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.

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INTRODUCTION

More than 10000 commercially dyes are utilized by plastic, food, cosmetic, paper and textile industries and their amount produced annually is about 7x10^4 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; Vijayaraghavan 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 (Jayaraj et al.,2011; Hameed and El-K Hiairy, 2008; Jain and Sikarwar, 2006). In present study aqueous solution of M.B. was used as a model compound to moniter 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 (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), 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

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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.

\[ qe = \frac{C_i - C_e}{m} \times \frac{V}{c_i} \]

Where \( C_i \) = initial concentration of M.B. (mg/L)
\( C_e \) = final concentration of M.B. (mg/L)
\( m \) = biomass (mg)
\( V \) = 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>Vilar et al., 2006.</td>
</tr>
<tr>
<td>Algal Waste</td>
<td>104.00</td>
<td>Khaled et al., 2005.</td>
</tr>
<tr>
<td>Ulva lactuca</td>
<td>16.60</td>
<td>Tahir et al., 2008.</td>
</tr>
<tr>
<td>Ulva lactuca</td>
<td>22.361</td>
<td></td>
</tr>
<tr>
<td>Sargassum spp.</td>
<td>21.881</td>
<td></td>
</tr>
<tr>
<td>Hydrida verticillata</td>
<td>198.00</td>
<td></td>
</tr>
<tr>
<td>Moss</td>
<td>185.00</td>
<td></td>
</tr>
<tr>
<td>Water hyacinth root</td>
<td>128.90</td>
<td></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 particle 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 in development of a successful method for biosorption. The lower pH of solution has more influence than the higher pH. Basic dye upon dissolution release coloured cation in solution and adsorption of these charged dye groups with adsorbent surface is primarily influenced by the surface charge on the adsorbent which in turn is influenced by pH of solution. (Kumar et al., 2006; Crini et al., 2007; Punjogahrn et al., 2008; Khaled et al., 2005). In present study dye adsorption increased rapidly with the pH and maximum removal occurred at pH 6 in all the selected biosorbers. The removal percentage then decreased as pH increased from 7 to 12 (Fig.1). Similar results were recorded in 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. 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 contact time and finally attained saturation. The process of adsorption reached equilibrium after 60min. 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

Percentage of dye removal increased rapidly with an increase in the adsorbent dose (Fig.3). As the surface area increased, 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 Hydrila, 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 Haiaiy, 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 by 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 (191975mg/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.

Effect of dye loading capacity

In order to analyse the reusability, the biomass after one batch experiment was separated by centrifugation dried and reused with fresh dye solution of same concentration (100mg/L). It was noticed that the algal biomass could be reused for five subsequent cycles (Fig. 7). The saturation of binding sites occurred after first two cycles whereas the removal % was higher and decreased in subsequent cycles. After 4th cycle of loading, the capacity of dye removal decreased drastically in all the materials in the present study, giving only 20-30 % dye removal. Similar observation for
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).

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

Robinson, T., McMullan, G., Marchant, R., & Nigam, P. 2001. Remediation of dyes in textile effluent, a critical review on

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