Thermodynamic study of Egg white albumin adsorption on charcoal derived from peach Nuclei and walnut shell

Abbas Hmood Al-Khafagy
University of Kufa, College of Education for Women, Dept. of Chemistry

(NJC)

(Recevied on 21/10/2009) (Accepted for publication 15/2/2010)

Abstract

In this study , the efficiency of waste charcoal derived from walnut shell and peach Nuclei from synthetic wastewater(EWA) has been studied . Batch adsorption experiments were carried out as a function of pH , adsorbent mass, EWA concentration, contact time and temperature .

The pH of each solution was not controlled , this is because the net interaction between the adsorbent and EWA could be disturbed by the buffer solution , therefore , the experiments were carried out in a pH 2 to 4 . These experiments were done under room temperature and showed that the optimum weight of charcoal derived from Walnut shell was 0.2gm , equilibrium time was 60min. , removal % (86.2) and K_d (86.2) , While optimum weight of charcoal derived from peach Nuclei was 0.05gm , equilibrium time was 120min. , removal % was(34.5) and K_d(138).

Thermodynamic parameters such as ΔH , ΔG , ΔS , were calculated . The adsorption process on charcoal derived from peach Nuclei was endothermic, while exothermic on charcoal derived from Walnut shell, the results were analyzed by the Langmiur and Freundlich equation .

Key Words :- Egg white albumin(EWA) , Langmiur and Freundlich adsorption , isotherm .

الخلاصة

بينت هذه الدراسة كفاءة الفحم المشتق من قشور الجوز ونوى الخوخ لازالة الفضلات المائية(البومين بياض البيض) وكذلك تم معرفة العوامل الموثرة في الامتزاز مثل الدالة الحامضية ، وزن السطح ألمـاز ، تركيـز ألبومين بياض البيض ، زمن الاتزان ودرجة الحرارة.

وتم دراسة دالة حامضية المحلول باستخدام محلول بفر منظم الناتجة من التداخل بين الـسطح المـاز والمادة ألمازة وبالمدى من 2 الى 14 وعند درجة حرارة المختبر وتبين من الدراسة إن أعظم وزن للامتزاز على سطح الفحم المشتق من قشور الجوز 0.2gm وبزمن اتزان 60 دقيقة ونسبه الإزالة 86.2% ومعامـل التوزيع 86.2 بينما اعظم وزن للامتزاز على سطح الفحم المشتق من نوى الخوخ كـان 0.05gm وبـزمن اتزان 120 دقيقة ونسبه الإزالة 34.5%ومعامل التوزيع 138 ،وتم حساب الدوال الثرموديناميكيـة فكانـت عملية الامتزاز ماصة للحرارة على سطح الفحم المشتق من نوى الخوخ بينما العملية باعثة للحـرارة علـى سطح الفحم المشتق من قشور الجوز وتم تحليل النتائج في ضوء معادلتي فرندلش ولانكماير.

Introduction

Water pollution is any human contamination of water that reduces its usefulness to humans and other organisms in nature. Pollutants such as herbicides , pesticides , fertilizers , hazardous chemical and albumin can make their way into our water supply [(1)]. [A real understanding of life's processes requires an understanding of how protein and other endogenous macromolecules perform their actions. Proteins can be viewed as copolymers consisting of different amino acids , connected through the so called peptide bond, the simplest amino acid characterization is in terms of their hydrophobic or hydrophilic nature[(2)].]

Over the years , intensive research has been fueled up to fabricate nanoscaled materials through bottom – up and top down approaches [(3-6)]. Protein adsorption on surfaces of biomaterials and medical implants is an essential aspect of the cascade of biological reactions taking place at the interface between a synthetic material and the biological environment. Type , amount and conformation of adsorbed proteins mediate subsequent adhesion , proliferation and differentiation of cells and are believed to steer foreign body response and inflammatory processes[(7-9)].

Hen egg white , known as albumen , contains more than 20 different proteins and is a rich source for a number of proteins with useful applications in health and pharmaceutical sectors[(10)] , these proteins vary significantly in size , concentration and other properties. Thus Hen egg white comprises over 50% of proteins present in albumin [(11)]. Although its exact function in egg whites is still unclear, its role in external secretion in humans is well established as the first non-immune defense that provides an early barrier against bacterial infections [(12,13)]. Egg white has been successful use in the food industry as the major foaming protein , this is possible due to the ability of the egg white to have homogenous foams of great volume , while improvement of foam stability in the presence of the other compounds or heating , therefore , the use of egg white in ceramics shape forming has many advantages in the processing , egg white is nontoxic , biodegradable , cheap , and widely available [(14)] .

Previous studies about egg white albumin of , had been studied the factors affecting the foaming properties of egg white [(15)], preparation and characterization of chicken egg white hydrolysate [(16)],while no work about adsorption egg white had been done.

Charcoal derived is often used as an adsorbent for the removal of a variety of egg white albumin , this sorbent is highly inert and thermally stable , it can also be used over a broad pH range [(17)].

In this work the total adsorption of EWA from aqueous solution on charcoal derived from walnut shell , peach Nuclei were evaluated by U.V.-Visible spectrophotometery

Material and Methods

Material

Egg White albumin were supplied by Sigma Chemical Co.

Instruments

1. Spectrophotometer T604 ,pg,Instruments ,LTD
2. Balance sensitive –W-Germany
3. PH-meter HANNA, Portugal
4. Oven memmert ,Edelstahi,Germany
5. Shaker Bath ,Indicator GCA,Chicago
6. Centrifugal ,Herouse, septch

Preparation of charcoal derived

The charcoal derived used in this study was prepared by pulverizing the walnut shell and peach Nuclei into the powder in the laboratory pulverizing , washed and dried in oven . It was then kept in furnace up to 600C° for two hours [18].

Preparation of EWA solution

A standard stock solution of Egg white Albumin (200ppm) was prepared by dissolving 0.04gm EWA in 250ml , the volumetric flask 250ml was completed to the mark with deionized water. Solutions of different concentrations were prepared by serial dilutions between (10-100ppm)

Adsorption experiments

Batch adsorption experiments were carried out in a series of volumetric flasks of 50ml capacity and added 0.05gm of charcoal derived from peach Nuclei while 0.2 gm of charcoal derived from Walnut shell with 20ml of the aqueous EWA solution at a constant temperature , water bath shaker for determined time interval at a constant speed of 180rpm. The adsorbent size of 600mm , was used in all experiments. The study on the effect of adsorbent size was performed using the initial EWA concentration of 100ppm. For the study on effects of initial metal concentration , temperature and adsorbent size , no adjustment of pH of the solutions were carried out. However , the study on effect of adsorbent dose was performed at optimum, pH .

The acidity of EWA solution was adjusted by addition drops of HCl or NaOH solutions .

All experiments were duplicated , after adsorption the mixture was filtered through qualitative filter papers. The concentrations of EWA in the solutions before and after equilibrium were determined by U.V.-Visible spectrometer. The amount of EWA adsorbed (Qe in mg/g) was computed using the following relation [19].

$$Qe=\frac{(Co-Ce)V}{m}$$

Where : C_o and Ce are EWA concentrations in ppm before and after adsorption for time , V is volume of adsorbate and m is the weight of adsorbent .

Results and Discussion

Contact time effect results (fig.1) indicate that removal efficiency increased with an increase in contact time before equilibrium is reached .

Other parameters such as dose of adsorbate, pH of solution and agitation speed were kept optimum , while temperature was kept at 292K . Optimum contact time of charcoal derived from walnut shell adsorbents was found to be 60min , compared to that of charcoal derived from peach Nuclei which was 120min . Greater availability of various functional groups on the surface of charcoal derived, which are required for interaction with anions and cations , significantly improved the binding capacity and the process proceeded rapidly[20].

Weight adsorbate effect of EWA sorption was studied by varying the amount of adsorbent from0.05 to 0.2gm while keeping other parameters (pH , contact time and agitation speed) constant . (Fig.2) presents the EWA adsorption amount for the two types of adsoebent used . It can be observed that adsorption amount of the adsorbent generally improved with increasing optimum weight (Fig. 2) .

Adsorption isotherm

To study the relationship between sorbed (Qe) and aqueous

concentration Ce at equilibrium (Fig.4), calcafor adsorption isotherms for EWA removal by charcoal derived .

The experimental data were analyzed according to the linearity of the Langmuir and Freundlich isotherm .

The Langmuir isotherm is represented by the following equation[21].

$$\frac{C_e}{Q_e} = \frac{1}{K_L} + \frac{a}{K_L} . C_e$$

Where :- C_e is the equilibrium concentration (mg/L) ,

Q_e is the amount adsorbed at equilibrium (mg/g),

And K_L and a are Langmiur constants related to adsorption efficiency and energy of adsorption, respectively. The linear plots of C_e/Q_e versus C_e suggest the applicability of the Langmiur isotherms. Values of k_l and a were determined from the slope and intercepts of the plots and are presented (Fig.8).

The Freundlich equation has also been employed for the adsorption of EWA on charcoal derived. The Freundlich isotherm was represented as [22] .

$$\text{Log } Q_e = \log K_f + \frac{1}{n} \log C_{eq}$$

where :- Q_e is the amount of EWA (mg/g),

C_e is the equilibrium concentration of EWA in solution (mg/L), and K_f and n are constants incorporating all factors affecting the adsorption capacity and intensity of adsorption , respectively. The linear plot of Log Q_e versus Log C_e shows that the adsorption of EWA follows the Freundlich isotherm (Fig.7). Values of equation constants were found and were complied in table (1).

pH effect

The pH dependence of EWA adsorption onto charcoal derived is shown in (Fig.3). As it is shown in figure , Q_e is high at pH=2 on charcoal derived from peach Nuclei while Q_e is high at pH=5 on charcoal derived from walnut shell . It is revealed that the adsorption capacity is high at optimum pH because of the dissolution of crystal structure and the competition between the protons and EWA for the exchange sites on the charcoal derived particle [23,24] .

Temperature effect

The adsorption capacity of the charcoal derived increases with increase in the temperature on charcoal derived from peach Nuclei , while decrease on charcoal derived from walnut shell of the system from 292-332 K. The adsorption capacity from 2.676-3.562mg/g on charcoal derived from peach Nuclei while from 8.650-6.690mg/g on charcoal derived walnut shell.

Thermodynamic parameters such as free energy(ΔG) KJ.mol^{-1} enthalpy (ΔH) KJ.mol^{-1} and entropy(ΔS) J. mol^{-1} were determined using the following equations[25-27] .

$$\text{Log } X_m = \frac{-\Delta H}{2.303RT} + \text{Constant}$$

$$\Delta G = -RT \ln \frac{C_e}{Q_e}$$

$$\Delta G = \Delta H - T\Delta S$$

X_m is the optimum adsorption capacity ,

Q_e is the adsorption amount ,

C_e is the concentration at equilibrium

T is the temperature in Kelvin and R is gas constant .

The ΔH value obtained from the slope of van't Hoff plots have been presented in table (2). From the order we could conclude that physisorption is much more favorable for EWA. The positive value of ΔH shows the endothermic nature of adsorption on charcoal derived from peach Nuclei while Negative of ΔH shows Exothermic of adsorption on charcoal derived from walnut shell . It governs the possibility of physical adsorption , in the case of physical adsorption , while increase the temperature of the system , the extent of EWA adsorption increases on peach Nuclei and adsorption decreases on walnut shell . This rules out the possibility of chemisorptions . However , the very low ΔH value depicts EWA are physisorbed onto adsorbent [28], the positive value of ΔG (table 2) shows that the adsorption is slowly Favourable for EWA . However, it indicates that the EWA adsorption is unspontaneous. The negative values of ΔS shows the decrease disorder and randomness at the solid solution interface of the adsorbent on walnut shell and the positive values of ΔS on peach Nuclei[29].

Determination of distribution Coefficient and removal percentage values

Calculation of determined distribution coefficient and removal percentage values were obtained from equation[30]:

$$\text{Re}movel\% = \frac{(Co - Ce)}{Co} x100$$

$$K_d = \frac{(Co - Ce)}{Co}.x \quad \frac{V}{m}$$

The removal and K_d values of EWA on charcoal derived from peach Nuclei increase from 34.5 to 66.9 % and K_d values from 138 to 267.9 when the temperature increased 292k to 332 k°, while the removal percentage of EWA on charcoal derived from walnut shell decrease from 86.2 to 66.9 and K_d values from 86.2 to 66.9 as shown in table(3).These results are in good agreement of the thermodynamic data (tables 2 and3).

Table (1):- Freundlich and Langmuir isotherms for ions using charcoal derived at 292K

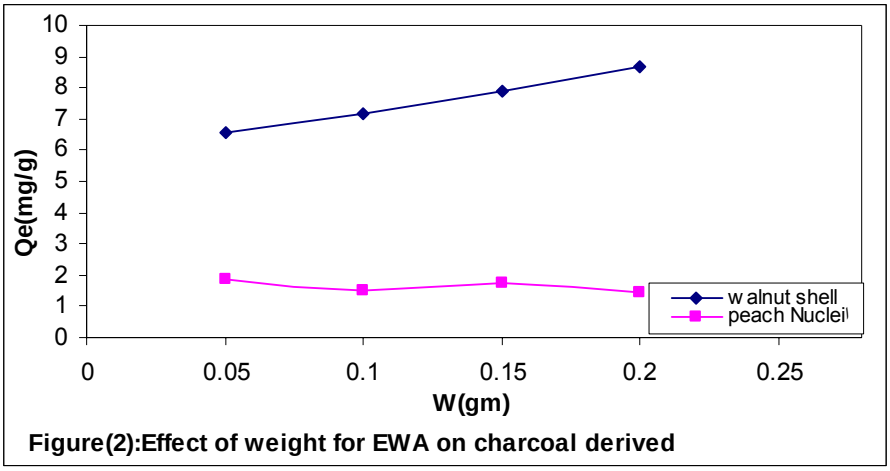
surface	K_f	n	R^2	a	k	R^2
Walnut shell	0.0033	0.335	0.9761	-0.063	0.0994	0.9491
Peach Nuclei	0.102	1.176	0.8367	-0.015	0.041	0.4753

Table(2):- thermodynamic values and constant of vant Hoff"s equation for ions using charcoal derived at 292K

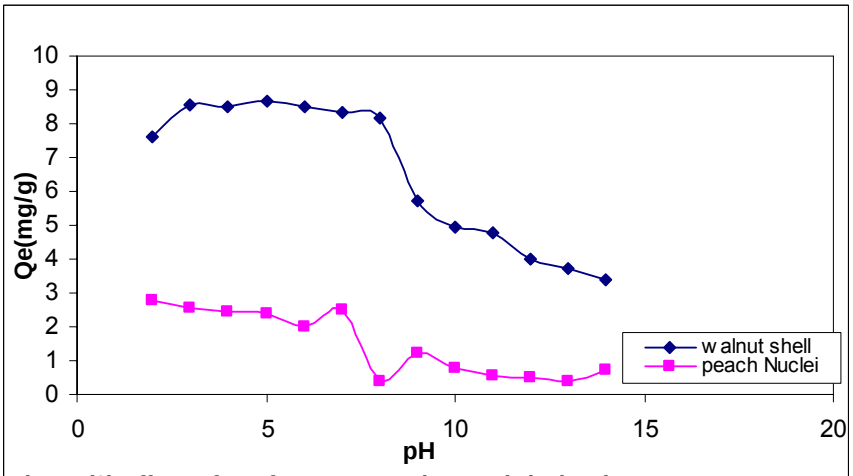
surface	**ΔH(Kj.mol^{-1})**	**ΔG(Kj.mol^{-1})**	**ΔS(j.mol^{-1})**
Walnut shell	-4.825	1.1339	-20.407
Peach Nuclei	6.471	6.106	1.25

Table (3):- removal % and K_d values of BSA on charcoal derived at 292K

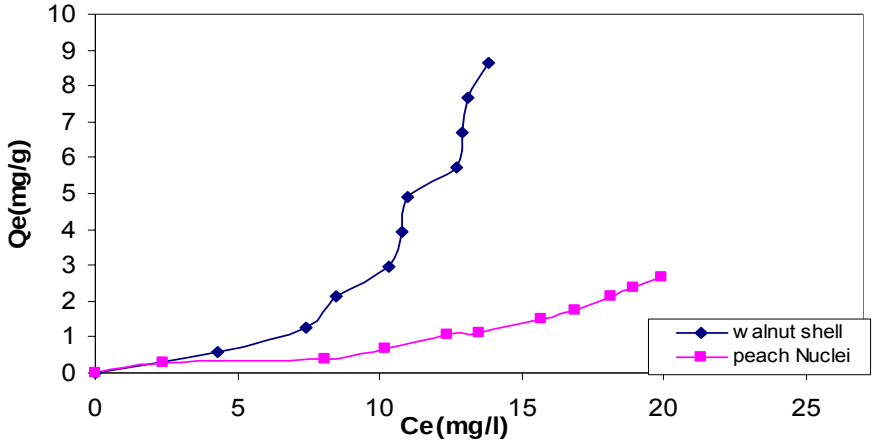
Temp.	Walnut shell		Peach Nuclei	
	Removal %	K_d	Removal %	K_d
292	86.2	86.2	34.5	138
302	85.7	85.7	37	148
312	84.7	84.7	57	228
322	80.2	80.2	59.2	236.9
332	66.9	66.9	66.9	267.9



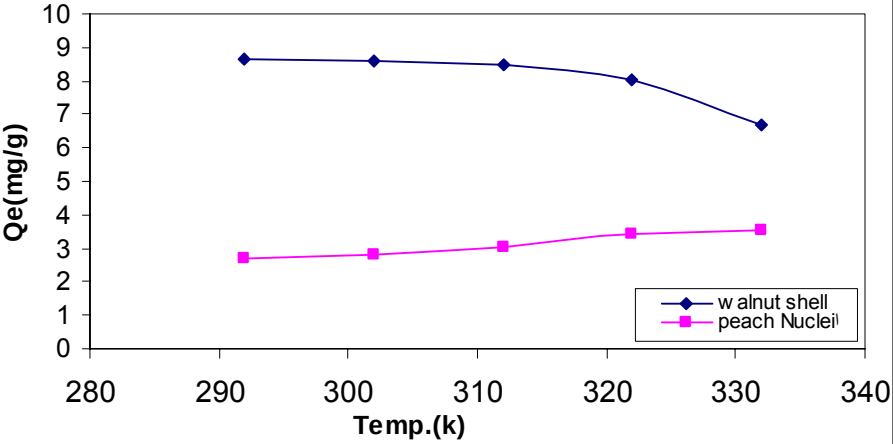
Figure(2):Effect of weight for EWA on charcoal derived



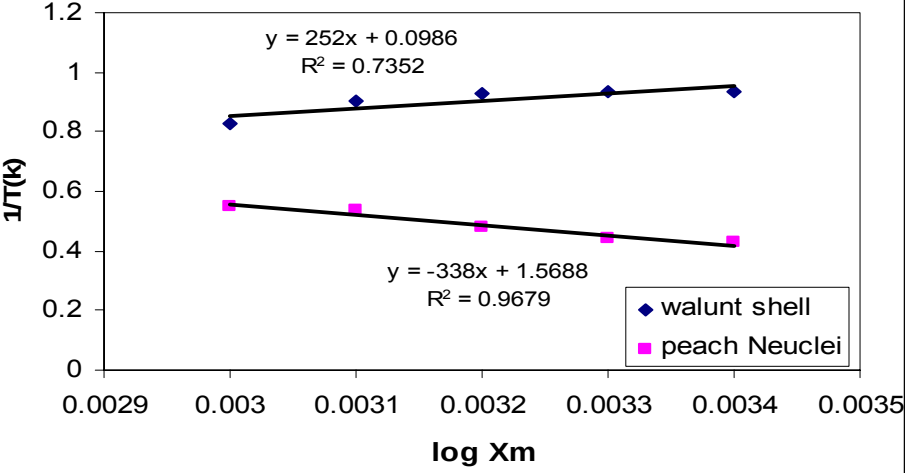
Figure(3):Effect of PH for EWA on charcoal derived



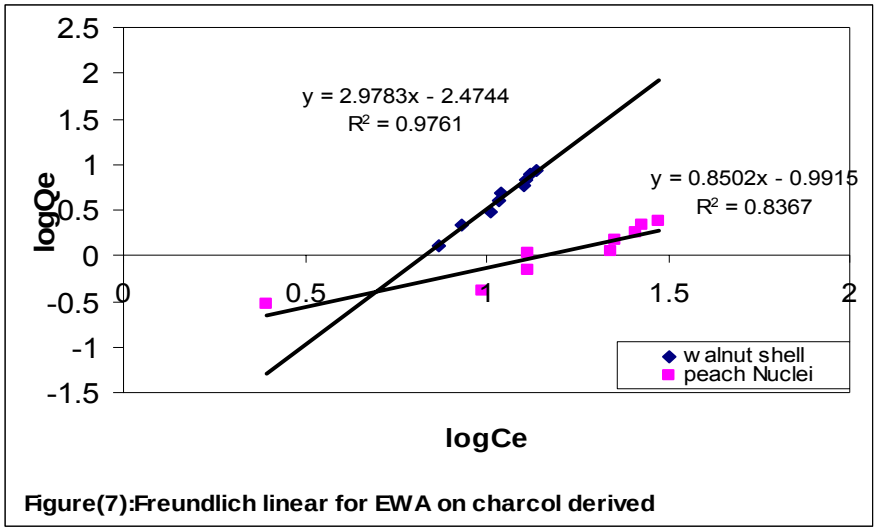
Figure(4):adsorption isotherms for EWA on charcoal derived



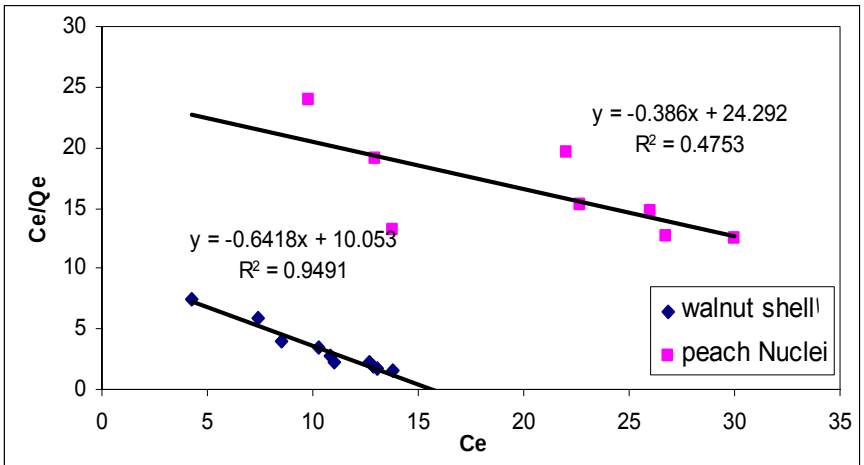
Figure(5):Effect of temperature for EWA adsorption on charcoal derived



Figure(6):Relation between log Xm verus 1/T for EWA on charcoal derived



Figure(7):Freundlich linear for EWA on charcol derived



Figure(8):Langmiur linear for EWA on chrcoal derived

References

1- Meger V. etal , ***Wat. , Sci. , Tech.*** , 1992, **16** , 1205 .

2- Roberto A. etal , ***J.R. Soc. , Inter***., 2008, **5** , 273.

3- Wang Y. etal. , ***Araip , Phys***., 1990, **92** , 6927.

4- Tanaka A. etal. , ***Araip , Phys. , Rev***., 1992, **B45**, 6587.

5- Hofmeistera H. , etal , ***J. Mater. , Res***., 2005, **20** , 1551.

6- Chen W. , Apple. , ***Phys. , Lett***., 2000, **88**, 5193.

7- Brunelt DM etal , Titanium in Medicine-Material Science , Surface Science , Berlin , Springer , (2001).

8- Bucciantini EG. etal. , Inherent Toxicity of Aggregates Implies a Common Mechanism for Protein Misfolding Disease. 416 , 507-11 , (2002).

9- Bonfield W. , Biomat. , ***Matter World*** , 1997, **5(1)** , 18.

10- Desert C. etal , J. , Comparison of Different Elect. Separations of Hen egg white, ***J. Agric***, 2001, **49(10)** , 4553.

11- Davis C. etal , High Value Opportunities From The Chicken Egg, 02, 094, (2002).

12- Ibrahim HR. , etal. , ***FEBS Lett*** , 2001, **506(1)** , 27.

13- Janeway CA. , In : Immunology , Garland Pub. , 35-43 , (2001).
14- Beneventi D. , etal , ***Colloids and Surfaces A: Physicochemical and Eng.*** , 2001, **189**, 65.
15- Kathernal L. etal. , ***j. , Food , Sci. , Czech***., 2004, **24(3)**, 110.
16- Blazc. etal , ***Acta. , Chem.. , Slov***. , 2004, **51**, 177.
17- Skrabakova S. etal. , ***Chem.. , Listy*** , 1995, **89** , 180.
18- Gaikwad R.W. , ***EJEAFChe*** , 2004, **3(4)**, 702.
19- Ngugen Q. etal , ***J. Fac. , Agr***., 2007, **52(2)**, 401.
20- Saifuddin M. , Elec. , ***J. of Biotech.***, 2005, **8** , 1 .
21- Viraji R.S. etal , ***Waste Management*** , 2001, **21**, 105.
22- Arivoli S.,etal, ***The Arabian J. Of Sci.,and Eng***., 2008, **34**, 1A.
23- Ali H.O. etal. , ***J. of Hazardous Materials***, 2006, **1313** , 59.
24- Murat A. etal , ***J. Micr. And Meso. , Materials***, 2006, **94**, 99.
25- Kapoor K.L. , Macmillam , ***India , Limited***, 1994, 449-481.
26- Panday K.K. etal. , ***Wat , Res***., 1985, **19(7)** , 869.
27- Atkins P. etal , ***Atkins Phy. , Chem. , Oxfored Unv.***, 2006, 100-102.
28- Sudha R. etal. , ***E-J. of Chem.***, 2007, **4(2)** , 238.
29- Namasivayam C. etal. , ***Env. Pollut.***, 1995, **89** , 1.
30-Fifield F.W,etal, ***Principles and Pratice of Analytical Chem..,Blackwell***, 2000, 85.