ISSN NO. 2320-5407

Journal homepage: http://www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH

RESEARCH ARTICLE

Removing the methylene blue dye from aqueous solutions by low cost materials

Jasim M. Salman[1], Noor A. Abdal-Hussein[2], Ali K. Al Muttairi[3]

1.Department of Biology, College of Science, University of Babylon, Iraq

2, 3..Environmental Researchers Center, University of Babylon, Iraq

Manuscript Info

Manuscript History:

Received: 25 February 2015
Final Accepted: 26 March 2015
Published Online: April 2015

Key words:

Methylene Blue, Adsorption, Watermelon Seed Shells, Water Treatment, Green chemistry

Corresponding Author

Jasim M. Salman

Abstract

In this paper we try to find a new and cheep method to remove metheylen blue from aqueous solutions, this study suggested water melon seeds shells as strong and cheep adsorbate , the experiments show that the best contact time (duration) is two hours which give a dye removal efficiency(R) = 66.83, and there is a direct correlation between the concentration of the adsorbate and the value of R , which Ranging from R=38.56 at concentration 0.5gm to R=82.27 at concentration 2.5 gm, the results also show that water melon seeds shells at concentration of 1.5 gm was able to remove M.B. from aqueous solution with concentration of 100mg/L With R=81.63, in this study also the effect of pH value on the adsorption process, the results show that the removal of M.B. increase with decrease of pH value, also the isotherm studies were conducted including Langmuir and freundlich models which were analyzed and the results fit with freundlich models more than Longmuir model.

INTRODUCTION

Watermelon (*Cucumis melo*), from the family of cucumber (Cucurbitacea), Watermelon is one of the major under-utilized fruits grown in the warmer part of the world, Watermelon is a very rich source of vitamins, Melon fruit contains large quantities of seeds The seeds can be cooked and dried and served as snacks eg. Egypt, Iran and might also be cooked, ground West Africa (Koocheki *et al*., 2007).

The effluent from textile industries contain a large amount of dyes such as methylene blue and congo red, the discharged by textile industries are first treated for the separation of dyestuff and then send to disposing end (Khan *et al*., 2005). the presence of dyes in water, even in very low quantities, is highly visible and undesirable; color interferes with penetration of sunlight into waters; retards photosynthesis; inhibits the growth of aquatic biota and interferes with gas solubility in water bodies (Shahryari *et al*., 2010).Methylene blue (MB) is a cationic dye with the chemical name tetramethy lthionine chloride, it has been widely used in a variety of clinical settings to identify anatomicand pathologic structures and to treat methemoglobinemia as well asaid in the diagnosis of and targeted therapy for cancer (Cragan, 1999).

There are three methods for treatmentof colored materials, including (1) physicalmethods employing precipitation, adsorption, andreverse osmosis; (2) chemical methods viaoxidation (using air oxygen; ozone, NaOC1, andH202 as oxidants) and reduction (e.g., Na2S204);and (3) biological methods including aerobic andanaerobic treatment(Banat *et al*., 2005). There are many studies deals with removal of methylene blue by adsorption (Kanawade and Gaikwad, 2011;Ur Rehman *et al*., 2012;Derakhshan *et al*., 2013), this study is attempt to find cheep and practical method to remove methylene blue from aqueous solutions.

Materials and Methods

Preparation of Adsorpate

Metheylene blue used in this study made by (SDFCL India) was used to prepare the stock solution by dissolving an accurate weight of the dye in distilled water and then we made series of dilution to obtain the desired concentrations for this work.

Preparation of Adsorbent

Dried water melon seeds were collected then we take only the seed shells and activate them by sinking it in diluted solution of phosphoric acid H_3PO_4(10%) for one hour and then dried in the oven at temperature 100c° until it dried completely then we used electrical mortar to grind the shells to a powder (El- Halwany,2013).

Batch Studies

Several experiments were conducted to determine the ability of water melon seeds shells to remove M.B. from aqueous solutions for all the experiments we use uv. Visiblespectrophotometer ( ) with wave length at 660 nm to measure the M.B. concentration.a series of concentrations of M.B. solutions (5, 10, 15, 20, 25) (Table 1) to draw the calibration curve, as shown in Fig. 1.

Table 1: the calibration curve

Concentrations (g/L)	Absorbance
5	0.092
10	0.192
15	0.304
20	0.386
25	0.508
30	0.591

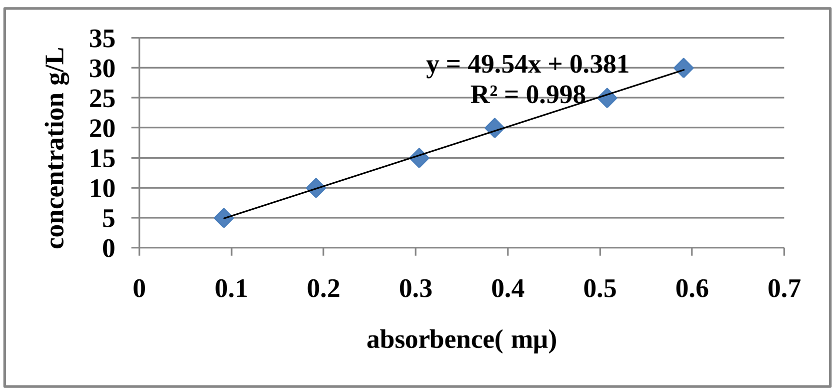


Figure 1: The Calibration Curve

Batch studies were carried out to investigate the effects of different parameters as follow (Hassan, 2013; El-Halwany, 2013; Hassan and Hassan, 2013).

Adsorption time

Five sample of aqueous solution of M.B. with concentration of 100 mg/L and volume of 50 ml in conical flask then we added 1.5 gm of the adsorpate to each one of them, and kept them in shaker for different time (30, 60, 90, 120, 150 mints respectively) to determine the effects of time on adsorption process, then the absorbance of the samples were determined be using UV. Visible spectrophotometer.

Water melon Seeds Shells concentration

Various concentration of adsorpate (0.5, 1, 1.5, 2, 2.5 gm) were added to five sample of aqueous solution of M.B. each one with concentration of 100mg/L and volume of 50ml respectively and the flasks were kept in shaker for 120 mints, the then we measure the absorbance of the samples by using UV. Visible spectrophotometer.

Methylene Blue concentration

For this experiment the concentration of adsobate used was 1.5mg/L which was added to added to dfive samples with different concentration of M.B. (20, 40, 60, 80, 100 mg/L) respectively, and then the flask were kept in the shaker for 120 mints, the absorbance of the samples were measured by using UV. visible spectrophotometer.

The effects of pH

1.5 gm of the adsorbent was added to three samples containing M.B. aqueous solutions with different pH value, the first one with pH value 3 (acidity) and the second solution with pH value 7 (neutral)and the third one with ph 10(alkaline) respectively, and then the flasks were kept in the shaker for 120 mints .

Isotherm Studies

For isotherm studies, accurately weighted amount (0.5, 1, 1.5, 2, 2.5) g/L of adsorbent (water melon seeds shell), Agitation was provided for 120 min which is more than sufficient time to reach equilibrium.

The adsorption capacity of adsorbent was calculated using the equation below [Wally *et al*., 2010]:

$qe = \frac{(ci - ce)v}{w}$....................................... (1)

Where:

qe: Adsorption capacity of the adsorbent (mg/g).

Ci: Initial concentration of adsorbate

(Mg /L).

Ce: Equilibrium concentration of adsorbate

After adsorption has occurred (mg /L).

V: Volume of solution (L).

W: Weight of adsorbent (g).

The dye removal percentage was calculated using equation (2) [Meisslamawy,2006].

$R\,\% = \frac{Ci - Ce}{Ci} * 100\%)$ ……………..(2)

Where:

R%: The metal removal percentage.

Ci : The initial concentration of metal (mg/L).

Ce: The residual concentration of metal after adsorption had taken place over a period of time **t** expressed as (mg/L).

Results and discussion

The fist experiment was done to determine the effects of contact time on the adsorption process (table 2), the results show that there is a an increase in the dye removal efficiency (R) rapidly at the initial stages with the increase of contact time and become slower near the final time stages, that can be due to the fact that a large number of vacant surface sites were available for adsorption during the initial stage of the adsorption process. Near the equilibrium, the remainingvacant surface sites were difficult to occupy due to, probably, the slow pore diffusion of the MB molecules on the adsorbents and the best contact time was 120 mints (Fig. 2) , this was similar to the results found by (Shahryari et al., 2010; Shailbu et al., 2014).

Table 2: the effects of contact time on adsorption process

Time(mints)	Absorbance	R
30	**1.193**	**40.52**
60	**0.945**	**52.8**
90	**0.881**	**56**
120	**0.662**	**66.83**
150	**0.668**	**66.53**
M.B. concentration= 100mg\L, Water Melon Seeds Shells dose = 1.5 gm.		

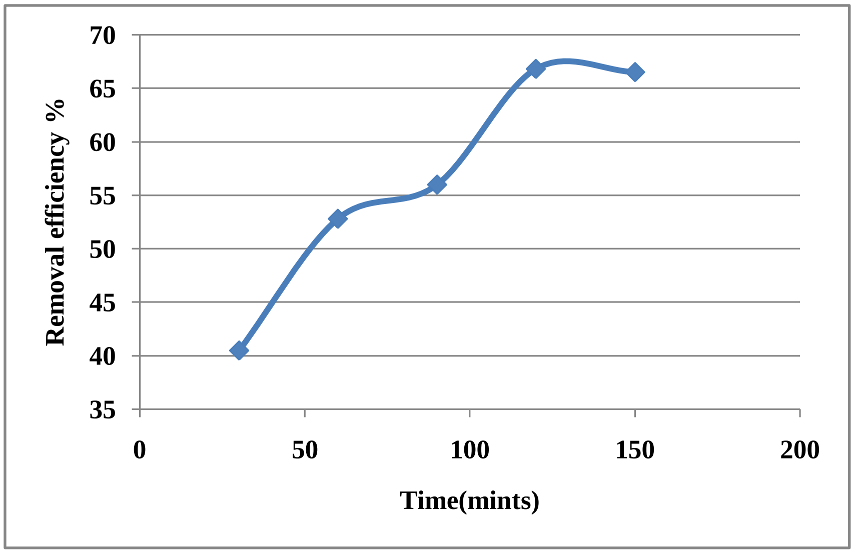


Figure 2: the effects of contact time on adsorption process

In the second experiment we try to find the effect of sorbent dose on the adsorption process on the water melon seeds shells (table3),the results show that the increase of sorbent dose from (0.5gm) to (2.5gm) led to increase the R from (38.56) to (82.27) respectively as shown in (Fig.3), and this could be due to fact that increasing the sorbent dose will led to increase the surface area available for adsorption , this Compatible with the results of (Porselvi *et al.*, 2014;Ramesh *et al*, 2014).

Table 3: the effects water melon seeds shells dose

Water melon seeds shells dose (gm)	Absorbance	R
0.5	**1.248**	**38.56**
1	**0.77**	**61.48**
1.5	**0.562**	**71.78**
2	**0.421**	**78.77**
2.5	**0.35**	**82.27**
M.B. concentration= 100mg\L, Contact time =120mints		

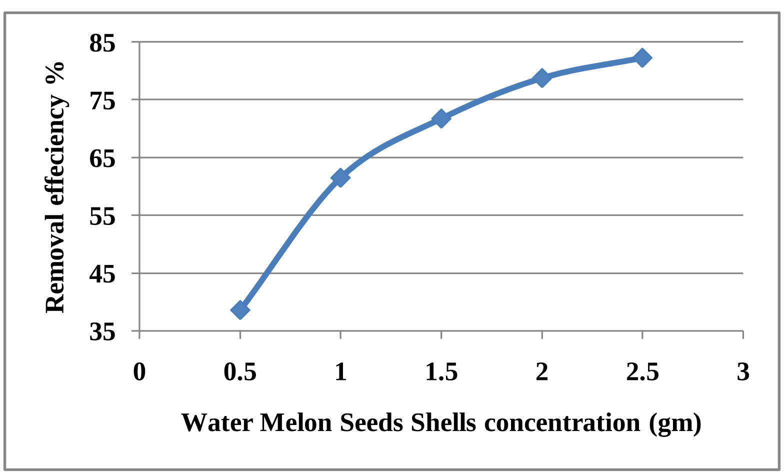


Figure 3: the effects water melon seeds shells dose on adsorption process

The third experiment was carry out toestimateefficiency of water melon seeds shells to remove the M.B. from aqueous solutions that contain different concentration of the dye (table 4), the results show that seeds shells of water melon was efficient in remove the M.B. even at the highest concentration of M.B. (100mg\L) with R (81.63), may be due to higher interactionbetween MB and adsorbent (Shahryari et al., 2010), as shown in (Fig.4)

Table 4: the effects of initial M.B. concentration.

M.B. concentration (mg\L)	Absorbance	R
20	0.063	82.5
40	0.104	86.17
60	0.246	79
80	0.484	69.55
100	0.363	81.63
Water Melon Seeds Shells dose = 1.5 gm, Contact time =120mints		

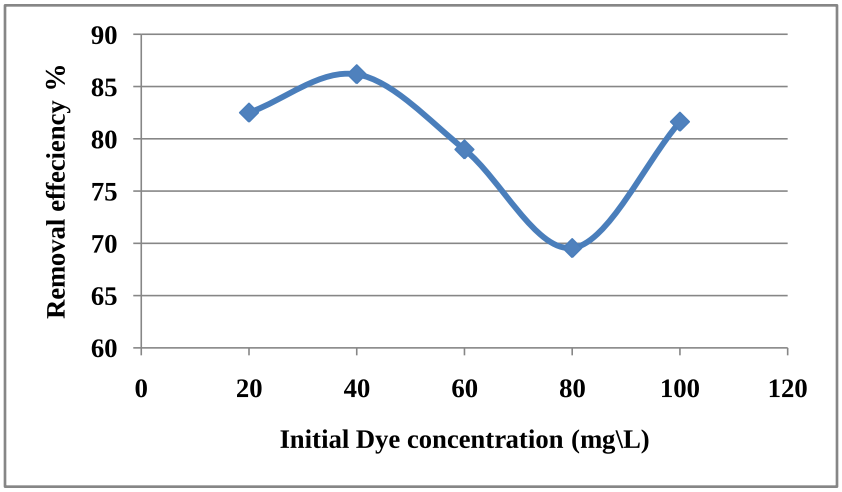


Figure 4: the effects of initial M.B. concentration on adsorption process

The fourth experiment was carry out toestimate efficiency of water melon seeds shells to remove the M.B. from aqueous solutions with different ph value, the first solution ph =2 (acidity), the second solution with pH=7 (neutral), the third solution with pH=10 (alkalinity) (table 5, Figure 5), the results show that seeds shells of water melon was efficient in remove the M.B at alkaline medium more than at neutral medium and the least at acidity medium and that can be explain due to the fact that the M.B. is a cataion dye, and also this can be attributed to the fact the at higher pH value the surface charges of the adsorbent have become more negatively charged at higher pH, which led to higher electrostatic interaction between negative charged adsorbent and positively charged M.B. molecules.(Acemioglu, B., et al., 2014).

Table 5: the effects of pH value

pH value	Absorbance	R
2	0.605	69.64
7	0.512	74.25
10	0.249	87.28
Water Melon Seeds Shells dose = 1.5 gm , M.B. concentration= 100mg\L, Contact time =120mints		

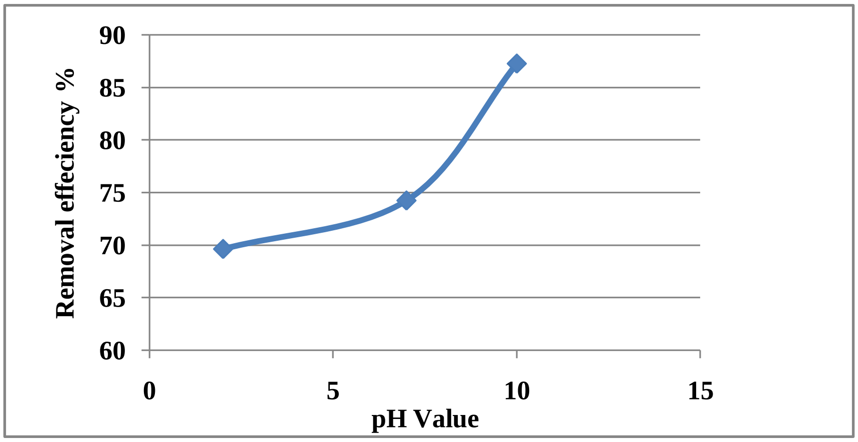


Figure 5: the effects of pH on adsorption process

Adsorption isotherm

The equilibrium data of MB was fitted to the Langmiur and Freundlichisothermmodels.These isotherms are expressed by the following equations

$qe = \frac{abce}{1+bce}$...........3

qe : The quantity adsorbed at equilibrium in (mg/g) .
Ce : The equilibrium concentration of adsorbate in (mg /L).
a and b: **a** is a Langmuir constant (mg/g) and **b** is also Langmuir constant in (L/mg)
$qe=k_fCe^{1/n}$.................4
qe : The quantity adsorbed at equilibrium in (mg/g) .
Ce : The equilibrium concentration of the adsorbate in (mg/L).
K*f*and n: The Freundlich experimental constants, **K*f***and **n** are indicators of the adsorption capacity and adsorption intensity, respectively

Figures 6 and 7 illustrate the use of the Langmuir, Freundlich models for adsorption of methylene blew at initial concentration of 100mg / l, stirring time 120 minutes and adsorbent dose from(0.5, 1, 1.5, 2,2.5). Langmuir isotherm was achieved by plotting log Ce versus ce/qe to give a straight line with a correlation coefficient (R^2) equal to 0.9816. Langmuir's constants (a) and (b) can be evaluated from the slope (1/a) and intercept (1/ab) of the linear equation. [Waly, et al., 2010; Meisslamawy,2006]

Freundlich isotherm was achieved by plotting log Ce versus log qe to give straight line with a correlation coefficient (R^2) equal to 0.9859. The slope of the line will give the value of 1/n and the intercept on the Y-axis gives the value of log K*f*[Kumar and Kirthika, 2009].

Figure 6:Langmuir isotherm adsorbtion model

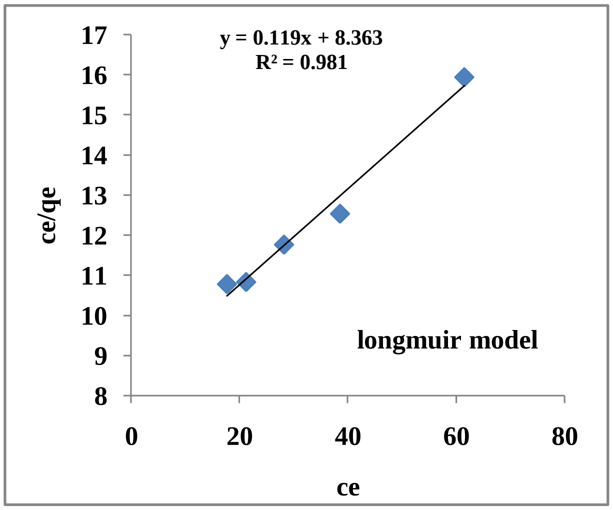
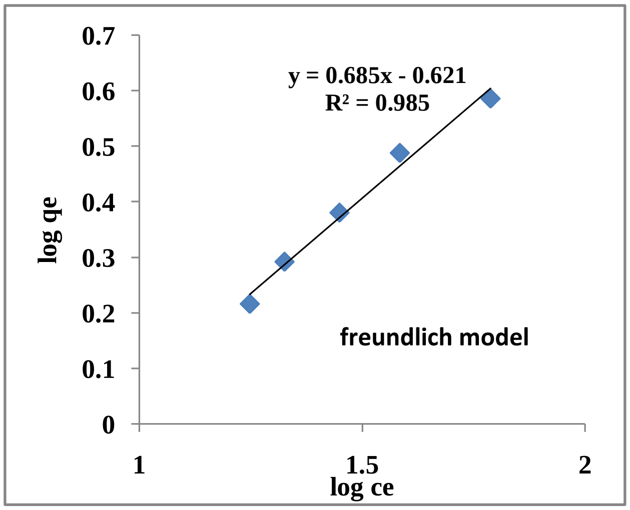


Figure 7 :freundlich isotherm adsorbtion model



The Langmuir and Freundlich isotherm constant are summarized in Table 6

Table 6: Langmuir &Freundlich isotherm constant

Langmuir		freundlich	
a	8.35	K_f	0.238
b	0.0143	1/n	0.6856
R^2	0.9816	R^2	0.9859

From the values of correlation coefficient of the three models, Freundlich isotherm fit very well with the experimental data as shown in Figure8

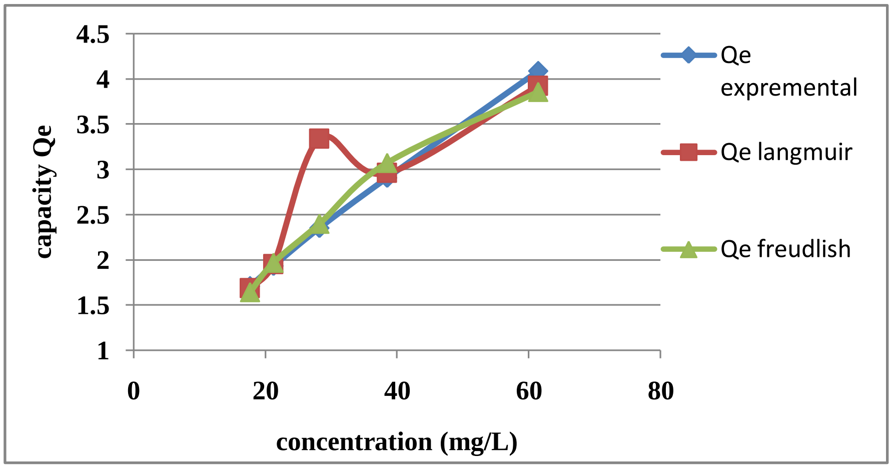


Figure8: Isotherm of MB on water melon seeds shell

Acknowledgment

The authors would like to grateful Environmental Research Center and University of Babylon for their support to this research.

References

Koocheki, A.; Razavi , S.A.M. ; Milani E. ; Moghadam T.M.; Abedini , M.; Alamatiyan, S. and Izadkhah.M.(2007). Physical properties of Watermelon seed as a function of moisture content and variety. Int.Agrophysics. Vol. 27, p.p. 349-359.

Khan, A. R. ; Tahir, H.; Uddin, F.; Hameed, U . (2005). Adsorption of Methylene Blue from aqueous Solution on the Surface of Wool Fiber and Cotton Fiber. J. Appl. Sci. Environ. Mgt. Vol. 9, No. 2, p.p. 29-35.

Shahryari, Z. ;Goharrizi, A. S. and Azadi, M.(2010). Experimental study of methylene blue adsorption from aqueous solutions onto carbon nano tubes. Int. J. Water Res. Environ. Eng. Vol.2, No.2, pp. 016-028.

Cragan, D.J. (1999) Teratogen Update: Methylene Blue.Teratology.Vol. 60, p.p.42–48.

Banat , F.; A1-Asheh b,S.; A1-Rawashdeh, M. and Nusair , M. (2005) .Photodegradation of methylene blue dye by the UV/H202and UV/acetone oxidation processes. Desalination.ELSEVIER. Vol. 181, p.p. 225-232.

Kanawade, S.M. and Gaikwad, R.W.(2011). Removal of Methylene Blue from Effluent by UsingActivated Carbon and Water Hyacinth as Adsorbent. International Journal of Chemical Engineering and Applications, Vol. 2 , No. 5 , 2011.

Ur Rehman M.S., Kim,I. and Han, J. (2012). Adsorption of methylene blue dye from aqueous solution by sugar extracted spent rice biomass. Elsever, Carbohydrate Polymers, Vol. 90, p.p. 1314–1322.

Derakhahan, Z. ;Baghapour, M. A.; Ranjbar, M. and Faramarzian, M. (2013). Adsorption of methylene blue from aqu Pumice Stone: Kinetics and Equilibrium Studies. Health Scope.Vol.3, p.p. 136–44.

El- Halwany, M. M.(2013). Kinetics and thermodynamics of activated sunflowers seeds shell carbon (SSSC) as sorbent material. J. Chromat Separation Techniq. Vol. 4, No. 5, doi: 10.4172/2157-7064.

Hassan, A. A. (2013). Removal of cadmium from aqueous solutions by Wheat Bran and sunflower shell. Journal of Babylon University/ Engineering Sciences. Vol. 21, No. 3.p.p. 866-875.

Hassan, A.A. and Hassan, Z. A. (2013). Methylene blue removal from aqueous solution by adsorption on eggshell bed. Euphrates Journal of Agriculture science. Vol.5, No. 2, p.p. 11-23.

Waly, T.A.; Dakroury, A.M.; El-sayed, G.O.; El-salam, S.A. (2010). Assessment removal of heavy metals ions from wastewater by cement kiln dust(CKD). J. American Sci., Vol. 6, No.12, p.p. 910-917.

Meisslamawy, H.A.J. (2006). Sorption capacity measurements of sulphuric acid in the active mass of the Iraq lead acid storage battery. M.Sc. thesis, College of Science for Women-University of Baghdad, Iraq.

Shaibu, S.E.; Adekola, F.A.; Adegoke, H. I. and Ayanda, O. S. A. (2014). Comparative Study of the Adsorption of Methylene Blue on to Synthesized Nanoscale Zero-Valent Iron-Bamboo and Manganese-Bamboo Composites. Materials . Vol. 7, p.p. 4493-4507.

Porselvi, V. M.; Kumar, G. S.; Meenakshi, S. and Kumaresan , S. (2014). Adsorption of methylene blue on to cissusqua drangularis. International Journal of Basic and Applied Chemical Sciences . Vol. 4, No.1, pp.51-57.

Ramesh S.T.; Gandhimathi R.; Elavarasi T.E.; Isai T. R.; Sowmya K. and Nidheesh P.V. (2014). Comparison of methylene blue adsorption from aqueous solution using spent tea dust and raw coir pith. Global NEST Journal, Vol 16, No 1, pp 146-159.

Acemioglu, B.; Ertas, M.; Alma, H. M. and Usta M. (2014). Investigation of the adsorption kinetics of methylene blue on to cotton wastes. Turk. J. Chem., Vol. 38, p.p. 454 – 469.

Kumar, P.S. and Kirthika, K . (2009). Equilibrium and kinetic study of adsorption of nickel from aqueous solution on to brael tree leaf powder. J. Eng. Sci. Tech., Vol.4, No.4, pp. 351-363.