

## Azo Dye Removal from Aqueous Phase by Surface Modified Agro-industrial Waste: Equilibrium and Kinetics studies

Man mohan<sup>1</sup>, V Kiran Kumar<sup>2</sup>, Arunima Rajeev<sup>3</sup> and S. Gajalakshmi<sup>4\*</sup>  
<sup>1,2</sup>Research Scholar, <sup>3</sup>M.Tech. scholar and <sup>4</sup>Assistant Professor

<sup>1, 3, 4\*</sup> *Bioremediation Lab, Centre for Pollution Control and Environmental Engineering, Pondicherry University, Pondicherry, India.605014.*

<sup>2</sup> *Bioelectrochemical Systems Lab, Centre for Pollution Control and Environmental Engineering, Pondicherry University, Pondicherry, India.605014.*

### Abstract

Azo dyes are well known recalcitrant and hazardous pollutants from dyeing industries which are essentially needed to be removed from the industrial effluents before discharged in the environment. Among many dye removal techniques, biosorption has gained attraction due to eco -friendliness and cost effectiveness. Biosorption of pollutant is surface phenomena which is resultant of the physicochemical interactions between biologically originated surfaces and the pollutant molecules. On the other hand, biomass from agro-industrial activities (e.g., rice straw, rice husk, wheat straw etc.) poses significant adversity on the environment, if traditional management practices are adopted. This study integrates the use of biomass for azo dye removal. It focusses on the utilization of rice straw biomass for removal of azo dye in the purview of sustainable environmental management. Biosorption of methylene blue dye (MB) by the use of rice straw and surface modified rice straw was studied. Rice straw powder (RSP) was treated with autoclaved sea water (RSP-ASW) and Sodium dithionite (RSP-SDT) and their characteristics was studied. Proximate analysis suggests the improvement in chemical composition by the treatments. The surface characterization with FTIR, PZC and SEM inferred the effect of modifying agents on RSP. Batch biosorption experiments were conducted to check the effect of operating parameters, viz., solution pH (pH3 – pH11), temperature (298K-318K), initial dye concentration (50 mg/L-200 mg/L), contact time (0 – 360 minutes), and adsorbent dosage (0.25 gm -1 gm) on MB removal. The preliminary investigations on sorption equilibrium of MB on pre-treated and untreated rice straw biomass showed the highest congruity with the Langmuir isotherm model, among the four adsorption isotherm models, viz., Freundlich, Langmuir, Temkin and DubininRadushkevich (D-R) isotherm models. The adsorption process follows the pseudo second order kinetics. The MB removal achieved was in the order RSP-SDT>RSP-ASW>RSP in all the adsorption experiments conducted. The maximum dye removal efficiency was 181.8 mg of MB / gm of RSP-SDT at neutral pH and room temperature.

**Keywords:** Agro-industrial waste, Azo dyes, Biosorption, Equilibrium, Adsorption isotherms, Adsorption kinetics model, and surface modification.

### 1. Introduction

Biologically originated surfaces has been vastly investigated for their possible applications in many areas of research and development such as mechanical strengthening and support[1], fuel and energy[2], separation technologies for filtration and adsorption[3], [4]. Dead plant, bacterial and fungal biomass consist chiefly of cell wall and other components. Plant cell walls are the complex extracellular polysaccharide secretions which consists of cellulose, hemicellulose, lignin, and many other

biopolymers[5], [6]. Although the basic structural components of cell wall are almost common but the evolutionary variations in composition give rise to topological, physical and chemical diversity at very large scale[7], [8]. These variations defines the specificity and uniqueness of the bio-surfaces[9]. Agricultural activities are considered to be the sources of unstanchable biomass generation[10]. These huge amount of biomass mainly consist of cell wall and other components[11]. Paddy cultivation and its post-harvest activities yields enormous amount of biomass such as rice grains, husk, straw and residual roots[6]. Traditionally, these agro-bio waste can be managed up to certain extent to support collateral activities like livestock feeding[12], biofuel generation[13]and bio fertilizer production[14]. But huge generation of biomass, less storage capacities and decreased intercrop durations has led to the asystematic and eco-unfriendly / unsustainable approaches of waste management in the developing world. Most of the biomass have been employed to *in-situ* biodegradation or incorporation[15] and open field burning[16] which affects negatively the fauna, flora and abiotic components of the environment[17]–[19].

Elevated levels of inorganic, organic synthetic chemicals in the effluents from the textiles and other coloring industries are the prominent sources of water pollution[20]. Azo dyes are the important class of color imparting components in the textile industries. Low manufacturing cost, broad range of colors, better fastness, very high intensity and better stability making them an exquisite choice in the world of textile coloring[21]. Toxicity and recalcitrance are the major problem associated with azo dyes containing effluents. Management of these toxic, carcinogenic and teratogenic effluent is always a key challenge for the sustainable industrial development. Exigency of research and development for economic and eco-friendly technologies has been set to overcome the long-lasting negative effects of these pollutants.

Dye removal from the textile effluent can be achieved by Fenton process, ozonation, photo chemical process, electrolysis, activated carbon, membrane filtration, ion exchange and biosorption process[22]. Biosorption is the affinity driven passive binding and concentrating the selected ions or other molecules on the surface of biomass from aqueous phase[23]. Gaad (2008) defines biosorption as “*any system in which the interaction between sorbate (i.e. atoms, metal ions, organic molecules etc.) and biosorbent (i.e. a solid surface of bio-matrices) eventuate in the increased sorbate concentration at solid-liquid interface and reduction in solution sorbate concentration*”[24]. It has been considered as a potent integrable technology in the existing set of treatment systems for the pollutant removal from aqueous phase[25]. Studies on the biosorption process mostly oriented towards dynamics, kinetics and energetics aspects to examine the efficiency and process optimization[26]. Physically and chemically surface transformation of biosorbents is an ongoing trend in biosorption research to enhance the performance by increasing the specificity, rate of reaction and endurance towards repetitive use of biosorbents[27]–[32].

The study presented here explores a sustainable process of hazardous wastewater treatment coupled with agro-industrial solid waste management. Lab scale batch experiments for biosorption of methylene blue dye (MB) on the surface modified rice straw biomass were carried out. Two different surface modification agents were used namely sodium dithionite solution (SDT) and autoclaved sea water (ASW). Modified rice straw was characterized by FTIR, SEM, and PZC then compared with raw rice straw. Studies on sorption equilibrium and kinetic were performed in order to investigate the effects of key factors i.e., contact time, adsorbent dosage, pH, and temperature on biosorption process. Adsorption isotherm models *viz* Langmuir, Freundlich, Temkin and Dubinin-Raduskevich (D-R) were tested to understand the system behaviour. Kinetics were described by using pseudo first order, pseudo second order and intraparticle diffusion models to derive adsorption kinetics parameters and rate constants for further optimization studies.

## 2. Materials and Methods

### Materials

The cationic azo dye 3,7-Bis(dimethylamino)phenothiazin-5-ium chloride popularly known as Methylene blue or Basic blue 9 (relative molecular mass 319.86 g/mole) was received from HiMedia Laboratories Pvt. Ltd, Mumbai, India. At natural pH and 298K temperature the solubility of dye in water is 43.6 g/L which gives maxima at 668nm[33]. Stock solution of 1g/L concentration was prepared by dissolving 1g Methylene blue crystalline powder in 1liter distilled water at room temperature and stored in amber bottle. Stock dilutions were prepared in fresh distilled water according to experimental requirements. Initial pH of the working solutions was adjusted by 1M NaOH and 1M HCl.

Rice straw was collected from a rice field from the locality of Kalapet, Pondicherry India (12.0295° N, 79.8577° E). Dust and other particulate removal were done by distilled water wash followed by sun drying. Sun dried biomass was cut into 1cm length followed by drying at 100°C in laboratory oven. Oven dried material was ground using electrical grinder, sieved through 0.25mm sieve by automatic sieving machine and stored in air tight plastic jar.

Surface modification of rice straw powder (RSP) was achieved by two different chemical pre-treatments; autoclaved sea water/saline (ASW) and sodium dithionite (SDT). Sodium dithionite was received from *Finar Limited*, Ahmedabad, Gujarat and Saline were collected from Pondicherry University beach, Bay of Bengal, India (12°00'50.0"N 79°51'38.4"E).

The sea water collected was filtered through Whatman® GF /A (1.6micron pore size) filter paper and autoclaved at 15lbs for 30 minutes in laboratory autoclave. Adequate amount of autoclaved sea water was mixed with RSP and the mixture was stirred for 4 hours at room temperature. Mixture was dewatered using muslin cloth and then washed with distilled water. Sea water treated rice straw powder (RSP-ASW) was oven dried at 105°C for 12 hours and stored in air tight jar. Appropriate amount of RSP was mixed with 0.5%w/w Sodium dithionite aqueous solution. The mixture was stirred for 4 hours at room temperature and subjected to filtration followed by thorough washing with distilled water. Washed rice straw powder (RSP-SDT) was oven dried at 105°C for 12 hours and stored in air tight jar for further use.

Proximate analysis (Moisture, volatile matter, Fixed Carbon and Ash content) of RSP, RSP-ASW and RSP-SDT was performed according to ASTM (E872-82) guidelines [34]–[36]. The salt addition method has been adopted for the point of zero charge (pzc) analysis[37]. A series of 20ml, 0.01M KNO<sub>3</sub> solution from pH 2 to pH 11 at the interval of pH 1 was prepared using 0.1M NaOH and 0.1M HNO<sub>3</sub> in closed Erlenmeyer flasks. Biomass (0.2g) was mixed in each flask containing solution and agitated at 130 rpm for 24 hours in incubator shaker at room temperature. The pzc was determined from the plot between ΔpH and initial pH of the solution.

$$\Delta\text{pH} = \text{initial pH} - \text{final pH}$$

Surface morphology of biosorbents were analysed by scanning electron microscopy (SEM). For specimen preparation, carbon sputtering technique was followed. The predominant functional moieties of biosorbent surfaces were identified using KBr pellet method in the wave number band ranges from 500 cm<sup>-1</sup> to 4000cm<sup>-1</sup> by FTIR (Thermo Nicolet Model- 6700) spectroscopy.

## Experimental design & Methodology

Batch adsorption experiments were conducted with  $3^3 \times 5^2$  factorial design in triplicate. Qualitative and quantitative analysis of Methylene blue aqueous solutions were carried out spectrophotometrically (LAB INDIA UV-VIS 3000+) throughout the experiments. Adsorption capacity and percent dye removal were calculated from the equation (1) and (2) respectively.

$$Q_{ads} = \frac{C_0 - C_e}{m} \times V \quad \text{-----}$$

(1)

$$\% \text{ Removal efficiency} = \frac{C_0 - C_e}{C_0} \times 100 \quad \text{-----}$$

(2)

Where,  $C_0$  (mg/L) is initial MB dye concentration,  $C_e$  (mg/L) is equilibrium MB dye concentration, volume of MB dye solution denoted as  $V$  (ml) and biosorbent dosage is denoted as  $m$  (mg).

The effect of initial concentration of dye was studied by taking 0.5g biosorbent in 50ml solution of three different initial concentrations 50 mg/L, 100mg/L and 200mg/L at natural pH. Then mixture was agitated in incubator shaker (GeNei, SLM-INC-OS-250) at 130rpm for 4 hours at room temperature. At equilibrium 5ml sample was centrifuged and supernatant was quantified. Adsorbent dosage was varied (0.25g, 0.5g, and 1g) to evaluate the effect of adsorbent dosage on dye uptake. In closed Erlenmeyer flask 0.5g biosorbent was mixed with 50ml MB solution of 100mg/L strength and kept in incubator shaker (130 rpm, 4 hours contact time) at three different temperatures 293K, 303K and 313K in order to evaluate the effect of temperature on the biosorption process.

A range of pH from 2 to 11 were taken to determine the effect of initial pH on the process. Adjustment of pH was done using small amount of 1M NaOH and 1N HCl. Dye solution of 100mg/L concentration (50ml) was mixed with 0.5g biosorbent dosage in various initial pH at the agitation speed of 130rpm for 4 hours at room temperature. The effect of contact time was studied by mixing 0.5g biosorbent with 50ml of dye solution (100mg/L) at pH 7. The solution was agitated at 130 rpm at room temperature for 240 minutes. Sampling was done at every 30 minutes of interval followed by centrifugation and spectrophotometric analysis.

## Adsorption equilibrium and Kinetics Studies

Critical information on the adsorption capacities, energetics, surface properties and mode of interactions between adsorbent and adsorbate can be obtained from the equilibrium isotherms[38]. Four vastly used i.e., Langmuir, Freundlich, Temkin, Dubininand Radushkevich (D-R) isotherm models has been employed and compared in this study. The empirical expressions of the isotherms and their linearized forms has been given in Table 1.

Langmuir isotherms predicts the monolayer adsorption capacities for the homogeneous surfaces whereas, Freundlich isotherms describes the heterogeneous adsorption systems[39], [40]. Temkin isotherms gives an insight in to the heat of adsorption and binding energy[41]. Dubinin-Radushkevich (D-R) isotherm model is generally applied to explain the adsorption on the heterogeneous surfaces and their Gaussian energy distributions for the intermediate concentration ranges[42].

Adsorption kinetics and dynamics was studied by employing reaction order depended models i.e., pseudo first order (PFO), pseudo second order (PSO) and Webber-Morris intraparticle diffusion model (IPD). PFO kinetic model[43]is generally used to elucidate the mechanism of adsorption in aqueous solutions. PSO kinetic model[44]is based on the

assumption that the sorption capacity is proportional to the number of active sites occupied on the biosorbent surface. IPD model is useful to describe the sorbate transport and site occupation on the sorbent porous surface in the aqueous phase[45]. The fundamental expressions and their linearized forms have been summarized in the Table 2.

**Table 1. Adsorption Isotherms and Corresponding Expressions.**

Isotherm	Isotherm Expression	Linearize Equation	Plot
Langmuir	$q_e = \frac{(q_m b C_e)}{(1 + K_L C_e)}$	$\frac{C_e}{q_e} = \left(\frac{1}{q_m}\right) C_e + \left(\frac{1}{K_L q_m}\right)$	$C_e$ versus $C_e/q_e$
Freundlich	$q_e = K_F C_e^{1/n}$	$\ln q_e = \ln K_F + \frac{1}{n} (\ln C_e)$	$\ln C_e$ versus $\ln q_e$
Temkin	$q_e = \frac{RT}{b} \ln (K_T + C_e)$	$q_e = B \ln K_T + B \ln C_e$	$\ln C_e$ versus $q_e$
D-R	$q_e = q_e \exp\left\{-B_D \left[RT \ln \left(1 + \frac{1}{C_e}\right)\right]^2\right\}$	$\ln q_e = \ln(q_t) - (2\beta \epsilon)$	$\epsilon$ versus $\ln q_e$

**Table 2. Kinetics Models for Biosorption Studies.**

Kinetics	Expression of Kinetics	Linear form of equation	Plot
PFO	$(dq_t/dt) = K_1 (q_e - q_t)$	$\ln(q_e - q_t) = \ln q_e - K_1 t$	$t$ versus $\ln(q_e - q_t)$ .
PSO	$(dq_t/dt) = K_2 (q_e - q_t)^2$	$(t/q_t) = (1/K_2 q_e^2) + (1/q_e) t$	$t$ versus $(t/q_t)$
IPD	$q_t = K_{in} t^{0.5}$	$q = K_{in} t^{0.5} + C$	$t^{0.5}$ versus $q_t$

### 3. Results and Discussion

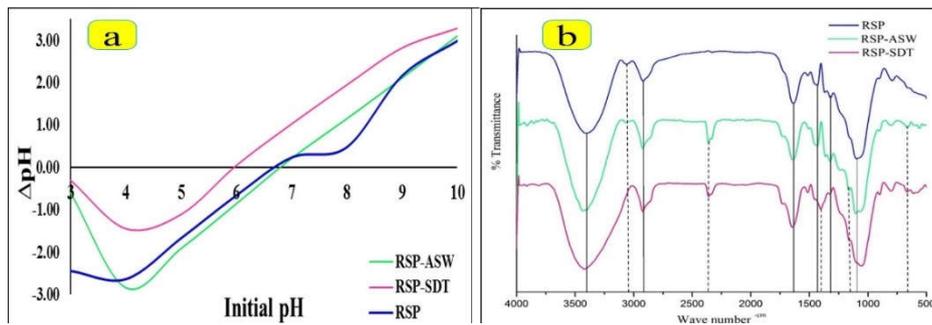
#### Effect of pre-treatments on the rice straw biomass

Proximate and ultimate characterization suggests the changes in the physicochemical properties of the rice straw (Table 3). Decrease in the ash content and fixed carbon indicates the solubilisation and runoff of small sized rice straw particles by the aqueous phase pre-treatment. Decrease in the moisture content can be attributed to the decrease in the hydrophilic sites on the RSP surface[46]. Point of zero charge studies shows deviation in the surface electrical charge of the pre-treated RSP (Figure 1a.). RSP-SDT is reported with the lowest pzc followed by RSP and RSP-ASW. The FTIR spectra of RSP and pre-treated RSP presented the major adsorption bands (wave number,  $Cm^{-1}$ ) associated with lignocellulose matrices. The combined FTIR plot (Figure 1b.) indicates effect of pre-treatment on the surface functional moieties in the fingerprint and functional group region of the spectra. Pre-treatment with ionic liquids has been reported to change amorphousity but there is no much deviation reported in the region of  $800-950cm^{-1}$  in the present study[47], [48]. Textural and topographical changes have been observed in the scanning electron micrographs (Figure 2.) which inferred the effect of pre-treatment agent on the RSP. Surface roughness and sharp crest and grooves have been reported which might be due to swelling of particles and silica exposure[49].

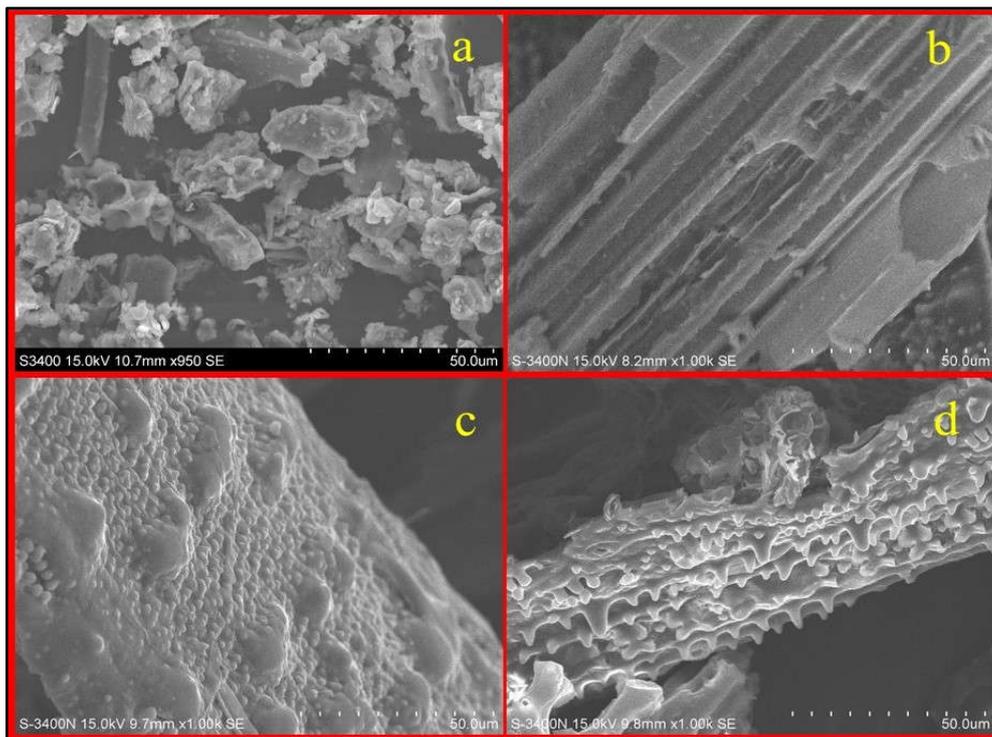
**Table 3. Proximate analysis of biosorbents.**

	RSP	RSP-ASW	RSP-SDT
<b>Parameter</b>			
Moisture %	6.90	6.44	3.71

Volatile Matter %	35.79	42.48	59.07
Fixed Carbon %	31.26	27.42	16.70
Ash %	26.05	23.66	20.52



**Figure 1. PZC analysis plot (a) and FTIR spectra (b) of RSP, RSP-ASW and RSP-SDT.**

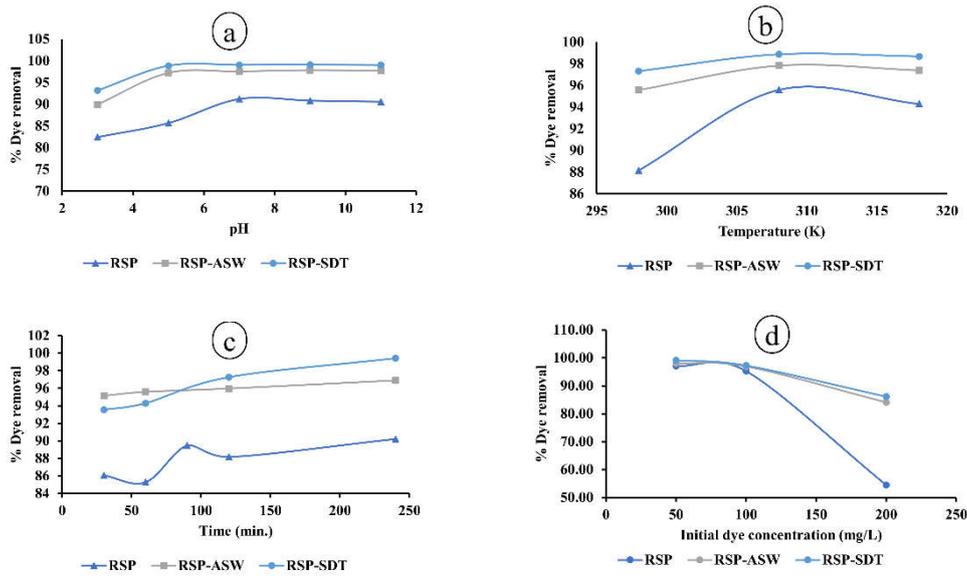


**Figure 2. Scanning Electron Micrographs of RSP (a, b), RSP-ASW(c) and RSP-SDT (d) at 1000x magnification.**

**Effect of operating parameters on MB biosorption**

Dye removal increases with the increase in the pH for RSP and pre-treated RSP (Figure3a.)[50]. The removal efficiency was found to be low at highly acidic pH but there is not significant difference reported in the range of pH 6 to pH11. Probability of competition between MB<sup>+</sup> and H<sup>+</sup> for the access to the adsorption sites can be inferred from the low removal efficiency at low pH. Above pzc, the biosorbent surface becomes

negatively charged which enhances the performance. The increase in temperature initially increases the dye removal and decreases with higher temperature (Figure 3b.). This can be attributed to the elevated kinetic energy of the dye molecules and diffusion speed in the biosorbent particles due to temperature increase[51]. Initial increase followed by saturation (at equilibrium) was observed in the dye removal with contact time (Figure 3c.). It suggests the initial monolayer coverage of dye molecules on the biosorbent surfaces. The decrease in the dye removal with initial dye concentration can be due to the increased tendency of aggregation of MB and increased mass transfer resistance (Figure 3d.). The increased adsorption based on adsorbent dosage may be due to the increased sorption surface and adsorption sites availability (Figure 5d)[52].



**Figure 3. Effect of Process Parameters on MB Biosorption on RSP and Pre-treated RSP. ( a= effect of initial pH, b= effect of temperature, c= effect of contact time and d= effect of initial dye concentration.**

The MB adsorption isotherms has been plotted (Figure 4a, 4b, 4c and 4d.) and computed parameters are tabulated in the Table.4. The Langmuir isotherm model indicates increase in the monolayer adsorption capacity ( $q_m$ ) in the order of RSP-SDT>RSP-ASW>RSP. Values of separation constant indicates favourability of biosorption process. Freundlich isotherm model fits best ( $R^2>0.99$ ) in the pre-treated adsorbents. Temkin isotherm assuming the linear decrease in the heat of adsorption of sorbate molecules is proportional to their coverage on the adsorbent surface[54].

D-R isotherm model is useful to distinguish between the physical nature and the chemical nature of the adsorption process. The mean free energy (E) values from the experimental data suggest the physical nature (range =  $0 < E > 8000 \text{ J.mole}^{-1}$ ) of MB adsorption on the RSP, RSP-ASW AND RSP-SDT. The equilibrium study parameters for all the biosorbents best fit with Langmuir isotherm model followed by Freundlich, Temkin and D-R isotherm models (Table4).

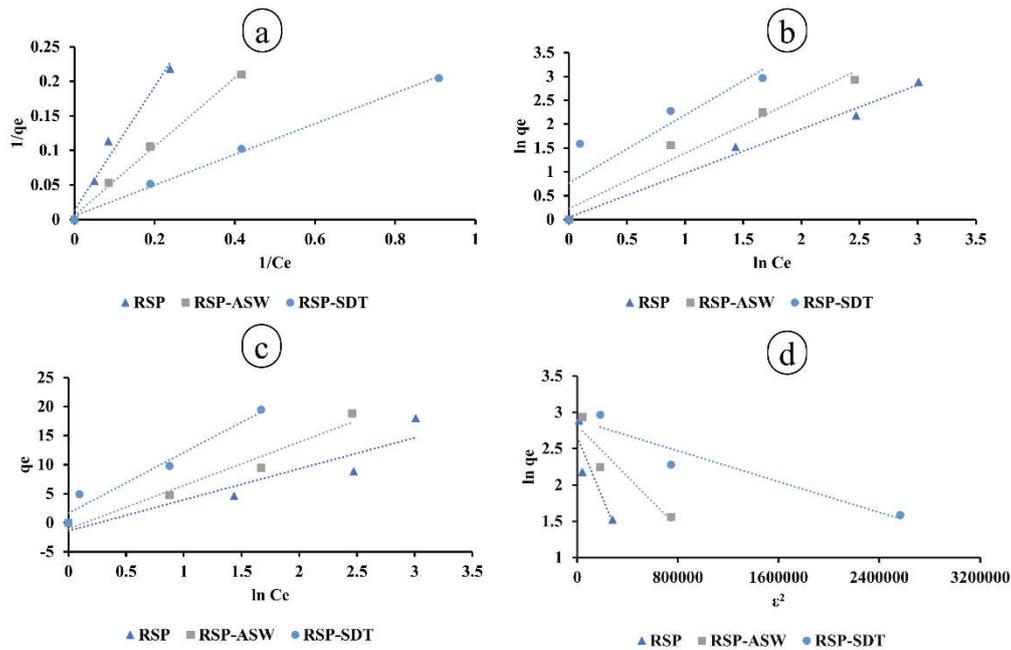


Figure 4. Equilibrium Isotherms for MB Dye Biosorption (a= Langmuir isotherms, b= Freundlich isotherms, c= Temkin isotherms and d= Dubinin and Raduskevich isotherms).

Table 4. Isotherm model parameters for MB dye biosorption by RSP and pre-treated RSP.

Parameter	Unit	RSP	RSP-ASW	RSP-SDT
<b>Langmuir isotherm</b>				
$q_m$	mg/gm	72.46	156.25	181.81
$b$	L/mg	0.0123	0.00318	0.0012
$R_L$	$R_{L50}$ mg/L	0.6187	0.8628	0.9424
	$R_{L100}$ mg/L	0.4479	0.7587	0.8911
	$R_{L200}$ mg/L	0.2886	0.6112	0.8037
$R^2$		0.9676	0.9959	0.9968
<b>Freundlich isotherm</b>				
$K_F$	mg/gm	1.05	1.25	2.16
$n$		1.082	0.856	0.702
$R^2$		0.9886	0.9619	0.7614
<b>Temkin isotherm</b>				
$K_T$		0.7672	0.8666	1.1699
$B$		5.3577	7.4623	10.446
$R^2$		0.8599	0.9605	0.9566
<b>Dubinin-Raduskevich isotherm</b>				
$q_s$	mg/gm	16.66	25.85	29.62
$K_{ad}$	$\text{mole}^2 / \text{Joule}^2$	$2 \times 10^{-6}$	$4 \times 10^{-6}$	$5 \times 10^{-7}$
$E$	Jules/mol	57.74	57.74	50
$R^2$		0.7444	0.8326	0.8643

The optimization of full-scale batch adsorption process requires adsorption kinetics model. Experimental data has been employed for biosorption kinetics modelling (Figure 5a, 5b and 5c). Pseudo second order reaction kinetics model shows the best adoptability of the experimental data than pseudo first order and intraparticle diffusion kinetics model. The kinetic model parameters, rate constants and regression coefficients has been computed and tabulated (Table 5). From Figure 15, it can be noted that none of the isothermline pass through the origin, So, it is clear that there is involvement of other mechanisms. Intraparticle diffusion can't be considered the only rate limiting step in the biosorption of MB on RSP, RSP-ASW and RSP-SDT[41].

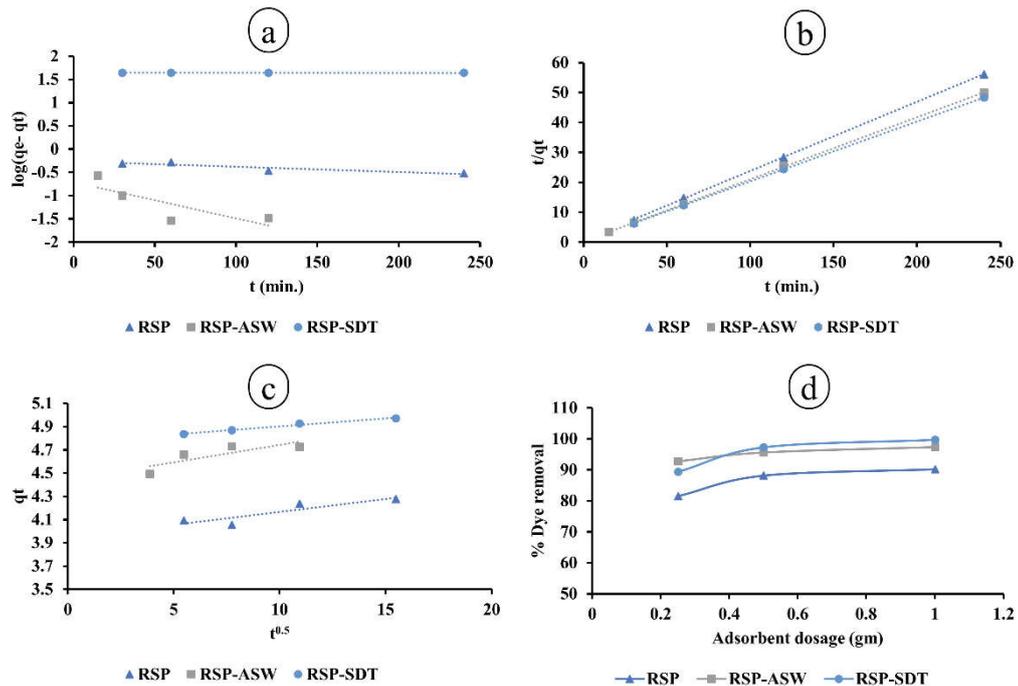


Figure 5. Kinetics Models for the Biosorption of MB dye from aqueous solution (a= PFO ,b= PSO, and c= IPD), Effect of Adsorbent Dosage on MB Dye Removal(d).

Table 5. Kinetic model parameters of MB adsorption by biosorbents.

Parameter	Unit	RSP	RSP-ASW	RSP-SDT
<i>Pseudo First Order kinetics model</i>				
$q_e$	mg/gm	7.661	0.492	5.176
$K_1$	$\text{min}^{-1}$	0.0011	0.0078	0.000006
$R^2$		0.8202	0.6366	0.9334
<i>Pseudo Second Order Kinetics model</i>				
$q_e$	mg/gm	4.323	4.826	4.995
$K_2$	$\text{mg} \cdot \text{gm}^{-1} \cdot \text{min}^{-1}$	0.0863	0.153	0.147
$R^2$		0.9999	0.9999	1
<i>Intraparticle Diffusion model</i>				
$K_i$	$\text{mg} \cdot \text{gm}^{-1} \cdot \text{min}^{-1/2}$	0.0223	0.0298	0.0137

C	mg/gm	3.944	4.4434	4.7642
R <sup>2</sup>		0.8026	0.6716	0.981

## Conclusion

Batch biosorption experiments were performed for methylene blue dye removal from aqueous solutions by rice straw and surface modified rice straw (RSP-ASW and RSP-SDT). The experimental result suggests that the surface modification of RSP increases the MB adsorption capacities in order of RSP-SDT > RSP-ASW > RSP. Langmuir isotherm model was found to be best fit from the equilibrium studies. The calculated adsorption capacity was found to be a maximum of 72.46mg/gm (RSP), 156.32mg/gm (RSP-ASW) and 181.81mg/gm (RSP-SDT). Biosorption kinetics can be explained by the pseudo second order kinetics model ( $R^2 > 0.99$ ). In a broad view, this preliminary investigations on the agroindustrial solid waste management coupled with wastewater treatment shows a sustainable approach to mitigate pollution.

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## References

- [1] M. H. Ramage *et al.*, "The wood from the trees: The use of timber in construction," *Renewable and Sustainable Energy Reviews*. 2017.
- [2] M. Ioelovich, "Recent findings and the energetic potential of plant biomass as a renewable source of biofuels - A review," *BioResources*. 2015.
- [3] S. V. Durgananda Singh Chaudhary, †, H.-H. Ngo, and W. G. S. and H. Moon\*, "Biofilter in Water and Wastewater Treatment," *Korean J. Chem.Eng.*, pp. 1054–1065, 2003.
- [4] S. De Gisi, G. Lofrano, M. Grassi, and M. Nocarnicola, "Charecterisitcs and adsorption capsities of low cost sorbents for waste water treatments: A review," *Sustain. Mater. Technol.*, pp. 10–40, 2016.
- [5] K. Keegstra, "Future Perspectives in Plant Biology Plant Cell Walls 1."
- [6] X. Li and C. Chapple, "Understanding Lignification: Challenges Beyond Monolignol Biosynthesis," *PLANT Physiol.*, vol. 154, pp. 449–452, 2010.
- [7] I. Sorensen, D. Domozych, and W. G. T. Willats, "How Have Plant Cell Walls Evolved?," *PLANT Physiol.*, 2010.
- [8] Y. M. Oh *et al.*, "Distinctive Bacterial Communities in the Rhizoplane of Four Tropical Tree Species," *Microb. Ecol.*, 2012.
- [9] Z. A. Popper, "Evolution and diversity of green plant cell walls," *Current Opinion in Plant Biology*. 2008.
- [10] "Approved by the World Agricultural Outlook Board," 2018.
- [11] P. K. Sath, S. Duhan, and J. S. Duhan, "Agro-industrial wastes and their utilization using solid state fermentation: a review," *Bioresources and Bioprocessing*. 2018.
- [12] R. Lantin, "RICE: Post harvest operations," 1999.
- [13] A. Bhatia and G. H. S, "Crop Residues Management with Conservation Agriculture: Potential, Constraints and Policy Needs," 2012.
- [14] D. R. . Patil, "Post Harvest technology of rice."
- [15] A. Dobermann and T. H. Fairhurst, "Rice Straw Management," 2002.

- [16] N. T. Kim Oanh *et al.*, "Particulate air pollution in six Asian cities: Spatial and temporal distributions, and associated sources," *Atmos. Environ.*, 2006.
- [17] M. Mohanty, "Rice residue-management options and effects on soil properties and crop productivity Climate Change effects on crops and cropping systems of central India: Carbon modelling and conservation agriculture View project CA-CRP; Hydrogels in water management in ."
- [18] G. Engling, J. J. Lee, Y. W. Tsai, S. C. C. Lung, C. C. K. Chou, and C. Y. Chan, "Size-resolved anhydrosugar composition in smoke aerosol from controlled field burning of rice straw," *Aerosol Sci. Technol.*, 2009.
- [19] A. Z. Oo *et al.*, "Methane and nitrous oxide emissions from conventional and modified rice cultivation systems in South India," *Agric. Ecosyst. Environ.*, 2018.
- [20] R. Kant, P. Bhatt, and A. Rani, "Textile dyeing and printing industry: An environmental hazard," *Asian Dye.*, 2013.
- [21] W. Herbst and K. Hunger, "22," *Ind. Org. Pigment. third Ed.*
- [22] A. Shitu, "Removal of Methylene Blue Using Low Cost Adsorbent: A Review," 2014.
- [23] B. Volesky, "Biosorption and me," *Water Research.* 2007.
- [24] G. M. Gadd, "Biosorption: Critical review of scientific rationale, environmental importance and significance for pollution treatment," *Journal of Chemical Technology and Biotechnology.* 2009.
- [25] M. Tsezos, "Biosorption of metals. The experience accumulated and the outlook for technology development," *Hydrometallurgy*, 2001.
- [26] Y. Liu and Y. J. Liu, "Biosorption isotherms, kinetics and thermodynamics," *Separation and Purification Technology.* 2008.
- [27] M. K. Dahri, L. B. L. Lim, M. R. R. Kooh, and C. M. Chan, "Adsorption of brilliant green from aqueous solution by unmodified and chemically modified Tarap (*Artocarpus odoratissimus*) peel," *Int. J. Environ. Sci. Technol.*, 2017.
- [28] S. G. Prabhu, G. Srinikethan, and S. Hegde, "Surface treated *Pteris vittata* L. pinnae powder used as an efficient biosorbent of Pb(II), Cd(II), and Cr(VI) from aqueous solution," *Int. J. Phytoremediation*, 2018.
- [29] T. D. Šoštarić *et al.*, "Study of heavy metals biosorption on native and alkali-treated apricot shells and its application in wastewater treatment," *J. Mol. Liq.*, 2018.
- [30] M. Bounaas *et al.*, "High efficiency of methylene blue removal using a novel low-cost acid treated forest wastes, *Cupressus semperirens* cones: Experimental results and modeling," *Particulate Science and Technology*, 2018.
- [31] D. S. P. Franco, E. H. Tanabe, and G. L. Dotto, "Continuous Adsorption of a Cationic Dye on Surface Modified Rice Husk: Statistical Optimization and Dynamic Models," *Chem. Eng. Commun.*, 2017.
- [32] S. Chowdhury, R. Mishra, P. Saha, and P. Kushwaha, "Adsorption thermodynamics, kinetics and isosteric heat of adsorption of malachite green onto chemically modified rice husk," *Desalination*, 2011.
- [33] "IARC MONOGRAPHS-108 156 1.1.3 Chemical and physical properties of the pure substance."
- [34] H. Singh, K. Sapra, and B. S. Sidhu, "Evaluation and Characterization of Different Biomass Residues through Proximate & Ultimate Analysis and Heating Value."
- [35] A. International and files indexed by mero, "Standard Test Method for Ash in Wood 1."
- [36] A. International and files indexed by mero, "Standard Test Method for Volatile Matter

- in the Analysis of Particulate Wood Fuels 1.”
- [37] E. N. Bakatula, D. Richard, C. M. Neculita, and G. J. Zagury, “Determination of point of zero charge of natural organic materials,” *Environ. Sci. Pollut. Res.*, 2018.
- [38] irvin langmuir, “Constitution and fundamental properties of solods and liquids,” 1916.
- [39] A. Mittal, L. Kurup, and J. Mittal, “Freundlich and Langmuir adsorption isotherms and kinetics for the removal of Tartrazine from aqueous solutions using hen feathers,” *J. Hazard. Mater.*, 2007.
- [40] B. H. H. K.Y. Foo, “Insights into the modeling of adsorption isotherm systems,” *Chem. Eng. J. J.*, pp. 2–10, 2010.
- [41] T. M. Elmorsi, “Equilibrium Isotherms and Kinetic Studies of Removal of Methylene Blue Dye by Adsorption onto Miswak Leaves as a Natural Adsorbent,” *J. Environ. Prot. (Irvine, Calif.)*, 2011.
- [42] E. R. García, R. L. Medina, M. M. Lozano, I. H. Pérez, M. J. Valero, and A. M. M. Franco, “Adsorption of azo-dye Orange II from aqueous solutions Using a metal-organic framework material: Iron-benzenetricarboxylate,” *Materials (Basel)*, 2014.
- [43] Y. S. Ho and G. Mckay, “A COMPARISON OF CHEMISORPTION KINETIC MODELS APPLIED TO POLLUTANT REMOVAL ON VARIOUS SORBENTS.”
- [44] Y. S. Ho and G. McKay, “Pseudo-second order model for sorption processes,” *Process Biochem.*, 1999.
- [45] V. V. and K. Vasanth Kumar, “46,” *J. Colloid. interface Sci.*, 2005.
- [46] T. C. Hsu, G. L. Guo, W. H. Chen, and W. S. Hwang, “Effect of dilute acid pretreatment of rice straw on structural properties and enzymatic hydrolysis,” *Bioresour. Technol.*, 2010.
- [47] S. H. Lee, T. V. Doherty, R. J. Linhardt, and J. S. Dordick, “Ionic liquid-mediated selective extraction of lignin from wood leading to enhanced enzymatic cellulose hydrolysis,” *Biotechnol. Bioeng.*, 2009.
- [48] T. N. Ang, G. C. Ngoh, A. S. M. Chua, and M. G. Lee, “Elucidation of the effect of ionic liquid pretreatment on rice husk via structural analyses,” *Biotechnol. Biofuels*, 2012.
- [49] N. Poornejad, K. Karimi, and T. Behzad, “Ionic Liquid Pretreatment of Rice Straw to Enhance Saccharification and Bioethanol Production,” *J. Biomass to Biofuel*, 2014.
- [50] L. S. Oliveira, A. S. Franca, T. M. Alves, and S. D. F. Rocha, “Evaluation of untreated coffee husks as potential biosorbents for treatment of dye contaminated waters,” *J. Hazard. Mater.*, 2008.
- [51] J. J. Salazar-Rabago, R. Leyva-Ramos, J. Rivera-Utrilla, R. Ocampo-Perez, and F. J. Cerino-Cordova, “Biosorption mechanism of Methylene Blue from aqueous solution onto White Pine (*Pinus durangensis*) sawdust: Effect of operating conditions,” *Sustain. Environ. Res.*, 2017.
- [52] N. Ahalya, “53,” pp. s189–s192, 2012.
- [53] C. Namasivayam, N. Muniasamy, K. Gayatri, M. Rani, and K. Ranganathan, “Removal of dyes from aqueous solutions by cellulosic waste orange peel,” *Bioresour. Technol.*, 1996.
- [54] E. O. Oyelude, F. Frimpong, and D. Dawson, “Studies on the removal of basic fuchsin dye from aqueous solution by HCl treated malted sorghum mash,” *J. Mater. Environ. Sci.*, 2015.