Exploring the efficacy of Base-Modified *Saccharum munja* biomass for adsorptive removal of cationic dyes from single and binary systems

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ABSTRACT

In the 21st century, anthropogenic activities, growing industrialization and unplanned urbanization have raised a serious concern about the deteriorating quality of water resources. The textile wastewaters that contain high number of Synthetic dyes reduce light transmission and adversely affect the photosynthetic activity of aquatic life, causing a highly toxic effect on living communities. Various technologies are available for the remediation of wastewater, among which adsorption is regarded as a green, clean, and versatile method. Herein, Base modified *Saccharum munja* was used for the adsorptive removal of Fuchsin Basic and Methylene Blue dye from single and binary systems. Response surface methodology was used to optimize the effect of different parameters such as contact time, initial dye concentration, biosorbent dosage, and pH on the % removal of dye. Further the kinetic and isotherm of the adsorption process were evaluated with the help of different models. Pseudo-Second-order was found to be best fitted among all the kinetic models. The value of experimental q_e = 87.92 mg/g was in good agreement with the calculated q_e = 88.8 mg/g of FB dye; For MB dye q_e experimental is 60.50 mg/g which is quite similar to calculated q_e 61.46 mg/g. Langmuir Isotherm model suited the best with the experimental data. Further, the adsorption process was also favourable under Freundlich Isotherm model as the value of 1/n falls between 0 and 1 also showing a significant fit to the results that suggested the occurrence of multilayer adsorption. The maximum adsorption capacity (q_{max}) for Fuchsin Basic and Methylene Blue dye obtained from Langmuir model was 178.89mg/g and 87.26mg/g respectively. In conclusion, Saccharum munja can significantly reduce the environmental pollution associated with dye wastewaters and provide a sustainable solution for dye removal.

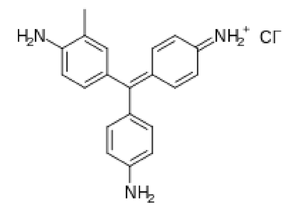
Keywords: Dyes, *Saccharum munja*; Wastewater; Adsorption; Biomass based composites.

1. INTRODUCTION

Globally, about 10,000 dyes are available whose annual production is above 7×10^5 tons which are used in textile, paper, food, and pharmaceutical industries to color their products. Out of the total annual dye consumption in textile industry about 10-15% of them are being discharged as waste into the environment. In India, textile industries have been consuming more than 100 L of water for processing of 1 kg textiles and as a result, they discharge considerable amount of colored wastewater which is responsible for pollution of surface and ground water resources in many regions of the country. Considering this aspect, different conventional and contemporary techniques such as photocatalysis, electrochemical degradation, coagulation-flocculation, adsorption, ozonation, membrane filtration, oxidation processes etc. have been reported for the elimination of dyes. Among these methods, adsorption with biomass-based green adsorbents is considered as the efficient method for the elimination of dyes from wastewater due to its merits of operational simplicity, cost-effectiveness, ability to adsorb wide pollutants, no secondary-pollution, simple regeneration and environmentally benign nature.

a)

b)



c)

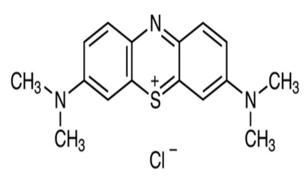


Figure 1 a) Toxicity caused by dyes b) Fuchsin basic dye structure c) Methylene blue dye structure

2. EXPERIMENTAL

2.1. Preparation of adsorbent

1g of Raw SM was dissolved in 40 ml of 0.1M Na_2CO_3 solution in a 250 ml conical flask. After that, the conical flask was placed in an ultrasonicator for 20 to 25 minutes at 60ºC temperature for the homogeneous mixing. Further, the mixture was heated with constant stirring on heating mental at 65ºC for 105 minutes; filtered out; washed several times with distilled water till neutral pH; dried in hot air oven. The dried and base modified SM (M-SM) was grinded, sieved, and stored in an airtight container for further use. It was further characterised with various instrumentational techniques to study the surface and morphological characteristics associated with the material.

2.2. Characterization of adsorbent

The surface morphology and functional groups existing over the SM adsorbent was analyzed with FESEM of JEOL make 7610F Plus and FTIR spectroscopy (Frontier, Perkin Elmer). XRD was performed on Empyrean X-ray Diffractometer.

2.2. Batch adsorption studies

Batch adsorption studies were carried out to investigate the effect of various parameters such as pH, dosage, concentration, temperature and contact time. For kinetic and thermodynamic exploration, fixed amount of the adsorbent was added to 10 mL of dye solution having an initial concentration of 100 mg/L, and the residual concentration of the supernatant was evaluated by a UV-visible spectrophotometer(at wavelength 547.2 nm) at predetermined intervals ranging from 0 to 45 min. Adsorption isotherm was studied with Freundlich, Langmuir, Temkin and D-R models at 40,60 and 80˚C. The quantity of each dye adsorbed by SM was calculated as:

Removal (%)=$(C_o-C_e)/C_o$ ×100

Adsorption capacity at equilibrium, q_e(mg⁄g)= $((C_o-C_e)\times V)/m$

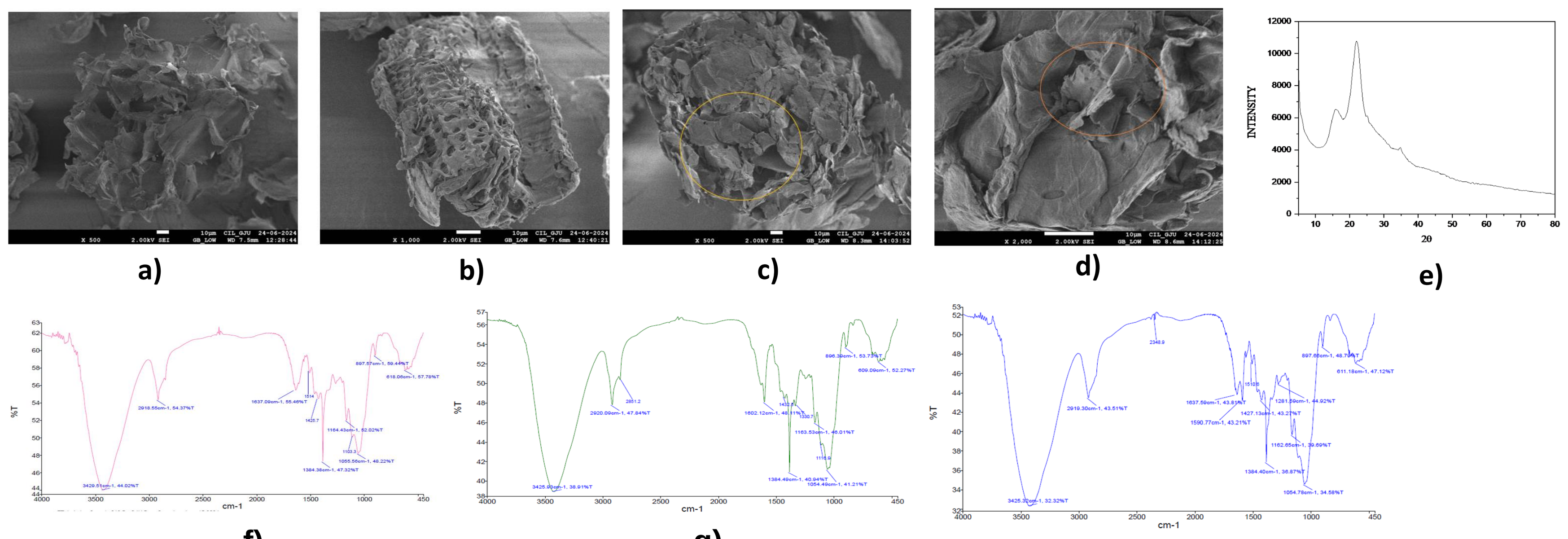
Adsorption capacity at any time t, q_t(mg⁄g)= $((C_o-C_t)\times V)/m$

Where, C_e, C_o and C_t are equilibrium, initial and concentration of dye at time, t respectively; m represents the amount of adsorbent in g and V is the volume of solution in L.

3. RESULTS AND DISCUSSIONS

3.1. Characterization of adsorbent

FESEM- Figure2 (a, b) shows the structural and surface morphology of M-SM. Where, (a) shows the flakes, rough structure and heterogeneous morphology of M-SM. (b) shows the porous opened structure of M-SM due to base. Fig. 2 (c) showing FB dye loaded and porous closed due to the adsorption of FB dye and (d) showing MB dye loaded and porous closed due to the adsorption of MB dye. **XRD- Fig. 2 (e)** shows the XRD pattern of M-SM. The XRD pattern of B-SM displayed two major peaks. The sharp peak, 2θ = 22.03° show crystalline region and the broad peak, 2θ = 15.77° show amorphous region. **FTIR- Figure 2 (f-h)** shows the FTIR spectra of M-SM, FB loaded M-SM and MB loaded M-SM, respectively. In **(f)**, the peak 3429.51cm^{-1} is due to the OH stretching or NH_2 group stretching. The peak 2918 cm^{-1} is assigned to CH asymmetric stretching. The peaks at 1637.09 cm$^{-1,}$ 1514 cm^{-1}, and 1425.7 cm^{-1} shows asymmetric and symmetric stretching vibration of C=O groups. At 1384.38 cm^{-1} the C-N stretching band was observed, and 1055.56 cm^{-1} was seen due to stretching to alcohols and carboxylic acid. In **(g, h)** After MB dye and FB dye adsorption, all the peak got shifted. The OH or NH_2 group peak were shifted from 3429.51 cm^{-1} to 3425.93 cm^{-1} and3425.32 cm^{-1}; the 2918 cm^{-1} got shifted to 2920.09 cm^{-1} and 2919.30 cm^{-1}; the 1637.09 cm^{-1}, 1514 cm^{-1}, and 1425.7 cm^{-1} were modified to 1602.12 cm^{-1}, 1637.59 cm^{-1} ;1432.5 cm^{-1}; and 1427.13. the 1384.38 cm^{-1}, and 1055.56 cm^{-1} gets altered to 1384.49 cm^{-1}, 1384.40 cm^{-1}; 1054.49 cm^{-1}, 1054.78 for MB and FB dye adsorption respectively



a) b) c) d) e) f) g) h)

Figure 2- Characterization studies

3.2. Batch adsorption studies

b)

Dye stock solutions was prepared by dissolving 0.125g of both FB and MB in 250ml of distilled water in two different volumetric flask. It was further diluted to make the dye solutions of varying concentration within range of 50-300 ppm. The pH of dye solution (2-11) was adjusted by using 0.01M NaOH and 0.01M HCl. The thermodynamic parameters and kinetics studies have been discussed in **Table 1** and the isotherm studies are listed below in **Table 2**.

Table 1- Thermodynamic and Kinetic studies

Thermodynamic parameters					
	ΔG (kJ/mol)			ΔS ($Jmol^{-1}K^{-1}$)	ΔH ($kJmol^{-1}$)
	313K	333K	353K		
FB	-3.291	-3.785	-4.656	33.74	7.32
MB	-6.648	-7.974	-8.823	54.83	10.44
Pseudo-second-order model					
	K_2		q_e (mg/g)		
FB	0.0425		87.92		
MB	0.0154		60.50		

Table 2- Isotherm studies

Model	Equations	Parameters	Parameter values	
			FB	MB
Langmuir model	$\frac{1}{q_e}=\frac{1}{q_{max}}+\frac{1}{K_L q_{max}}1/C_e$	q_{max} (mg/g), maximum adsorption capacity	178.89	87.26
		K_L (L/mg), Langmuir constant	0.056	0.0295
Freundlich model	$\ln qe = \ln k_f + \frac{1}{n} lnCe$	K_F (mg/g) $(L/mg)^{1/n}$, Freundlich constant	8.78	7.183
Temkin model	$q_e = \frac{RT}{b_T} lnK_T + \frac{RT}{b_T} lnC_e$	K_T, equilibrium binding constant	1.707	2.029
D-R model	$\ln V_{ads} = lnV_t - \left(\frac{RT}{\epsilon}\right)^2 ln^2\left[\frac{p^o}{p}\right]$	β Dubinin-Radushkevich isotherm constant	6.616	49.966
		R is the ideal gas constant (8.314 J/ mol) T (K) is the absolute temperature		

4. CONCLUSIONS

- M-SM biosorbent was very effective for the removal of hazardous Fuchsin basic and Methylene blue dye .
- Experimental data was well fitted with pseudo-second order kinetics and thermodynamic studies revealed endothermic nature of adsorption.
- The desorbed dyes were recovered making the whole process eco-friendly.

International Conference on
Composite Materials for Environment Protection & Remediation
(ICCMEPR - 2024) 02-03 July, 2023