Int J Pharm Bio Sci 2013 July; 4(3): (B) 325 - 333

Research Article Chemical Engineering

International Journal of Pharma and Bio Sciences

ISSN 0975-6299

REMOVAL OF METHYLENE BLUE BY USING *GREWIA ORBICULATA ROTTL .* *(* ZINGROOL TREE) AS BIOSORBENT

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ABSRACT

This investigation handles the adsorption of methylene blue dye from aqueous solution using "*Grewia orbiculata* Rottl." Leaves. Effects of different parameters such as agitation time, adsorbent size, adsorbent dosage, initial concentration of methylene blue in aqueous solution, volume, pH of aqueous solution on removal of methylene blue are determined. From these investigations, one gram of "*Grewia orbiculata* " Leaf powder of 82.5μm size is found to remove 90% of 20 mg/l methylene blue from 30ml of aqueous solution in 30min. These results indicate that adsorption of methylene blue is increased with an increase in adsorbent dosage and decrease in adsorbent size. A significant increase in percentage removal of methylene blue is observed as pH value increased from 4 to 7.28 and percentage removal is marginally increased from 1 to 4. The percentage removal decreased as pH value increased beyond 7.28. Freundlich and Langmuir isotherm models describe the adsorption data very well indicating favorable adsorption of methylene blue adsorbent. Freundlich isotherm is relatively more suitable than Langmuir isotherm. Hence based on results obtained it is found that *Grewia orbiculata* Leaf powder is effective in methylene blue removal and can be appreciably considered as most versatile, economical and feasible adsorbent for removal of methylene blue from aqueous solutions.

KEY WORDS: Methylene blue dye , *Grewia orbiculata* Ro*ttl*, Biosorption, Langmuir and Freundlich isotherm.

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INTRODUCTION

Dyes have long been used in dyeing, paper and pulp, textiles, plastics, leather, cosmetics and food industries. Color stuff discharged from these industries poses certain hazards and environmental problems. These colored compounds are not only aesthetically displeasing but also inhibiting sunlight penetration into the stream and affecting aquatic ecosystem. Dyes usually have complex aromatic molecular structures which make them more stable and difficult to biodegrade. Furthermore, many dyes are toxic to some microorganisms and may cause direct destruction or inhibition of their catalytic capabilities.[1] There is requirement on industry to minimize environmental release of color, even in cases where a small but visible release might be considered as toxicologically rather innocuous. A major source of release of color into the environment is associated with the incomplete exhaustion of dyes onto textile fiber from an aqueous dyeing process and the need to reduce the amount of residual dye in textile effluent has thus become a major concern in recent years. An alternative approach to addressing the problem of color in textile dyeing effluent has involved the development of effluent treatment methods to remove color. These methods inevitably add to the cost of the overall process and some present the complication associated with the possible toxicity of degradation products.[2] A variety of low cost adsorbents like blast furnace flue dust, activated carbon, crab shell, chitosan, coconut jute carbon, apple residues, peat, fly ash, sawdust, jack fruit peel, banana and orange peels, rice husk, tree fern, tanning gel particles etc. have been investigated for their effectiveness in removing of methylene blue. The interesting features of newly developed adsorbents are their highly versatility, high uptake and high tolerance for organics and regeneration. The present investigation looks into a specific process for the removal of methylene blue by adsorption using an economically low cost adsorbent developed from an easily, freely and abundantly available Zingrool tree (round leaved Indian lenden) leaves powder [3](*Grewia orbiculata* Rottl.).This plant is classified as Endemic to Deccan Peninsula(Peninsular India).

This study presents the optimum values for the following parameters

1. Agitation time
2. Adsorbent size
3. Adsorbent dosage
4. Initial concentration of adsorbate in the aqueous solution
5. Volume of aqueous solution
6. pH of aqueous solution

EXPERIMENTAL PROCEDURE

Preparation of the adsorbent

The matured *Grewia orbiculata* leaves are collected from Chowdavaram. Those are washed with distilled water to remove dust and soluble impurities and dried under sun light till leaves became crisp. The dried leaves are ground and powdered by using domestic mixer and the resulting powder is sieved to different sizes by using BSS standard sieves using sieve shaker. The size fractions 82.5 μm, 97.5 μm, 115 μm, 137.7 μm, 165 μm and 215 μm are preserved in bottles for use as adsorbent[4].

Preparation of Methylene blue stock solution (aqueous solution)

Analytical Reagent grade methylene blue ($C_{14}H_{18}N_3SCl$) dye powder is purchased from Kamphasol (Mumbai). One gram of powder is dissolved in 1 L of distilled water to prepare 1000 mg/l of stock solution. Samples of different concentrations of methylene blue are prepared from this stock solution by appropriate dilutions. 100 mg/l of methylene blue solution is prepared by taking 100 ml of 1000 mg/l solution is in a 1L volumetric flask and made up to mark with distilled water. Similarly solutions with different dye concentrations such as 5 mg/l, 10 mg/l, 20 mg/l, 40 mg/l, 60 mg/l, 80 mg/l are prepared by appropriate dilutions[4].

Effect of agitation time

30 ml of aqueous solution is taken in a 250 ml conical flask and 0.5 gm of adsorbent having a size of 82.5 μm is added. This sample is shaken on an orbital shaker at 160 rpm at room temperature for 1 min. similarly few more

samples are prepared in conical flasks and adding 0.5 gm of adsorbent and exposed to varying agitation times (2, 4, 8, 12, 15, 20, 25, 30, 35, 40, 45, 50, 55, and 60 min). These samples are filtered separately with Whatman filter papers and the filtrates are analyzed in UV spectro photometer at 665 nm wavelength to obtain final concentrations of methylene blue. The percentage removal of methylene blue is calculated as $(C_0 - C_t) X 100 / C_0$. Graphs are plotted between the agitation time and % removal of methylene blue to identify the optimum agitation times[5].

Effect of adsorbent dosage

30 ml of aqueous solution is taken in a 250 ml conical flask and 0.5 gm of adsorbent having size 82.5 µm is added. This sample is shaken on an orbital shaker at room temperature for optimum agitation time. Similarly few more samples are prepared in conical flaks and adding dosages 1 gm, 1.5 gm, 2 gm, 2.5 gm and 3 gm of adsorbent and agitated for optimum time. These samples are filtered separately and the filtrates are analyzed in UV spectro photometer to get final concentrations of methylene blue. The % removal of methylene blue is calculated as $(C_0 - C_t) X 100 / C_0$.[6]

Effect of adsorbent size

30 ml of aqueous solution is taken in a 250 ml conical flask and 0.5 gm of adsorbent having size 82.5 µm is added. This sample is shaken on an orbital shaker at room temperature for optimum agitation time. Similarly a few samples of solution are taken adding adsorbent of different sizes such as 97.5 µm, 115 µm, 137.5 µm, 165 µm and 215 µm and agitated for optimum time. These samples after agitation are filtered separately and the filtrates are analyzed in UV spectro photometer to obtain final concentrations of methylene blue[6].

Effect of initial concentration of methylene blue in aqueous solution

30 ml of aqueous solution containing 20 mg/l of methylene blue is taken in a 250 ml conical flask and 1 gm of 85.5 µm size adsorbent is added. The sample is kept in continuous contact for optimum agitation time (30 min) by shaking on an orbital shaker at room temperature. The sample is settled and filtered. The final concentration of the filtrate is calculated by using UV spectro photometer. The similar procedure is repeated for other concentrations of aqueous solution 10, 20, 40, 60, 80 and 100 mg/l.[7]

Effect of volume of the aqueous solution

30 ml of aqueous solution containing 20 mg/l of methylene blue is taken in a 250 ml conical flask and 1 gm of 82.5 µm size adsorbent is added. The sample is kept in continuous contact for optimum agitation time (30 min) by shaking on an orbital shaker at room temperature. The sample is settled and filtered. The final concentration of the filtrate is calculated by using UV spectro photometer. The similar procedure is repeated for other volumes of aqueous solution 10, 20, 40, 60, 80 and 100 ml.[8]

Effect of pH of the solution

To study the influence of pH on methylene blue adsorption, 30 ml of aqueous solution is taken in each of 11 conical flasks. The pH values of the solutions are adjusted to 1, 2.2, 4, 5.4, 6.2, 7.28, 8.3, 9.6, 11.2, 12.4 and 14 in separate flasks by adding required amounts of 0.1 N HCl and 0.1 N NaOH. In these, 1 gm of 82.5 µm size adsorbent is added separately. The samples are shaken on an orbital shaker at room temperature for optimum agitation time. Then samples are allowed to settle and are filtered. The methylene blue concentrations of the filtrates are determined by using UV spectro photometer.[9]

RESULTS AND DISCUSSION

Effect of agitation time

The optimum agitation time is determined by plotting the % removal of methylene blue against agitation time in fig.1 for different dosages at the interaction time intervals of 1 min to 60 min. The % adsorption is found to increase up to 30 min and thereafter, negligible increase in % removal is noticed with agitation time. It is noticed that the rate of adsorption is faster in the initial stages because adequate surface area of the adsorbent is available for the adsorption of methylene blue. As the time increases, more amount of methylene blue gets adsorbed onto the surface of the adsorbent and surface area decreases. The maximum % adsorption is attained at 30 min of agitation. The % removal of methylene blue becomes almost constant after 30 min. All other experiments are conducted at this optimum agitation time[10].

Effect of adsorbent size

The percentage removal of methylene blue from aqueous solution with various particle sizes(82.5 µm, 97.5 µm, 115 µm, 137.5 µm, 165 µm and 215 µm) are obtained at 0.5 gm. The results are shown in fig.2 with % removal of methylene blue increased as the adsorbent particle size decreases from 215 µm to 82.5 µm. This is due to number of active sites on the adsorbent are better exposed to the adsorbate[11].

Effect of adsorbent dosage

The percentage removal of methylene blue is drawn against adsorbent dosage different in fig.3.. Percentage removal of methylene blue increases from 72.5% to 90% for the adsorbent size 82.5 µm, as dosage increased from 0.5 gm to 3 gm. Such behavior is obvious because the number of active sites available for dye removal would be more as amount of the adsorbent increases.

Effect of initial concentration of methylene blue in aqueous solution

The effect of initial concentration of methylene blue in the aqueous solution on the percentage removal of methylene blue is shown in fig.4. The percentage removal of methylene blue is decreased from 90% to 35% by increasing the initial concentration of methylene blue in the aqueous solution from 5 mg/l to 100 mg/l. Such behavior can be attributed due to the increase in the amount of adsorbate to the unchanging number of available active sites on the adsorbent (since the amount of adsorbent is kept constant).

Effect of volume of the aqueous solution

Change in % removal of methylene blue with variation in the volume of the aqueous solution from 20 ml to 100 ml is shown in fig. 5 for an adsorbent dosage of 1 gm of 82.5 µm size for an optimum agitation time of 30 min. From this plot, it is clear that % removal of methylene blue is gradually decreased from 95% to 65%. As the volume of the aqueous solution increases, the amount of methylene blue present in the solution also increases. This implies that % removal by unaltered surface area of adsorbent decreases as the amount of methylene blue in the solution is increased.

Effect of pH of the aqueous solution[18]

pH influences the surface charge of the adsorbent, the degree of ionization and the species of adsorbate. So pH is an important factor controlling the process of adsorption. In the present investigation, adsorption data are obtained in the pH range of 1 to 14 for methylene blue initial concentration of 20 mg/l and 1 gm of 82.5 µm size adsorbent. The effect of pH of the aqueous solution on % removal of methylene blue is drawn in fig.6. The % removal of methylene blue dye is increased from 65% to 95% as pH is increased from 1 to 7.28. The graph reveals that % removal increased significantly from 4 to 7.28 . Increase in the percentage adsorption is marginal for values 1 to 4. This is due to partial hydrolysis of ions resulting in the formation of $M(OH)^+$ and $M(OH)_2$. $M(OH)_2$ would have been adsorbed on the non polar surface than on $M(OH)^+$. The % removal is decreased for pH value above 7. In the present investigation, the maximum % removal of methylene blue is obtained for 1 gm of 82.5 µm size adsorbent at optimum agitation time. The principal driving force for dye ion adsorption is the electrostatic interaction (i.e) attraction between adsorbent and adsorbate. The greater the interaction, adsorption of dye will be more. With an increase in interaction, the dye ions replace H^+ ions bond to the adsorbent for forming part of the surface functional groups such as –OH, -COOH etc. As the electro-negativity of Grewia Orbiculata leaf powder is greater, more methylene blue ions are adsorbed.

Freundlich isotherm for adsorption of methylene blue

The Freundlich relationship is an empirical equation. It does not indicate a finite uptake capacity of the adsorbent and can thus only be applied in case of low and intermediate concentration ranges. However, it is easier to handle mathematically in more complex calculations[12].

The Freundlich isotherm is given by $q_e = K_f C_e^n$

Taking logarithms on both sides $\log q_e = \log K_f + n \log C_e$ where K_f and n are known as Freundlich constants. Freundlich isotherms are drawn between log q_e and log C_e in figs.7. The resulting line have the correlation coefficient of 0.99

Langmuir isotherm for adsorption of methylene blue[13]

Since the chemical forces fall off very rapidly with distance, it is probable that chemisorption does not extend beyond a single layer of adsorbate on the surface of the solid. It can be anticipated as first pointed out by Langmuir that chemisorbed adsorbate layers may be only one molecule thick. The Langmuir is most widely used two-parameter equation. The relationship is given by

$q_e / q_m = b C_e / (1+bCe)$

where C_e concentration of the adsorbate at equilibrium, q_e is the amount adsorbed at equilibrium per unit mass of adsorbent, q_m is the maximum amount adsorbed per unit mass of adsorbent and b is the coefficient related to affinity. Equation (5) can be rearranged as

$(C_e / q_e) = 1/bq_m + C_e/q_m$

From fig.8 between (C_e / q_e) and C_e, we can calculate the slope $(1/q_m)$ and the intercept $(1/bq_m)$. Further analysis of Langmuir equation is made on the basis of separation factor, R_L

Figure 1 Effect of agitation time

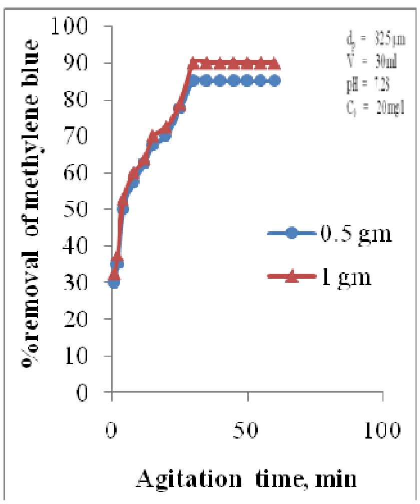

Figure 2 Effect of adsorbent size

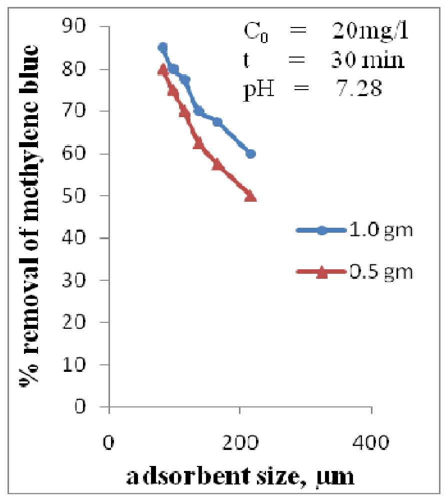

Figure 3 Effect of adsorbent dosage

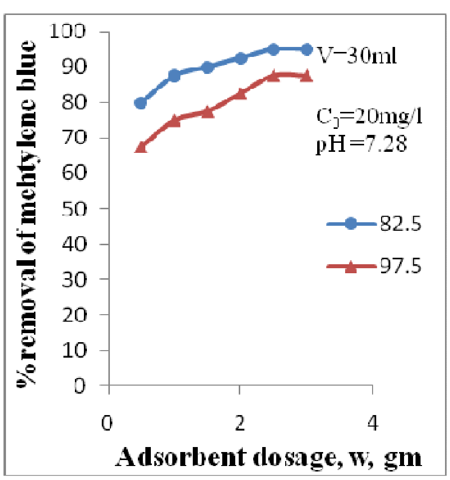

Figure 4 Effect of initial dye concentration

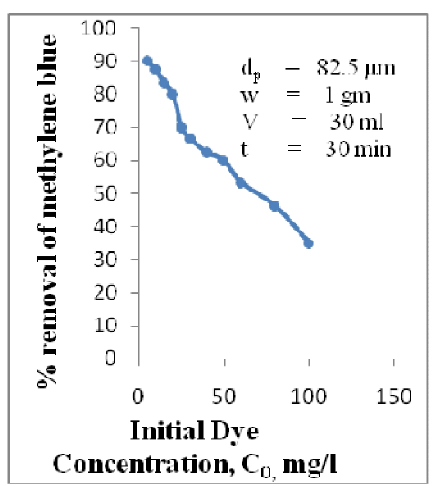

Figure 5 Effect of Volume of aqueous solution

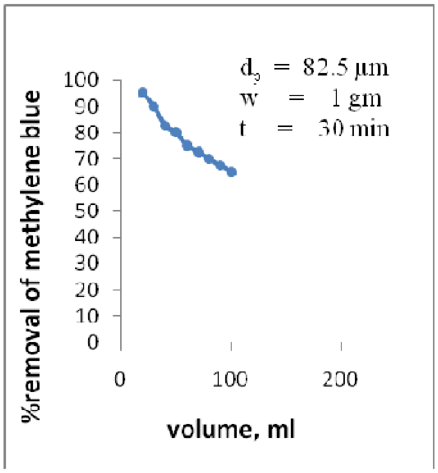

Figure 6 Effect of pH

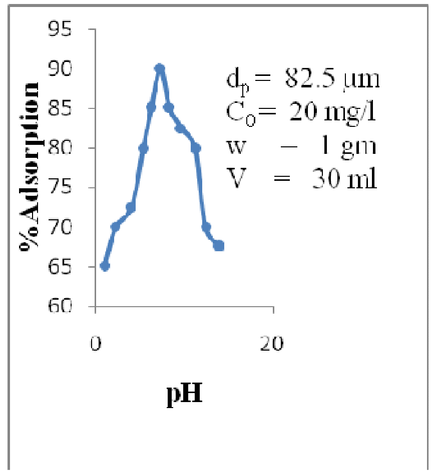

Figure 7 Freundlich isotherm

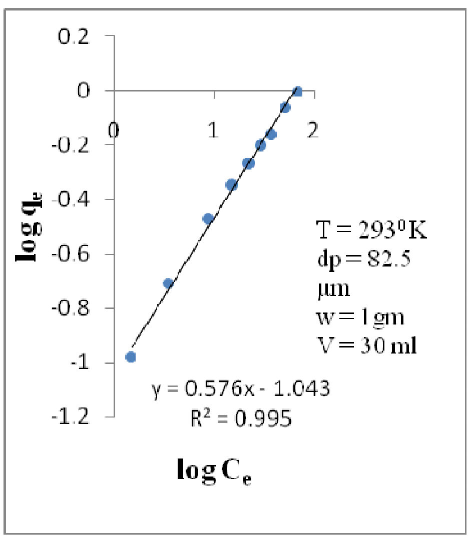

Figure 8 Langmuir isotherm

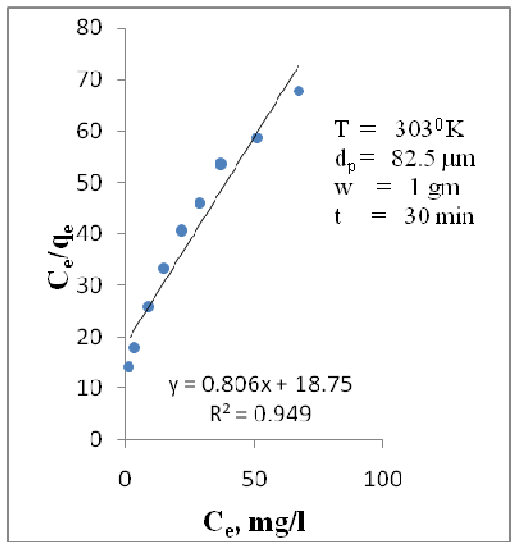

Table.1
Effect of agitation time on % removal of methylene blue

S.No.	Agitation time, t, min	Final Concentration, C_t, mg/l	% Removal of Methylene Blue
1	1	14	30
2	2	13	35
3	4	10	50
4	8	8.5	57.5
5	12	7.5	62.5
6	15	6.5	67.5
7	20	6	70
8	25	4.5	77.5
9	30	3	85
10	35	3	85
11	40	3	85
12	45	3	85
13	50	3	85
14	55	3	85
15	60	3	85

Table.2
Effect of adsorbent size on % removal of methylene blue

S.No	adsorbent size, μm	Final concentration, Ct mg/l	%adsorption
1	82.5	3.0	85
2	97.5	4.0	80
3	115	4.5	77.5
4	137.5	6	70
5	165	6.5	67.5
6	215	8	60

Table.3
Effect of adsorbent dosage on % removal of methylene blue

S.No.	Adsorbent Dosage, (w) gm	Final Concentration of Methylene Blue, mg/l	%Removal of Methylene Blue
1	0.5	4	80
2	1	3.5	87.5
3	1.5	3	90
4	2	2.5	92.5
5	2.5	2	95
6	3	2	95

Table.4
Effect of initial dye concentration on % removal of methylene blue

S.No.	Initial Concentration, C_0, mg/l	Final Concentration, C_t, mg/l	%removal of methylene blue
1	5	0.5	90
2	10	1.25	87.5
3	15	2.5	83.33
4	20	4	80
5	25	7.5	70
6	30	10	66.6
7	40	15	62.5
8	50	20	60
9	60	28	53.3
10	80	43	46.25
11	100	65	35

Table.5
Effect of volume of aqueous solution on % removal of methylene blue

S.No.	Volume of aqueous solution, V, ml	Final Concentration, mg/l	%removal of methylene blue
1	20	1	95
2	30	2	90
3	40	3.5	82.5
4	50	4	80
5	60	5	75
6	71	5.5	72.5
7	80	6	70
8	90	6.5	67.5
9	100	7	65

Table.6
Effect of pH on % removal of methylene blue

S. No.	pH	Final Concentration, C_t, mg/l	% Adsorption
1	1.0	7	65
2	2.2	6	70
3	4	5.5	72.5
4	5.4	4	80
5	6.2	3	85
6	7.28	2	90
7	8.3	3	85
8	9.6	3.5	82.5
9	11.2	4	80
10	12.4	6	70
11	14	6.5	67.5

CONCLUSIONS

The analyses of the experimental data result in the following conclusions.

1. The optimum agitation time for the methylene blue adsorption is 30 minutes.
2. The percentage removal of methylene blue from the aqueous solution increases with a decrease in the particle size of the adsorbent.
3. The percentage removal of methylene blue from aqueous solution is augmented with increase in weight of the adsorbent.
4. Increase in the volume of aqueous solution results in gradual decrease of the percentage removal of methylene blue.
5. Higher the Initial concentration of methylene blue in the aqueous solution, the percentage removal of methylene blue is decreased.
6. Percentage removal of methylene blue from aqueous solution is increased significantly with increase in pH value from 4 to 7.28. Increase in % removal is marginal between pH value 1 to 4. The % removal decreases for pH beyond 7.28.
7. In the range of variables studied, percentage removal is increased from 65% to 90%.
8. The data are well represented by Freundlich and Langmuir isotherms indicating favorable adsorption of methylene blue by the adsorbent. Freundlich isotherms are relatively more suitable than Langmuir isotherms.

REFERENCES

1. A. Bennani Karim, B. Mounir, M. Hachkar, M. Bakasse and A.Yaacoubi, "Adsorption of Malachite Green dye onto raw Moroccan clay in batch and dynamic system" *Canadian Journal on Environmental, Construction and Civil Engineering* Vol. 2,pp. No.2 2011.
2. A. Hebeish, M. A. Ramadan, E. Abdel-Halim, A. Abo-Okeil, "An effective adsorbent based on sawdust for removal of direct dye from aqueous solutions", *Clean Techn Environ Policy*, 13:713–718, 2011.
3. A. M. Ben Hamissa, M. C. Ncibi, B. Mahjoub and M. Seffen, "Biosorption of metal dye from aqueous solution onto Agave americana (L.) fibres", *Int. J. Environ. Sci. Tech.,* 5 (4), pp. 501-508, 2008.
4. Ahmet Demirak, Ömer Dalman, Ezel Tilkan, Dilek Yıldız, Evşen Yavuz, Cansu Gökçe, "Biosorption of 2,4 dichlorophenol (2,4-DCP) onto Posidonia oceanica (L.) seagrass in a batch system: Equilibrium and kinetic modeling" *Microchemical Journal* 99, pp 97–102, 2011.
5. Ana Me´ndez, Sandra Barriga, Antonio Saa and Gabriel Gasco, "Removal of malachite green by adsorbents from

paper industry waste materials", *J Therm Anal Calorim* 99, pp. 993–998, 2010.

6. Arh-Hwang Chen and Shin-Ming Chen, "Biosorption of azo dyes from aqueous solution by glutaraldehyde-crosslinked chitosans", *Journal of Hazardous Materials* 172, pp. 1111-1121, 2009.
7. Russo M.E., Marzocchella A., Olivieri G., Prigione V., Salatino P., Tigini V. and Varese G.C., "Characterization of dyes biosorption on fungal biomass".9th international conference on chemical and process engineering110-119may2009
8. B. D. Bhole, Bratati Ganguly, Anusha Madhuram,Deepti Deshpande and Jui Joshi, "Biosorption of methyl violet, basic functions and their mixture using dead fungal biomass", *Current science*, vol. 86, no. 12, 25 june 2004.
9. B.H. Hameed, R.R. Krishni and S.A. Sata, "A novel agricultural waste adsorbent for the removal of cationic dye from aqueous solutions", *Journal of Hazardous Materials* 162, pp. 305–311, 2009.
10. Baoe Wang and Xiu Guo, "Reuse of waste beer yeast sludge for biosorptive decolorization of reactive blue 49 from aqueous solution", *World J Microbiol Biotechnol* , 27, pp.:1297–1302, 2011.
11. Bao-E. Wang, Yong-You Hu, Lei Xie and Kang Peng, "Biosorption behavior of azo dye by inactive CMC immobilized Aspergillus fumigatus beads", *Bio resource Technology* 99, pp. 794–800, 2008.
12. Bellir Karima, Bencheikh Lehocine Mossa And Meniai A-Hassen, "Removal of Methylene Blue from aqueous solutions using an Acid Activated Algerian Bentonite: Equilibrium and Kinetic Studies", *International Renewable Energy Congress* November 5-7, 2010 – Sousse, Tunisia.
13. Catherine Faur, H´El`Ene M´Etivier-Pignon And Pierre Le Cloirec, "Multicomponent Adsorption of Pesticides onto Activated Carbon Fibers", *Adsorption 11*, pp. 479–490, 2005.
14. Chulhwan Park, Myunggu Lee, Byunghwan Lee, Seung-Wook Kim, Howard A. Chase, Jinwon Lee and Sangyong Kim, "Biodegradation and biosorption for decolorization of synthetic dyes by Funalia trogii", *Biochemical Engineering Journal*, 2006.
15. M. Sarioglu and U.A. Atay, "Removal Of Methylene Blue By Using Biosolid", *Global NEST Journal*, Vol 8, No 2, pp 113-120, 2006.
16. S.Abirami, S.Srisudha and P.Gunasekaran, "Biosorption of Chromium from Tannery effluent using Biomass of Sargassum wightii (greville)", *Int J Pharm Bio Sci 2012 July*; 3(3): (B) 584 - 595
17. Rout Chadetrik , Saza Radhi naif and Vikas Beniwal "Sorption Potential of Penicillium Janthinellum for removal of cu(ii) from Electroplating industrial effluent)", *Int J Pharm Bio Sci 2013 Jan; 4(1): (B) 847 - 858*