International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.9, No.06 pp 560-566, 2016

Experimental study to removal of methylene blue dye from aqueous solution by adsorption on eco-frendliy materials

Jasim M. Salman[1]*, Maysam A. Baiee[2] , Alaa R. Omran[3]

[1]Department of Biology ,College of Science ,University of Babylon , Hilla, 5001, Iraq.
[2]College of Ecology ,AL-Qasim Green University , Hilla, 5001, Iraq.
[3]Environmental Research Center, University of Babylon , Hilla, 5001, Iraq.

Abstract : The aim of percent work is examination ability of aquatic plant (*phragmiate australies*) as adsorbent material of removal methylene blue dye from aqueous solution. Aqutic plant was collected from local habitat in iraq as low cost, available, active adsorbent. Batch experiments were conducted to obtain optimum removal conditions, such as concentration of dye, adsorbent dosage, contacted time, and pH of dye solution. The results show higher efficiency of removal was 94% , the equilibrium time was 80 min, and the removal dye efficiency in the basic media was higher than the efficiency in the acidic media.
Keywords: Adsorption, Removal, Methylene Blue dye , Zero point Charge, Textile effluents, *phragmiate australies.*

Introduction

Recently industries utilize many species of synthetic dyes that found in their waste water which pass out to the environment, casing many environmental problems, due to complex aromatic structure which its make have higher resistance toward under ambient circumstances (bio, thermal photo- degradation)[1]. One of the most important these dye is the Methylene Blue dye [3,7-bis(Dimethylamino)-phenazathionium chloride Tetramethylthionine chloride], have chemical formula ($C_{16}H_{18}ClN_3S.3H_2O$), is hetrocyclic aromatic compound[1,2]. Methylene blue (MB) is a cationic thiazine dye that have blue color in the oxidized state but it is colorless in its reduced state (leucomethylene blue). The two states (methylene blue and leucomethylene) are found as redox couple in equilibrium as electron donor-acceptor couple or oxidation-reduction system[3].

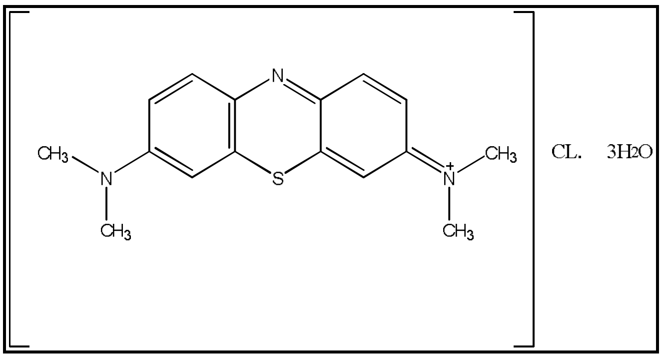

Fig.1.Structure for Methylene Blue dye

There are many methods that use to treatments the methylene blue dye involve physical, chemical, and biological technologies but the adsorption is play an important role in the water treatment, due to low cost (espitilay the natural adsorbent use), ease applied, and efficient[4,24-29]. In recent a few years the use of plant residuals in the adsorption of methylene blue was used in many study, because these materials represent natural siliceous materials in addition to good others properties such as availability, low cost, and eco- friendly adsorbent[5]. There are many study deal with the adsorption of textiles dyes on the various aquatic plants, can be listed some in the following table:-

Table.1. Examples of some aquatic plants was used as adsorbents materials .

No	Adsorbents	Name of researchers	year
1	*Hydrilla verticillata*	Low et al.	1994 [6]
2	water hyacinth roots	Varghese et al.	2004 [7]
3	water hyacinth roots	Soni et al.	2012 [8]
4	water hyacinth shoot	Inengite et al	2014 [9]
5	*Lemna minor*	Salman et al.	2016 [1]
6	*Phragmites australis*	Omran et a.l	2016 [10]

These ciliceous plants wastes containing high percentage of cellulose which have active functional groups like O-H, C=O aldehydes or ketones and phenolic O-H. these groups represent active site on the raw material which use as adsorbent in the removal contaminates process in the aquose phase[11, 1].

The aim of the present work was to highlight the utilize of a plant waste (*Phragmites australis*) as natural, eco-friendly, available, and low cost material in removing Methylene Blue dye from aqueous solution under different operating conditions was investigated.

Experimental study

The samples of aqutic plant were collected from ranning water system in Hilla city middle of Iraq. The specimens washed by running tap water for removing the impurities like soils, dust etc. then it washed by distilled water. The powder Dried at room temperature for ten days and then convert to powder by pulverized mill. The products powder washing with water (to remove color) till the washing solution become colorless and dried at 25 ^{o}C for 24 hours. The function groups in the powder were obtain by using a PerkinElmer Tensor 27 Fourier transform infrared spectrometer (Germany), dried, *Phragmites australis* powder (2 mg) was mixed thoroughly with KBr (300 mg) and then pressed in vacuo to homogeneous disc with a thickness of about 0.9 mm.

The stok solution (1000mg/L) of Methylene blue (MB) dye [Chemical formula=$C_{16}H_{18}ClN_3S.3H_2O$, was obtained by sigma-alderich chemicals] was prepared by dissolving accurate weighed of powder dye in the distilled water. The experimental solutions were prepared from stok solution by dilutions.

0.5g of *Phragmites australis* powder (i.e. adsorbent) were weighted and put each Wight into 250ml conical flasks. Added for each conical 50ml solution methylene blue dye. The conical flasks shaken continuously for different times to reach equilibrium concentration. The suspended particles of adsorbent were separated by used centrifuge, and the final absorption corresponding each solutions by using spectrophotometer (UV/VIS-JENWAY,1600, German). The removal percentage calculated from the equation:

$$removal\% = (A^{\circ} - A)\ A^{\circ} \times 100\ldots$$

(A^{o} and A is the absorption of concentration of dye before and after adsorption respectively.)

Resultes and Disscation

Achieved washing adsorbent process were play major roles in this research: first to remove impurities from the adsorbent, and second to release the color of material and avoided interfere spectrophotometrically with wave length of methylene blue, this case recognized by analyzed washing solution spectrophotometrically after each one washing time. After second washing time the absorbance was negligible at 663nm. So the per-treatment of two washing cycles were adequate[13].

The elemental composition and the types of functional groups of Phragmites australis powder that are represents active site for the molecules of dye adsorption was obtained by elemental analysis, FTIR. The FTIR spectra of the tar are given in Fig. 2, and Fig. 3. the type of function groups and their corresponding discretions are tabled in Table 2. The band between 3390 cm^{-1} indicating the presence of O–H (stretching vibrations)[14] alcohols and phenols are present in the structure of adsorbent, which appears in the position 3433.29 cm^{-1} after adsorption due to interaction with methylene blue dye. The bands at 2923 and 2957 cm^{-1} are show the presence of aliphatic structure in the Phragmites australis powder[15]. While the bands at 2855 and 2915 cm^{-1} is indicative the present saturated C-H symmetrical and asymmetrical stretching .The band at 1635.6 cm^{-1} is represented to the bending vibration of absorbed water on the fibers of hemicellulose component due to this fibers have high affinity for water adsorption [15,16], while this band was appears in the position 1533.29 cm^{-1} after adsorption due to replace water and interaction methylene blue dye with adsorbent. The 1265 cm^{-1} band refers to the stretching vibration of ethers[15]. The bands at 700–900 cm^{-1}. The C=O stretching vibrations at 1732 cm^{-1} denoting the presence of the carbonyl groups[17] refer to ketones, phenols, carboxyl acids and aldehydes, which appears in the position 1570.29 cm^{-1} after adsorption due to interaction with methylene blue dye.

Table 2: Infrared spectrum data of *Phragmites australis* powder after and befor adsorption

No	Frequency cm^{-1} Befor adsorption	Assignment	Frequency cm^{-1} After adsorption
1	3390.86	O-H Alcohol	3433.29
2	2960 and 2922.16	aliphatic structure	……………..
3	1732.08	C=Ostretching vibrations	1570
	1635.64	O-H bending (of H_2O)	1533
4	1371.39	O-H bending	1367.53
5	1250.22	C-O stretching	1274.95
6	1161.15	C-OH bending	1180
7	1103.28	C-O-H(OH association)	
8	1060.85	C-OH bending	1060.
9	1045.42	C-O-C stretching (pyranose ring skeletal)	1041.56

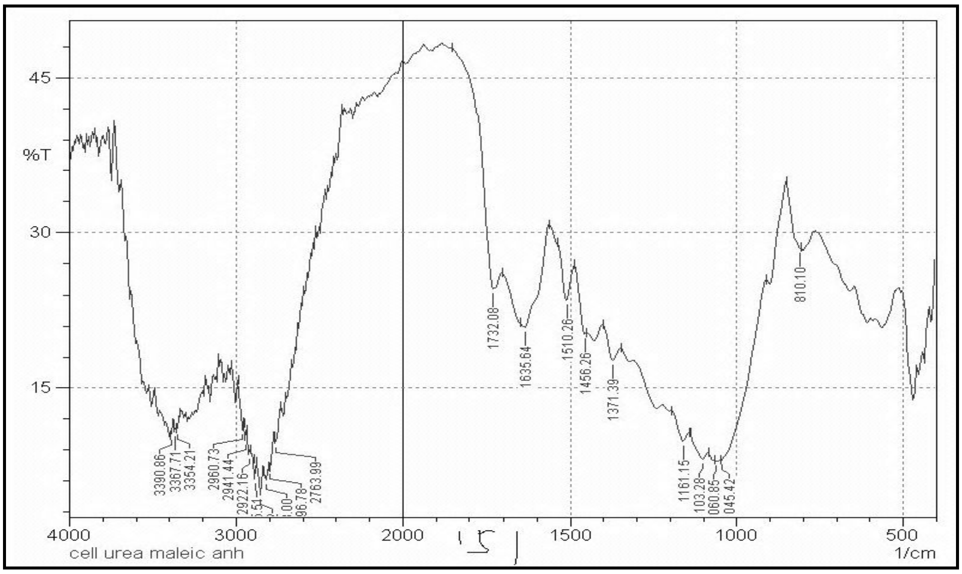

Fig. 2. FTIR *Phragmites australis* powder befor adsorption.

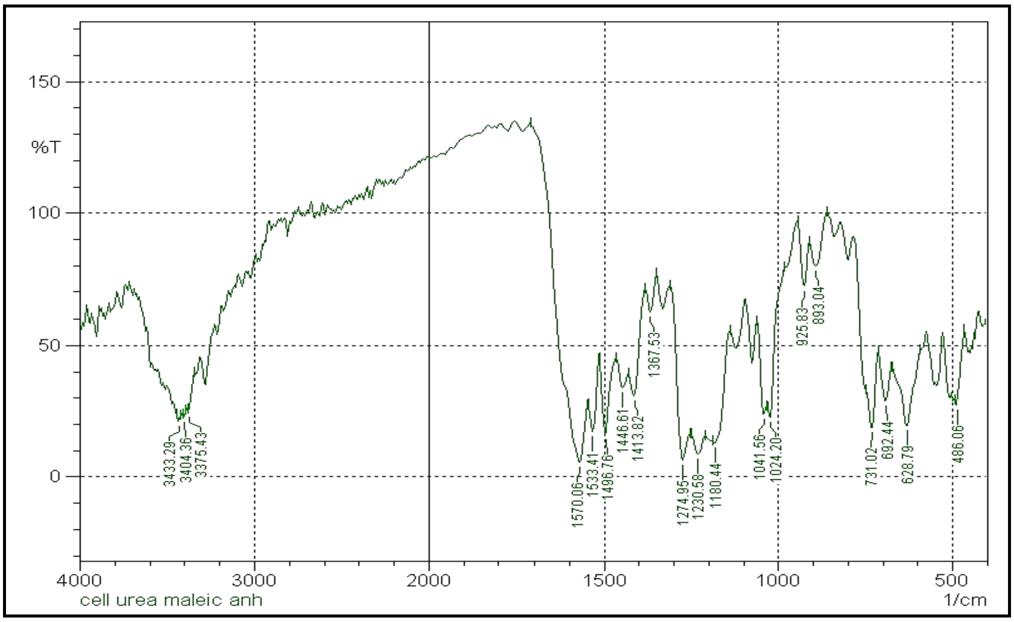

Fig. 3. FTIR *Phragmites australis* powder after adsorption.

The influence of methylene blue dye concentration and contact time on the removal percentage by use Phragmites australis powder as adsorbent were studies with different contact time (10-90 min) and with different concentration of adsorbate 10, 20, 40mg/L at pH-6.0, room temperature (22±2°C) and adsorbent dose-2g/L. The results are shown in Fig.(4).

When the concentration of adsorbate is raise from 10 to 50 ppm the removal percentage decreases from (94 %) to (69 %). this increases the Available driving force to overcome all of mass transfer resistance, and the enhances of adsorbtion capacity of Phragmites australis powder with increasing concentration of adsorbate because this led to raising interaction between adsorbate and adsorbent[18, 19]. Generally the results shown the removal percentage was raising with contact time progress. At the initial stage, there was a rapid adsorption of the dyes. It aboves that the removal of dye was rapid at the first 20mins, due to strong attraction between active site available on the surface of the adsorbent and dye molecules[10].

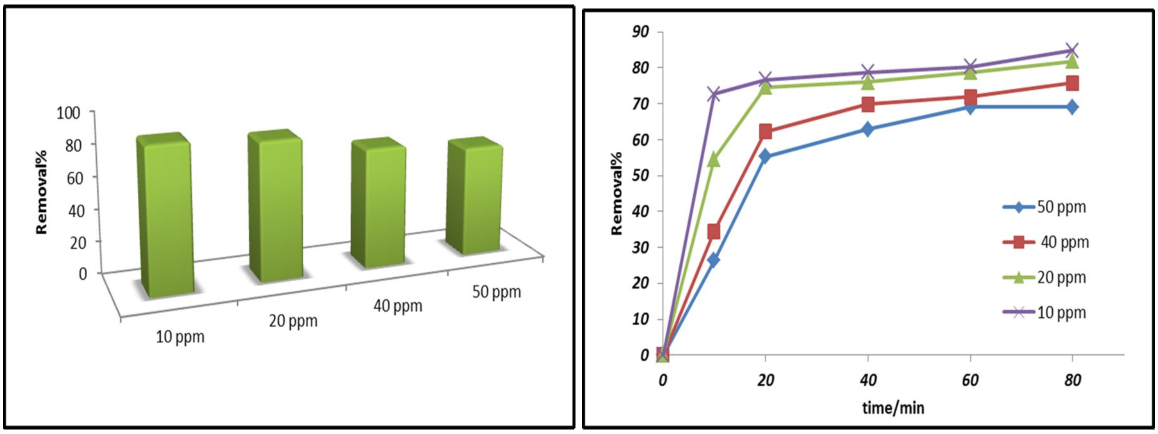

Fig.(4) Effect of contact time and methylene blue dye concentreation on removal efficiency at constant adsorbent dose of 2g/L and neutral pH.

The effect of *Phragmites australis* dosage on removal adsorbate was cried out for adsorbent dose (2, 4, 6g/L) at operation condition contact time of 90 min with initial concentration of dye 50mg/L at room temperature (22±2°C) and pH-6.0. The obtained results are illustrated in Fig.5. The data obvious that the removal dye efficiency increases with high dosage at constant operation condition because increase adsorbent dose lead to increasing available active sites due to increasing the surface area of adsorbent[20,21].

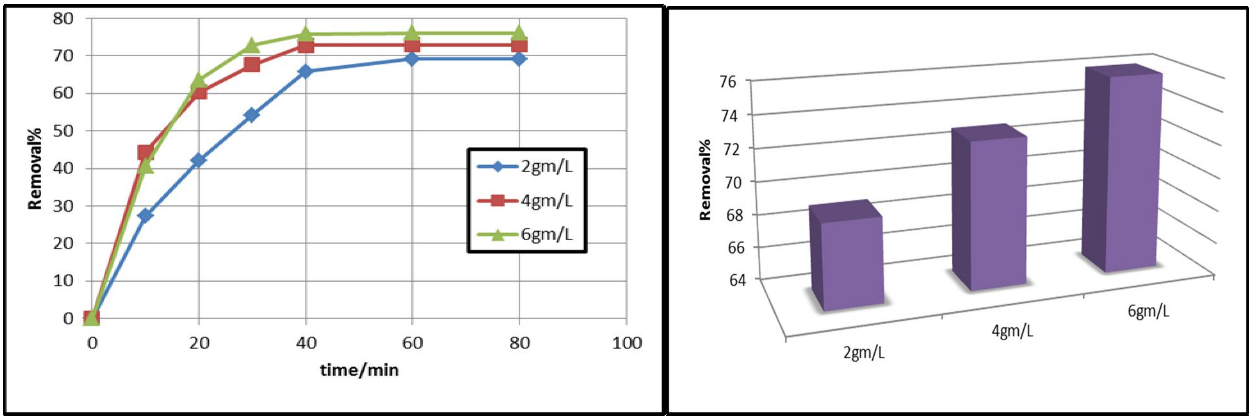

Fig.5. The effect of the absorbent dose on the removal of methylene blue and reaction time initial dye concentration 50 mg/L at pH-6.0, room temperature (27±2°C).

The pH of effluent has direct effect on the removal pollutants process from aqeouse solution, The effect pH of solution on removal of methylene blue has been studies by changing the pH over a range of (4-9) at constant operation condition concentration of dye 50 ppm. optimum Phragmites australis powder dosage is 4 gm/L and contact time of 90 min, the data are which obtained shown in Fig. (6). The results oboveouse the removal methylene blue efficiency in the acidic medium is low and gradually icreased to the basic medium. In the acidic medium (the zero of poit charge of Phragmites australis powder was 6.5 [18]) due to low negatively active site avlibile on the Phragmites australis powder. While in the this medium there are much more positively active site [22], this generation electrostatic repulsion positively charged dye cations[15,23]. also migth be because presence of positively hydrogens ions which interfering with dye cations for the available adsorption sites [21,23].

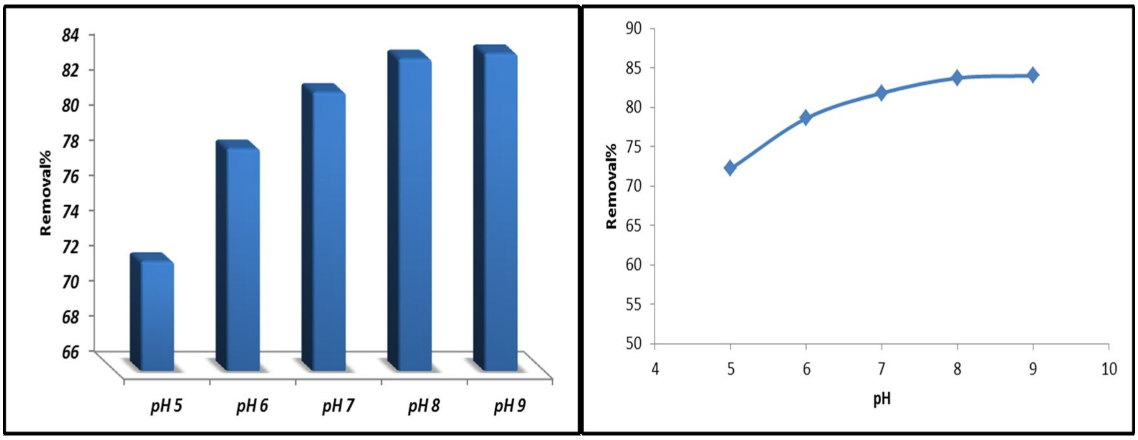

Fig.6. The effect of the pH of solution absorbent on the removal of methylene blue and reaction time initial dye concentration 50 mg/L at pH-6.0, room temperature (27±2°C), and Absorbent dose 4gm/L .

Conclusion

The waste Phragmites australis powder have higher adsorption capaity to absorb methylene blue dye The optimum operating condition were 10 mg/l initial dye concentration, 6 gm/L adsorbent dosage, in the basic pH the absorbent have adsorption capacity more then acidic medium and equlibreuim time 80 min .

Acknowledgements

The authors acknowledge the Environmental Research Center, University of Babylon for their assistance and facilities used to complete this work.

References

1. Salman. J.M, Amrin. A.R, Jouda. S.A, Use of aquatic plant (*lemna minor*) as adsorbent materials to removal of methylene blue dye from aqueouse solution Journal of advance chemical scinces2016, 2(1),192-194.
2. Wiklund L, Basu S, Miclescu A, Neuro- and cardioprotective effects of blockade of nitric oxide action by administration of methylene blue. Ann N Y Acad Sci; 2007, 1122: 231-244.
3. Faber P, Ronald A, Millar BW. Methylthioninium chloride: pharmacology and clinical applications with special emphasis on nitric oxide mediated vasodilatory shock during cardiopulmonary bypass. Anaesthesia; 2005, 60: 575-587.
4. Mohammed M.A, Shitu A, and Ibrahim, Removal of methylene blue using low cost Adsorbent: A Review, Research Journal of Chimical Scinces, 2014, 4(1), 91-102.
5. Ahmed M.N. & Ram R.N, Removal of basic dye from wast water using silica as adsorbent, Environ, Pollut, 1992, 77, 79-86.
6. Low K.S, Lee C.K, and Heng L.L, Sorption of basic dyes by Hydrilla Verticillata, Environ. Tech, 1994, 14, 115-124.
7. Varghese S, Vinod V.P, and Anirudhan T.S, Kinetics and Equilibrium Characterizaation of phenols Adsorption onto a novel Activated Carbon in water treatment, Indian J. Chem. Tech, 2004, 11, 825-833.
8. Soni M, Sharma A.K, Srivastava J.K, and Yadav J.S, Adsorptive Removal of Methylene blue Dye from an Aqeouse Solution using Water Hyacinth Root Powder as a Low cost Adsorbent, international journal of chemical Scinces and Application, 2012, 3(3), 338-345.
9. Inengite A.k, Abssi C.Y, and Johnny D.B, Equilibrium Studies of Methylene blue Dye Sorption by Dride Water Hyacinth Shoot, Environment and Natural Resouces Research, 2014, 4, 4.
10. Alaa R. Omran, Maysam A. Baiee, Sarab A. Juda, Jasim M. Salman, Ayad F. AlKaim, removal of Congo red dye from aqueous solution using new adsorbent surface developed from aqutic plant*(Phragmites australis),* Internitonal Journal of Chem Tech Research 2016, 5(9), 334-342.
11. Rasool. K, Lee. D. S, Characteristics, kinetics and thermodynamics of Congo Red biosorption by activated sulfidogenic sludge from an aqueous solution, Int. J. Environ. Sci. Technol. 2015, 12:571–580.
12. Abu-Saied. M.A, Abdel-Halim, E.S, Moustafa Fouda M.G, Al-Deyab. S. Salem, Preparation and Characterization of Iminated Polyacrylonitrile for the Removal of Methylene Blue from Aqueous Solutions Int. J. Electrochem. Sci, 2013, 8, 5121 – 5135.
13. Bulut, Y., Aydın, H., A kinetics and thermodynamics study of methylene blue adsorption on wheat shells, Desalination, 2006, 194, 259–267.
14. Fuchsman. C.H, Peat Industrial Chemistry and Technology, Academic Press, 1980.
15. Nimkar. D. A, Chavan. S. K, Removal of Congo red Dye from Aqueous Solution by Using Saw Dust as an Adsorbent, 2014, (4) 1, 47-51.
16. Hale S., Pyrolysis of Phragmites Australis and characterization of liquid and solid products, Journal of Industrial and Engineering Chemistry, 2008, 14, 573–577.
17. Salman J.M, Amrin. A.R, F.M. Hassan, Jouda. S.A, Removal of congo red dye from aqueous solution by using natural materials . Mesop. environ. j., 2015, 1 (3) 82-89.
18. Zahra. H, A. Mohammad, Z.Zuainal, F. Ahmadun, and H. Mohd Removal Methyl Orange from Aqueous Solutions Using Dragon Fruit (*Hylocereusundatus*) ,Foliage Chem Sci Trans, 2013, 2(3), 900-910.
19. Mehdi. S; Halimah. M; Nashriyah. M. and Ismail. B.S "Adsorption and Desorption of Paraquat in Two Malaysian Agricultural Soils" American-Eurasian Journal of Sustainable Agriculture, 2009, 3, 3,555-560.
20. Yusuf. M, F.M.Elfghi, S.K.Mallak, Kinetic studies of Safranin-Oremoval from aqueouse solution using Pineapple Peels, iranica journal of energy& Environment, 2015, 6(3), 173-180.
21. Marius S.S., Benoit C., Igor C., Mariana D. and Stelian P., Removal of an Acid Dye from Aqueous Solution by Adsorption on a Commercial Granular Activated Carbon:Equilibrium, Kinetic and Thermodynamic Study, 2011, 12, 4, pp. 307-322.
22. Salman, J.M, Amrin A.R, Jouda, S.A., Aquatic crusteans shell as adsorpents for paraquate pesticide removal from its aqueous solution by thermal activation , Mesop. Environ. J.. 2015, 1 4, 75-83.
23. Hameed, B.H Evaluation of papaya seeds as a novel non-conventional low-cost adsorbent for removal of methylene blue. J. Hazard. Mater., 2009, 162, 939–944.

24. R.Sudha, P. Premkumar, Lead Removal by Waste Organic Plant Source Materials Review, International Journal of ChemTech Research,2016, Vol.9, No.01 pp 47-57.
25. Kouame Kouame Victor, Meite Ladji, Adjiri Oi Adjiri, Yapi Dope Armel Cyrille, Tidou Abiba Sanogo, Bioaccumulation of Heavy Metals from Wastewaters (Pb, Zn, Cd, Cu and Cr) in Water Hyacinth (*Eichhornia crassipes*) and Water Lettuce (*Pistia stratiotes*), International Journal of ChemTech Research ,2016, Vol.9, No.02 pp 189-195.
26. Senthamil Selvan K, Palanivel M, A Case study approach on Municipal Solid Waste generation and its impact on the soil environment in Dharapuram Municipality, Tamilnadu, India, International Journal of ChemTech Research,2016, Vol.9, No.02 pp 196-204.
27. M. Mohamed Sihabudeen, A. Abbas Ali and A. Zahir Hussain, Removal of Heavy Metals from Ground Water using Eucalyptus Carbon as Adsorbent, International Journal of ChemTech Research ,2016, Vol.9, No.03 pp 254-257.
28. G.BabuRao, M. Krishna Prasad, K. Kishore Kumar, Biosorption of Copper (II) from Aqueous Solution using Oscillatoria.Splendida, International Journal of ChemTech Research,2016, Vol.9, No.03 pp 290-295.
29. A. Naga Babu, G.V. Krishna Mohan and K. Ravindhranath, Removal of Chromium (VI) from Polluted waters using Adsorbents derived from Chenopodium album and Eclipta prostrate Plant Materials, International Journal of ChemTech Research ,2016, Vol.9, No.03 pp 506-516.

*****