PUBLICATIONS

Papers published in research journals


Papers presented at conferences / competitions

Also presented at 7th *Maharashtra State Inter University Research Convention Avishkar*, Jan. 2013, Dr. Balasaheb Sawant Kokan Krishi Vidyapith, Dapoli.

Also presented at 8th *Maharashtra State Inter University Research Convention Avishkar* Jan. 2014, North Maharashtra University, Jalgaon.

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Biosorption of Malachite Green from Aqueous Solution by Green Seaweeds

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Abstract

Water pollution and toxicity of hazardous chemical compounds are major concerns today in the developing countries due to rapid industrialization and urbanization. In the present study removal of an industrial dye Malachite Green using dried biomass of green seaweeds was attempted. The process of dye adsorption was found to be controlled by various factors such as pH, contact time, adsorbent dose, initial concentration of dye, agitation speed and particle size of biomass used. The removal capacity was >80% in all the green algal materials used for investigation (*Ulva lactuca, Caulerpa taxifolia, Chaetomorpha media and Enteromorpha intestinalis*). The removal % and removal efficiency was maximum when 100mg fine biomass of Chaetomorpha media was used in the dye solution having 100 mg/L concentration at pH 8 and agitation speed 150 rpm. The process required one hour for removal of 88 % dye. Protonation of biomass using 0.1M HCL was able to enhance the removal percentage of dye more than 90% in all the materials.

Keywords - biosorption, Caulerpa, Chaetomorpha, Enteromorpha, Malachite Green, Ulva.

Introduction:

Effluents from various industries form an important source of dyes (Aksu,2005). Normally dyes have complex aromatic molecular structure which makes them more stable and more difficult to biodegrade (Seshadri et.al.1994). Many dyes and their breakdown products may be toxic for living organisms (Kannan and Sundaram, 2001).Therefore decolorization of dyes is important before the discharge of effluent. Removal of dye has been attempted extensively using physico-chemical methods such as coagulation, ultra filtration, electro-chemical adsorption, photo-oxidation activated carbon adsorption etc. (Kannan and Sundaram, 2001; Bhattacharya and Sharma, 2004). But these technologies are not efficient, satisfactory and also cost effective. Use of low cost, easily available biomaterials for the adsorption of dyes is practiced as an alternative method and several botanical, low cost materials have directly been used as an adsorbent for removal of dyes from wastewater. (Jayaraj et. al, 2011; Hameed and El-K Haiary, 2008).

Malachite Green (M.G.) is a basic, cationic, triphenyl methane dye. It has been extensively used in industries for dyeing leather, silk, wool, jute and in distilleries. It is used as a fungicide and antiseptic in aquaculture industries (Zhang and Zhang, 2008). M.G. has been proved to cause adverse effect on the immune and reproductive system of mammals and is known for its cytotoxic, genotoxic and carcinotoxic potentials (Bekci,2009).Though the use of this dye has been banned in several countries and not approved by US Food and Drug Administration, it is still used in many parts of the world due to its low cost, easy availability, efficiency and lack of
proper alternatives (Papinutti et al., 2006; Hameed and El-K Haiary, 2008; Yonar and Yonar, 2010).

In present study aqueous solution of M.G. dye was used as a model compound to monitor biosorption using dried biomass of a few green seaweeds, viz *Ulva lactuca, Caulerpa taxifolia, Chaetomorpha media* and *Enteromorpha intestinalis* as an adsorbent. The purpose of this work was to evaluate and compare adsorption capacity of selected green seaweeds with respect to the effect of pH, contact time, adsorbent dose, initial concentration of dye, agitation speed and particle size on the process of dye adsorption.

**Materials And Methods:**

**Collection and Preparation of biomass (adsorbent):**

Mature green thalli of *Ulva lactuca* (L.), *Caulerpa taxifolia* (Vahl) C. Agarth., *Chaetomorpha media* (C.Agarth) Kutz. and *Enteromorpha intestinalis* (L.)Knee. 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), coarse (0.84 to 2mm) and large particles (above 2mm). This powdered material was stored in airtight containers in a cool and dry place for further use.

**Procurement and Preparation of M.G.:**

Malachite green was obtained from Merck Specialities Pvt. Ltd, Mumbai. 

**Commercial Name** – basic green, aniline green, fast green.

**IUPAC Name** – N-{4-[4-(demethylamino)-phenyl]phenylmethylene}2,5-

**Cyclohexadienyl-ylidene} N-Methyl – methanaminium chloride**

**Structural Formula** -

Stock solution of M.G. was prepared by dissolving accurately weighed sample of dye in distilled water to get a concentration of 1000 mg /L and diluted as per requirement.

**Batch adsorption experiments:**

These experiments were carried out at room temp. using diluted stocks solution of M.G. to the required initial concentration, (Low et. al.1993). Exactly 50 ml. M.G. solution of known concentration range was shaken at a specific agitation speed with required biomass dose for specific contact time. For all the batch experiments a fine biomass was used except for study of effect of particle size. All experiment were carried out at room temperature (27° ± 2°C).

Initial and final concentration of dye were measured at 618 nm on a double beam UV-Visible Spectrophotometer (Systronics, 2205). The percentage of dye removal and amount of dye adsorbed (mg/g) was calculated using following formulae.

\[
\text{Removal} \% = \frac{C_i - C_e}{C_i} \times 100
\]

\[
q_e = \frac{(C_i - C_e \times V)}{m}
\]

Where \(C_i\) = initial concentration of M.G.(mg/L) 
\(C_e\) = final concentration of M.G.(mg/L) 
\(m\) = biomass (mg)
qe = uptake efficiency (mg/g)

v = volume of dye solution (ml)

Effect of pH was studied by changing pH of dye solution from 1 to 10 using either 1 M HCl or 1 M NaOH. The experiment was run for optimum time using 100 mg fine biomass was added in 50 ml of 100 mg/L dye solution.

Effect of Contact time was analyzed by adding 100 mg fine biomass in 50 ml dye solution (100mg/L) at respective optimum pH. The final concentration of dye was recorded, after every ten min. upto 120 min.

Effect of biomass dose was analyzed by increasing the amount of biomass from 50 to 500 mg and keeping all other parameters at optimum value. In order to study the effect of concentration, 100 mg biomass was added in 50 ml of dye solution and concentration of dye was increased from 50 to 500mg/L, keeping pH and contact time at optimum values.

The effect of agitation speed was analyzed by arranging experiment at varying speed from 50 to 250 rpm at optimized conditions. Similarly influence of particle size on the process of biosorption was studied by using fine, coarse and large particle biomass for adsorption of M.G.

In order to analyze loading capacity of biomass, four cycles of biosorption were monitored using the same biomass. (100 mg fine biomass was used in 50 ml of aqueous solution containing 100mg/L M.G. dye). The pH, time and speed were maintained at optimum values.

For protonation, fine algal biomass was treated with 0.1M HCL for three hours and then dried in shade. This biomass (100mg) was used for batch experiment at optimized pH and time conditions.

Results and Discussion:

Removal of M.G. and efficiency of the process of biosorption varied in different algal materials with respect to different factors.

Effect of pH –

The study of pH is important for development of a successful method for biosorption. In many cases, the adsorption of basic dyes decreased at lower pH due to occurrence of proton in acidic medium. (Kumar et al., 2006; Crini et al., 2007; Punjongham et al., 2007). In the present study dye adsorption was found unfavorable between pH values 1-4. Maximum removal of Malachite green was observed at pH 8 in C. media, E. intestinalis and C. taxifolia while it was at pH 7 in U. lactuca (Fig.1). Similar type of observations are recorded in, Pithophora and Enteromorpha (Sivamani et al. 2009; Jayaraj et al. 2011) for M.G. and in Ulva and Sargassum for methylene blue (Tahir et al., 2008 and Khaled et al.2005).

At lower pH, number of negative charges on adsorbent get decreased and number of positive charges increase which did not favour the adsorption of positively charged dye cations due to electrostatic repulsion. According to Hamdaoui (2006), low adorption of malachite green at acidic pH is due to the presence of excess H+ ions competing with dye cations for the adsorption sites of adsorbent.
Effect of contact time –

The removal efficiency of dye varied as per the time of contact (Fig.2). It was observed that maximum adsorption of M.G. took place during first 30 min. in all the materials and the rate of biosorption decreased thereafter. The equilibrium of process was marked by the maximum removal percentage of dye which varied in different algal biomass used. The dye removal profile followed three distinct phases. Initially the rate of removal was less, which increased progressively with progression of contact time and finally attained saturation. The process of adsorption reached equilibrium after 75 min. in U. lactuca, 60 min. in C. media, 45 min. in E. intestinolis and 90 min. in C. taxifolia. From the result it was noted that 30 min of contact time was sufficient for initial acclimatization. The rate of dye removal was rapid during the first 30 min. in all the materials. After that the rate of dye removal slowly decreased and reached saturation.

Effect of adsorbent dosage –

It was observed that there is a sharp increase in dye removal percentage with an increase in the adsorbent dose (Fig.3). Increased dye adsorption may be due to an increase and availability of exchangeable dye binding sites and/or surface area. This study is in good agreement with the results obtained for Azadirachta indica, Enteromorpha for M.G. removal and Ulva and Sargassum for methylene blue removal (Bhattacharrya and Sharma, 2003; Jayaraj et al., 2011; Khaled et al., 2005).
Effect of Initial Concentration of M.G. –

In present study the efficiency (qe) increased with an increase in dye concentration however removal percentage decreased to 50% (Fig.4). The same observations were made for other adsorbents like Hydrilla, Pithophora and Enteromorpha for M.G. removal and for Ulva and Sargassum for removal of methylene blue (Khaled et al.2005; Tahir et al.2008; Sivamani et al. 2009; Rajeshkannan et al. 2010; Jayaraj et al. 2011). According to Hameed and El-K Haiary, 2008, the initial concentration of dye provides an important driving force hence higher initial concentration of dye enhances the adsorption capacity.

Effect of Agitation speed –

In the batch experiment agitation speed plays an important role in affecting the external boundary film and distribution of the solute in the bulk solution. As the speed of agitation was increased from 50 to 250 rpm in present study the dye removal percentage also increased (Fig.5). At the lowest speed of 50 rpm removal percentage was about 50% in all the materials which crossed 80% after increasing the agitation speed up to the 150 rpm. The removal percentage of dye did not change thereafter by increasing the speed of agitation.

Effect of Particle size –

The contact surface between an adsorbent and dye plays an important role in the process of adsorption. According to Blazquez et al. (2005), solid sorption capacity as well as the time required to reach equilibrium are mostly related to the morphology. The fine powdered biomass exhibited a maximum dye removal % in all green seaweeds in the present study (Fig.6). This may be due to a larger surface area of fine powdered particles, which could adsorb more amount of dye (Aliabadi et al., 2006). Similar observation is recorded by Hii et al. (2012) for removal of rhodamine B by Turbinaria.

The efficiency of dye removal did not vary much and was maximum in C. media (44.03 mg/g) followed by C. taxifolia (43.10 mg/g), U. lactuca (42.49 mg/g) and E. intestinalis (41.65 mg/g).

Effect of dye loading capacity –

In order to judge the reusability of biomass, the biomass from one batch was separated by centrifugation after the desired time and reused with fresh dye solution of same concentration (100mg/L).

It was noticed that the algal biomass could be reused up to four subsequent cycles (Fig. 7). The saturation of binding sites occurs earlier (first or second cycle), where the removal % is also higher and decreases in subsequent cycles. After 3rd
cycle of loading, the capacity of dye removal decreased drastically in all the materials in the present study, giving about 20-30% dye removal. These observations are supported by Gajare and Menghani (2012) for removal of M.G using natural grown algal biomass from river water.

**Effect of protonation**

The process of protonation increased dye removal % significantly in all the materials, (Fig.8). This increase is due to a structural modification and action of mineral acids causative protonation of functional groups responsible for the biosorption. Similar observations are made by Vijayaraghavan and Yun (2008) in *Laminaria* for C.I.Reactive Black.

Adsorption capacity of the algal biomass used in present study was much better than several other biomaterials used (Table.1). It was about 50% of natural grown algal biomass and activated carbon of *Enteromorpha*.

**Table 1: Adsorption capacity of different adsorbent materials.**

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>q(mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated Carbon of</td>
<td>27.78</td>
<td>Santhi <em>et.al.</em>, 2010(A)</td>
</tr>
<tr>
<td>Epicarp of <em>Ricinus communis</em></td>
<td>25.91</td>
<td>Santhi <em>et. al.</em>, 2010(B)</td>
</tr>
<tr>
<td><em>Annona squamosa</em> seeds</td>
<td>30.86</td>
<td><em>Santhi et.al.</em>, 2009</td>
</tr>
<tr>
<td>peel of <em>Cucumis sativa</em> fruit</td>
<td>63.85</td>
<td>Sharma <em>et.al.</em>, 2009</td>
</tr>
<tr>
<td>Rice husk activated carbon</td>
<td>28.8042</td>
<td>Mane <em>et.al.</em>, 2007</td>
</tr>
<tr>
<td>Rice Husk ash</td>
<td>38.4774</td>
<td><em>Wang et.al.</em>, 2008</td>
</tr>
<tr>
<td>Rice bran coarse particles</td>
<td>75.6484</td>
<td></td>
</tr>
<tr>
<td>Wheat bran coarse particles</td>
<td>36.45</td>
<td><em>Kumar and Sivansan</em>, 2007</td>
</tr>
<tr>
<td>Mango seed husk</td>
<td>55.3</td>
<td><em>Baek et.al.</em>, 2010</td>
</tr>
<tr>
<td>Coffee beans</td>
<td>38.45</td>
<td><em>Kumar and Sivansan</em>, 2007</td>
</tr>
<tr>
<td>Rubber wood sawdust</td>
<td>25.67</td>
<td>Bakci <em>et.al.</em>, 2009</td>
</tr>
<tr>
<td><em>Caulerpa racemosa</em></td>
<td>90</td>
<td>Gajare and Menghani, 2012</td>
</tr>
<tr>
<td>Naturally grown algal biomass</td>
<td>94.74</td>
<td>Jayraj <em>et.al.</em>, 2011</td>
</tr>
<tr>
<td>Activated carbon of <em>Enteromorpha</em></td>
<td>44.03</td>
<td>Present study</td>
</tr>
<tr>
<td>Dried biomass of</td>
<td>43.10</td>
<td></td>
</tr>
<tr>
<td><em>Chaetomorpha media</em></td>
<td>42.49</td>
<td></td>
</tr>
<tr>
<td><em>Enteromorpha intestinalis</em></td>
<td>41.65</td>
<td></td>
</tr>
</tbody>
</table>
Conclusion:
The present study is attempted to search for a low cost adsorbent for removal of toxic dyes. Removal and disposal of naturally grown seaweed biomass is also today's environmental concern. This study gives solution for both the problems. All materials used in the present study have shown a remarkable potential for removal of dye from aqueous solutions. Chemical treatment to the biomass was found to enhance the biosorptive capacity of the biomass. The study also revealed that contact time required for equilibrium was very less as compared to other biomaterials. Certainly these results will open a new research area in control of water pollution.

References:


RESEARCH ARTICLE
BIOSORPTION OF METHYLENE BLUE FROM AQUEOUS SOLUTION ONTO GREEN SEAWEEDS

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ABSTRACT

Due to rapid industrialization and urbanization, presence of hazardous chemical compounds causing water pollution is of common occurrence in developing countries. Use of biosorption technology for removal of dyes from industrial waste water is rapidly gaining attention due to its effectiveness and ease of application. In the present study removal of an industrial dye, Methylene Blue using dried green seaweeds has been attempted. The process of dye adsorption was found to be controlled by factors such as pH, contact time, adsorbent dose, initial concentration of dye, agitation speed and particle size of biomass used. The removal capacity was >83% in all the green algal materials used for investigation (Ulva lactuca, Caulerpa taxifolia, Chaetomorpha media and Enteromorpha intestinalis). The removal % and removal efficiency was maximum when 100mg fine biomass of Chaetomorpha media was used in the dye solution having 100 mg/L concentration at pH 6 and agitation speed of 200 rpm. The process required one hour for removal of 94.3 % dye. Protonation of algal biomass using 0.1M HCL was able to enhance the ability of dye adsorption in all the algal materials.

INTRODUCTION

More than 10000 commercially dyes are utilized by plastic, food, cosmetic, paper and textile industries and their amount produced annually is about 7x10^6 metric tons per year (Celekli et al.,2013). The effluent of these industries results in coloured wastewater. 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; Jayarajahvan and Yan, 2008). Physico-chemical methods used for removal of these dyes such as coagulation, ultra filtration, electro-chemical adsorption, photo-oxidation, activated carbon adsorption are not convenient (Kannan and Sundaram, 2001; Bhattacharya and Sharma, 2004; Aksu et al.,2008). Use of low cost, easily available biomaterials for the adsorption of dyes is practiced as an alternative method and several botanical, low cost materials have directly been used as an adsorbent for removal of dyes from wastewater (Jayarajahvan et al.,2011; Hameed and El-K哈利, 2008; Jain and Sikarwar, 2006). In present study aqueous solution of M.B. was used as a model compound to monitor biosorption using dried biomass of green seaweeds viz Ulva lactuca, Caulerpa taxifolia, Chaetomorpha media and Enteromorpha intestinalis as adsorbents. The purpose of this work was to evaluate and compare adsorption capacity of selected green seaweeds with respect to the effect of pH, contact time, adsorbent dose, initial concentration of dye, agitation speed and particle size on the process of dye adsorption.

MATERIALS AND METHODS

Collection and Preparation of biomass (adsorbent)

Mature green thalli of Ulva lactuca (L.), Caulerpa taxifolia (Valil) C. Agarth., Chaetomorpha media (C.Agarth) Kutz. and Enteromorpha intestinalis (L.)Knee. 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), medium ( 0.84 to 2mm) and coarse grade powder (above 2mm).This powdered material was stored in airtight containers in a cool and dry place for further use.

Procurement and Preparation of M.B

Methylene Blue was obtained from Merck Specialities Pvt. Ltd, Mumbai. Stock solution of M.B. was prepared by dissolving accurately weighed sample of dye in distilled water to get a concentration of 1000 mg/L and diluted as per requirement.

Batch adsorption experiments

These experiments were carried out using diluted stock solution of M.B. to the required initial concentration, at room temp. 27 ± 2 °C (Low et al.,1993). Exactly 50 ml M.B. solution of known concentration range was shaken in a conical flask at a specific agitation speed with required biomass dose for specific contact time. For all the batch experiments the fine biomass was used except for study of effect of particle size. Initial and final absorbance of dye was measured on a double beam UV-Visible spectrophotometer. The removal % and removal efficiency was calculated using the below mentioned formulas.

Removal % = [(C0-C)/C0] x 100

Removal efficiency = [(C0-C)/C0] x 100
Spectrophotometer (Systronics, 2205) at 618 nm. The initial and final concentrations were obtained from the standard graph by the interpolation technique. In all batch experiment the extent of removal of the dye and amount adsorbed (qe) was calculated using following formulae.

$$\text{Removal} \% = \frac{c_i - c_f}{c_i} \times 100$$

$$qe = \frac{m}{v} \times \frac{c_i - c_f}{v}$$

Where \(c_i\) = initial concentration of M.B. (mg/L)
\(c_f\) = final concentration of M.B.(mg/L)
\(m\) = biomass (mg)
\(q_e\) = uptake efficiency (mg/g)
\(v\) = volume of dye solution (ml)

Effect of pH was studied by changing pH of dye solution from 1 to 10 using either 1 N HCl or 1 N NaOH. The experiment was run for optimum time with 100 mg fine biomass in 50 ml of 100 mg/L dye solution. Effect of Contact time was analyzed by adding 100 mg fine biomass in 50 ml dye solution (100mg/L) at respective optimum pH. The final concentration of dye was recorded, after every ten min., up to 120 min. Effect of biomass dose was analyzed by increasing the amount of biomass from 50 to 500 mg and keeping all other parameters at optimum value. In order to study the effect of concentration, 100 mg biomass was added in 50 ml of dye solution and concentration of dye was increased from 50 to 500mg/L, keeping pH and contact time at optimum values. The effect of agitation speed was analyzed by arranging the experiment at varying speed from 50 to 250 rpm at optimized conditions.

**Table 1** Comparison of adsorption capacity of green seaweeds with other low cost adsorbent

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>qe (mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caulerpa racemosa Var.</td>
<td>3.40</td>
<td>Cengiz S and Cavas, 2008</td>
</tr>
<tr>
<td>cylindrica</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sargassum maticum</td>
<td>279.2</td>
<td>Rubin et al., 2005.</td>
</tr>
<tr>
<td>Gelidium</td>
<td>171.00</td>
<td>Vitar et al., 2006.</td>
</tr>
<tr>
<td>Algal Waste</td>
<td>104.00</td>
<td></td>
</tr>
<tr>
<td>Ulva lactuca</td>
<td>16.603</td>
<td>Khaled et al., 2005.</td>
</tr>
<tr>
<td>Ulva lactuca</td>
<td>22.361</td>
<td>Tahir et al., 2008.</td>
</tr>
<tr>
<td>Sargassum spp.</td>
<td>21.881</td>
<td></td>
</tr>
<tr>
<td>Hydrilla verticillata</td>
<td>198.00</td>
<td>Low et al., 1993</td>
</tr>
<tr>
<td>Moss</td>
<td>185.00</td>
<td></td>
</tr>
<tr>
<td>Water hyscinth root</td>
<td>128.90</td>
<td>Low et al., 1995</td>
</tr>
<tr>
<td>Chaetomorpha media</td>
<td>191.975</td>
<td></td>
</tr>
<tr>
<td>Enteromorpha intestinalis</td>
<td>171.775</td>
<td>Present Study</td>
</tr>
<tr>
<td>Ulva lactuca</td>
<td>171.025</td>
<td></td>
</tr>
<tr>
<td>Caulerpa taxifolia</td>
<td>165.825</td>
<td></td>
</tr>
</tbody>
</table>

Similarly influence of particle size on the process of biosorption was studied by using fine, coarse and large biomass for adsorption of M.B. In order to analyze loading capacity of biomass, four cycles of biosorption were monitored using the same biomass. The biomass was washed dried and reutilized for next cycle after every use. For protonation, fine algal biomass was treated with 0.1N HCL for three hours and then dried in shade. This biomass (100mg) was used for batch experiment at optimized pH and time conditions.

**RESULTS AND DISCUSSION**

Removal of M.B. and efficiency of the process of biosorption varied in different algal materials with respect to different factors.

**Effect of pH**

The pH of the solution was an important controlling parameter development of a successful method for biosorption. The low pH of solution has more influence than the higher pH. Basic dye upon dissolution release coloured cation in solution adsorption of these charged dye groups with adsorbent surface primarily influenced by the surface charge on the adsorbent which in turn is influenced by pH of solution. (Kumar et al., 2006; Cr et al., 2007; Punjongham et al., 2008; Khaled et al., 2005). The present study dye adsorption increased rapidly with the pH at maximum removal occurred at pH 6 in all the select biosorbents. The removal percentage then decreased as pH increased from 7 to 12 (Fig. 1). Similar results were recorded Ulva lactuca and Sargassum (Khaled et al., 2005; Tahir et al., 2008; Rubin et al., 2005); in Pithophora spp. (Vasant Kumar et al., 2004) in Gelidium (Vitor et al., 2006) and in Caulerpa racemosa (Cengiz and Cavas, 2008).

**Effect of contact time**

The removal efficiency of dye varied as per the time of contact (Fig. 2). It was observed that maximum adsorption of M.B. to place during first 30 min. in all the materials and the rate biosorption decreased thereafter. The equilibrium of process w marked by the maximum removal percentage of dye which varies in different algal biomass used. The dye removal profile follow three distinct phases. Initially the rate of removal was less, which increased progressively with contact time and finally attained saturation. The process of adsorption reached equilibrium after 60 min. in all the algal biomass. The rate of dye removal was rapid during the first 45 min. in all the materials. After that the rate of dye removal slowly decreased and reached saturation.
Effect of adsorbent dosage

The percentage of dye removal increased rapidly with an increase in the adsorbent dose (Fig.3). As the surface area increased, the availability of exchangeable sites also increased. There was no change observed in removal % above 100 mg biomass.

Effect of Initial Concentration of M.B

In the present study the dye uptake capacity (qe) increased with an increase in dye concentration however removal percentage decreased by 25 to 30% (Fig.4). The maximum removal percentage and qe were observed at 100 ppm concentration in all algal biomass. The same observations were made for other adsorbents like Hydrilla, Pithophora and Enteromorpha for M.G. removal and for Ulva and Sargassum for removal of methylene blue (Khaled et al., 2005; Tahir et al., 2008; Sivamani et al., 2009; Rajeshkannan et al., 2010; Jayaraj et al., 2011). According to Elmeed and El-K Haiary, 2008, the initial concentration of dye provides an important driving force hence higher initial concentration of dye enhances the adsorption capacity.

Effect of Agitation speed

In the batch experiment agitation speed acts as an important factor affecting the external boundary film and distribution of the solute in the bulk solution. In present study the dye removal percentage slowly enhanced with increase in speed from 50 to 250 rpm. (Fig.5).

Effect of Particle size

In the process of adsorption, the contact surface between an adsorbent and dye plays an important role. Solid sorption capacity as well as the time required to reach equilibrium are mostly related to the morphology (Blazquez et al., 2005). In the present study the fine powdered biomass exhibited a maximum dye removal % in all green seaweeds (Fig.6). This may be due to a larger surface area of fine powdered particles, which could adsorb more amount of dye (Aliabadi et al., 2006). Similar observation is recorded for removal of rhodamine B by Turbinaria. by Hii et al., (2012) The efficiency of dye removal did not vary much and was maximum in C. media (191.975mg/g) followed by U. lactuca (171.025mg/g), E. intestinalis (171.775mg/g), and C. taxifolia (165.825mg/g). The values can be compared with other biosorbents mentioned in Table 1.
natural grown algal biomass have recorded Gajare and Menghani (2012).

**Effect of protonation**

The dye removal improved in all the materials by the process of protonation, (Fig.8). This is due to a structural modification and action of mineral acids cause protonation of functional groups responsible for the biosorption. An overall 5-6% increase in removal of M.B. occurred due to protonation in present study. Similar observations are made by Vijayaraghavan and Yun (2008) in *Laminaria* for C.I. Reactive Black, in *Sargassum muticum* for M.B. (Rubin et al., 2005).

![Fig.7 Effect of dye loading capacity on biosorption of M.B.](image)

![Fig.8 Effect of protonation on biosorption of M.B.](image)

**CONCLUSION**

Green seaweeds can be used effectively for removal of M.B. from waste water. The biomass is reusable and protonation improves the dye removal capacity of biosorbent. Dye removal percentage and dye uptake efficiency qe was found in following order Chaetomorpha media > Enteromorpha intestinalis > Ulva lactuca > Caulerpa taxifolia.

**References**


Khaled A, Sikairy A. E. Abelwahab O. and Nemr A. E. 2006 Biosorption of basic blue nine from water solution by mari alga Ulva lactuca. Egyptian J. Aquatic Research 31: 130-140


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Original Research Article

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

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ABSTRACT

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.

Introduction

A huge amount of commercial dyes are used in plastic, food, textile, cosmetic, paper industries for production of over $7 \times 10^6$ 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; Bhattacharyya 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 Kunakshwar, (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.

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°C ± 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.

Removal % - \( \frac{C_i - C_e}{C_i} \times 100 \)

\[ q_e = \left( \frac{C_i - C_e}{C_i} \right) \times \frac{m}{v} \]

Where \( C_i \) = initial concentration of dye (mg/L)
\( C_e \) = final concentration of dye (mg/L)
\( m \) = biomass (mg)
\( q_e \) = uptake efficiency (mg/g)
\( v \) = volume of dye solution (ml)
Technical information of Methylene Blue and Malachite Green is given below

<table>
<thead>
<tr>
<th></th>
<th>Methylene Blue</th>
<th>Malachite Green</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>UPAC Name</strong></td>
<td>3,7-bis(Dimethylamino)-phenothiazin-5-iium chloride</td>
<td>N-[4-[4-(demethylamino)-phenyl]phenylmethylene]2,5-Cyclohexadienyl-ylidene N-Methyl-methanaminium chloride</td>
</tr>
<tr>
<td><strong>Commercial Name</strong></td>
<td>Basic blue 9, Methylthioninium chloride, Chromosmon, Swiss Blue, Methylene Blue.</td>
<td>basic green, aniline green, fast green.</td>
</tr>
<tr>
<td><strong>Molecular Formula</strong></td>
<td>$C_{16}H_{18}N_3Cl$</td>
<td>$[C_{6}H_{5}C(C_{6}H_{4}N(CH_{3})<em>{2})</em>{2}]Cl$</td>
</tr>
<tr>
<td><strong>Structural Formula</strong></td>
<td><img src="image" alt="Structural Formula" /></td>
<td></td>
</tr>
</tbody>
</table>

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*
**Table 1** Isotherm and Kinetic model Constants for biosorption of dyes from their binary solution by *Ulva lactuca*.
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 those of Shanthi and Mahalakshmi (2012); Vijayaraghavan, 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 in turn 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 heterogeneous 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 (Lajergren, 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 R² 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

\[ qt = K_i t^{1/2} + C \]

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*.

**References**


K. Sven.


