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Effective Adsorbents Based on Biomaterials for Removal of Methylene Blue Dye from Water

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Biomaterials prepared from barks of *Ficus benghalensis, Tamarindus indica* and *Acasia nilotica indica* are investigated as adsorbents for the removal of methylene blue dye from waste waters using batch methods of extraction. Various physico-chemical parameters are optimized for the maximum removal of the dye. The extractions are found to be pH sensitive. Substantial adsorption is noted at high pHs. With simulated waters, 100 % removal of the dye is observed at pH 8/10 and at other optimum conditions of extraction with all the adsorbents developed. The optimum time needed for the maximum extraction of the dye is found to be in the order: *Ficus benghalensis* (120 min) > *Tamarindus indica* (90 min) > *Acasia nilotica indica* (30 min). The adsorption capacities of *Ficus benghalensis sorbent, Tamarindus indica sorbent* and *Acasia nilotica indica* sorbent are 50.0 mg/g, 66.7 mg/g and 100 mg/g respectively. In case of the *Acasia nilotica indica* sorbent, even at low pHs, substantial removal of the dye is effected. Co-anions (five fold excess) are least interfered while cations like, Ca^{2+}, Mg^{2+} and Cu^{2+} have interfered to some extent but in no case, % removal has not come down below 90 %. It is interesting to note that Fe^{2+} and Zn^{2+} have maintained the maximum extraction synergistically. The developed procedures were successfully applied to real water samples too.

Keywords: Methylene blue dye, Pollution control, Bioadsorbents, Applications.

INTRODUCTION

Removal of dyes from polluted waters is one of the main thrust areas of pollution control. If the dye is degradable with time, it is of less threat to the environment. But most of the synthetic dyes are widely used in various industries such as paper, textile, plastic and cosmetic industries. The presence of even traces of these toxic dyes or their byproducts in water is causing threat to aquatic life. Hence their removal methods assume importance [1-4].

Methylene blue (MB) is a cationic synthetic dye and is widely used in industries as colouring agent and it is not biodegradable. The contamination of water with this dye, even in traces, is hazardous to aquatic life [5]. Various treatment methods based on biodegradation, membrane separation, ultra filtration, oxidation, reverse osmosis and photodegradation are reported in literature [6-8]. Adsorption methods are reported to be effective. The biosorbents pertaining to *Ficus carica* [9], fly ash based geopolymers [10,11], activated carbon coated with ZnO nano particles [12], biocomposite alginate beads [13], chitosan based zeolite [14], activate carbon of *Eupharbia rigida* [15], tea waste [16], flakes of chitosan [17], H_3PO_4 activated carbon of *Pistachio shells* [18], leaf powders of *Azadirachta indica* [19], stem and leaf powders of *Tridax procumbens* and *Phyllanthus niruri* [20], $ZnCl_2$ activated corn husk carbon [21] are reported.

Several research groups investigated various unconventional bioadsorbents derived from plant materials for the removal of diverse pollutants and successful methodologies are reported to literature for fluoride [22-27], chromium(VI) [28-30], zinc(II) [31], ammonia [32,33], aluminum(III) [34,35], nitrite [36,37], phosphate [38] and dyes [20,39-41].

While various materials are being investigated as adsorbents for the removal of methylene blue dye, we noticed the strong affinity between methylene blue and the bark powders of *Ficus benghalensis, Tamarindus indica* and *Acasia nilotica indica.* In the present work, these biosorbents are investigated to establish the optimum conditions for the effective removal of methylene blue dye from polluted waters.

EXPERIMENTAL

Analytical grade chemical and double distilled water were used in this investigation. A stock solution of 500 ppm of methylene blue solution was prepared and was suitably dilute as per the requirement.

Adsorbents: Barks powders of various plants were tried for the removal of methylene blue from synthetically prepared polluted water by optimizing various physico-chemical parameters *viz.*, pH, concentration of sorbent and time of equilibration. It has been observed that the barks powders of *Ficus benghalensis, Tamarindus indica, Azadirachta indica,* have affinity towards methylene blue ions.

Ficus benghalensis, the banyan, is extensively grown tree in India and has aerial roots reaching the ground with age and it belongs to *Moraceae* family. *Tamarindus indicia* is a long-lived tropical evergreen tree with a spreading crown and feathery evergreen foliage and fragrant flowers yielding hard yellowish wood and long pods with edible chocolate-coloured acidic pulp and it belongs to *Fabaceae* family. It is grown in all parts of India. *Acasia nilotica indica* is one of the species of acacia belongs to *Fabaceae* and is a medium sized deciduous tree with crooked and forked trunk and is grown well in South Asia.

The barks powders of *Ficus benghalensis, Tamarindus indica* and *Acasia nilotica indica*, were cut, washed with tap water followed by distilled water and then sun dried. The dried materials were powdered to a fine mesh of size: < 75 μ and activated at 105 °C in an oven and these materials were employed in this investigation.

Adsorption experiment: Batch methods of extraction procedure was adopted [42,43]. Definite amounts of sorbents were taken in 1 L stopper bottles containing 500 mL of methylene blue solution of known concentration. pHs of the solutions were adjusted with dil. HCl/dil. NaOH using pH meter. Then the samples were agitated in mechanical shakers. After marked times, the solutions were settled and filtered. The solutions were assayed for the methylene blue spectrophotometrically at λ_{max} at 661 nm where the Beer-Lambert's law is obeyed. The absorbencies were measured at 661 nm using UV-visible spectrophotometer (Systronics make). The ODs of unknown solutions were referred to standard graphs of "OD *vs.* Concentrations" that was prepared using the method of least squares to obtain the residual concentrations of the dye in the agitated solution.

Effect of interfering ions: The effect of the presence of common co-ions that present in natural water *viz.*, sulphate, fluoride, chloride, nitrate, phosphate, carbonate, Ca(II), Mg(II), Cu(II), Zn(II) and Ni(II) on the % of extraction, was assessed by preparing synthetic mixtures of methylene blue and of the interfering ions (in five folds) and subjecting thus obtained synthetic simulated water for the extraction of methylene blue dye using the developed adsorbents at the optimum extraction conditions.

Applications of the developed biosorbents: The methodologies developed in this work were applied to the real sewage/effluent samples of dye-based industries at Hyderabad and Mangalore. For this purpose, samples were analyzed for the actual amounts of methylene blue and then the samples were fed with known amounts of methylene blue.

RESULTS AND DISCUSSION

The effect of various physico-chemical parameters such as pH, time of equilibration and sorption concentration on the extraction ability of the sorbents derived from barks of *Ficus benghalensis, Tamarindus indica* and *Acasia nilotica indica* are investigated.

Effect of agitation time: For an adsorbent at constant pH, the % removal of the dye increases with time and after certain agitation time, an equilibrium state is achieved and it remains constant (Figs. 1-3). For instance, with *Ficus benghalensis* adsorbent, % of extraction of methylene blue at the pH: 10 is found be 32.1 % at 10 min, 48.0 % at 20 min, 79.0 % at 30 min, 80.3 % at 40 min, 84.1 % at 50 min, 85.0 % at 60 min, 88.0 % at 70 min 90.0 % at 80 min, 91.0 % at 90 min, 97.5 % at 100 min, 99.1 % at 110 min and 100 % above 120 min.

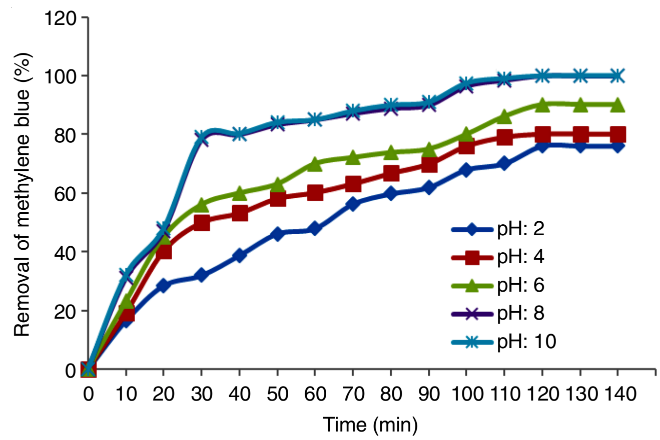

Fig. 1. Equilibration time *vs.* % removal of methylene blue

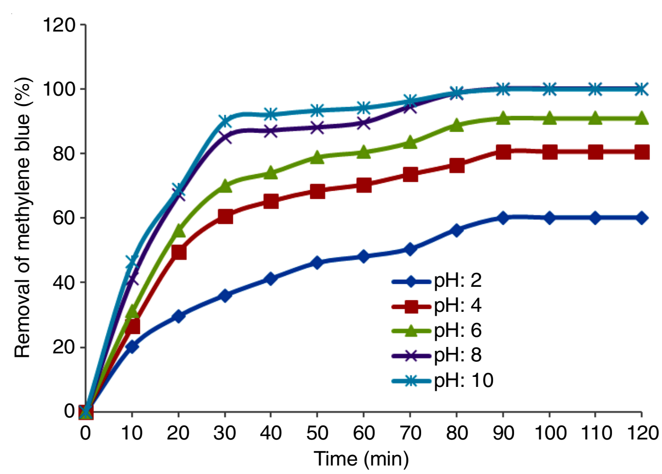

Fig. 2. Equilibration time *vs.* % of removal of methylene blue

With *Tamarindus indica* adsorbent, % of extraction of methylene blue dye at pH 10 is found to be 46.5 % at 10 min, 68.9 % at 20 min, 90.0 % at 30 min, 92.1 % at 40 min, 93.4 % at 50 min, 94.2 % at 60 min, 96.3 % at 70 min, 98.9 % at 80 min and 100 % above 90 min. In the case of *Acasia nilotica indica* sorbent, the % of extraction at pH: 8/10, is found to be 95.8 % at 10 min, 99.4 % at 20 min and 100 % above 30 min.

It is interesting to note the optimum time for the maximum removal of the dye is observed to be 120 min for *Ficus*

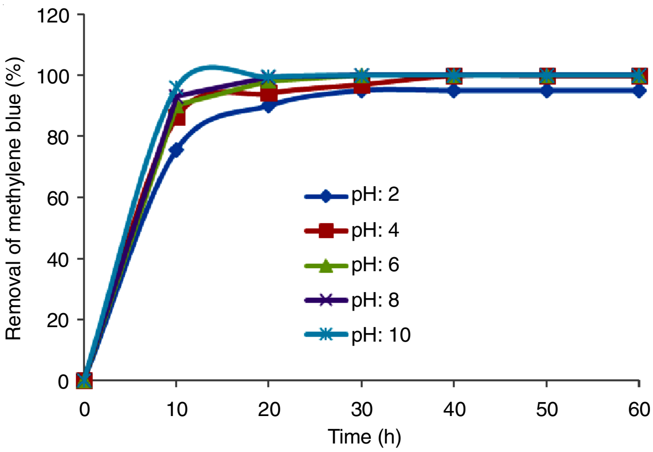

Fig. 3. Equlibration time *vs.* % removal of methylene blue

benghalensis, 90 min for *Tamarindus indica* and 30 min for *Acasia nilotica indica* sorbents.

Effect of pH: The percentage of removal is pH sensitive. As the pH increases, % removal is increased. It is found to be 76.1 % at pH: 2; 80.2 % at pH: 4; 90.1 % % at pH: 6; 100 % at pHs: 8 and 10 after an equilibration period of 120 min for the *Ficus benghalensis* sorbent (vide Fig. 4); With *Tamarindus indica* adsorbent, the % of removal is: 60.0 % at pH: 2; 80.5 % at pH: 4; 91.0 % at pH: 6 and 100.0 % at pH: 8 and 10 after an agitation time of 90 min (vide No. 5). With *Acasia nilotica indica* adsorbent, the % of removal is: 95.0 % at pH: 2; 97.0 % at pH: 4; 100 % above pH: 6 at an equilibration time of 30 min (vide Fig. 4). The *Acasia nilotica indica* sorbent is found to be quite effective even at low pHs.

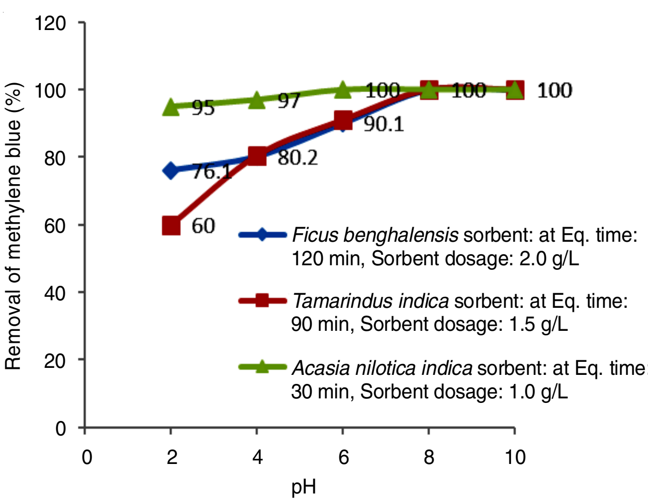

Fig. 4. pH *vs.* % Removal of the methylene blue

Sorbent dosage: The optimum concentration of the adsorbent needed for the complete extraction (100 %) of the dye (100 mg/L) is: 2.0 g/L for *Ficus benghalensis* sorbent, 1.5 g/L for *Tamarindus indica* sorbent and 1.0 g/L for *Acasia nilotica indica* sorbent (vide Fig. 5). The adsorption capacity is of the order: *Acasia nilotica indica* (100 mg/g) > *Tamarindus indica* (66.7 mg/g) > *Ficus benghalensis* (50.0 mg/g).

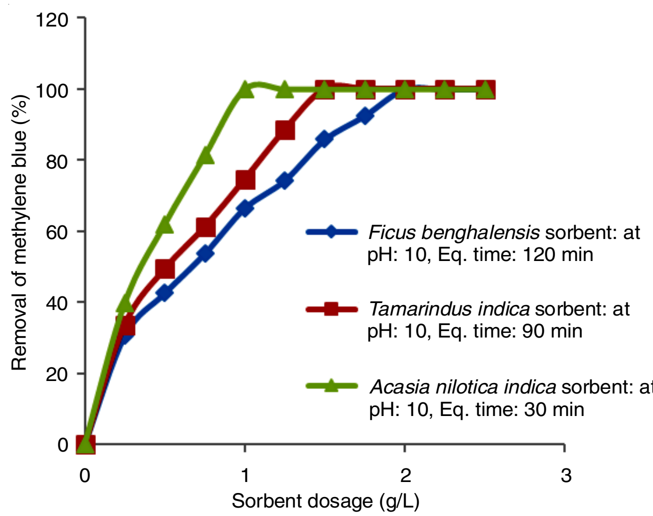

Fig. 5. Sorbent dosage *vs.* % removal of methylene blue dye

Interfering ions: The extractability of methylene blue in presence of fivefold excess of common ions found in natural waters has been investigated and presented in Table-1. Anions marginally effected the % of extraction of methylene blue with all the adsorbents developed in this work at the optimum extraction conditions. In the case of cations, Fe^{2+} and Zn^{2+} have not shown interference while Ca^{2+}, Mg^{2+} and Cu^{2+} have interfered to some extent.

The biosorbents have -OH/COOH groups and their dissociation is pH dependent as per the equilibrations:

At high pH values:

$$\text{Adsorbent-OH} \rightleftharpoons \text{Adsorbent-O}^- + H^+$$

$$\text{Adsorbent-COOH} \rightleftharpoons \text{Adsorbent-COO}^- + H^+$$

TABLE-1
EFFECT OF INTERFERING IONS ON THE EXTRACTABILITY OF METHYLENE BLUE WITH DIFFERENT BIO-SORBENTS

Adsorbent and its concentration	Maximum extractability at optimum conditions	Extractability of methylene blue in presence of fivefold excess of (50 ppm) interfering ions at optimum conditions: Conc. of methylene blue: 10 ppm[@] (%)									
		SO_4^{2-}	PO_4^{3-}	Cl^-	CO_3^{2-}	F^-	Ca^{2+}	Cu^{2+}	Fe^{2+}	Zn^{2+}	Mg^{2+}
Ficus benghalensis sorbent	100.0 %; pH: 8 or 10; Agitation time: 120 min; Sorbent conc.: 2.0 g/L	97.0	97.5	98.5	100. 0	97.5	94.0	915	100.0	100.0	93.0
Tamarindus indica sorbent	100.0 %; pH:8 or 10; Agitation time: 90 min; Sorbent conc.: 1.5 g/L	90.5	98.0	98.5	100.0	98.5	91.0	92.3	100.0	100.0	92.5
Acasia nilotica indica sorbent	100.0 %; pH:8 or 10; Agitation time: 30 min; Sorbent conc.: 1.0 g/L	98.0	97.5	98.0	100.0	99.0	93.0	92.8	100.0	100.0	93.5

[@]Average values of five estimations; Standard deviation = ± 0.75

TABLE-2
% EXTRACTION OF METHYLENE BLUE FROM DIFFERENT INDUSTRIAL EFFLUENTS WITH BIO-SORBENTS DEVELOPED

Bio-sorbent	% of Extractability of methylene blue[@]				
	5.0 ppm	10.0 ppm	15.5 ppm	20.5 ppm	24.5 ppm
Ficus benghalensis (pH: 8; Equilibration time: 120 min and sorbent concentration: 2.0 g/L)	92.0	92.0	95.0	95.0	94.0
Tamarindus indica (pH: 8; Equilibration time: 90 min and sorbent concentration: 1.5 g/L)	91.0	91.0	94.0	96.5	92.0
Acasia nilotica indica (pH: 8; Equilibration time: 30 min and sorbent concentration: 1.0 g/L)	95.0	92.5	95.0	94.5	93.0

[@]Average values of five estimations; Standard deviation = ± 0.80

At low pH values:

$$\text{Adsorbent-OH} + H^+ \rightleftharpoons \text{Adsorbent-}\underset{\text{H}}{\text{O}^+\text{H}}$$

At low pH values, the surface of the adsorbents are positively charged while at high pH values, it is negatively charged. Hence, the adsorption of methylene blue, a cation, is less favoured at low pHs and it is more favoured at high pHs. This is reflected in the % of extraction of the dye as the pH varied.

The decrease in the rate of adsorption with time of agitation may be due to the more availability of adsorption sites per dye cation, initially and are progressively consumed with time due to the formation of adsorbate film on the active sites of adsorbents.

The observations made in interference studies are as per the expectations. At high pH values, as the surface of the adsorbent is negatively charged, anions are less adsorbed onto the surface and so, the co-anions are not interfered with the adsorption of the dye. But some co-cations, *viz.*, Ca^{2+}, Mg^{2+} and Cu^{2+} that compete with cationic methylene blue for the adsorption sites on the adsorbents, have shown some inference. It is interesting to note that Zn^{2+} and Fe^{2+} have not interfered. Zn^{2+} ion forms zincate anions at high pHs and these negatively charged zincate anions are less adsorbed onto the negatively charged surface of the adsorbents and hence, no interference. In the case of Fe^{2+}, the cation is precipitated as hydrated ferrous hydroxide at high pH onto the surface of the adsorbents and this newly formed surface along with the surface of the bioadsorbents offer additional adsorption sites and hence, complete adsorption of the dye is observed.

Applications: The procedures developed in this investigation are applied to real water samples as described under "experimental" and the results are depicted in the Table-2. It can be noted from the Table-2 that the present developed adsorbents are successful and the % of removal is: 92.0 to 95.0 % for *Ficus benghalensis* sorbent; 91.0 to 96.5 % for *Tamarindus indica* sorbent and 92.5 to 95.0 % for *Acasia nilotica indica* sorbent.

Comparison of the present findings with the previous works: The adsorption capacities of *Ficus benghalensis sorbent, Tamarindus indica sorbent* and *Acasia nilotica indica* sorbent are found to be 50.0, 66.7 and 100 mg/g, respectively. Hither to reported adsorbents in the literature, optimum pH condition of extraction and their adsorption capacities (mg/g) are presented in Table-3 along with the present findings. It may be inferred that the present developed adsorbents have more adsorption capacity than many reported adsorbents. Further, these adsorbents are based on plants that are widely grown in India.

TABLE-3
COMPARISON OF METHYLENE BLUE DYE ADSORPTION CAPACITY WITH PREVIOUS WORKS

Adsorbent	Optimum pH	q_e (mg/g)	Ref.
Ficus carica bast	8.0	47.62	[9]
Geo polymer based on fly ash	6.0	50.7	[10]
Monoliths of geo polymer	5-7	15.4	[11]
ZnO nanoparticles coated activated carbon	9.0	66.66	[12]
Bio-composite alginate beads	6.5	33.58	[13]
Chitosan modified zeolite	7.0	37.04	[14]
Euphorbia rigida-based AC	6	114.5	[15]
Tea waste	7.2	85.16	[16]
Pistachio shell-based AC	7.0	129.0	[18]
Ficus benghalensis sorbent	8.0	50.0	Present work
Tamarindus indica sorbent	8.0	66.7	
Acasia nilotica indica sorbent	8.0	100.0	

Conclusion

• Adsorbents derived from barks of *Ficus benghalensis, Tamarindus indica* and *Acasia nilotica indica* plants are investigated for this sorption nature towards methylene blue dye by varying various physicochemical parameters. The conditions for the maximum removal of the dye from polluted water are optimized.

• With synthetic simulated waters, 100 % removal of the dye is observed with *Ficus benghalensis* adsorbent at the extraction conditions: pH: 8/10, agitation time: 120 min and dosage of adsorbent: 2 g/L With *Tamarindus indica* sorbent, 100 % removal is noted at: pH: 8/10, agitation time : 90 min and dosage of adsorbent: 1.5 g/L. *Acasia nilotica indica* sorbent is observed to be more effective at the optimum conditions: pH: 8/10, agitation time: 30 min and adsorbent dosage: 1.0 g/L.

• Optimum equilibration time: The time needed for the maximum extraction of the dye is found to be in the order: *Ficus benghalensis* (120 min) > *Tamarindus indica* (90 min) > *Acasia nilotica indica* (30 min).

• The optimum sorbent dosage is least for *Acasia nilotica indica* 1.0 g/L and it is 1.5 g/L for *Tamarindus indica* sorbent and 2.0 g/L for *Ficus benghalensis* sorbent for extracting 100 % of the dye from water having 100 ppm of the dye.

• Even at low pHs, substantial removal of the dye is removed with *Acasia nilotica indica* sorbent. This is an interesting observation

• Co-anions ions (five fold excess) have not effected the % removal of methylene blue dye at optimum extraction conditions. But cations *viz.,* Ca^{2+}, Mg^{2+} and Cu^{2+} have interfered to some extent but in no case, % removal has not come down below 90 %. It is interesting to note that Fe^{2+} and Zn^{2+} have maintained the maximum extraction synergistically.

• The procedures are applied to real water samples collected from industrial effluents and found to be successful as envisaged from Table-2.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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