Adsorption Characteristics of Beans Peel powder   as New Adsorbent for Cr(III) Removal from Aqueous Solution

Hassan A. Habeeb Alshamsi* and Salam H. Alwan Altaa

Department of Chemistry, College of Education, University of Al-Qadisiyah, Iraq

_____

ABSTRACT

Heavy metals in drinking water are ones of the most important environmental problems in many countries . Up to now many different methods have been used to remove these heavy metals from drinking water. One method is using of local cheep substrates for adsorption of these heavy metals from drinking water. In this study beans peel was used as an adsorbent for removing Cr(III) ions from aqueous solutions. The amounts of adsorbed ions were estimated by using flame atomic absorption spectrophotometer . The effects of initial metal ions concentration , pH , existing salt and temperature were study. The adsorption isotherms are of L-curve type according to Giles classification and the experimental data were best fitted to Langmuir , Freundlich and Temkin isotherm models. The adsorption phenomenon was examined as a function of temperature (20,30, 40 and 50°C) and various thermodynamic parameters (ΔH^o, ΔS^o and ΔG^o) have been calculated. The thermodynamic parameters of metal ion- beans peel systems indicated the adsorption processes is spontaneous .The results indicated that the adsorption extent of Cr(III) ions onto beans peel increased with increasing the pH of solution and it was decreased with increasing ionic strength of solution.

Key words: Langmuir, Freundlich, Chromium(III), isotherm, thermodynamic, kinetics

_____

INTRODUCTION

Pollution of the aquatic environment by inorganic chemicals has been considered a major threat to the aquatic organisms . Heavy metals are among the most common environmental pollutants, and their occurrence in waters and biota indicate the presence of natural or anthropogenic sources. Their accumulation and distribution in soil, water and environment are increasing at an alarming rate causing deposition and sedimentation in water reservoirs .heavy metals receive particular concern considering their strong toxicity even at low concentrations[1-3]. Chromium is one pollutant in the environment occurring in air, rocks, soil, water and biological materials, It is also used in metal plating , tanneries, and oil well drilling. These sources annually release 106 tones of chromium in the form of fly ash, industrial effluents, particulates, dust and fumes into air, soil and water[4-5] . Chromium has been considered as one of the top 16th , toxic pollutants and because of its carcinogenic and teratogenic characteristics on the public, it has become a serious health concern [6-7]. different methods such as chemical precipitation, ion exchange, distillation , solvent extraction , lime , sand and carbon filters and … have been used for water treatment [8-9]. Because of high performance and ease of use , adsorption is introduced as one of the most applied methods[10] . In this method heavy metals are adsorbed in the pore surface of adsorbent which is insoluble in water. One of the most common adsorbent for heavy metals, is activated carbon , which because of its high cost of activating processes is very expensive in recent years cheap adsorbents have been attractive to many of researchers. Cheap adsorbents are widely and easily in reach and their preparation cost is low. These adsorbents are mainly a waste result of industrial and agicultural activity and have cellulose base[11-12]. Adsorption technology is easy to use, no need for processing and complex reforming processes , efficient and selective for heavy metals.

_____

MATERIALS AND METHODS

2.1 **Materials***:*
Hydrochloric acid , sodium chloride and sodium hydroxide were supplied by Fluka , Chromium nitrate were supplied by BDH.

2.2 **Instrumentation:**
Atomic Absorption Spectrophotometer, EA3000A, Euroea , Italy was used for determination of Cr ions. A digital pH-Meter, BL 210S , Sartorius Ag Gottingen, Germany was used for the pH adjustments. A K&K Scientific shaker water bath, CL002, Korea was used for shaking the adsorption batches. A Janetzi – T5 Centrifuge, CL008, Belgium was used for separation of adsorbent before analysis.

3. Adsorption experiments
3.1 Preparation of the beans Peel
Grinding beans peel in the form of powder was washed with excessive amounts of distilled water ; several washings were performed to remove dust and impurities . The powder was then dried under sunlight for 5 hours and then in an oven at 120^oC for a period of 1.5 hour and kept in airtight containers, then sieve the powder so that the particle size of 150µm .

3.2 Adsorption Isotherm
Solutions of metal ions (10ml) of known concentrations 50-500ppm were added to stoppered flasks containing 0.2 g of beans peel . The flasks were shaken in a thermostatically controlled water bath at a speed of 150 rpm . till equilibrium is attained 45 min for Cr (III) ions . These times are sufficient for the adsorption process to reach equilibrium in each case . After the equilibrium time elapsed , the suspensions were centrifuged at 3000 rpm for 10 min. The clear supernatants were assayed for metal , after appropriate dilution , spectrophotometrically by using atomic absorption spectrophotometer. Equilibrium concentrations were obtained by comparing the experimental data with the calibration curve. The quantity of metal adsorbed was calculated according to the following equation[13] **:**

$$\mathbf{Q_e} \textbf{ or } \quad \frac{x}{m} = \frac{V(C_o - C_e)}{m} \qquad\qquad \text{………………..(1)}$$

Where Q_e is the sorption capacity (mg/g), x is the quantity adsorbed (mg), m is the weight of adsorbent (g), C_o is the initial concentration (mg/L), C_e is the equilibrium concentration (mg/ L), V is the volume of solution (L).

3.3 Desorption Isotherm
The elution extent of the adsorbate was determined using distilled water as elution media . Solutions of different concentrations of each adsorbate (10 mL) were added to flasks containing 0.2 g of surface . The flasks were placed in time 30 min a constant temperature bath at 20^oC . After equilibrium , the suspensions were centrifuged and the supernate was decanted carefully and set a side for assay. A 10 ml portion of distilled water was added ; after shaking for 30 min , the suspensions were centrifuged. The clear supernate was again decanted and the adsorbate content was determined [14-15] . The amount of desorbed was calculated according to the following equation**:**

$$\textbf{The amount desorbed (mg/g)} = \frac{C_{ed} \times V}{m} \qquad\qquad \text{......................(2)}$$

3.4 Effect of Temperature
Adsorption experiment was repeated in the same manner at different temperatures (20,30, 40 and 50 ^oC) to estimate the basic thermodynamic functions of the process**.**

3.5 Effect of pH
Adsorption experiment was carried out as mentioned previously as a function of pH using a fixed concentration of metals ions. Hydrochloric acid and sodium hydroxide were used to adjust the pH vale in the range from 1 to 6.8 . The pH of the suspensions at the commencement of the adsorption was measured as well as at the end of experiment using pH-meter.

3.6 Effect of Ionic Strength
The effect of the addition 0.01-0.3 g of sodium chloride to solutions containing fixed concentration of metal ions equilibrated with 0.2 g of beans peel were investigated under the same experimental conditions described before **.**

RESULTS AND DISCUSSION

4.1 Effect of contact time
The removal of Cr(III) by the beans peel powder is examined at different time intervals as shown in Figure 1.As can be seen ,during first 2 minutes ,the Cr(III) % removal increase extremely with prolonged time and reaches value of 99%. Above first 2 minutes, no significant change of Cr(III) %removal is observed and a maximum value was 99.4% at 30 min. Depending on the results, it can be concluded that the adsorption equilibrium is reached after 30 minutes**.**
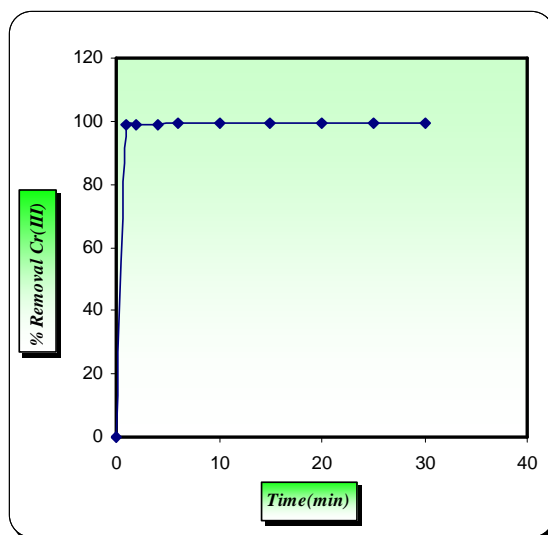

Figure 1: Effect of contact time

The results showed that the percentage of metal ions removed from aqueous solution increases with time to end this surface saturation ions used which was 45 min .

4.2 Effect of Particle Size
The effect of particle size at adsorbent particles of sizes illustrated in Figure 2 has been studied.

It is noticed t from Figure 2 ,the increase in particle size decreased the adsorption capacity at a fixed adsorbent dosage ,the decrease in particle size increase the Cr(III) removal. The increase or removal rate by small size particle is due to greater accessibility to pores and to the greater surface area per unit of adsorbent mass.
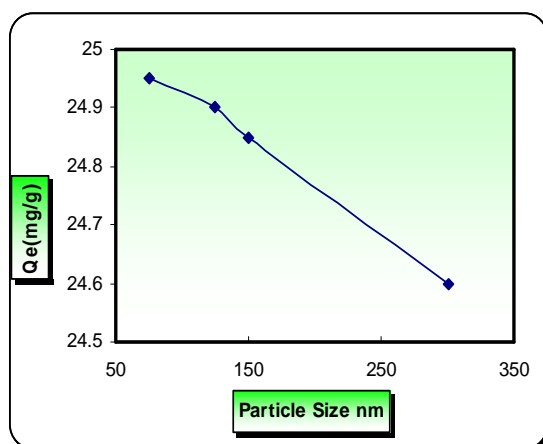

Figure 2 : Effect of particle size

_____

4.3 Adsorption and desorption Isotherm
Studied the time required to reach equilibrium concentration in adsorption metal ions on the surface of beans peel in different times was 0-120 min . when the temperature 20 ^{o}C and constant concentration of ion (500 mg /L) and using that particle size of 150 µm . Results of the study showed that the time required to reach equilibrium concentration is 45 min for Cr(III) ions. The plot show amount of adsorbent versus equilibrium conc. to give the general shape of isotherm adsorption and desorption as shown in Figure 2. It is clear that adsorption isotherm follow product (L) according to Giles classification, as well less energy adsorption increase the covered part of the surface and adsorption increases with increasing concentration of material adsorbent..
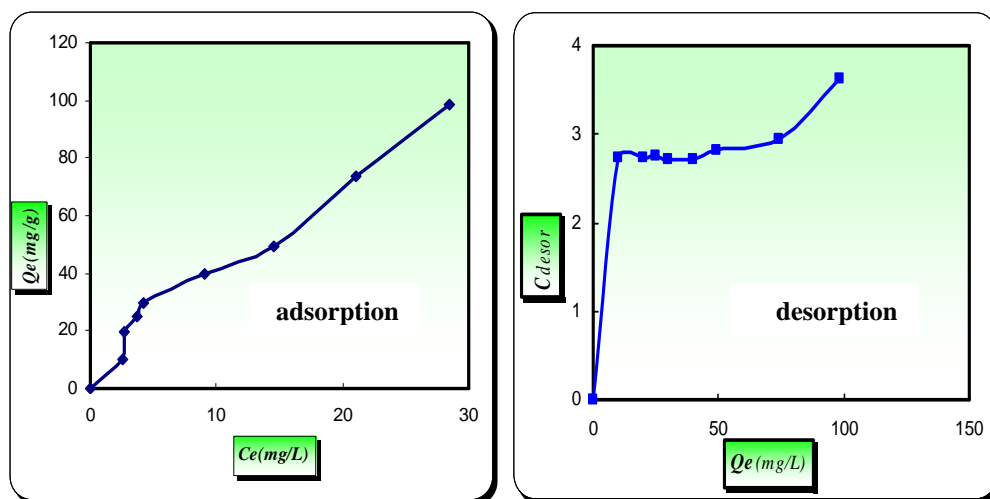

Figure 3: adsorption and desorption isotherms

Figure (3) shows the linear relationship of Ce / Qe versus Ce according to Langmuir isotherm[16,17] . The values of Langmuir constants as well as the correlation coefficient are presented in Table 1. Although drawing logQe versus logCe (Figure 3) illustrates the adsorption of Cr (III) on the surface of the adsorbent material according to Freundlich isotherm[18] . The drawing Qe versus lnCe (Figure 4) explains adsorption of Cd (II) on the surface of the adsorbent material according to Timken Isotherm[19] . The results of three isotherms are summarized in Table 1.

$$\frac{Ce}{Qe} = \frac{1}{q_m.k_L} + \frac{1}{q_m}.Ce$$
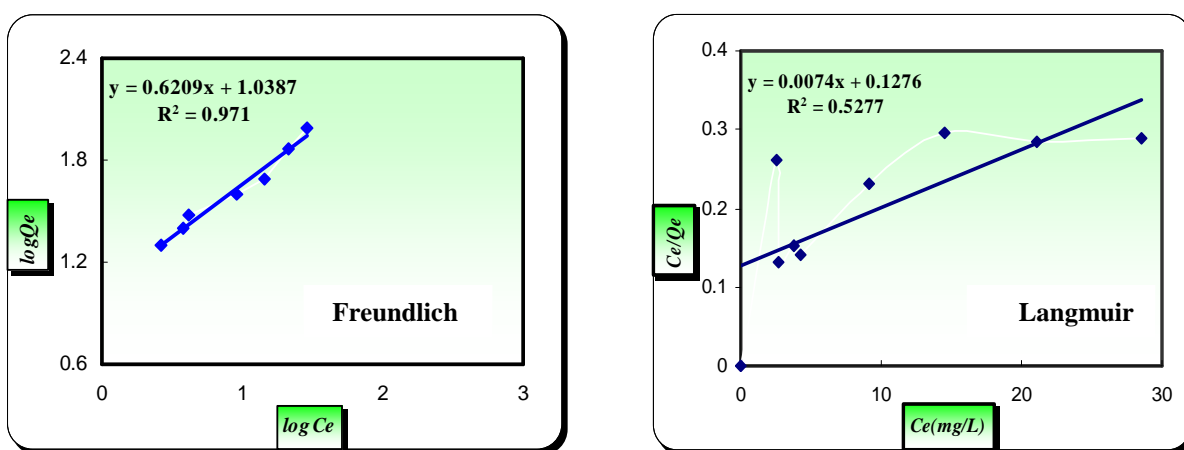
...............(3)

Figure 4 : Langmuir and Freundlich Isotherm
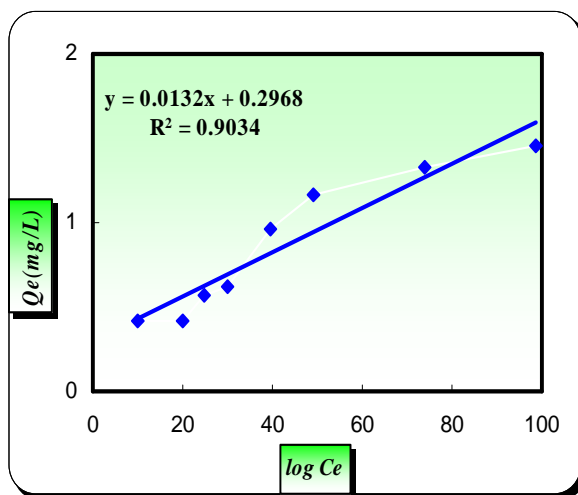
_____

Figure 5 : Temkin Isotherm

Table 1: Constants for Langmuir, Freundlich and Timken

Metal ion	Langmuir equation			Freundlich equation			Timken equation		
	K_L	a	r^2	K_F	n	r^2	K_T	B	r^2
Cr (III)	8.628	0.0009	0.527	2.825	1.610	0.971	44.800	0.620	0.904

4.4 Adsorption Kinetic

Both kinetic models ,pseudo first and pseudo second order using equations 4 and 5 respectively have been applied [20,21] and the results are shown in Figure 5**.**

$$\log Q_e - Q_t = \log Q_e - k_1 t \qquad\qquad\qquad\qquad \textbf{4}$$

where *Qe* and *Qt* are the adsorption capacity (mg/g) at equilibrium and at time t respectively, and k_1(min^{-1}) is the pseudo-first order rate constant of the adsorption. By plotting of $\log(Qe-Qt)$ versus *t* a straight line can be obtained as Figure 5 shows . *k₁* and correlation coefficient can be determined **.**

$$t/Qt = (1/h) + (1/Qe)t \qquad\qquad\qquad\qquad \textbf{5}$$
$$h = k_2 Q_e^2$$

hence *h*(mg g^{-1}min^{-1}) can be regarded as the initial adsorption rate and *k₂* is the rate constant for pseudo-second-order adsorption (g mg^{-1}min^{-1}) . Plotting of *t/Qt* versus *t* gives a straight line . *k₂* and correlation coefficient can be determined
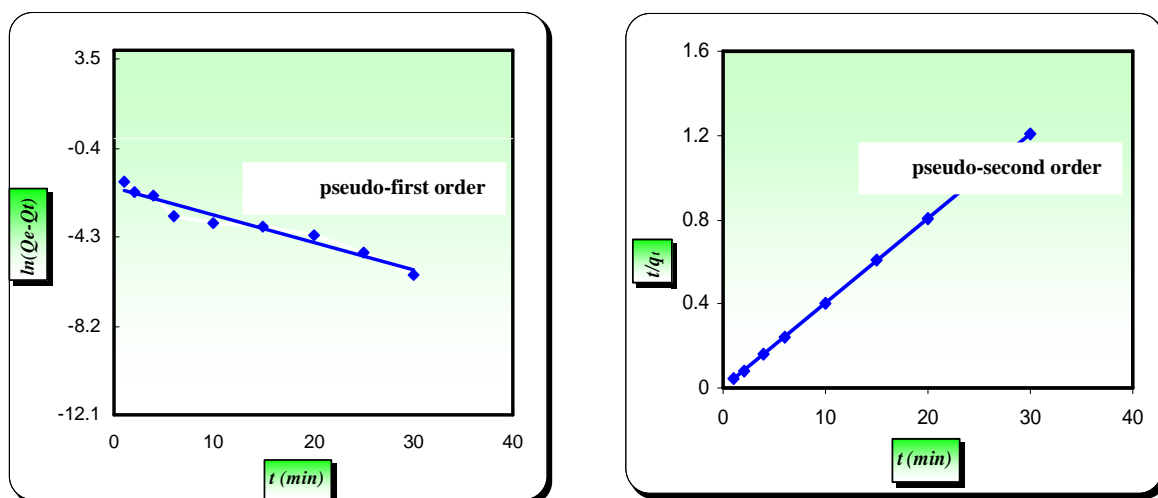

Figure 6: Pseudo-first and pseudo second order kinetic models

_____

The kinetic constants and correlation coefficients for both models account in the Table 2. The correlation coefficients values to model the second place - a relatively high pseudo, and that the amount of the adsorbent calculated by this model close to the value that has been determined through experiments. While the value of the correlation coefficient for the model first pseudo system adsorption unconvincing in. Therefore , the model second - pseudo be more appropriate to describe the kinetics of adsorption of metal ions on the surface of the peel beans**.**

Table 2: kinetic constants of pseudo-first and pseudo-second order models

Metal ion	pseudo-first order			pseudo-second order			
	k_1	Q_e	r^2	k_2	Q_e	h	r^2
Cr(III)	0.121	0.121	0.947	4.040	24.875	2500.000	1.000

4.5 Effect of Temperature on Adsorption
The effect of temperature on the metal ion adsorption on the surface of the beans peel in different temperatures (20, 30, 40 and 50 ^oC) was investigated . It is through the use of equation 1 to calculate the amount of adsorbent . The plot of amount of adsorbent (Q_e) versus equilibrium concentration (C_e) for the purpose of obtaining isotherm adsorption per degree temperature as shown in Figure 7, and indicate that the amount of adsorbent (Q_e) increase with increasing temperature**.**
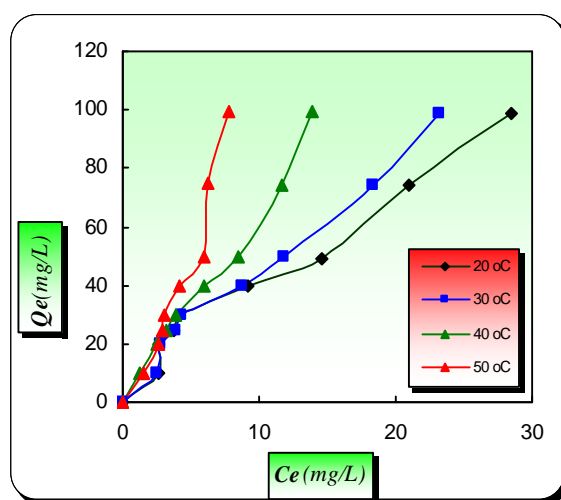

Figure 7: Effect of temperature

Thermodynamic functions of adsorption process were calculated and the results showed in a table 3, which illustrates the adsorption process is "endothermic process" as the temperature increases leading to increased kinetic energy of the molecules adsorbed on the surface adsorbent leading to disengagement metal ion surface .The results showed the adsorption of the chemical type [22]**.**

Table 3: Values of thermodynamic functions and equilibrium constant

Metal ion	$\Delta H^o (kJ.mol^{-1})$	ΔG^o $(kJ.mol^{-1})$	ΔS^o $(J.mol^{-1}. k^{-1})$	Equilibrium Constant
Cr(III)	3151.921	-11892.900	51.347	131.914

4.6 Effect of pH
Several different acidic functions were used 1.0-6.8 to study the effect of pH on adsorption of metal ions on the surface of the beans peel at 20°C and concentration (500 mg/L) . Through the use of equation (1) was extracted values Qe were drawn against the acidic function as shown in Figure 8.
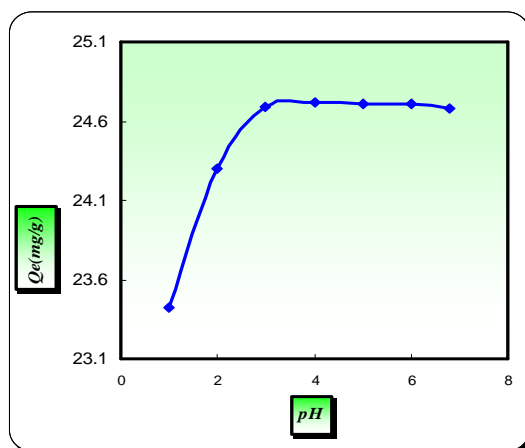
_____

Figure 8 : Effect of pH

This can be explained by noting that the amount of adsorbent increases with increasing pH vale above 6.8 ions begin degradation , leading to the formation of hydroxides insoluble like Cr (OH)$_3$. Due to the fact that protons strong competing sorbate because of the higher concentration and high mobility and partly to the fact that the solution pH influences the sorbent surface charge . Any sorbent surface creates positive or negative charge on its surface. In acidic medium the adsorbent surface was highly protonated , which was not favorable for metal ion uptake. At higher pH values, the adsorbent surface began acquiring a net negative charge making the situation electrostatically favorable for a higher uptake of metal ion [23,24] **.**

4.6 Effect of Ionic Strength
Figure 9 shows the effect of different sodium chloride concentrations (0.01, 0.05, 0.1, 0.15, 0.2, 0.25 and 0.3 gm) upon adsorptive capacity of surface of the beans peel at 20°C**.** As figure illustrates ,the increasing of salt concentration causing a decreasing in Q$_e$.
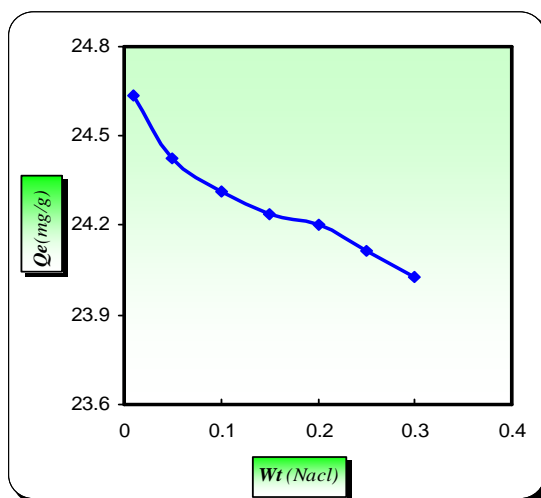

Figure 9: Effect of salt concentration

This can be clarified by a competition between the sodium ions and chromium ions in the adsorption on the surface including sodium ions characterize by a smaller size comparing with metal ions. So the adsorption of sodium ions is faster than the adsorption of metal ions [25]**.**

REFERENCES

[1] K. M. Mohiuddin ,Y. Ogawa, H. M. Zakir , K. Otomo , N. Shikazono , *Int. J. Environ. Sci. Tech.*, **2011**,8 , 723.
[2] M.A. Momodu ,C.A. Anyakora. *Res. J. Environ. Earth Sci*.**,2010** , 2, 39.
[3] O. B.Olafisoye, T. Adefioye , O. A. Osibote., *Pol. J. Environ. Stud*., **2013**,22, 1431 .
[4] R.H. Krishna and A.V.V.S Swamy , *E-J. Chem*., **2012,**9,1389.
[5] A. Bielicka, I. Bojanowska, A. Wiśniewski , *Pol. J. Environ. Stud*. , **2005**, 14, 5.

_____

[6] V.D. A. Cardoso, A.G.D. Souza, P.P.C. Sartoratto ,L.M. Nunes**,** *Colloid,Surf. A: Physicochem. Eng. Aspects*,**2004**,248, 145.

[7] Z. Krejpcio, *Pol. J. Environ. Stud.* , **2001**,10, 399 .

[8] D.B. Weirich, R. Hari, H. Xue, P. Behra ,L . Sigg,*Environ Tech* ,**2002**,36, 328 .

[9] D.Zhou, L. Zhang, J. Zhou , S. Guo, *Water Res.* **2004,** 38, 2643.

[10] J.C. Igwe . *Terres. Aqua. Environ. Toxicol.* **,2007**,2,60.

[11] S. Tangjuank, N. Insuk, V. Udeye , J. Tontrakoon, *Int. J. Phys. Sci.* ,**2009**,4,412.

[9] Y.S. Ho, C.C. Wang, *Process Biochem.*,**2004,** 39 ,759.

[13] H. A.H. Alshamsi , S. H. Alwan, *Res. J. Pharm. Bio. Chem. Sci.*,**2015**, 6, 985 .

[14] A. Pandeya, D. Berab, A. S., L. Ray,*Chem. Special. Bioavail.*,**2007**,19,17.

[15] Y.S. Ho, C.T. Huang, H.W. Huang ., *Process Biochem.* ,**2002**, 37, 1421.

[16] L. S .Al-Hayder, M. H. AL-Juboory, *J. Chem. Pharm. Res.* , **2015,** 7,1138.

[17] I. Lanqmiur, *J. Am. Chem. Soc.* **1918**,40,1361.

[18] H.M.F.Freundlich , *Z. für Phys. Chem.*,**1906**,57A,385.

[19] M.J.Tempkin, V.Pyzhev.*Acta.Physioshim.URSS*, **1940**,12,217.

[20] P.S. Kumar, K Kirthika, *J. Eng. Sci.Tech.*,**2009**,4,351.

[21] O.S. Ayanda, O. Adeyi, B. Durojaiye, O. Olafisoye, *Pol. J. Environ. Stud.*,**2012**,21,1147.

[22] S. H. Hasan, K. K. Singh, O. Prakash, M. Talat, Y. S. Ho , *J. Hazard. Mater.*,**2008**,152 , 356**.**

[23] K.S.Geetha, S. L .Belagali, J.Bio.Innov. , **2016**, 5, 83.

[24] I.Ghodbane, L. Nouri, O. Hamdaoui, M. Chiha, *J. Hazard. Mater.***, 2008,**152,148.

[25] D.M. Borrok, J.B. Fein, *J. Colloid .Inter. Sci.*,**2005**, 286, 110.