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Original Research Paper
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Enteromorpha intestinalis: Low Cost Biosorbent for Methylene Blue and Malachite Green from Binary Solution

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ABSTRACT

Biosorption of Methylene Blue (M.B.) and Malachite Green (M.G.) from binary solution onto dried biomass of green seaweed *Enteromorpha intestinalis* (L.) Knee was investigated. The biosorption was analyzed with respect to the pH, initial concentration of dye, agitation time and adsorbent dose. Removal percentage of both the dyes was maximum in 100 ppm dye solution at pH 7 when 100 mg adsorbent was used for one hour. 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 from the beginning of dye-solid interaction. Therefore biosorption might involve monolayer surface coverage and heterogeneous adsorption mechanism. Thus *Enteromorpha intestinalis* can be used as a low cost adsorbent for both dyes from a binary mixture.

KEYWORDS : Binary mixture, *Enteromorpha intestinalis*, Malachite Green, Methylene Blue.

Introduction

A huge amount of commercial dyes are used in plastic, food, textile, cosmetic, paper industries for production of over $7x10^5$ metric tons per year to colour final products (Celekli *et.al.,*2013) which results in production of coloured waste water. Even a very small amount of dye present in water (less than 1 ppm) is highly visible and undesirable (Banat *et.al.*,1996; Robinson *et.al.*,2001). Many of the dyes are carcinogenic and pose a serious hazard to aquatic living organisms (Vijayaraghavan and Yan, 2008) and cause the destruction of aquatic communities in ecosystem (Kuo, 1992; Walsh *et.al.*, 1980).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 and 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 (Kanan and Sundaram,2001; Senthil *et.al.*, 2003; Bhattacharya and Sharma, 2004; Aksu *et.al.*, 2008).

Among these techniques, adsorption is widely used for effluent treatment (Derbyshire *et.al.,* 2001; Ho and Mc. Kay 2003; Jain *et.al*.,2003). Bacteria, fungi, algae, industrial waste, agricultural waste and polysaccharide materials are used as biosorbents for dye removal. Use of marine algae commonly known as seaweeds as biosorbent is attracting researchers. They contain alginate gel in their cell wall as the most important constituent. Marine algae have been identified as potent metal biosorbents due to the presence of binding sites such as carboxyl, sulfonate, amine and hydroxyl groups (Davis *et.al.,* 2003; Celekli *et.al.*, 2011, 2013).

In present study aqueous binary solution of Malachite Green and Methylene Blue dyes was used as a model compound to monitor biosorption using dried biomass of green seaweed *E. intestinalis* The purpose of this work is to evaluate dye adsorption capacity and mechanism of adsorption of dye in binary system by *E. intestinalis*.

Materials and Methods

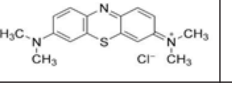
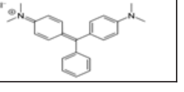
Collection and Preparation of biomass (adsorbent):

Mature green thalli of *Enteromorpha intestinalis* were collected from **Kunakeshwar**, (16.40° N, 73.19°E), in Sindhudurga district of Maharashtra (India) and washed with filtered sea water, and then fresh water for several times to remove sand, dirt and epiphytes. After drying in shade at room temp., the algal material was ground to a powder and then sieved through different mesh size to obtain fine (0.1 to 0.84mm) particles. This powdered material was stored in airtight containers in a cool and dry place for further use.

Procurement and Preparation of Binary dye solution:

Methylene blue (M.B.) and Malachite Green (M.G.) were obtained from Merck Specialties Pvt. Ltd, Mumbai.

Technical information of Methylene Blue and Malachite Green is given below.

	Methylene Blue	Malachite Green
IUPAC Name	3,7-bis (Dimethylamino) –phenothiazin–5-ium chloride	– [4-[[4-(demethylamino) -phenyl] phenylmethylene] 2, 5-Cyclohexadienl- ylidene] N- Methyl – methanaminium chloride
Commercial Name	Basic blue 9, Methylthioninium chloride, Chromosmon, Swiss Blue, 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.

Batch adsorption experiments:

These experiments were carried out at room temp. 27°± 2°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. 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 (λ 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.

$$\text{Removal \%} = \frac{Ci-Ce}{Ci} \times 100$$

$$= \frac{(Ci - Ce) \times v}{m}$$

Where Ci = initial concentration of dye (mg/L)
Ce = final concentration of dye (mg/L)
m = biomass (mg)
qe = uptake efficiency (mg/g)
v = volume of dye solution (ml)

Effect of various experimental parameters on adsorption of M.B. and M.G. dyes from binary mixture using dried biomass of *E. intestinalis* as an adsorbent was studied under different experimental conditions, such as pH, contact time, initial concentrations of dye, adsorbent dose.

Results and Discussion:
Removal of M.B. and M.G. from aqueous binary solution on dried *E. intestinalis* 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 *E. intestinalis* is given in fig.1. Increase in pH initially increased the removal % up to pH 7. Hence pH 7 was selected for further experiments. Shanthi and Mahalakshmi (2012) have reported maximum adsorption of M.B. and M.G. dyes on tamarind kernel power at pH 6.8. In the present study maximum removal of M.B. and M.G. reported was 87.33% and 85.33% respectively. Individual dye adsorption studies revealed that optimum pH for M.B. removal was 6 for *E. intestinalis* (Deokar and Sabale, 2014a).

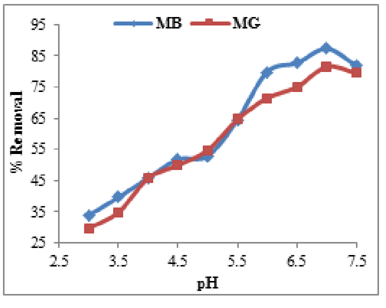


Fig.1-Effect of pH on biosorption of dyes from Binary by Enteromorpha intestinalis

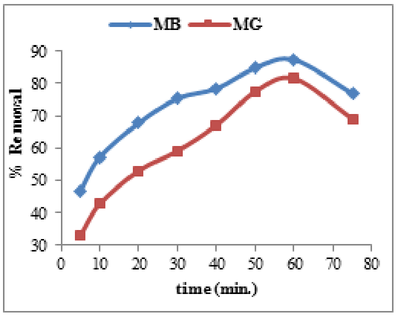


Fig.2- Effect of agitation time biosorption of dyes Binary solution by Enteromorpha intestinalis

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. Within first five minutes M.B. removal was near about 45 % in *E. intestinalis*. The % removal of binary mixture of dyes at 60 minutes of contact time was 85.33 % for M.G. and 87.55% for M.B. by *E. intestinalis*. 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 Shanthi and Mahalakshmi (2012); Vijayraghavan, Mao and Yun (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 intern facilitates the adsorption process. Celekli *et al.* (2013) has reported an increase in dye uptake of Reactive Red (120) and Reactive Yellow (80) binary system by *Spirogyra majusula* by increasing initial concentration.

D. Effect of biomass dose: The adsorption was recorded for 60 min using 100 mg/L binary dye solution at pH 7. *E. intestinalis* could remove about 80% dyes by increasing the biomass to 100 mg, the percentage of removal of dyes was enhanced by about 5 to 15 % in different biomaterials. This was the maximum removal of both M.B. and M.G. obtained in the present study. A further increase in the biomass caused a decline in the removal and also uptake of both the dyes. Same result was observed when *U. lactuca* was used as a biosorbent. (Deokar and Sabale, 2014b).

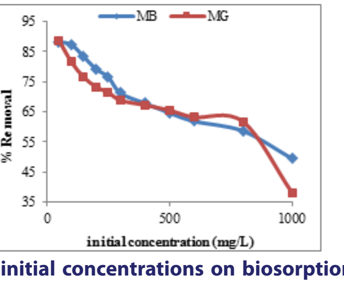


Fig.3 Effect of initial concentrations on biosorption of Binary solution by Enteromorpha intestinalis

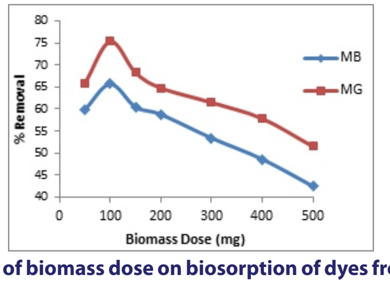


Fig.4 Effect of biomass dose on biosorption of dyes from Binary solution by Enteromorpha intestinalis

E. Adsorption Isotherms: Adsorption isotherm describes relationship between the amount of a substance adsorbed and its concentration in the equilibrium solution. It gives the qualitative information of nature of solute-surface interaction at a constant temperature. In order to understand the process and mechanism, experimental data, were analyzed with the help of adsorption models. In this study Langmuir (Langmuir, 1918) and Freundlich (Freundlich, 1907) 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 *et. al.*, 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). Freundlich isotherm allowed for desorbing the adsorption of low strength solution (Marungreneng and Pavasant, 2006). K_f is constant indicative of the relative adsorption capacity of adsorbent, n is constant indicative of intensity of the adsorption. High K_f 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 was 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.

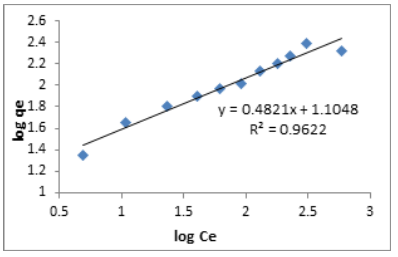


Fig.5 Frenlich model for removal of M.G. from binary Solution by *Enteromorpha intestinalis*

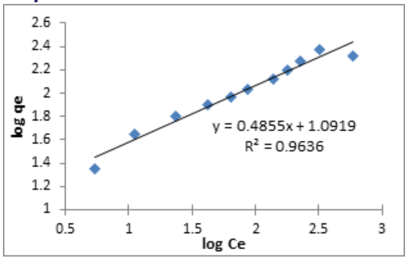


Fig.6 Frenlich model for removal of M.B. from binary solution by *Enteromorpha intestinalis*

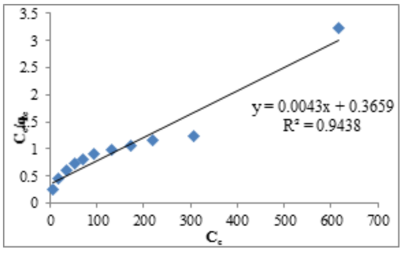


Fig. 7 Langmuir model for removal of M.G. from binary solution by *Enteromorpha intestinalis*

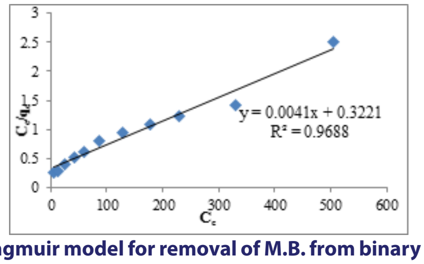


Fig. 8 Langmuir model for removal of M.B. from binary solution by Enteromorpha intestinalis

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 *Enteromorpha intestinalis*. *E. intestinalis* for removal of M.G. Values of experimental q_e were in tune with q_e obtained by isotherm graphs. R_L values ranged from 0 to1 and confirmed a favorable adsorption for both dyes.

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 *Enteromorpha intestinalis* with respect to contact time, initial dye concentration and pH. Pseudo first-order (Lagergren, 1898) and Pseudo second-order kinetics (Ho and Mckay,1999) 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. Values of q_e obtained from the plot of pseudo second order kinetic model were found very close to the q_e values calculated from experimental data. R^2 values obtained from pseudo second order kinetic model were higher than those recorded for pseudo first order kinetic model. The pseudo second order kinetic model was found suitable in the present study for M.B. and M.G. adsorption from binary solution by *E. intestinalis*. Such observations are reported earlier in various studies using different binary dye solutions (Senthil Kumar *et.al.*, 2006; Mane *et.al.*, 2007; Li *et.al.*, 2008; Deokar and Sabale, 2014b).

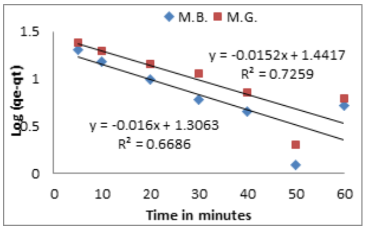


Fig.9 Pseudo first- order model for removal of dyes from binary mixture by E. intestinalis

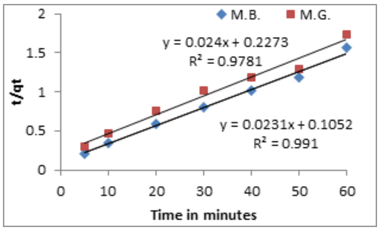


Fig.10 Pseudo Sec-order model for removal of dyes from binary mixture by E. intestinalis

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 Chakravarti, 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 (Battacharya and Sharma, 2005).

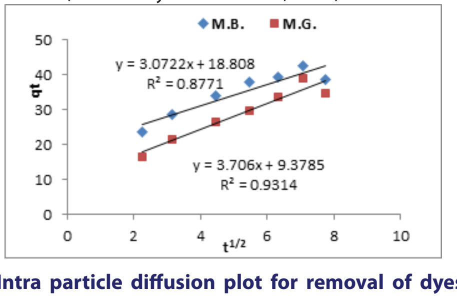


Fig.11 Intra particle diffusion plot for removal of dyes from binary mixture by *Enteromorpha intestinalis*

Conclusion:

The present study showed that *Enteromorpha intestinalis* (L.) Knee had 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 *Enteromorpha intestinalis*.

Table.1 Isotherm and Kinetic model Constants for biosorption of dyes from their binary solution by ***Enteromorpha intestinalis*** (L.) Knee .

Models	Parameters	Dye	
		Methelyne Blue	Malachite Green
Langmuir	Graphical q_m (mg/g)	250	250
	Experimental q_m(mg/g)	238.52	247.00
	b(1/mg)	$12.61x10^{-3}$	$13.07x10^{-3}$
	R^2	0.966	0.960
	R_L	0.931-0.136	0.932-0.110
Freundlich	n	2.062	2.074
	K_f	12.331	12.705
	R^2	0.963	0.962
Pseudo-first-order	Graphical q_e (mg/g)	22.23	25.004
	Experimental q_e (mg/g)	43.662	40.775
	$k_1 x10^{-3}$ (min^{-1})	9	14
	R^2	0.837	0.965
Pseudo-second-order	Graphical q_e(mg/g)	43.478	41.66
	$k_2 x\ 10^{-3}$	0.576	0.483
	R^2	0.987	0.993
Intra particle diffusion	K_{id} (mg $g^{-1}min^{-1}$)	2.648	3.406
	R^2	0.931	0.968

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