[18,19] .Many variables such as the molecular volume of the dye ,its planarity and its ability to bind to the adsorbents, among others, can effect the degree of adsorption .

More Leshman's Stain is adsorbed GeO_2 than Y_2O_3. This difference most be related to the higher affinity of the dye for the GeO_2 surface than Y_2O_3 surface, as the surfaces of the two adsorbents have similar pore volume. Also this may be due to a tendency for the dye molecule to escape from the solid phase of GeO_2 than Y_2O_3 to the liquid phase of dye with an increase in temperature of the solution[20,21]

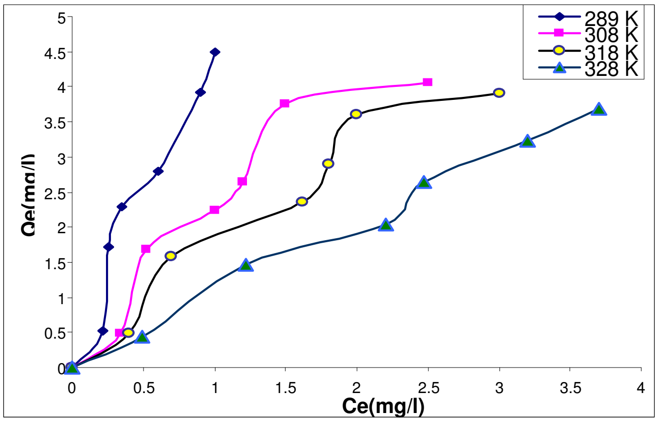

Figure-7
Effect of temperature on the adsorption capacity of Leshman's Stain with GeO_2 at pH=7

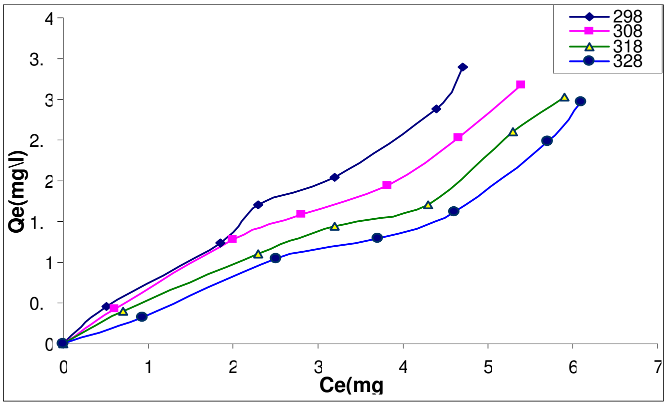

Figure-8
Effect of temperature on the adsorption capacity of Leshman's Stain with Y_2O_3 at pH=7

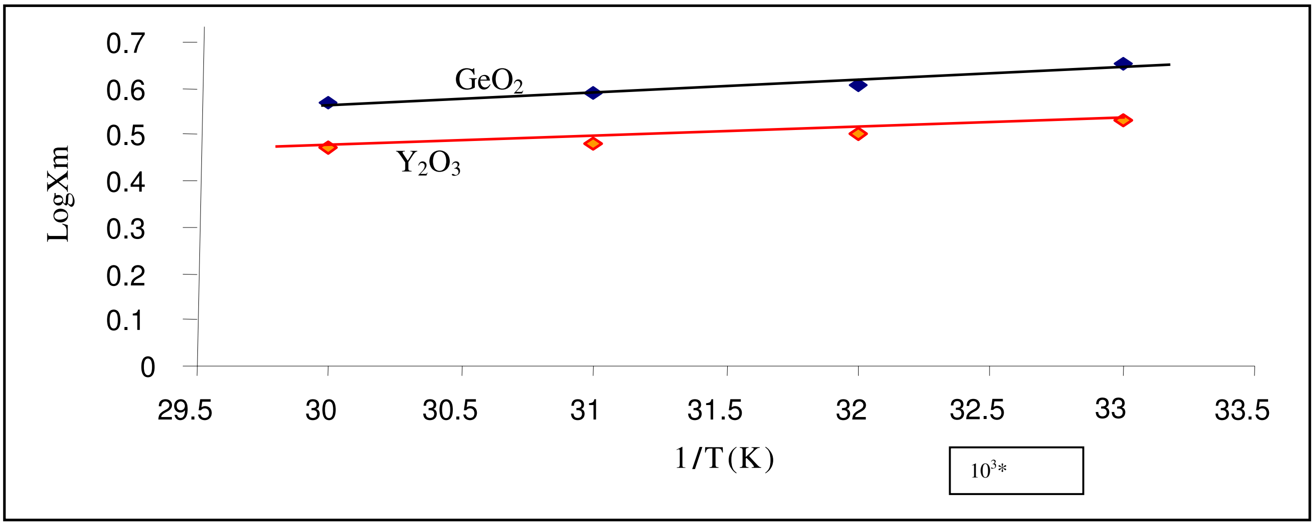

Figure-9
Relationship between the Log Xm and 1/Tof dye with GeO_2 and Y_2O_3 as an adsorbe

Conclusion

The results showed that the adsorption of Leshman's Stain onto GeO_2 andY_2O_3 was found to be effective, efficient and promising .The Leshman's Stain was adsorbed well by two adsorbents and the equilibrium data were fitted by the Freundlich and Longmiur isotherms where the data were slightly better by the Freundlich isotherm for the dye in terms of regression values (R^2).

References

1. WHO. Guide Lines for drinking-water quality, 2WHO, Geneva, **(1984)**
2. G.M. Walker & L.R Weatherley, *Process Biochem*, **32**,327-335 **(1997)**
3. Moreika R.F. ,M.G.Peruch andN.C.Kuhene, *Braz. J. Chem. Eng*., **15**, **(1998)**
4. safarik I., Nymburska K. and safarikova M., *J.Chem. Tech. Biotechnol*., **69**, 1-4 **(1997)**
5. Lee J., Ryn S. and Kim S.K., Surface Science**, 481,** 163-171 **(2001)**
6. Svetla D., Oyvind B., Elsebeth S. and Lundqvist I.B., *Physical Review*, **B74**, 155402 **(2006)**
7. Adamson H.W., Physical Chemistry of Surface ,4th edition , Wiley –Inter Science, New York, **(1982)**
8. Giles C.H., Adsorption form Solution at the Solid-liquid Interface, eds, E.D. Parfitt . Academic Press, London **(1983)**
9. R.K., *J.Chem.Tech.Biotchnol*,**35A**, 195-207 **(1985)**

10. Rytwo G., Serban C. and Margulies L., *Clays clay Miner*, **39**, 551-555 **(1991)**

11. Hang P.T. and Brindley G.W., *Clays clay Miner*, **18**, 203-212 **(1970)**

12. Gregg J. and Sing W., Adsorption surface area and porosity, 2nd edition, Academic press London, 61-84 **(1982)**

13. Oguz I. and Fatma T., *Turk. J. Chem*, **24**, 9-19 **(2000)**

14. Hussain M.J., Abbas H. and Lekaa K.H. **(2006)**

15. Panday K.K., Gup P., Singh V.N. Wat., *Res*., **19(7)**, 869 **(1985)**

16. Weber W.J., Asce A.M. and Morris D. Div. Am, *soc. Civ, Eng*, **31**, 89 **(1963)**

17. Dancan J., BSC., Introduction to colloid and surface chemistry .3rd Ed, **(1980)**

18. Chu C.H. and Chen K.M., *Process Biochem*, **37,** 595-600 **(2010)**

19. Ahmed N.M. and Ram R.N., *Environ Pollut*. **77,** 79-86 **(1992)**

20. Al-Asheh B.F.S. and Al-Makhadmeh L., *Process Biochem*, **39**, 193-202 **(2003)**

21. Y.HO and Mckay, *Trans. Chem*,**76**, 183-191**(1998)**