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Utilization of Effective Microorganisms based water hyacinth compost as biosorbent for the removal of basic dyes

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ABSTRACT

The water hyacinth plants are renewable natural biomass, proliferate ubiquitously, and abundant in water bodies often posing environmental nuisances. To overcome this problem, a novel approach that utilizes water hyacinth plant has to be arrived. This research work mainly deals with application of low cost, non-conventional, newly developed novel biomaterial, Effective Microorganisms (EM) based Water Hyacinth Compost as biosorbent for the removal of basic dyes from aqueous solution. Biosorption of basic dyes like Methylene Blue (MB), Malachite Green (MG), and Basic Blue 41 (BB41) was investigated using a biosorbent of EM based Water Hyacinth Compost. The biosorbent material was analyzed for physico-chemical composition such as pH, moisture content, organic carbon, nitrogen, etc. and also the biosorbent was characterized before and after adsorption using FTIR and SEM. The batch study was performed to optimize the operational parameters such as pH, biosorbent dosage, biosorbent particle size, and initial dye concentration. The maximum experimental removal efficiency of adsorbent was obtained as 98.9, 98.4, and 89.1% for MB, MG, and BB41, respectively. Two and three parameter adsorption models were used for the mathematical description of the biosorption equilibrium and isotherm parameters were evaluated. The study confirms that the EM-based water hyacinth compost can be used as an effective biosorbent for the removal of basic dyes.

Keywords: Water Hyacinth; Compost; Biosorption; Basic Dyes; Isotherms

1. Introduction

Many industries such as textile, paper, food processing, dyeing, and cosmetics use dyes to color the products. The effluents from these industries are usually polluted by dyes. These dyes usually have aromatic complex structure which makes it very difficult towards degradation. These effluents are mixed with the natural water bodies such as rivers, streams and ecosystem which cause the serious effects on environment such as esthetic pollution, eutrophication, and perturbation in aquatic life. Dye wastewater is usually treated by physical or chemical treatment processes that include chemical coagulation/flocculation,
precipitation, ozonation, adsorption, oxidation, irradiation, ion exchange, and photodegradation [1]. Some of these techniques have shown to be effective, although they have limitations. Among these are: excess amount of chemical usage, or accumulation of concentrated sludge with disposal problems; expensive plant requirements and operational costs; lack of effective color reduction; and sensitivity to a variable wastewater input [2].

Basic dyes, which are predominantly used in coloring acrylic fiber, are generally more toxic than other classes of dyes [3,4]. Acute exposure to Methylene Blue (MB) can cause increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice, quadriplegia, and tissue necrosis in humans [5]. Malachite Green (MG) is highly toxic, highly residual, teratogenic, carcinogenic, mutagenic, creates other side effects to fresh water organisms [6,7] and enters food chain and alarmed the health hazards against human being. The use of Basic Blue (BB) dye can cause eye burns to human and animals, irritation to gastrointestinal tract with symptoms of nausea, vomiting and diarrhea, and also can cause methemoglobinemia, cyanosis, convulsion, tachycardia, and dyspnea [8]. Thus, the removal of basic dyes from the environment is worthwhile noting.

To conflict these problems, the environmental friendly measures are required. Among the different conventional wastewater treatment techniques, biosorption is found to be an efficient and cost-effective technique. The possibility of recovery of adsorbate and adsorbent has made the biosorption process more attractive [9]. Since past several decades, the application of adsorption process has become the focus of intense research and utilization of waste materials as potential adsorbents is gaining stern consideration towards solid waste management [10].

Nowadays research has indicated that biosorption is one of the most promising technologies and the removal of dyes by different kinds of biosorbent materials has been receiving more attention [11–13]. Table 1 shows the adsorptive capacity of various biosorbents for the selected basic dyes. The water hyacinth (Eichhornia crassipes) is a floating macrophyte and its growth is enormous in the water bodies of Tamil Nadu, India. It is listed as one of the most productive plants on earth and is considered one of the world’s worst aquatic plants [14]. The water hyacinth growth forms dense mats that avert river traffic, block irrigation canals, interfere with hydel power projects and destroy rice fields [15].

Composting is the biological degradation of organic matter under aerobic conditions to a relatively stable humus-like material called compost [16]. The micro-organisms present in the organic materials are responsible for decomposition. The decomposition by Effective Microorganisms (EM) is safe and simple way of improving the composting system. EM is a mixture of groups of organisms that has a reviving action on human being, animals, and the natural environment [17] and described as a multi-culture of coexisting anaerobic and aerobic beneficial microorganisms [18]. EM can ensure high-quality compost as the microbial inoculant increases the production of aerobic bacteria and increases the composting speed. The main species involved in EM include lactic acid bacteria, photosynthetic bacteria, yeasts, actinomycetes, and fermenting fungi [19].

The aim of the present investigation is to explore the possibility and effectiveness of utilizing EM-based water hyacinth compost (EMWHC) as an alternative, low-cost adsorbent for the biosorptive removal of Methylene Blue, Malachite Green, and Basic Blue 41 dyes from aqueous solution. To the best of our knowledge, this study is the first attempt on EM-based Water Hyacinth Compost onto the biosorption process.

2. Materials and methods

2.1. Adsorbent

EM-based water hyacinth compost was prepared from waste water hyacinth plant and it was collected from nearby ponds and channels. The compost bed was prepared by forming the number of layers with cow dung, water hyacinth waste, and saw dust which were moist by EM in a compost bin.

EM is available in dormant state which procured from a local vendor and requires activation before application. Activation involves the addition of water, jaggery, and dormant EM as recommended by Sekaran et al. [20]. About 45 days, the volume of compost bed had dropped substantially due to thermodhilic process and the temperature was within the ambient temperature. At this point, the matured compost was collected and dried. This derived EMWHC can be used for various applications especially as biosorbent. The prepared adsorbent was air dried for 24 h and oven dried at a temperature of 70°C for 2 h and sieved.

2.2. Characterization of adsorbent

The composition of EMWHC was characterized and analyzed by the following procedures. The pH of biosorbent was measured by pH meter (Ecosan, EUTECH Instruments), Moisture Content by oven dry method, Organic Carbon by Walkely and Black
titration method, Nitrogen and Phosphorous by UV–
visible spectrophotometer (Merck, Spectroquant Phara
300), and Potassium by digital flame photometer. The
physicochemical composition of EMWHC is summa-
rized in Table 2. FTIR (Perkin–Elmer Paragon 500
FTIR) spectra of EMWHC samples were obtained by
preparing the samples as KBr disk and examined
within the range 400–4,000 cm\(^{-1}\) to identify the specific
functional groups responsible for the biosorption. To
determine the morphological structure and surface
characteristics of EMWHC and dyes-loaded EMWHC,
the samples were coated under vacuum, with a thin
layer of gold examined by Scanning Electron Micro-
scopy (FESEM S-4700, Hitachi).

2.3. Adsorbate

Basic dyes of MB, Malachite Green, and BB41 were
purchased from Merck India Ltd. and Sigma–Aldrich
Chemicals with wavelength of 665, 618, and 609 nm,
respectively. The dyes were used as commercial salts
without further purification. The dye stock solutions
were made up to a concentration of 2,000 mg/L by
dissolving an accurately weighed quantity of dye in
deionized water and was subsequently diluted to the
required concentrations. The pH of working solutions
were adjusted to the desired pH values by 0.1 M HCl
and 0.1 M NaOH.

3. Results and discussion

3.1. FTIR Study

The functional groups that are responsible for
adsorption present in the EM-based water hyacinth
compost and MB, MG, and BB41-loaded composts
were analyzed by FTIR and the spectra are illustrated
in Fig. 1. The FTIR spectra exhibit a number of absorp-
tion peaks, indicating the complex nature of adsorbent
examined before and after adsorption of dyes. The
quantity of the characteristic functional groups can be
identified by the steepness of the peaks. The absorp-
tion peaks about 3,000 cm\(^{-1}\) represents the presence of

<table>
<thead>
<tr>
<th>Dye</th>
<th>Adsorbent</th>
<th>Uptake/removal efficiency</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylene Blue</td>
<td>Coco-peat</td>
<td>212.8 mg/g</td>
<td>[38]</td>
</tr>
<tr>
<td></td>
<td>Saw dust</td>
<td>236.16 mg/g</td>
<td>[39]</td>
</tr>
<tr>
<td></td>
<td>Corynebacterium glutamicum</td>
<td>99.7%</td>
<td>[40]</td>
</tr>
<tr>
<td></td>
<td>Waste sludge</td>
<td>99%</td>
<td>[41]</td>
</tr>
<tr>
<td></td>
<td>Wheat straw</td>
<td>396.9 mg/g</td>
<td>[42]</td>
</tr>
<tr>
<td></td>
<td>Rice husk</td>
<td>312.0 mg/g</td>
<td>[43]</td>
</tr>
<tr>
<td>Malachite Green</td>
<td>Activated carbon (mesophorous)</td>
<td>99%</td>
<td>[44]</td>
</tr>
<tr>
<td></td>
<td>Activated carbon from Cassia fistula</td>
<td>28.81%</td>
<td>[45]</td>
</tr>
<tr>
<td></td>
<td>Saccharomyces cerevisae</td>
<td>17 mg/g</td>
<td>[46]</td>
</tr>
<tr>
<td></td>
<td>Mangrove barks</td>
<td>129.87 mg/g</td>
<td>[47]</td>
</tr>
<tr>
<td></td>
<td>Anaerobic granular sludge</td>
<td>61.73 mg/g</td>
<td>[48]</td>
</tr>
<tr>
<td></td>
<td>Coffee bean</td>
<td>95%</td>
<td>[49]</td>
</tr>
<tr>
<td>Basic Blue 69</td>
<td>Peat</td>
<td>195 mg/g</td>
<td>[50]</td>
</tr>
<tr>
<td>Basic Blue 9</td>
<td>Aspergillus niger</td>
<td>8.5 mg/g</td>
<td>[51]</td>
</tr>
<tr>
<td>Basic Blue 9</td>
<td>Activated sludge</td>
<td>256.41 mg/g</td>
<td>[52]</td>
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<tr>
<td>Basic Blue 54</td>
<td>Pine wood AC</td>
<td>1,119 mg/g</td>
<td>[53]</td>
</tr>
<tr>
<td>Basic Blue 69</td>
<td>Bagasse pith</td>
<td>152 mg/g</td>
<td>[54]</td>
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</table>

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Level</th>
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<td>pH</td>
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<tr>
<td>Moisture content</td>
<td>52 %</td>
</tr>
<tr>
<td>Electrical conductivity</td>
<td>1.74 dSm(^{-1})</td>
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<tr>
<td>Temperature</td>
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</tr>
<tr>
<td>Manganese</td>
<td>56 mg/L</td>
</tr>
<tr>
<td>Copper</td>
<td>28 mg/L</td>
</tr>
<tr>
<td>Zinc</td>
<td>54 mg/L</td>
</tr>
<tr>
<td>Organic Carbon</td>
<td>13.5% by dry mass</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.64% by dry mass</td>
</tr>
<tr>
<td>Phosphorous</td>
<td>0.21% by dry mass</td>
</tr>
<tr>
<td>Potassium</td>
<td>0.045% by dry mass</td>
</tr>
<tr>
<td>C:N ratio</td>
<td>21.1</td>
</tr>
</tbody>
</table>
amine groups. The bands between 3,500 and 3,300 cm\(^{-1}\) are reported to occur due to amine group stretching vibrations superimposed on the side of hydroxyl group band [21]. The spectra showing the peak at 1,107 cm\(^{-1}\) indicates the carboxyl groups, 1,729 cm\(^{-1}\) indicates the C–O stretching, 862 cm\(^{-1}\) specifies the aromatic, and 500–750 cm\(^{-1}\) indicates the alkane groups [22].

3.2. SEM Study

The morphological structure of EM WHC and the dyes loaded EMWHC are presented in Fig. 2(a)–(d). The SEM image (Fig. 2(a)) clearly shows that the control EMWHC was not smooth and has large number of pores resulting in increased surface area for bonding of dyes [23]. The images of Fig. 2(b)–(d) confirmed that the pores present in the control EMWHC were occupied by the dyes of MB, MG, and BB41 which was confirmed from the smooth surface.

3.3. Effect of pH

In the aqueous solution, pH is one of the most significant parameter which affects the process of dye removal. The solution pH influences the surface charge of adsorbent, the degree of ionization processes of the dye molecules, and also the effluent chemistry. In addition, it is directly related to competition ability of hydrogen ions with adsorbate ions to active sites on the adsorbent surface [24].

The effect of pH on the decolorization of dyes such as MB, MG, and BB41 were evaluated at different pH conditions ranging from 2 to 9, and the results are described in Fig. 3. The decolorization efficiency of dyes in batch mode (dye concentration 100 mg/L, desired adsorbent dosage and agitation speed 150 rpm) increased notably from pH 2 to 8 for MB and MG, whereas from 2 to 7 for BB41. The maximum removal efficiency of dyes (95.3% for MB, 98.4% for MG, and 90.2% for BB41) was obtained at pH 8, 8, and 7, respectively. Then the removal efficiency was decreased with the increase in pH to 9. Thus, the pH value was optimized for the selected dyes as 8 for MB, MG, and 7 for BB41. At low pH, the sorption was unfavorable, probably because of excess H\(^+\) ions competing for sorption sites. Increasing solution pH increases the number of hydroxyl groups thus, increases the number of negatively charge sites, and enlarges the attraction between dye and adsorbent surface [25].

The point of zero charge (pHpzc) was determined by solid addition method [26]. pHpzc gives very significant information about the type of surface active centers. The pHpzc of EMWHC biomass was found to be 6.7. Below pHpzc, the biosorbent acquires a positive charge which favors the attachment of dye anions to the surface of biosorbent. Above pHpzc, the biosorbent gets a negative charge and the electrostatic repulsion between dye anions and negatively charged functional groups results in lower dye removal [27].

3.4. Effect of dosage

To evaluate the optimum dosage, the decolorization of dyes was measured in an aqueous solution with adsorbent dosage varied from 2 to 10 g/L (optimum pH, dye concentration 100 mg/L and agitation speed 150 rpm). The results are illustrated in Fig. 4.
and show the maximum removal efficiency of dyes (96.3% for MB, 98.44% for MG and 92.35% for BB41) with the EMWHC at the dosage of 4 g/L. By increasing the amount of adsorbent, access to the residual sites for dye adsorption was restricted. In addition, the effective surface area for adsorption decreased due to the partial aggregation of adsorbent at high adsorbent dosages leading to a decrease in the adsorption capacity of dyes [28]. From the maximum removal effi-

Fig. 2. SEM images of (a) EMWHC Control and loaded with (b) MG, (c) MB, and (d) BB41.

Fig. 3. Effect of pH on removal of MB, MG, and BB41.

Fig. 4. Effect of adsorbent dosage on removal of MB, MG, and BB41.
ciency, it has been decided to use 4 g/L as optimum adsorbent dosage.

3.5. Effect of initial dye concentration

The initial dye concentration provides the necessary driving force to overcome the resistances to the mass transfer of dye between the aqueous and solid phases [29]. The effect of initial dye concentration was experimentally studied by varying the concentration of dyes (from 50 to 1,000 mg/L) by EM WHC. From Fig. 5, the adsorption capacity decreased when the concentration of solution increased. The maximum removal efficiency of dyes was observed at lower dye concentration of 50 mg/L as 98.6, 98, and 88.3% for MB, MG, and BB41, respectively. At 1,000 mg/L, the removal efficiencies were recorded as 70.4, 59.1, and 55.7% for MB, MG, and BB 41, respectively. At lower dye concentrations, solute concentration to biosorbent site ratio is higher, which cause an increase in color removal and at higher concentrations, lower adsorption yield is due to the saturation of adsorption sites [30].

3.6. Effect of particle size

Adsorbent particle size has significant role in exhibit the active sites in the adsorption process. The adsorbent particle sizes from 0.6 to 2.36 mm were used to optimize the size with the optimal parameters of pH, dosage, and initial dye concentration and the results are presented in Fig. 6. The maximum removal efficiencies were recorded at the particle size of 1.18 mm for MB, MG, and at 0.75 mm for BB 41. The increase in sorption depends on the large external surface area for smaller particles. Apparently, reductions in particle size resulted in increased external surface area of the adsorbent particles yielding more binding sites for dye adsorption and therefore, more efficient adsorption [31]. In order to compete the industrial applications and the recycling of adsorbent, the optimum size of particle was selected as 1.18 mm.

3.7. Sorption isotherms

The isotherm models are widely used to describe the equilibrium between biosorption capacity (\(q_e\)) and sorbate concentration (\(C_e\)) at a constant temperature [32]. The two parameter models of Langmuir and Freundlich isotherms and three parameter models of Redlich–Peterson, Toth, and Sips isotherms were discussed as follows:

Langmuir model:

\[ Q = \frac{Q_{\text{max}} b_L C_f}{1 + b_L C_f} \]  (1)

Freundlich model:

\[ Q = K_F C_f^{1/n_F} \]  (2)

Redlich–Peterson model:

\[ Q = \frac{K_{RP} C_f}{1 + a_{RP}^{d_{RP}} C_f} \]  (3)

Toth model:

\[ Q = \frac{Q_{\text{max}} b_T C_f}{[1 + (b_T C_f)^{1/n_T}]} \]  (4)

Sips model:

\[ Q = \frac{K_S C_f^{d_s}}{1 + a_S C_f^{d_s}} \]  (5)

where \(Q\) is the equilibrium dye uptake (mg/g); \(C_f\) is the final dye concentration (mg/L); \(Q_{\text{max}}\) is the maximum dye uptake (mg/g), \(b_L\) is the Langmuir equilibrium coefficient (L/mg), \(K_F\) is the Freundlich coefficient (L/g\(^{1/n_F}\)), \(n_F\) is the Freundlich exponent, \(K_{RP}\) is the Redlich–Peterson isotherm coefficient (L/g), \(a_{RP}\) is the Redlich–Peterson isotherm coefficient.
(L/mg)_{BP}^{\beta}, \beta_{RP} is the Redlich–Peterson model exponent, b_T is the Toth model constant (L/mg), n_T is the Toth model exponent, K_S is the Sips model isotherm coefficient (L/g), \alpha_S is the Sips model coefficient (L/mg), and \beta_S is the Sips model exponent.

The average percentage error between the experimental and the predicted values is calculated using,

\[
\% \text{ Error} = \frac{\sum_{i=1}^{N} (Q_{\text{exp.i}} - Q_{\text{cal.i}}/Q_{\text{exp.i}})}{N} \times 100
\]

where \( Q_{\text{exp}} \) and \( Q_{\text{cal}} \) represent the experimental and calculated uptake values, respectively, and \( N \) is the number of measurements.

The experimental equilibrium uptakes and their predicted values by five different models, Langmuir, Freundlich, Redlich–Peterson, Toth, and Sips for the three basic dyes are plotted in Fig. 7. The five isotherm model constants and correlation coefficients with percentage error were evaluated for the dyes MB, MG, and BB41 are presented in Table 3.

The derivation of the Langmuir isotherm assumes ideal monolayer adsorption on a homogenous surface. From the observed data, the correlation coefficient \( R^2 \) for the Langmuir model was greater than those for Freundlich model, suggesting the monolayer coverage of the EMWHC surface by dye molecules [33]. According to Langmuir isotherm, the maximum uptake was obtained as 295.65, 153.0, and 158.04 mg/g for MB, MG, and BB41, respectively.

The Freundlich isotherm is used for non-ideal adsorption on heterogeneous surfaces. The heterogeneity arises from the presence of different functional groups on the surface, and the various adsorbent–adsorbate interactions [34]. From the Fig. 7 it was evident that, the maximum predicted uptake for all the dyes were observed for Freundlich isotherm compared with other two- and three-parameter isotherms. The values of Freundlich constant \((1/n)\) for the examined basic dyes were predicted as 0.29, 0.32, and 0.44, which is less than 1 indicates the favorable dye adsorption. This indicates the fact that the active sites on sorbents have different affinities to dye molecules [35]. However, the prediction of isotherm data by the Freundlich model was not agreeable because of high % error (Table 3).

In order to improve the suitability of isotherm data, the three parameter models of Redlich–Peterson, Toth, and Sips were used. The Redlich–Peterson model is a combination of Langmuir and Henry’s model which incorporates three parameters \( (K_{RP}, n_{RP}, \text{ and } \beta_{RP}) \) and thus can be applied to either homogeneous or heterogeneous systems [36]. When \( \beta_{RP} = 0 \), the model reduces to the Langmuir model, while \( \beta_{RP} = 1 \), the model transforms to Henry’s law form. From the data obtained, \( \beta_{RP} \) was estimated as 0.88, 0.97, and 0.88 for MB, MG, and BB41, respectively, which are close to unity indicating that the isotherms are approaching the Langmuir, but not the Henry isotherm. The Redlich–Peterson model resulted in better \( R^2 \) (0.99) and low % error (<5.51%) values. The Toth model derived from potential theory has proven useful in describing sorption in heterogeneous systems. It assumes an asymmetrical Quasi-Gaussian energy distribution with a widened left-hand side, i.e. most sites have sorption energy less than the mean value [37].
The Toth model exhibited higher $R^2$ (0.99) values and less % error for the dyes MB, MG, and BB 41. The Sips model is postulated with the assumptions that surface active sites are of different strengths and that one molecule of adsorbate interacts with one active site [38]. At low and high sorbate concentrations, the Sips model effectively reduces to the Freundlich and Langmuir equations, respectively. The Sips model parameter $\beta_S$ was estimated as 0.69, 0.99, and 0.88 for MB, MG, and BB 41, respectively. Based on the correlation coefficient and % error values, MB adsorption was well explained by Sips model, MG removal was described well by Langmuir model, and Redlich–Peterson model fitted well with the experimental data of BB 41 adsorption.

4. Conclusion

The effectiveness of EM-based water hyacinth compost onto the removal of basic dyes MB, malachite green, and BB41 was investigated.

(1) It is evident that water hyacinth, an abundantly available organic waste material, can be converted as compost using EM.

(2) The maximum removal efficiency of EMWHC onto MB, MG, and BB41 was observed as 98.9, 98.4, and 89.1%, respectively.

(3) The experimental results revealed that, the maximum uptakes (286.15 mg/g for MB, 147.81 mg/g for MG, and 139.29 mg/g for BB 41) were exhibited at the optimum operating conditions.

(4) Two- and three-parameter isotherms were modeled for dyes adsorption. Based on correlation coefficients and percentage error values, Sips isotherm model described the experimental data well.

(5) The EMWHC can be used as a good biosorbent for MB, Malachite Green, and BB41 and it is suggested for the removal of basic dyes from wastewater.

(6) The present study concludes that EM-based water hyacinth compost could be employed as a low-cost, novel, and green biosorbent in removing the dyes from textile effluents.

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