Investigation of the adsorptive efficiency of Base modified Saccharum munja biomass for Safranine O and crystal violet dyes in single and binary systems

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ABSTRACT

With expanding populations, anthropogenic activities and climate change, water scarcity has become a significant issue that necessitates immediate efforts towards wastewater remediation. Textile wastewater loaded with organic dyes is harmful to aquatic life and disrupts photosynthetic activity. To address this issue, there are various technologies for treatment of wastewater. Among them, adsorption by using biomass-based composites is widely adopted technology due to its various characteristics such as eco-friendly, cost-effectiveness, low operation time and no harmful secondary pollutants. Herein, we have utilized the base treated *Saccharum munja* for the removal of Safranine O dye and Crystal Violet dye from water. The as-synthesized composite was characterized by using various technologies to explore the associated physicochemical characteristics. Response surface methodology was used to optimize the effect of various parameters such as initial dye concentration, biosorbent dosage, and pH. Moreover, the kinetics and isotherm of the adsorption process were evaluated using various models. The best-fitted model was found to be the Pseudo-Second-Order model among all the kinetic models. The experimental value of q_e, which is equal to 87 mg/g, was quite similar to the calculated value of q_e, which is equal to 88.261mg/g for SO dye; For CV dye q_e experimental is 92.66mg/g which is quite similar to calculated q_e 93.37mg/g. The Langmuir Isotherm model was found to be the most suitable for SO dye and Freundlich isotherm model was found to be the most suitable for CV dye. Further, the adsorption process was also favorable under Freundlich isotherm model as the value of 1/n falls between 0 and 1 also showed a good fit with the results and suggested multilayer adsorption. The maximum adsorption capacity (q_{max}) for Safranine O and Crystal Violet dye obtained from the Langmuir model was found to be 126.90 mg/g and 143.67 mg/g respectively. In conclusion, Saccharum munja can effectively reduce environmental pollution caused by dye wastewater and offer a sustainable solution for dye removal.

Keywords: Organic Dyes; *Saccharum munja*; Wastewater; Isotherm; Kinetics; Thermodynamics;

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 colour 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 coloured 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.

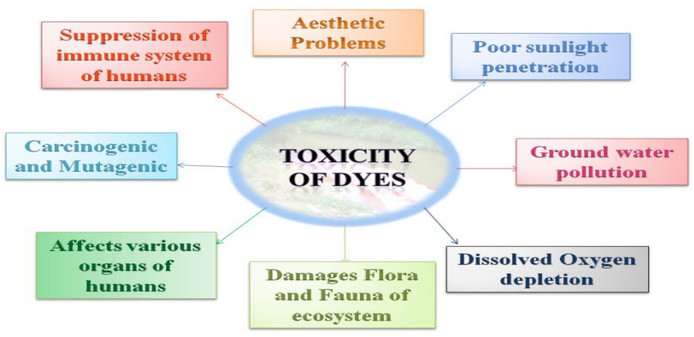

Figure 1 Toxicity caused by dyes

2. EXPERIMENTAL

2.1. Preparation of Base Modified adsorbent

1 g of raw SM was dissolved in 40 ml of 0.1M Na_2CO_3 solution in a flask. Further, it was ultrasonicated for about 20 to 25 minutes at a temperature of 60 degrees Celsius. This helps to mix everything evenly. Next, the mixture was heated by continuously stirring at 60 degrees Celsius for 90 minutes. After that, the solid part was filtered and washed with distilled water till neutral pH. The obtained product was dried in a hot air oven. Once dried, the obtained biosorbent was grinded; sieved to get fine particles

2.2. Characterization of adsorbent

The surface morphology and functional groups existing over the B-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. The point of zero charge (pH_{PZC}) of SM was determined using the pH-drift method.

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 for Safranine O and Crystal Violet dyes (at wavelength 520 and 580 nm) respectively at predetermined intervals ranging from 0 to 30 min. Adsorption isotherm was studied with Freundlich, Langmuir, Temkin and D-R models at 40˚C. The quantity of each dye adsorbed by SM was calculated as:

Removal (%)=$(C_o-C_e)/C_o \times100$

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)= $((C_0-C_t)\times V)/m$

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

Figure 2(a, b) FESEM image of B-SM revealed the porous structure which was mainly responsible for the dye adsorption. Figure 2(c, d) shows SO and CV dyes loaded and porous closed due to dye adsorption. XRD pattern of B-SM was shown in figure 2 (e0 FTIR technique was applied to identify the surface states of B-SM as shown in **Figure 2 (f)**. A broad peak at 3429 cm^{-1} was observed in the case of B-SM corresponding to the -OH. The presence of a peak at approximately 2918 cm^{-1} was due to the methylene group C-H. The peak at 1647.09 cm^{-1} ,1514 cm^{-1} were related to C=O stretching. The peak at 1384.38 cm^{-1} was attributed to C-N stretching and the peak at 1055.56 cm^{-1} . The B-SM adsorbent shows two diffraction peaks at 15.77˚ and 22.03˚. The sharp peak, 2θ = 22.03° show crystalline region and the broad peak, 2θ = 15.77° show amorphous region and figure 2(g, h) shows FTIR Pattern after SO and CV dyes adsorption

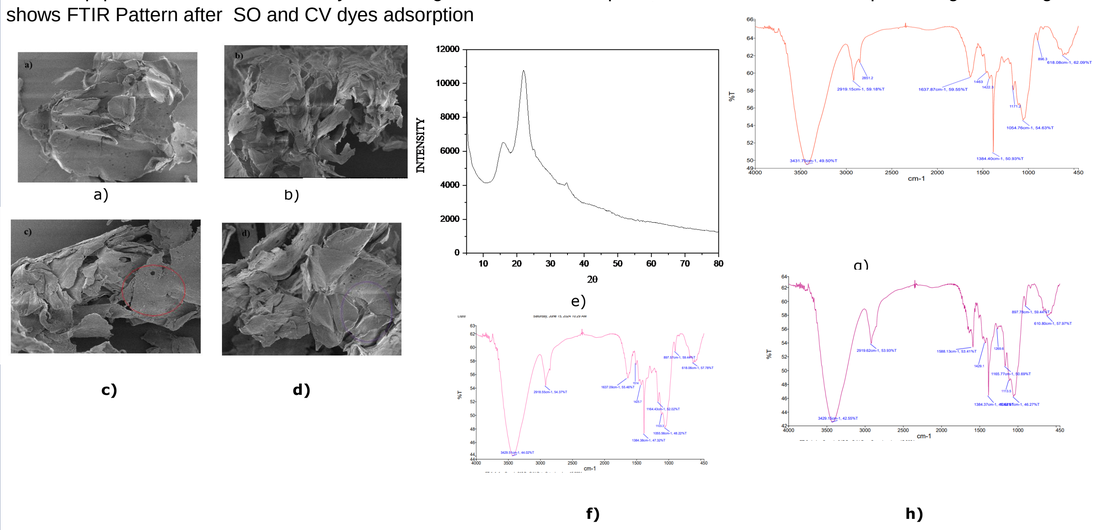

Figure 2- Characterization studies

3.2. Batch adsorption studies

The adsorptive behaviour of the B-SM for the removal of Safranine O and Crystal Violet dyes were studied between pH 2 to 11 and the concentration of dyes vary within the range of 50-300 ppm. The thermodynamic and kinetic studies have been discussed in Table 1 and isotherm studies for single and binary systems are discussed in Table 2 and 3, respectively.

Table 1- Thermodynamic and Kinetic studies

Thermodynamic parameters					
	ΔG (kJ/mol)			ΔS ($Jmol^{-1}K^{-1}$)	ΔH ($kJmol^{-1}$)
	313K	333K	353K		
SO	-3.989	-1.686	-0.866	-79.54	-28.66
CV	-5.042	-6.604	-8.577	87.96	22.54
Pseudo-second-order model					
	K_2		q_e (mg/g)		
SO	0.0215		87		
CV	0.029		92.66		

Table 2- Isotherm studies in single system

Model	Equations	Parameters	Parameter values	
			SO	CV
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	126.9	143.67
		K_L (L/mg), Langmuir constant	0.153	0.158
Freundlich model	$\ln qe = \ln k_f + \frac{1}{n} lnCe$	K_F (mg/g) $(L/mg)^{1/n}$, Freundlich constant	9.68	9.13
Temkin model	$q_e=\frac{RT}{b_T}lnK_T+\frac{RT}{b_T}lnC_e$	K_T, equilibrium binding constant	1.76	2.61
D-R model	$lnq_e=lnq_D-\beta E^2$	β Dubinin-Radushkevich isotherm constant	2.13	12.83
		R is the ideal gas constant (8.314 J/ mol) T (K) is the absolute temperature		

Table 3- Isotherm studies in binary system

Model	Equations	Parameters	Parameter values	
			SO	CV
Modified Langmuir model	$\frac{1}{q_{e,A}}=\frac{1}{Q_A^0}+\frac{1}{Q_A^0 K_L}\left[\frac{1}{C_{e,A}}+\frac{K_{L,B}C_{e,B}}{C_{e,A}}\right]$	Q_A^0 , maximum adsorption capacity for component A	119.33	135.68
		K_L, Langmuir constants	0.243	0.446

4. CONCLUSIONS

•B- SM biosorbent was very effective for the removal of hazardous Auramine O dye.

• Experimental data was well fitted with pseudo-second order kinetics and thermodynamic studies revealed spontaneous and exothermic nature of adsorption.

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