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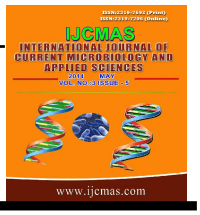

Original Research Article

Biosorption of Methylene Blue and Malachite Green From Binary Solution onto Ulva lactuca

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A B S T R A C T

Adsorption of Methylene Blue (M.B.) and Malachite Green (M.G.) onto dried biomass of *Ulva lactuca (L.)* was attended in this study. The adsorption process was analyzed with respect to the initial concentration of dye, pH, contact time and adsorbent dose. Removal percentage of both the dyes was maximum in 100 ppm dye solution at pH 6 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 right from the beginning of dye-solid interaction. Therefore the adsorption might involve monolayer surface coverage and heterogeneous adsorption mechanism. Thus *Ulva lactuca* can be used as a low cost adsorbent for removal of both dyes from a binary mixture**.**

Keywords

Adsorption, binary mixture, Malachite Green, Methylene Blue, *Ulva lactuca*.

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 *Ulva lactuca* (L.) The purpose of this work is to evaluate dye adsorption capacity and mechanism of adsorption of dye in binary system by *Ulva lactuca* (L.).

Materials and Methods

Collection and Preparation of biomass (adsorbent)

Mature green thalli of *Ulva lactuca* (L.) were collected from Kunakeshwar, (16.40^{o} N, 73.19^{o}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.

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:

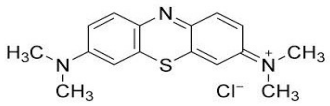
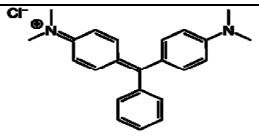
These experiments were carried out at room temp. $27^{o} \pm 2^{o}$ C using diluted binary stocks solution of M.B. and M.G. to the required initial concentration, (Low *et.al.*, 1993). Exactly 50 ml. binary solution of known concentration range was shaken at a specific agitation speed with a required fine biomass dose for specific contact time. 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.

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

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

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)

Technical information of Methylene Blue and Malachite Green is given 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, 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		

Effect of various experimental parameters on adsorption of M.B. and M.G. dyes from binary mixture using dried biomass of *Ulva lactuca* 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 *Ulva lactuca* 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 *Ulva lactuca* 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 65.68% and 75.35% respectively.

B. Effect of contact 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 75.35 % for M.G. and 65.68 for M.B. by *Ulva lactuca.* The variation in dye removal % is represented in fig.2.

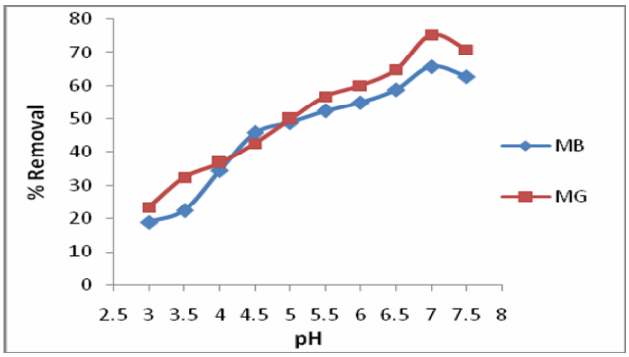


Fig.1-Effect of pH on biosorption of dyes from Binary solution by *Ulva lactuca*

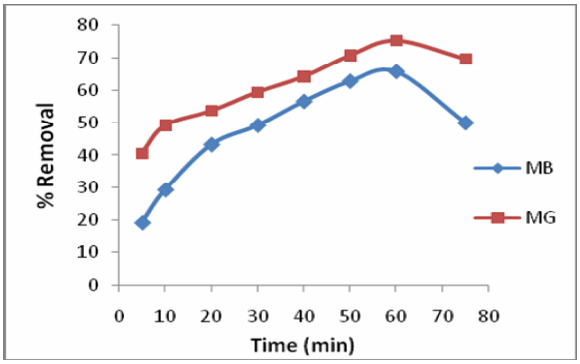


Fig.2- Effect of contact time biosorption of dyes from Binary solution by *Ulva lactuca*

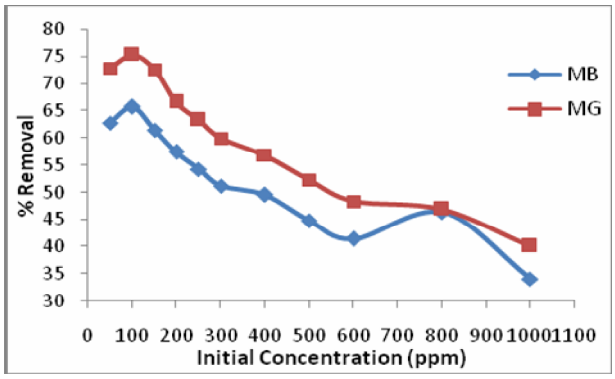


Fig.3 Effect of initial concentrations on biosorption of Binary solution by *Ulva lactuca*

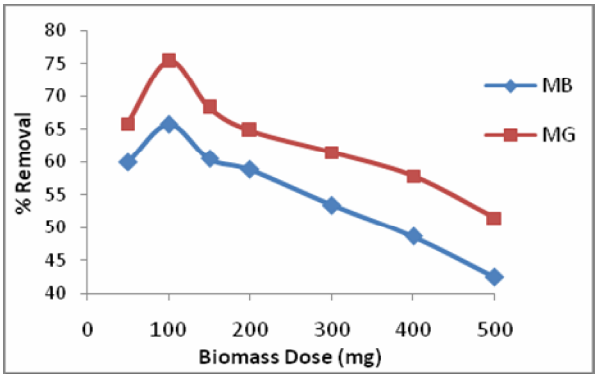


Fig.4 Effect of biomass dose on biosorption of dyes from Binary solution by *Ulva lactuca*

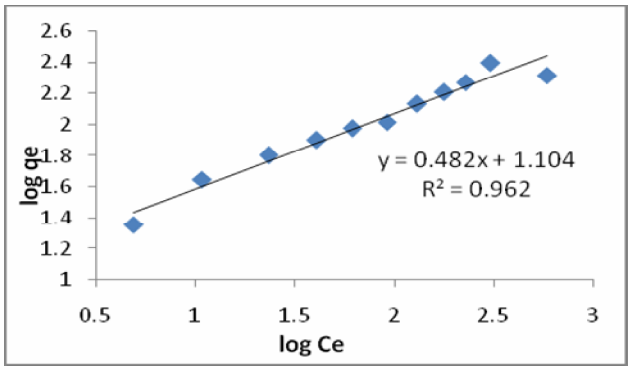


Fig.5 Frenlich model for removal of M.G. from binary Solution by *Ulva lactuca*

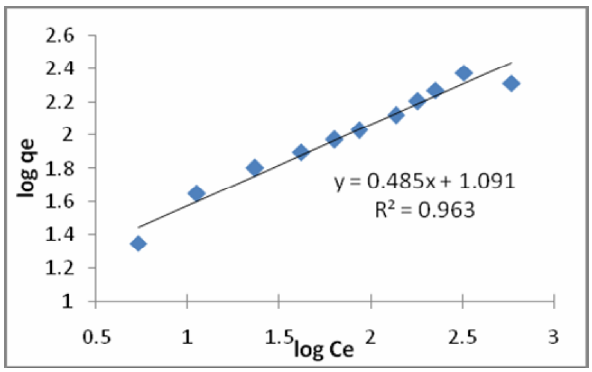


Fig.6 Frenlich model for removal of M.B. from binary solution by *Ulva lactuca*

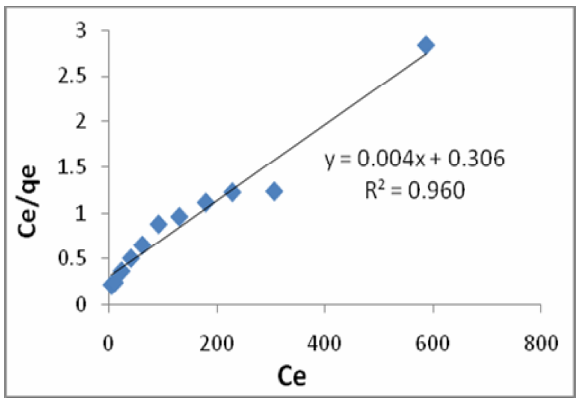


Fig. 7 Langmuir model for removal of M.G. from binary solution by *Ulva lactuca*

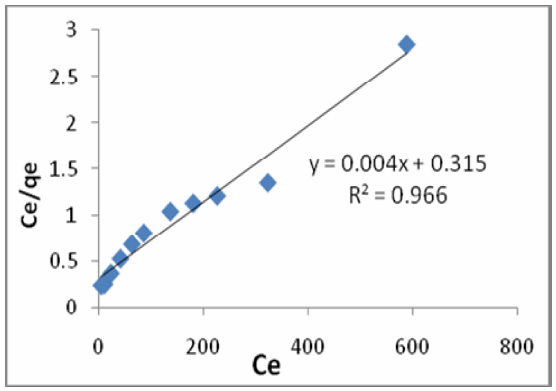


Fig. 8 Langmuir model for removal of M.B. from binary solution by *Ulva lactuca*

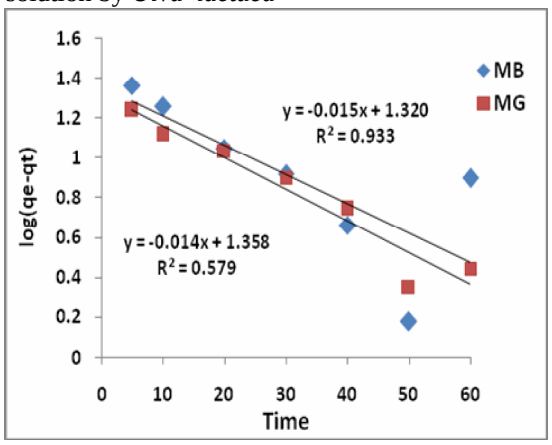


Fig.9 Pseudo first- order model for removal of dyes from binary solution by *Ulva lactuca*

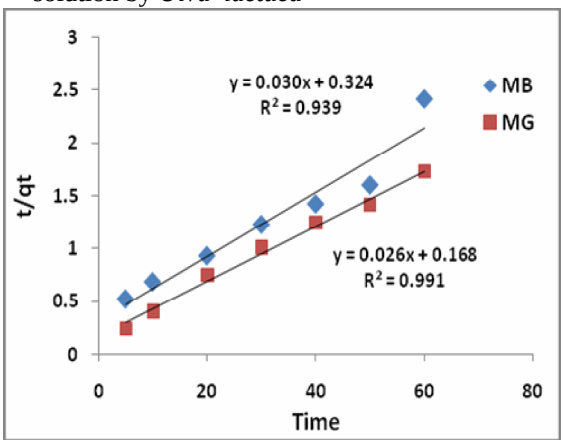


Fig.10 Pseudo Sec-order model for removal of dyes from binary solution by *Ulva lactuca*

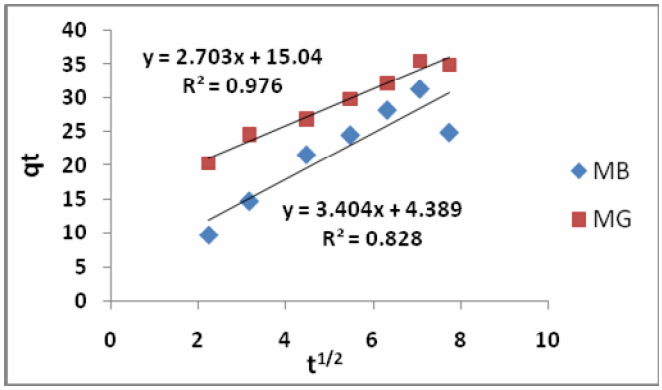


Fig.11 Intra particle diffusion plot for removal of dyes from binary solution by Ulva lactuca

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

Models	Parameters	Dye	
		Methelyne Blue	Malachite Green
Langmuir	q_m(mg/g)	200	200
	b(1/mg)	$5.4348x10^{-3}$	$8.5470x10^{-3}$
	R^2	0.910	0.962
	q_m exp.(mg/g)	185.56	187.44
Freundlich	K_f	3.9811	6.7298
	n	1.6921	1.873
	R^2	0.960	0.967
Pseudo-first-order	q_e exp.(mg/g)	32.84	37.675
	k_1x10^{-3} (min^{-1})	14	15
	q_e calc. (mg/g)	22.8034	20.893
	R^2	0.579	0.933
Pseudo-second-order	k_2 x 10^{-3}	0.9	0.676
	q_e calc.(mg/g)	33.33	38.462
	R^2	0.939	0.991
Intra particle diffusion	K_{id} (mg $g^{-1}min^{-1}$)	3.404	2.703
	R^2	0.824	0.976

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 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.

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 (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). 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.

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 *Ulva lactuca.*

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 *Ulva lactuca* 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. It was observed that kinetics of adsorption of M.G. and M.B. in binary solution by *Ulva lactuca* 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 (Senthil Kumar *et.al*., 2006; Mane *et.al*., 2007; Li *et.al*., 2008).

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).

The present study showed that *Ulva lactuca* 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 *Ulva lactuca* .

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