CHAETOMORPHA MEDIA (C. AGARTH): LOW COST BIOSORBENTS FOR REMOVAL OF METHYLENE BLUE AND MALACHITE GREEN FROM BINARY SOLUTION

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ABSTRACT:

In the present investigation, the use of abundantly available, low-cost, highly efficient and eco-friendly biosorbent *Chaetomorpha media* (C.Agarth) has been reported as an alternative to the current expensive methods of removing of Methylene Blue (MB) and Malachite Green (M.G.) dyes from aqueous binary solution. The effects of different variables viz pH, agitation time, adsorbate concentration, adsorbent dose, agitation speed etc. were investigated for ascertain optimal experimental conditions. Correlation coefficient values were close to unity which suggested that adsorption data were in favor of Langmuir and Freundlich models. Pseudo second-order kinetic model was found favorable to describe the adsorption behavior of both the dyes. The intra particle diffusion was a prominent process right from the beginning of dye-solid interaction. Therefore the adsorption might involve monolayer surface coverage and heterogeneous adsorption mechanism. Present investigation and comparison with other reported adsorbents concluded that, *C. media* may be applied as a low-cost attractive option for removal of both dyes from a binary mixture**.**

Keywords: Adsorption isotherm; Biosorption; binary mixture; *Chaetomorpha media*; Kinetic study;Malachite Green and Methylene Blue

INTRODUCTION:

The large quantities of Dyes are used in many industries including leather, textile, cosmetics, paper, printing, plastic, pharmaceuticals, food, etc. to colour their products, and their amount produced annually is about $7x10^5$ metric tons per year (Çelekli, *et. al*., 2013) which generates wastewater, characteristically high in colour and organic content. The two third of the total dye stuff production was carried by textile industry alone (Azhar *et. al*., 2005 and Garg *et. al*., 2003) The contaminants in wastewater even at a very small concentration of less than 1ppm of dye are highly toxic, undesirable and may be carcinogenic causing serious hazards to aquatic ecosystem. (Banat *et. al*., 1996; Robinson *et. al*., 2001 and Vijayaraghavan. and Yun ,2008) Therefore it is necessary to develop an effective and appropriate technique to remove the dyes from the waste water before discharging to natural water stream. Dyes are resistant to aerobic digestion, stable to light/ heat/ oxidizing agents, raising difficulties in treating coloured waste water. (Kumar *et. al*., 2006; Sun & Yang, 2003). Removal of dye has been attempted by conventional physico-chemical methods such as adsorption, coagulation, precipitation, filtration and oxidation etc. but these are not so effective/economic and also not eco-friendly (Kannan and Sundaram ,2001; Senthil *et. al*., 2003; Bhattacharyya and Sharma, 2004; Aksu *et. al*., 2008) Among these techniques, adsorption is widely used for effluent treatment. (Derbyshire *et. al*., 2001; Ho, and McKay, 2003; Jain, *et. al*., 2003) Bacteria, fungi, algae, industrial waste, agricultural waste and polysaccharide materials are used as biosorbents for dye removal. Marine algae are commonly known as seaweeds, the utilization of it as biosorbent is attracting researchers. They contain alginate gel in their cell wall as the most important constituent. Due to the presence of binding sites such as carboxyl, sulfonate, amine and hydroxyl groups, marine algae have been well-known as powerful metal biosorbents. (Davis *et. al*., 2003; Çelekli *et. al*. 2011; 2013) The aqueous binary solution of Methylene Blue and Malachite Green dyes was used as a model compound to monitor biosorption using dried biomass of green seaweed *Chaetomorpha media* (C.Agarth) in present study. The purpose of this work is to evaluate dye adsorption capacity and mechanism of adsorption of dye in binary system by *Chaetomorpha media*.

MATERIALS AND METHODS:

A. Preparation of adsorbent and dye solution: Fresh and mature thalli of *Chaetomorpha media* were collected from Kunakeshwar and Malvan in Sindhudurga District along the West coast of Maharashtra during growing season (August to February). This material was washed, dried in shade at room temperature, powdered using grinder, then passed through different sieves to obtain fine (0.1 to 0.84 mm) particles. The powdered material was stored in airtight plastic containers at room temperature and used for batch experiments.

B. Procurement and Preparation of Binary dye solution:

Methylene blue (M.B.) and Malachite Green (M.G.) were obtained from Merck Specialties Pvt. Ltd, Mumbai. Stock solutions of M.B. and M.G. were prepared by dissolving accurately weighed sample of dye in deionized water to get a concentration of 1000 mg /L. Then test solutions were prepared by dilution of M.B. and M.G. stock solutions as per requirement.

Batch adsorption experiments:

These experiments were carried out at room temp. 27o ± 2 o C using diluted binary stocks solution of M.B. and M.G. to the required initial concentration. (Low *et. al.*,1993) Exactly 50 ml. binary solution of known concentration range was shaken at a specific agitation speed with a required fine biomass dose for specific contact time. Difference between Initial and final concentrations of dye solution were measured by recording absorbance on a double beam UV-Visible Spectrophotometer (Systronics, 2205) at 618 nm and 668 nm (max. values for M.B. and M.G. dyes) respectively. In all the batch experiment the extent of removal of the dye in terms of the values of percentage removal of dye and amount of dye adsorbed (qe) was calculated using following formulae.

C. Determination of dye removal efficiency:

The percent removal of dye during biosorption process was determined using the following formula.

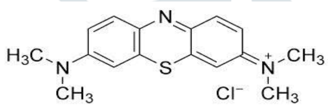
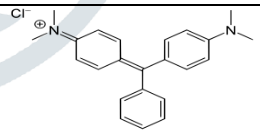
Dye Removal percent = $(C_i - C_e) / C_i \times 100$

Dye Uptake capasity during the biosorption was calculated as follows

$$q_e = (C_i - C_e) \times V / M$$

Where C_i is initial concentration of dye (mg/L),C_e is final concentration of dye (mg/L), M is weight of adsorbent (mg), V is volume of adsorbate (ml), q_e is amount of dye adsorbed (mg/g)

Scientific information of Methylene Blue and Malachite Green is as below.

	Methylene Blue	Malachite Green
UPAC Name	3,7-bis(Dimethylamino)–phenothiazin–5-ium chloride	N- [4-[[4-(demethylamino) - phenyl] phenylmethylene] 2, 5-Cyclohexadienl-ylidene] N- Methyl – methanaminium chloride
Commercial Name	Basic blue 9, Swiss Blue Chromosmon, Methylthioninium chloride, Methylene Blue,.	basic green, aniline green, fast green.
Molecular Formula	$C_{16}H_{18}N_3SCl$	$[C_6H_5C(C_6H_4N(CH_3)_2)_2]$ Cl
Structural Formula		

Stock solutions of M.B. and M.G. were prepared by dissolving accurately weighed sample of dye in deionized water to get a concentration of 1000 mg /L. Then test solutions were prepared by dilution of M.B. and M.G. stock solutions as per requirement.

RESULTS AND DISCUSSION:

Removal of M.B. and M.G. from aqueous binary solution on dried *Chaetomorpha media* varied with respect to different factors.

A. Effect of Initial pH: Variation in pH closely affects several functional groups such as amino, carboxyl etc. on the surface of algal cell wall which are responsible for binding of dye molecules. (Aksu and Karabayir, 2008;Marungrueng and Pavasant,2006) Effect of pH on adsorption of basic dyes with *Chaetomorpha media* is given in fig.1. Increase in pH initially increased the removal % up to pH 7. Hence pH 7 was selected for further experiments. Maximum adsorption of M.B. and M.G. dyes on tamarind kernel power at pH 6.8 has reported (Shanthi and Mahalakshmi 2012). In the present study maximum removal of M.B. and M.G. reported was 85.65% and 79.93% respectively. Deokar (2016), reported pH 6 was optimum pH for biosorption of Methylene Blue onto *Chaetomorpha media.*

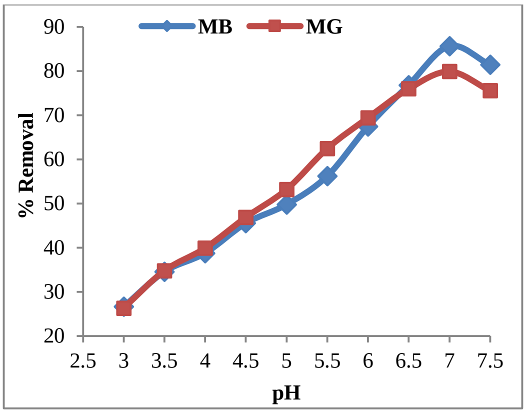


Fig.1-Effect of pH on biosorption of dyes from Binary solution by *C.media*

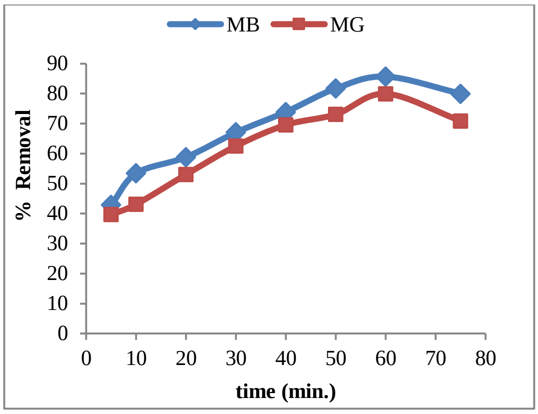


Fig.2- Effect of Agitation time on biosorption of dyes from Binary solution by *C. media*

B. Effect of Agitation time: The % removal of dyes from binary solution of M.G and M.B. increased with increase in contact time and reached a maximum value after one hour. The % removal of binary mixture of dyes at 60 minutes of contact time was 79.93% for M.G. and 85.65% for M.B. by *Chaetomorpha media*. The variation in dye removal % is represented in fig.2.

C. Effect of initial concentration of dye: At optimum initial concentration of dye i.e. 100 ppm the removal percentage of both the dyes was maximum. Further rate of removal of dye decreased with increase in the initial concentration. This is because of formation of monolayer at the lower initial concentration of dye over the surface of adsorbent. This variation is represented in fig.3. The results are in good agreement with these of reports. (Shanthi and Mahalakshmi 2012; Vijayaraghavan *et. al*. 2008) According to Aksu and Tezer (2005), increase in the initial dye concentration increases the number of dye ions in aqueous solution and thus enhances the number of collisions between dye ions and the seaweeds, which inturn facilitates the adsorption process.

D. Effect of adsorbent dose: The effect of variation of adsorbent dose was studied by keeping pH, contact time and concentration of dye constant (fig.4). When adsorbent dose increased the sorption capacity of M.G and M.B. also increased. 100 mg adsorbent dose was found to be the optimal adsorbent dose. This may be due to the higher availability of sorption sites for higher sorbent dosage.

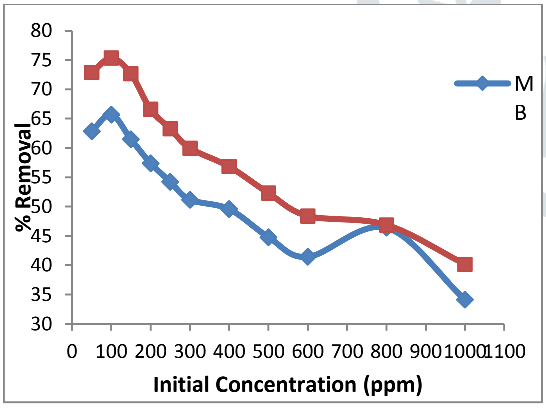


Fig.3 Effect of Dye concentrations on biosorption of Binary solution by *Chaetomorpha media*

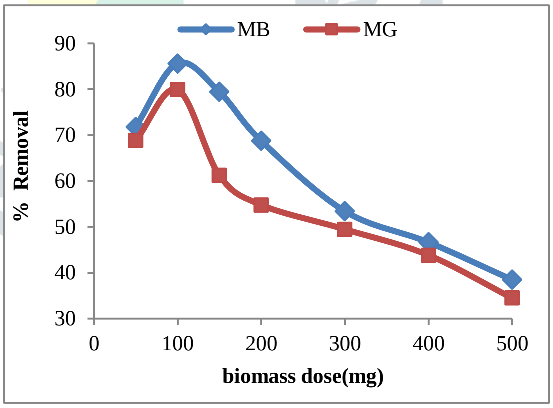


Fig.4 Effect of biomass dose on biosorption of dyes from Binary solution by *Chaetomorpha media*

E. Adsorption Isotherms: In order to understand the process and mechanism, experimental data, were analyzed with the help of adsorption models. In this study Langmuir (1918) and Freundlich (1906) models have been used to describe biosorption isotherms. These models are simple, well established and have physical meaning and are easily interpretable.

The model constants and correlation coefficients (R^2) obtained from both isotherm models are listed in Table.1.The linear relationship evidenced by the R-values (close to unity) indicates the applicability of these two isotherms and the monolayer coverage on adsorbent surface. Freundlich equation suggests multilayer adsorption and the sorption energy exponentially decreased on completion of the sorption centers of an adsorbent (Bekci, 2009).

It is assumed that the stronger binding sites are initially occupied with the binding strength decreasing with increasing degree of site occupation (Davis *et. al*. 2003; Deokar, 2016). Freundlich isotherm allowed for desorbing the adsorption of low strength solution (Marungrueng and Pavasant, 2006). Kf is constant indicative of the relative adsorption capacity of adsorbent, n is constant indicative of intensity of the adsorption. High Kf and n values indicate the binding capacity has reached its highest value and affinity between biomass and dye molecule was also higher. The value of n were greater than 1 representing efficient and beneficial adsorption. As per Freundlich constants the adsorption of M.G. was maximum than M.B. in binary solution in present study.

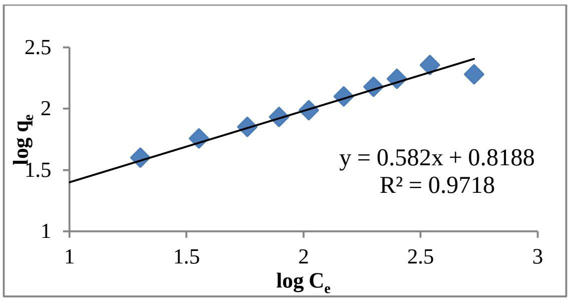


Fig.5 Frenlich model for removal of M.B from binary solution by *Chaetomorpha media*

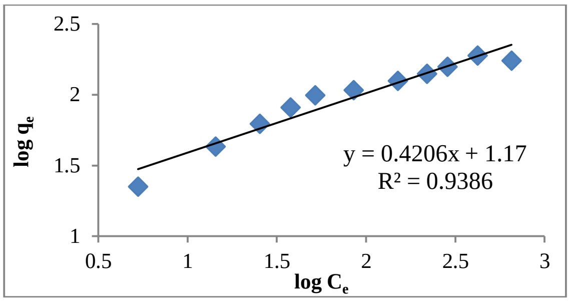


Fig.6 Frenlich model for removal of M.G. from binary Solution by *Chaetomorpha media*

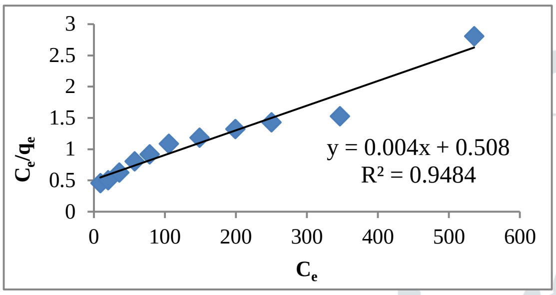


Fig. 7 Langmuir model for removal of M.G. from binary solution by *C. media*

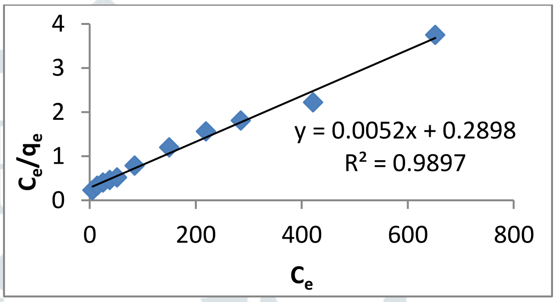


Fig. 8 Langmuir model for removal of M.B. from binary solution by *C. media*

The Langmuir model assumes monolayer coverage and constant adsorption energy while Freundlich equation deals with heterogenous surface adsorption. The applicability of both Langmuir and Freundlich isotherms to this study implies that both monolayer sorption and heterogeneous surface adsorptions exist in the experiment. This may be due to the different surface condition s on the two sides of the thallus of *Chaetomorpha media*.

F. Kinetic modeling: Adsorption kinetics of M.B. and M.G.dyes has been carried out in the present study to understand the adsorption behavior of dried *Chaetomorpha media* with respect to contact time, initial dye concentration and pH . Pseudo first-order (Lagergren, 1898) and Pseudo second-order kinetics (Ho and McKay,1998), models were used to describe the behavior of batch adsorption experiment. Values of Pseudo first and second-order kinetic constants are presented in Table.1. It was observed that kinetics of adsorption of M.G. and M.B. in binary solution by *Chaetomorpha media* is better described by Pseudo –second order kinetic model than Pseudo –first order. The linearity of the plot also shows the applicability of Pseudo –second order kinetic model, which has regression coefficient of R^2 equal to 0.939 and 0.991 for M.B. and M.G. respectively. The calculated qe based on Pseudo –second order kinetic model of M.B. and M.G. removal agreed very well with the experimental data. In contrast qe (cal.) values of Pseudo –first order kinetic model didn't match the experimental values of both dyes. Such observations are reported earlier in various studies using different binary dye solutions (Senthilkumar *et. al.*, 2006; Mane *et. al.*, 2007; Li *et. al.*, 2008; Deokar and Sabale, 2014)

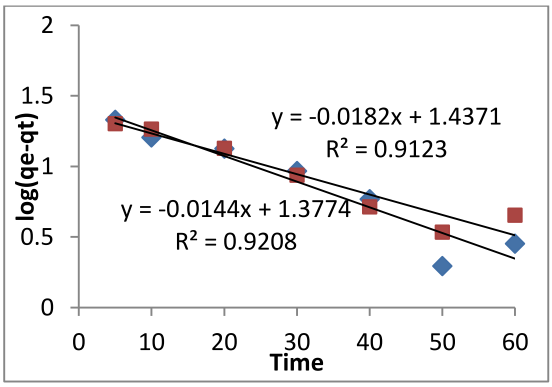


Fig.9 Pseudo first- order model for removal dyes binary mixture by *C. media*

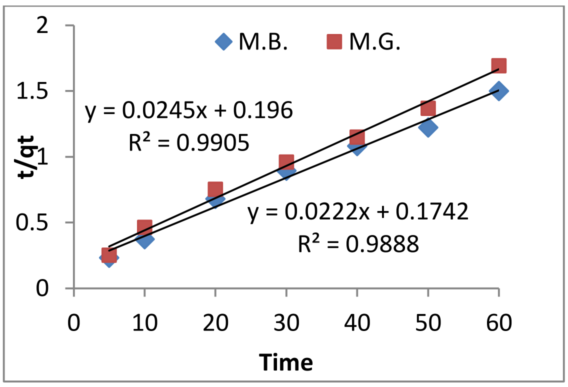


Fig.10 Pseudo Sec-order model for removal of dyes from binary mixture by *C.media*

G. Intra particle Diffusion Study: The adsorbent or dye species are most probably transported from the bulk of solution in to the solid phase through intra particle diffusion process, which is rate determining step in the adsorption process. In the present adsorption system it was explored by using the intra particle diffusion model (Weber and Chakravarthi, 1967; Brandt *et. al.*, 1993), which is explained by the equation

$$qt = Kidt^{1/2}+C$$

Where C is constant, Kid is intra particle diffusion rate constant (mg/g min $^{1/2}$), qt is the amount adsorbed at a time (mg/g), t is time (min). Intra particle diffusion rate constant was determined from the slope of the linear gradients of the plot qt Vs $t^{1/2}$ as shown in fig. 11 and table.1. as the plot does not show two or more intersecting lines the present work indicated that intra particle diffusion was a prominent process right from the beginning of dye-solid interaction, Surface adsorption and intra particle diffusion were concurrently operating during M.G. and M.B. adsorption from binary solution (Bhattacharyya and Sharma,2004; Deokar and Sabale, 2014)

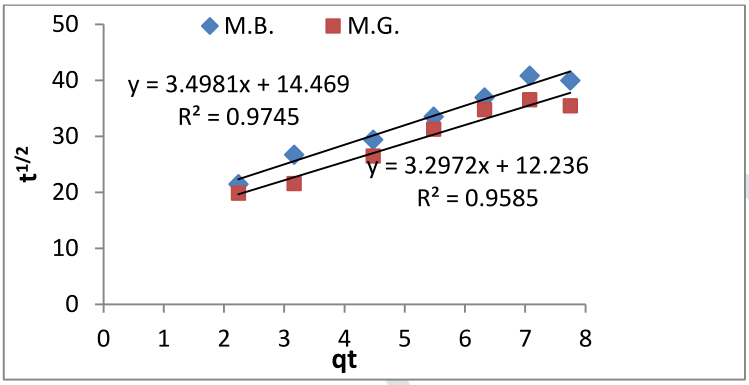


Fig.11 Intra particle diffusion plot for removal of dyes from binary mixture by *C. media*

CONCLUSION:

The present study showed that *Chaetomorpha media* having a great potential for binary uptake of M.G. and M.B. dyes from aqueous solution. Behavior of batch adsorption kinetics was well described by pseudo second-order kinetic model. The values of R^2 (close to unity) indicated that both Langmuir and Freundlich isotherm models were suitable for adsorption of M.G. and M.B. and the monolayer coverage on adsorbent surface. The values of R were in the range of 0 to 1 indicating that the adsorption process is favorable using the biomass of *Chaetomorpha media*.

Table.1 Isotherm and Kinetic model Constants for biosorption of dyes from their binary solution by *Chaetomorpha media*.

Models	Parameters	Dye	
		Methelyne Blue	Malachite Green
Langmuir	q_m(mg/g)	200	250
	b(1/mg)	18.25 x10^{-3}	7.87 x10^{-3}
	R^2	0.989	0.948
	q_m exp.(mg/g)	189.16	226.95
Freundlich	K_f	14.791	6.576
	n	2.381	1.718
	R^2	0.938	0.971
Pseudo-first-order	q_e exp.(mg/g)	42.825	39.962
	k_1x10^{-3} (min^{-1})	18	14
	q_e calc. (mg/g)	27.35	23.82
	R^2	0.912	0.920
Pseudo-second- order	k_2 x 10^{-3}	0.484	0.576
	q_e calc.(mg/g)	45.455	41.667
	R^2	0.939	0.991
Intra particle diffusion	K_{id} (mg $g^{-1}min^{-1}$)	3.498	3.297
	R^2	0.974	0.958

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