

Thermodynamic Study of Fe⁺³, Cr⁺³ and Cd⁺² Ions Adsorption on Charcoal Derived from Walnut Shell

*L. H. Khdeem

*Chemistry Department, College of Education for Women,
Kufa University, Al-najaf al-ashraf, Iraq
E-Mail: *lekaa_ab07@yahoo.com

ABSTRACT

In this study a commercial charcoal derived walnut shell was used for the adsorption of ions by U.V-Visible absorption spectroscopy technique. Various operating parameters studied were adsorbent dosage, pH, contact time and temperature. The effect of contact time was investigated and found that the adsorption process of Fe⁺³, Cr⁺³ ions on charcoal derived from walnut shell surface was reached at completed equilibrium within 60 min while the adsorption of Cd⁺² was reached equilibrium within 30 min. The effect of the weight of the charcoal derived on the adsorption process was studied a group weight in the range (0.05-0.2 g). The extent of the adsorption found to decreased the temperature increased i.e, exothermic adsorption. The thermodynamic parameters ΔG , ΔH , ΔS were calculated and explained in the mean of the chemical structure of the adsorbate which the values of removal percentage% and Distribution ratio (Kd). The Freundlich and Langmuir isotherm equations were applied to the data and values of parameter of these isotherms equations were evaluated the adsorption.

Keywords: Fe⁺³, Cr⁺³, Cd⁺² ions, Adsorption, Walnut shell, isotherms. Freundlich, Langmuir

1. INTRODUCTION

The fact that using organic compounds and heavy metal in different industry branches becomes more and popular nowadays causes the increase in the pollution of water. These impurities often occur in many waters simultaneously. At the same time, the maximum values of their permissible concentrations have become decreased in drinking waters¹.

The pollution caused by heavy metal was detrimental effect on the environment all over the world. For example, a variety of toxic effects on aquatic organisms can be produced by endangering ecosystems; human health can be directly or indirectly influenced by multiple channels such as touching with skin, drinking water, and food chain². Adsorption on low cost-adsorbent for removal of toxic metals from wastewater was investigated extensively³. Chromium and its compounds are toxic metals introduced into natural water from a variety of industrial wastes. The major sources are from leather tanning, textile dyeing, electroplating and metal finishing industries which cause severe environment and public health problems⁴. Cadmium is one of the most toxic metals affecting environment. It is extensively used by many industries such as electroplating, painting and battery manufacture. Effluents discharged from these industries contain undesired amount of cadmium⁵. The harmful effects of Cd⁺² can be included as the following: a number of acute and chronic disorders, such as itai-itai disease, renal damage, emphysema, hypertension and testicular atrophy⁶. The present of iron in ground and industrial water becomes toxic at high level and then may cause environmental and human health problems^{7,8}. Several methods were proposed for the removal of metal ions as ions exchange⁹, filtration¹⁰, coagulation¹¹, electrochemical deposition¹², and adsorption¹³. Some of the adsorption processes developed for removal of metal ions using biosorbents include tea waste^{14,15}, food waste¹⁶, sugarcane bagasse¹⁷, degreased coffee seeds¹⁸, saw dust¹⁹⁻²¹, eucalyptus bark²², mango peel waste²³, rice husk²⁴, leaf powders²⁵⁻²⁸, tobacco dust²⁹, coconut shell³⁰.

The aim of this study was to investigate the effect on removal of ions adsorbed on charcoal derived from walnut shell. The influence of experimental parameters such as pH, contact time, adsorbent dose, temperature. The adsorption process is studied from isotherm standpoint.

2. EXPERIMENTAL

2.1 Materials

(CrCl₃.6H₂O, CdCl₂.H₂O) were purchased from B.D.H. (97% Purity), and (Fe₂(SO₄)₃) were purchased from fluka (98% purity).

2.2 Instruments

The following instruments were used through out the work

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

2.3 Preparation of charcoal derived

The charcoal derived used in this study was prepared by pulverizing the walnut shell into powder by laboratory pulverize, washed and dried in oven. It was then kept in furnace up to 600C° for two hours³¹.

2.4 Preparation of ions solutions

Standard stock solutions of 500 ppm of Fe⁺³, Cr⁺³, Cd⁺² ions were prepared by dissolving 0.1g of ions compounds in a minimum amount of distilled water in a 200ml volumetric flask and volume was made up to the mark with distilled water. Solutions of different 5-50ppm concentrations were prepared by serial dilutions from the stock solution. Absorbance values of these solutions were measured at the selected λ_{\max} value for each ion and plotted against the concentration values. The Calibration curves in the concentrations range that fall in the region of applicability of Beer-Lambert's law were employed.

2.5 Methods

Removal of ions from aqueous solution on charcoal derived was performed by batch method by shaking 0.1g of charcoal derived with 35ml of Cd⁺², Cr⁺³ ions solutions and 0.15g of charcoal derived with 20 ml of Fe⁺³ ion solution with initial metal ion concentration of 50ppm.

The suspensions were examined, each at different temperature of 292, 302, 312, 322, 332 K . At each temperature, shaking of suspensions was interrupted at different contact time 30, 60, 90, 120, 150, 180, 210 min and the suspensions were filtered The concentration of ions remained in the adsorption were determined using U.V-Visible spectrophotometer .The particle size of charcoal derived used of 600 μ m .The effect of pH on adsorption of ions onto charcoal derived was investigated by varying the solution pH from 2 to 14.

2.6 Calculating the quantity adsorbed

The quantities of ions adsorbed were calculated according to the following equation ⁽³²⁾

$$Q_e = \frac{V_{sol} (C_o - C_e)}{m}$$

Q_e = the amount of adsorption (mg/g)

C_o = initial concentration (mg/L)

C_e = equilibrium concentration (mg/L)

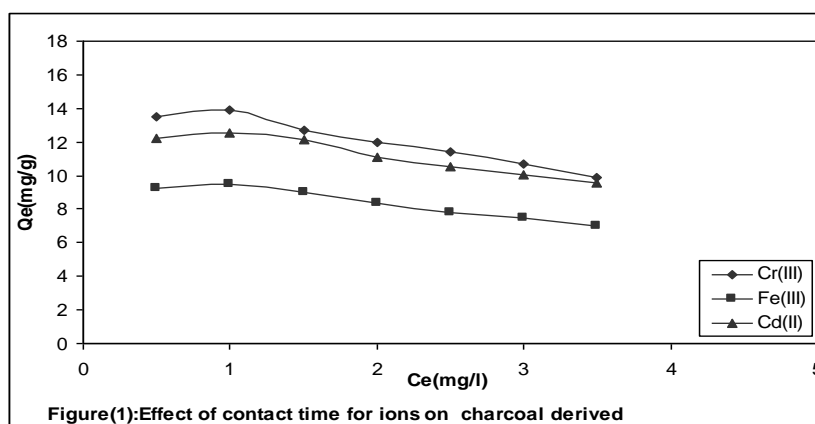
V = volume of solution (L)

M = weight of charcoal derived (g)

3. RESULTS AND DISCUSSION

3.1 Influence of contact time

The nature of the adsorption of ions on charcoal derived as a function of time at a fixed initial concentration 50ppm was studied, for each ion at different times between 30, 60, 90, 120, 150, 180, 210 min .From the experimental data, it was observed that the amount of adsorption increasing, with optimum contact time up to 30 min of Cd⁺², and 60 min for Fe⁺³, Cr⁺³. The amount of adsorption was ranged between 9.473-13.895 mg/g of ions, because of charcoal derived contain atoms which bonded with ions³³, Figure-1.

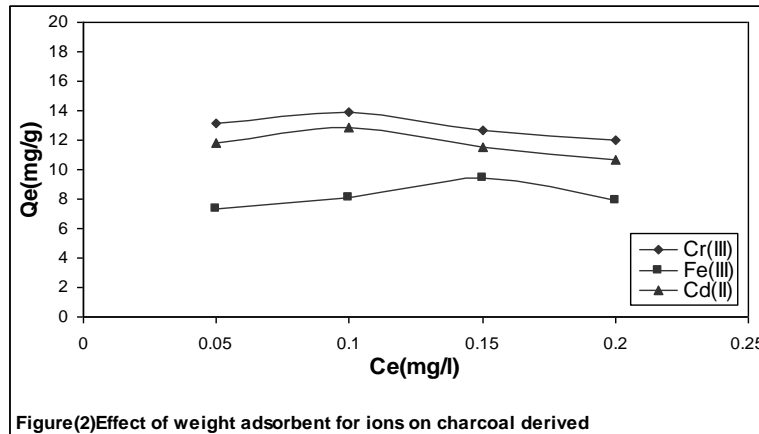


Figure(1): Effect of contact time for ions on charcoal derived

3.2 Effect of weight of charcoal derived

The effect of the weight of the charcoal derived on the adsorption process was studied using several weights ranged between 0.05-0.2g at optimum pH at room temperature. It was found that the amount of adsorption increasing of

optimum weight from charcoal derived in the Cr^{+3} , Cd^{+2} 0.1g and the adsorption capacity 13.895mg/g, 12.810mg/g, while 0.15g of Fe^{+3} and the adsorption capacity 9.473mg/g. This means any increase in the weight of adsorbent had no effect because of the perfect saturation of centers of adsorbent by ions compounds Figure-2.

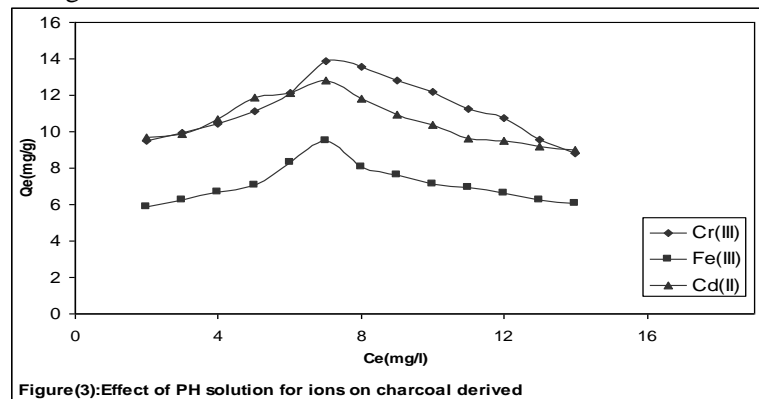


Figure(2):Effect of weight adsorbent for ions on charcoal derived

3.3 Effect of pH Solution

Adsorption experiments were performed over a range of pH 2-14 for the best initial ions concentration 50ppm and optimum contact time 30, 60 min.

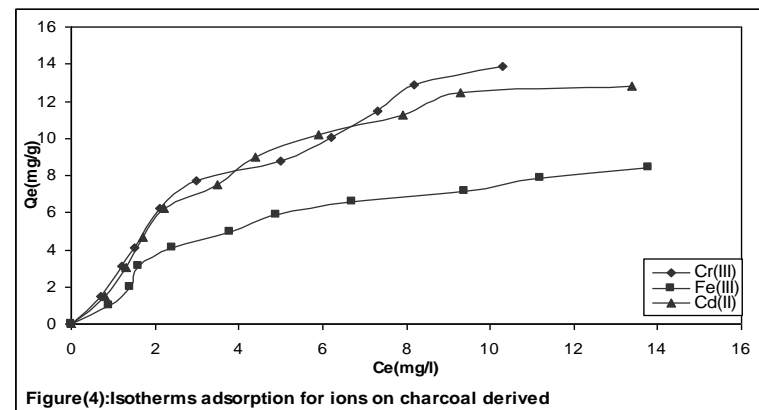
The maximum amount of adsorption by ions Cd^{+2} , Cr^{+3} and Fe^{+3} were 12.180mg/g, 13.895mg/g and 9.473mg/g respectively, at pH =7, the negative charge of charcoal, become contend between H^{+} ion and ions which bonded with oxygen atoms, the decrease amount of adsorption above and low pH=7. The results may be considered in general as a consequence of the competition between solvent – surface, solvent – solute and solute – surface interaction as the pH varied³⁴ Figure-3.



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

3.4 Adsorption of metals on charcoal derived

The adsorption of Fe^{+3} , Cd^{+2} and Cr^{+3} on charcoal derived as a function of their concentration were studied at 292⁰k by varying the metal concentration from 5-50 ppm, while keeping all other parameters constant. The results are shown in Figure-4.

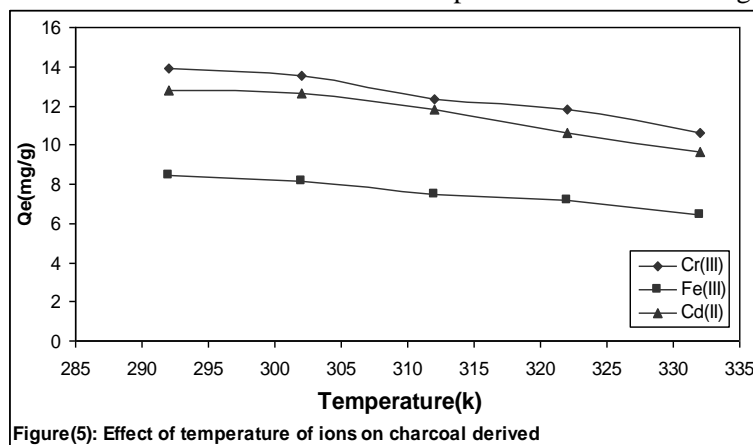


Figure(4):Isotherms adsorption for ions on charcoal derived

The amount of adsorption for ions increasing with increasing equilibrium concentration in aqueous solutions. The results indicate that energetically lost favorable sites become involved with increasing equilibrium concentration in the aqueous solution.

3.5 Effect of temperature

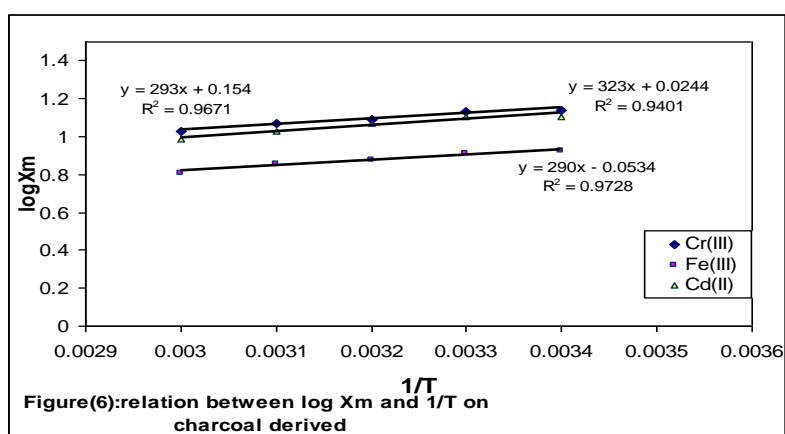
The temperature dependence of ions on charcoal derived was studied at different temperature 292, 302, 312, 322, 332 K. The considerable decrease in the amounts of ions adsorbed with temperature confirms the exothermic nature of the process. The enhancement of adsorption capacity of charcoal derived, with decreasing temperature is attributed to the possible decrease in the number of active sites available for adsorption on the surface³⁵ Figure-5.



Figure(5): Effect of Temperature of ions on charcoal derived

3.6 Thermodynamic parameters

The thermodynamic parameters for the adsorption of ions on charcoal derived such as ΔH , ΔG and ΔS were studied. The heat of adsorption (ΔH) may be obtained from the equation³⁶ Figure-6.



Figure(6): Relation between log Xm and 1/T on charcoal derived

The change in free energy (ΔG) could be determined from the equation³¹.

$$\Delta G = -RT \ln K_{\text{ads}}$$

$$K_{\text{ads}} = q_e / C_e$$

Table-2: Thermodynamic values and surface coverage for ions using charcoal derived at 292K

Ions	$\Delta H(\text{KJ.mol}^{-1})$ -	$\Delta G(\text{KJ.mol}^{-1}.\text{k}^{-1})$	$-\Delta S(\text{J.mol}^{-1}.\text{k}^{-1})$	θ
Cr^{+3}	6.384	5.55	40.86	0.79
Fe^{+3}	5.177	1.42	22.59	0.72
Cd^{+2}	6.189	2.45	29.58	0.73

The change in entropies (ΔS) and surface coverage was calculated from Gibbs equation³⁷ Table-2 shows that ΔH , ΔG , ΔS value of ions adsorption.

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

$$\theta = 1 - C_e/C_o$$

Where θ is the surface coverage C_o, C_e are initial and equilibrium dye concentrations respectively .

3.7 Adsorption isotherm

The experimental dates are analyzed according to the linear form of the Freundlich and Langmuir isotherm. The Freundlich isotherm is represented by the following equation³⁸.

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

Where:

Q_e is the amount of ions adsorption (mg/g)

C_e is the equilibrium concentration of ion (mg/L)

k, f are the constants equation.

In incorporating all factors affecting the adsorption capacity and intensity of adsorption, respectively. Linear plot of $\log Q_e$ versus $\log C_e$ as shown in Figure-7 shows that the adsorption of ions follows also the Freundlich isotherm.

The numerical value of $1/n > 1$ indicates that adsorption capacity is only slightly suppressed at lower equilibrium concentration. That isotherm does not predict any saturation of the sorbent by the sorbate: thus infinite surface coverage is predicted mathematically, indicating multilayer adsorption on the surface³⁹.

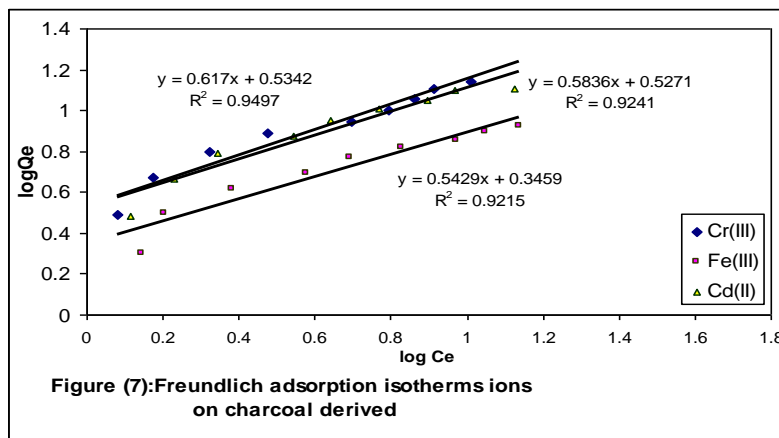


Fig-7: Freundlich adsorption isotherms ions on charcoal derived

The Langmuir equation is also applied to study the behavior of the adsorption of ions on charcoal derived. The Langmuir isotherm is represented as⁴⁰

$$\frac{C_e}{Q_e} = \frac{1}{K_1} + \frac{a}{K_1} \cdot C_e$$

Where

C_e is the equilibrium concentration of ions in solution

Q_e is the amount of ions adsorption

k_1, a are Langmuir constants related to sorption capacity and intensity of adsorption respectively. A linear plot is obtained when C_e/Q_e is plotted against C_e over the entire concentration rang of ions investigated Figure-8. The values of Freundlich and Langmuir constants and R^2 are given Table-1.

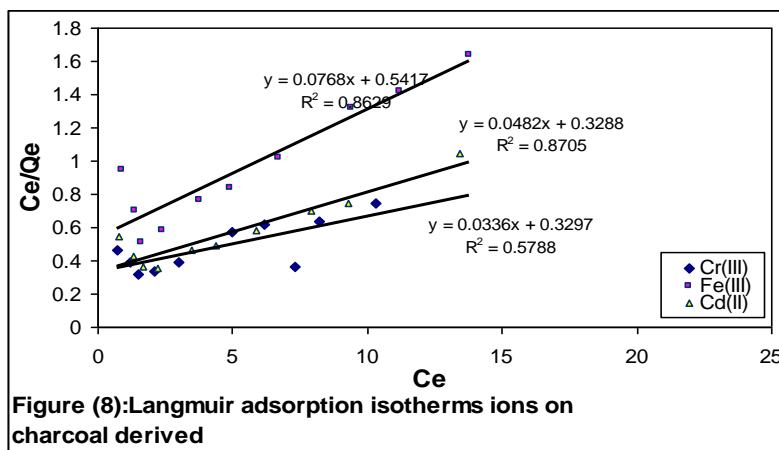


Fig-8: Langmuir adsorption isotherms ions on charcoal derived

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

Ions	K_f	n	R^2	a	k	R^2
Cr^{+3}	3.421	1.620	0.9497	0.101	3.033	0.5788
Fe^{+3}	2.217	1.842	0.9215	0.142	1.846	0.8629
Cd^{+2}	3.365	1.713	0.9241	0.146	3.041	0.8705

3.8 Determined distribution Coefficient and removal percentage values

The distribution Coefficient and removal percentage values were calculated from equation ⁽⁴¹⁾.

$$Removal \% = \frac{(C_o - C_e)}{C_o} \times 100$$

$$K_d = \frac{(C_o - C_e)}{C_o} \times VIM$$

The removal and K_d values of Cr^{+3} ion on charcoal derived from walnut shell decrease from 97.4 to 60.6 % and K_d values from 340.9 to 212.1 when the temperature increased 292k to 332 k, Cr^{+2} ion decrease from 73.2 to 55.2% and K_d values from 256.2 to 193.2 and Fe^{+3} ion increase from 72.4 to 55.2 % and K_d values from 253.4 to 193.2 are shown in Table-3.

Table-3: Removal % and K_d values of ions on charcoal derived at different temperature

Temp.	Cr^{+3}		Cd^{+2}		Fe^{+3}	
	K_d	Removal %	K_d	Removal %	K_d	Removal %
292	340.9	97.4	256.2	73.2	253.4	72.4
302	270.2	77.2	253.4	72.4	243.6	69.6
312	246.4	70.4	236.6	67.6	225.4	64.4
322	325.9	67.4	212.1	60.6	214.9	61.4
332	212.1	60.6	193.2	55.2	193.2	55.2

4. REFERENCES

- Joanna, L., Ewa, O., Ewa, N., and Malgorzata, K., J. Desalination, (2008), 223,249-255.
- Yuan, F., Ji-Lai, G., Guang-ming, Z., Qiu-Ya, N., Hui-Ying, Z., Cheng-Gang, N., Jiu-Hua, D., Ming, Y., Chemical Engineering journal, (2010), 162, 487, 494.
- Oyedeyi, O., and Osinfade, G., J. of Environmental Science and Technology, (2010), 4(6), 382-387.
- Mane, P. C., Bhosle, A. B., Dehmukh, P. D., Jangam, C. M., Advances in Applied Science Research, (2010), 1(3), 212-221.
- Rao, K. S., Anand, S., Venkaleswarlu, P., Journal of industrial and Engineering Chemistry, (2011), 17,174-181, <http://dx.doi.org/10.1016/j.jiec.2011.02.003>.
- Eakkachai, K., Nuthakarn watchara, W., Kitirole, W., Journal of Metals, Materials and Minerals, (2010), 20, 3, 73-76.
- Sarin, P., Snoeyink, V. L., Bebee, J., Jimk, K., Beckett, M. A., Kriven, Water, Res. (2004) 38, 1259-1269.
- Das, B., Hazarika, P., Saikia, G., Kalita, H., Goswami, D. C., Das, H. B., Dube, S. N., J. Hazard. Mater., (2007), 141, 834-841, <http://dx.doi.org/10.1016/j.jhazmat.2006.07.052>.
- Dizge, N., Kaskinler, B., Barlas, H., Journal of Hazardous Materials. (2009), 167,916-926, <http://dx.doi.org/10.1016/j.jhazmat.2009.01.073>.
- Fatin-Rouge, N., Dupont, A., Vidonne, A., Dejeu, J., Fievet, P., Foissy, A., Water Research, (2006), 40, 1303-1309, <http://dx.doi.org/10.1016/j.watres.2006.01.026>.
- El-Samrani, A. G., Lartiges, B. S., Villieras F., Water Research, (2008), 42, 951-960, <http://dx.doi.org/10.1016/j.watres.2007.09.009>.
- Chen, J. P., Lim, L., Chemosphere, (2005), 60, 1384-1392, <http://dx.doi.org/10.1016/j.chemosphere.2005.02.001>.
- Aguado, J., Arsuaga, J. M., Arencibia, A., Lindo, M., Gascan, V., Journal of Hazardous materials, (2009), 163, 213-221, <http://dx.doi.org/10.1016/j.jhazmat.2008.06.080>.
- Mahvi, A. H., Naghipour, D., Vaezi, F., Nazamara, S., Am. Journal Apple, (2005), Sci, 2, 372.
- Cay, S., Uganik, A., Ozasik, A., Sep. Purif, Techno, (2004), 1, 38, 273.
- Zheny, W., Wang, F., Yanga, Q., Dengb, P., Zenga, G. M., Hazardous Mater, (2008), 157, 490, <http://dx.doi.org/10.1016/j.jhazmat.2008.01.029>.
- Ibrahim, S. C., Hanafia, K. M., Yahya, M. A. Z., American Eurrsian, J. Agric, Environ, (2006), 1(3), 179.
- Kaikake, K., Hoaki, K., Sunada, H., Dhakal, R. P., Baba, Y., Bioresour, Technol, (2007), 98, 2787, <http://dx.doi.org/10.1016/j.biortech.2006.02.040>.

19. Memon, S. Q., Memon, N., Shaw, S. W., Khuhawar, M. Y., Bhangar, M. I. J., Hazard Mater. B., (2007), 139, 116, <http://dx.doi.org/10.1016/j.jhazmat.2006.06.013>.
20. Naiya, T. K., Chowdhury, P., Bhattacharya, A. K., Das, S. K., Chem., Eng, (2009), 148, 68.
21. Jeon, C., Kim, J. H., J. Ind., Eng., Chem, (2009), 15(6), 910.
22. Ghodbane, I., Nouri, L., Hamdaoui, O., Chiha, M., J. Hazard Mater, (2007), 152,148, <http://dx.doi.org/10.1016/j.jhazmat.2007.06.079>.
23. Iqbal, M., Saeed, A., Zafar, S. I., J. Hazard Mater, (2009), 164, 161, <http://dx.doi.org/10.1016/j.jhazmat.2008.07.141>.
24. Kumar, U., Bandyopadhyay, M., Bioresour. Technol, (2006), 97, 104, <http://dx.doi.org/10.1016/j.biortech.2005.02.027>.
25. Pao, K. S., Anand, S., Venkateswarlu, P., Bioresources, (2010), 5(1), 438.
26. Pao, K. S., Anand, S., Venkateswarlu, P., Korean J. Chem. Eng, (2010), 27(5), 1547.
27. Pao, K. S., Anand, S., Venkateswarlu, P., Adsorp. Sci, Technol, (2010), 28(2), 163.
28. Pao, K. S., Anand, S., Venkateswarlu, P., India J. Chem Technol, (2010), 17(5), 329.
29. Aldrich, C., Bioresource Technology, (2008), 99, 5595-5601, <http://dx.doi.org/10.1016/j.biortech.2007.10.042>.
30. Pino, G. H., de Mesquita, L. M. S., Torem, M. L., Pinto, G. A., Min., Eng., (2006), 19, 380-387, <http://dx.doi.org/10.1016/j.mineng.2005.12.003>.
31. Gaikwad, R. W., EJEAF Chem., (2004), 3(4), 702-709.
32. El Sayed, G. O., Dessouki, H. A., Ibrahim, S. S., Chemical Sciences Journal, (2010), 30, CSJ-9.
33. Qadeer, R., J. of Zhejjang, Univ., Sci., (2005), 6B(5), 353-356.
34. Adamson, A., Phy. Chem. of Surfaces, (1984), 369-398.
35. Anoop, K. K., Indian J. Chem. Technol., (2002), 9, 32.
36. Orawan, S., Wanna, I., Laemthong, C., Doungporn, C., Kanokrat, N., Songklanakarin, J. Sci., Tech., (2002), 24, 2.
37. Bekkouche, S., J. of Science Chemistry Desalination, (2004), 166, 355-362, <http://dx.doi.org/10.1016/j.desal.2004.06.090>.
38. Horsfall, M., Spiff, A. I., Biomass. Bull. Chem, Soc., (2005), 19(1), 89-102.
39. Hasany, S. M., J. Radioanal, Nucl., Chem., (2002), 252, 477.
40. Zaid A., Mohammed A.S., J. Mex., Chem., Soc., (2008), 52(2), 108-115.
41. Yoshita, A., Lu, J. L., Ye, J. H., and Liang, Y. R., Journal of Biotechnology, (2009), 8(10), 2212-2217.