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Abatement of Textile Dyes Using Surfactant Modified Adsorbent from Agricultural Waste Sawdust

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Abstract

The increased adsorption of anionic dyes on agricultural residues, such as sawdust and sawdust treated with cationic surfactant, presents an intriguing occurrence within the realm of surfactant- driven environmental technology. This research investigates into the efficacy of sawdust (SD) and surfactant modified sawdust as adsorbents for the removal of anionic dyes such as acid orange-2 (AO) from aqueous solutions. Surfactant treated sawdust samples were prepared by treating sawdust with cationic surfactant having different length of alkyl group such as tetra ethyl ammonium bromide (TEAB), hexa decyl ammonium bromide (CTAB). The adsorption of acidic dyes demonstrated a substantial improvement following surfactant treatment and also the chain lengths of alkyl group in surfactant have synergistic effect on adsorption process. The pH level was observed to significantly impact the adsorption process, with the optimal pH for acidic dye adsorption falling within the 2-3 range. Adsorption mechanism and useful insights of the process was carried out by applying the Langmuir and Freundlich adsorption isotherm frameworks. The results suggested that modified sawdust with surfactants has the potential to function as an economical adsorbent in the removal of acid dyes.

Keywords: *Anionic Dyes Adsorption; Agricultural Waste; Surfactant Modified Sawdust; Wastewater Treatment;*

1. Introduction

Introduction of dyes and pigments into the ecosystem constitute a significant source of aesthetic pollution and disturbance to aquatic life. Due to their chemical composition, dyes resist light, oxidizing agents, and heat, they are biologically non-degradable (Husain Q et.al 2006). Dyes may be classified as cationic, anionic, and non-ionic. Additionally, they possess mutagenic and carcinogenic properties, contributing to severe health issues such as kidney dysfunction, reproductive system disorders, liver complications, and central nervous system damage (Bruno Lellis et al., 2014, Khatri et al., 2018) It is of paramount significance to remove dyes from wastewater effluent in order to uphold sustainability through the application of physical, chemical, and biological methodologies, either individually or in conjunction (Kapoor et al 2021, Mahalakshmi et al.2019). Due to economic considerations, Conventional wastewater treatment methods, including coagulation ultrafiltration, ozonation, sedimentation, reverse osmosis, and flotation, face challenges in effectively treating wastewater (Veli et al 2006). Adsorption has advantage over other wastewater treatment technique due to its cost-effectiveness, high efficiency,

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simplicity, ease of implementation, and insensitivity to toxic substances (Sahoo et al 2020, Amalina et al 2022,). Although activated carbon is widely used for effluent treatment, its extensive application in water and wastewater industries comes at a significant cost (Sh Husien et al 2022). Agricultural waste materials have gained importance, often deemed of little or no economic value and posing disposal challenges. Various agricultural waste materials including sawdust have been investigated for their efficacy in removing different dyes from aqueous solutions (Namasivayam et al 2002, M. Nasrullah. 2019). Earlier studies have used sawdust as an effective adsorbent for the removal of various pollutants including dyes from wastewater (Kayode et al 2022, Sunil Bajpai et al 2012). Nevertheless, exploring the adsorption of anionic dyes on sawdust in aqueous solutions remains limited due to low adsorption capacity for acidic dyes (Najeeb ur Rahman et al 2021). In this study, we delved into the efficacy of sawdust and surface-treated sawdust in removing anionic dyes such as acid orange 2 through adsorption. Acid Orange-2 (AO-2) is a sulfonated azo dye commonly utilized in commercial applications and has served as a prominent model compound for research for the removal study of azo dyes. The study explored the effect of surfactant chain length on the adsorption of dyes by surfactant modified sawdust. The influence of initial concentration, temperature, and pH on the adsorption of dyes by both sawdust and surfactant-treated sawdust was also examined. Two models for the equilibrium data, the Langmuir and Freundlich isotherm equations, were employed.

2. Materials and Methods

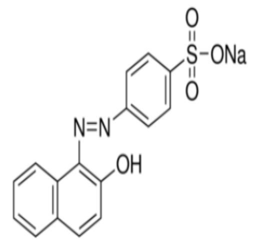
2.1.Adsorbent

The primary source to obtain sawdusts was from local saw mill. To eliminate water soluble contaminants, the sawdusts were soaked in distilled water for 72 hours and then washed repeatedly with water. It is next sieved with ASTM standard sieves 100 mesh to get sawdust of particle size ≤150 µm. The treated materials were dried using hot air oven at <80^{0}C for at least 2 hour to get sawdust with 10 % moisture. Tetra ethyl ammonium bromide (TEAB), Cetyl trimethyl ammonium bromide (CTAB) used for modification of sawdust was purchased from S. D Fine Chemicals, India [1-3].

2.2.Adsorbate

The acid dyes acid orange-2 (AO-2), provided by Clariant Chemicals, India, were used in the adsorption studies [4]. The dyes identification information and molecular weights are depicted in Table 1 [5].

Table 1 Characteristics of Acid Orange 2

Molecular Formula	$C_{16}H_{11}N_2NaO_4S$ (sodium salt)
Molar Mass	350.32 g/mol
CAS Number	633-96-5
Chemical Structure	

2.3.Methods

2.3.1. Surface Modification of Sawdust with Cationic Surfactant

15 g of sawdust was treated with 500 ml of 0.02 M (cation exchange capacity (CEC) of tetra ethyl ammonium bromide (TEAB) and hexa decyl trimethyl ammonium bromide (CTAB) surfactant solution of sawdust in a 1000 ml flask and it was agitated for eight hours [6-9]. It was then washed with distilled water repeatedly until it was free from chloride ion in the filtrate as indicated by a precipitation test with $AgNO_3$.It is dried at <80^{0}C for at least 2 hour and stored in air tight container. The surfactant treated sawdust with two surfactant used TEAB, CTAB are represented as TEA SD and CTA SD respectively [10-13].

2.3.2. Adsorption Studies

A batch adsorption procedure was conducted to evaluate the effects of initial adsorbent dose, dye concentration, pH, temperature, and contact time. In this experiment, 0.05 g of adsorbent was mixed with 50 ml of dye solution in an Erlenmeyer flask at room temperature. To investigate the influence of each parameter, one parameter was varied while keeping

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the others constant at their optimal conditions: pH 7.0, agitation speed of 150 rpm, contact time of 120 minutes, and dye concentration of 200 mg/L. After adsorption, the solutions were centrifuged, and the absorbance of the supernatant was measured at the maximum wavelength (λmax) to determine the dye content. The amount of dye adsorbed (q) was calculated using a mass balance equation.

$$q = (Co - Ce)\, v/m$$

Where Co and Ce are the initial and equilibrium concentration of dye in the solution respectively (mg/L), V is the volume of solution (L), m (g) is the mass of adsorbent used [14].

2.3.3. Characterization Methods

The elemental analysis, surface morphology study by scanning electron microscopy, and FT-IR study of sawdust and surfactant treated were determined by sophisticated instrumental facility IIT Bombay, Mumbai India. The cationic exchange capacity (CEC) and anion exchange capacity (AEC) of the prepared sawdust (Maria Jokova et al 1997). The zeta potential study for point of zero charge was carried out by zeta meter at institute of chemical technology (ICT), Mumbai, India [15].

3. Results and Discussion

3.1. Characterization of the Adsorbents

The characteristics of the adsorbents used are provided in Table 2. The point of zero charge (pHpzc) was determined to be 5.5, meaning that at pH values above 5.5, the surface of the sawdust will carry a negative charge, and at pH values below 5.5, it will carry a positive charge [16-18].

Table 2 Characterization Results for Sawdust

Percent Volatile Matter	12.5
pH_{pzc}	5.5
Particle size	≤150 μm
BET surface area (m^2g^{-1})	2.5
pH (1% suspension)	6.5
% Carbon	52
% Nitrogen	2.2
% Oxygen	6.8

3.2. Scanning Electron Microscopy (SEM) Study

Using SEM study the surface morphology of sawdust and surfactant treated sawdust were studied. The SEM micrographs of untreated sawdust and surfactant-treated sawdust are presented in Figure 1a and Figure 1b, respectively. The SEM image of the surfactant-treated sawdust distinctly exhibits a smooth porous structure, revealing coating of surfactant molecule on the sawdust surface. This could be also confirmed by increase in surface area of surfactant treated sawdust 2.95 m^2g^{-1} in BET surface area measurement which provides a high surface area and adsorption capacity for the adsorption of dye [19].

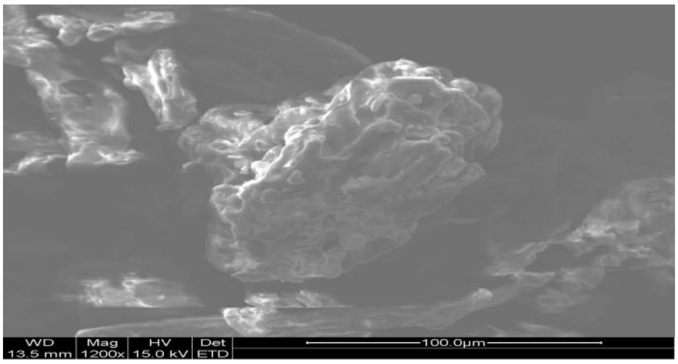

Figure 1(a) SEM Image of Sawdust

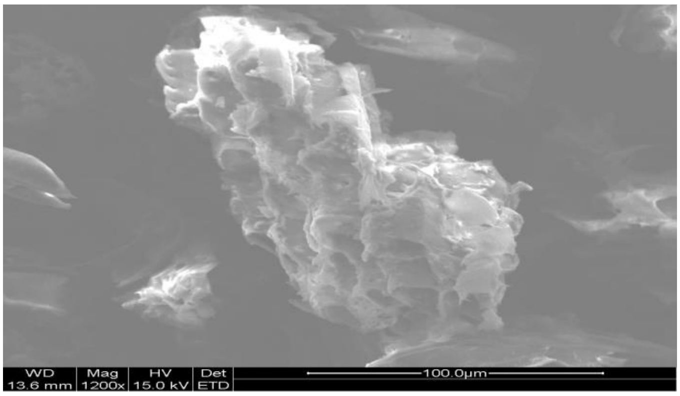

Figure 1(b) SEM Image of Surfactant Treated Sawdust

3.3. FTIR Analysis

To obtain corroborative evidence of the modification of sawdust through surfactant treatment, FT-IR spectra were analyzed within the range of 400-4000 cm^{-1}. Figure 2 illustrates the FT-IR spectra for both untreated and surfactant-modified sawdust. The band

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in the 3300 to 3400 cm^{-1} region indicates –OH stretching, while the band around 1650 cm^{-1} corresponds to H-O-H bending. Additionally, beyond the intrinsic signals of the materials, the modified sorbents display bands in the 2853-2934 cm^{-1} range, attributed to the C−H stretching vibrations from the long alkyl chains in the surfactant molecules. These findings clearly indicate that the surfactant has been adsorbed onto the sorbent surfaces. In addition to this strong absorption band around 1400 to 1500 cm^{-1} correspond to ammonium ion of surfactant molecule which shows the presence of surfactant (P.B Rai et.al 2008) [20].

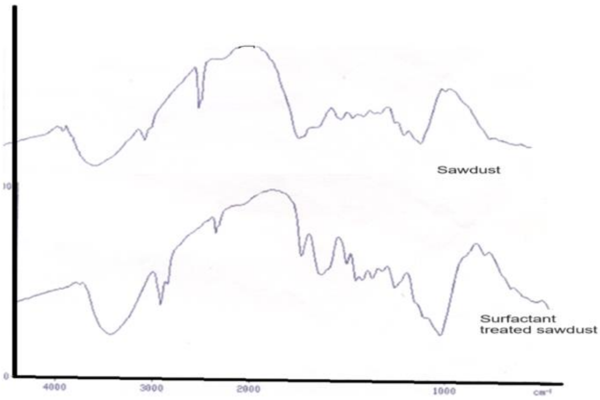

Figure 2 **FT-IR Spectra of Sawdust and Surfactant Treated Sawdust**

3.4.Impact of Initial Dye Concentration

The effect of initial dye concentration on the adsorption process using sawdust and surfactant-treated sawdust was examined through a batch study, with results presented in Figure 3. The study observed that dye removal efficiency increased as the dye concentration rose from 50 ppm to 200 ppm. However, beyond this concentration, the adsorption capacity reached a saturation point. Additionally, the amount of AO2 adsorbed on surfactant-treated sawdust showed that adsorption increased with the increase in chain length of the alkyl group present in the surfactant used for modification. This suggests that longer alkyl chains enhance the adsorption capacity of the treated sawdust. The lower adsorption of AO2 on the sawdust surface is attributed to electrostatic repulsion between the negatively charged sawdust surface and the anionic dye molecules. Conversely, the increased adsorption of dyes on surfactant-treated sawdust can be explained by hydrophobic interactions and the partitioning of dyes with the surfactant-treated sawdust. The higher adsorption observed with longer alkyl chain lengths in surfactants, from TEA SD to CTASD, can be attributed to the increased hydrophobicity of the adsorbent.

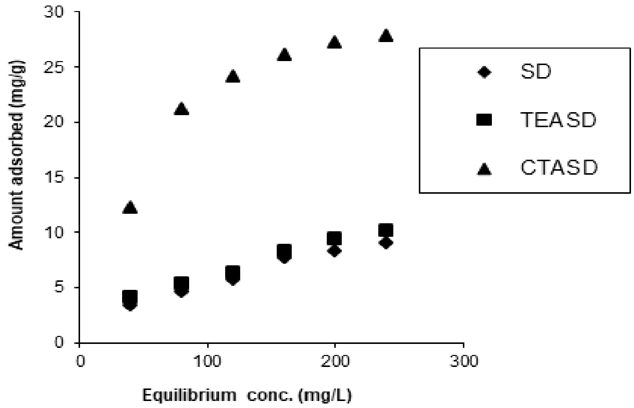

Figure 3 **Adsorption Equilibrium Study of AO2 On Sawdust and Surfactant Treated Sawdust**

3.5.Effect of pH

The solution's pH significantly impacts AO2 removal because it affects the charge on the adsorbent surfaces. Figure 4 shows the effect of pH on AO2 adsorption on both untreated and surfactant-treated sawdust. The point of zero charge (pHpzc) for sawdust is 5.5, meaning the sawdust surface will carry a net negative charge at pH values above this point.

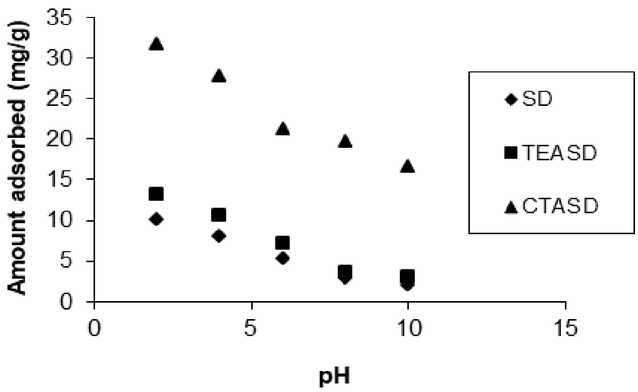

Figure 4 **Effect of pH on Adsorption of AO2 On Sawdust and Surfactant Treated Sawdust**

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The results indicate that AO2 removal by both untreated and surfactant-treated sawdust decreases as pH increases. At lower pH levels, the adsorbent surface has a net positive charge, which promotes the adsorption of negatively charged AO2 molecules through electrostatic attraction. Conversely, at pH levels above 5.5, the sawdust surface becomes negatively charged, causing electrostatic repulsion with AO2 molecules and thereby reducing adsorption capacity. However, surfactant-treated sawdust exhibits higher AO2 adsorption at higher pH levels. This increased adsorption is due to hydrophobic interactions between the adsorbent surface and the dye molecules, rather than ion-dipole or dipole-dipole interactions (Qian Li et al 2010).

3.6.Effect of Contact Time and Temperature

The effect of contact time on the adsorption of acid orange 2 onto sawdust and surfactant-treated sawdust was investigated and represented in Figures 4a and 4b. It can be seen that the rate of adsorption is highest within the first 45 minutes, suggesting a chemical adsorption process. After reaching equilibrium, no further dye removal was observed, indicating that additional treatment does not enhance adsorption. The primary factor influencing dye removal from aqueous solutions is the migration of dye molecules from the external surfaces to the internal sites of the adsorbent particles (. Maximum adsorption of acid dyes onto sawdust was observed at 80 minutes, beyond which there is no significant increase in adsorption. Temperature does not affect the equilibrium time.

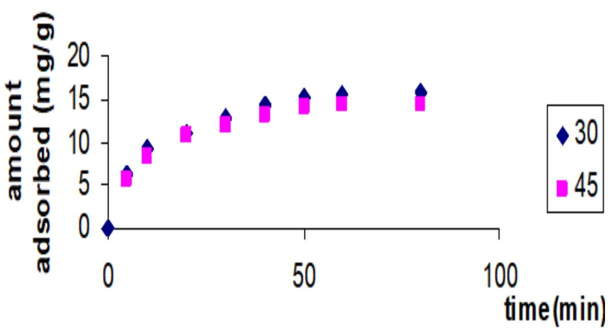

Figure 4(a) Effect of Contact Time and Temperature On Adsorption of AO2 On Sawdust

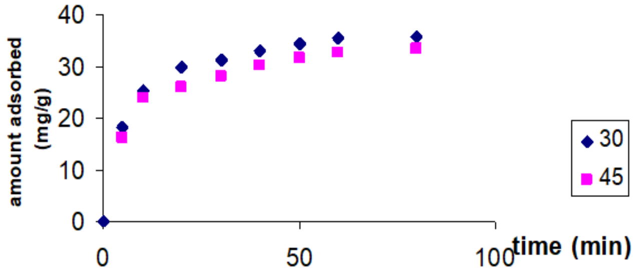

Figure 4(b) Effect of Contact Time and Temperature On Adsorption of AO2 on CTA SD

This phenomenon can be attributed to the increased mobility of dye molecules and the rise in the number of active sites for adsorption as the temperature increases. The decline in adsorption capacity with rising temperature suggests that the adsorption process is exothermic. This decrease in capacity is likely due to the weakening of adsorptive forces between the dye molecules and the active sites on the adsorbent surface as the temperature rises (Budnyak, T. M et al 2020). The effect of temperature on the adsorption isotherms of AO8 is clearly demonstrated, showing a substantial reduction in adsorption with increasing temperature.

3.7.Adsorption Isotherm Study

The equilibrium data for the adsorption of Acid Orange 2 dyes onto both sawdust and surfactant-treated sawdust were analyzed using the linear forms of the Langmuir and Freundlich isotherm equations (Langmuir, I. (1916), Freundlich, H.M.F. (1906)). The linear form of the Langmuir isotherm equation can be represented as

$$C_e/q_e = 1/Q_0 b + C_e/ Q_0$$

Where q_e is the equilibrium concentration of the adsorbate in the solid phase (mg/g), Ce is the equilibrium concentration of the adsorbate in the liquid phase (mg/L), and b are the Langmuir constants. The Freundlich isotherm equation is another widely used model in adsorption studies and is expressed as follows:

$$\ln q_e = \ln K_f + 1/n \ln C_e$$

Where, C_e is equilibrium concentration of the solute in solution (mg/L), q_e is amount adsorbed at

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equilibrium and K_f are constants for given adsorbate/adsorbent When C_e /q_e is plotted against C_e , a straight line is obtained with a slope of $1/Q_0$ and an intercept of $1/bQ_0$. As indicated in Table 1, the Langmuir adsorption isotherm model provided the best fit, shown by the highest R^2 values compared to the Freundlich isotherm.

Table 3 Freundlich and Langmuir Constant for Adsorption Isotherm

Langmuir constant				
Adsorbate	Adsorbent	Q_0 (mg/g)	b (L/mg)	R^2
Acid Orange 2	SD	15.15	0.006	0.985
	TEASD	18.86	0.005	0.988
	CTABSD	30.30	0.030	0.996
Freundlich constant				
Adsorbate	Adsorbent	K_f (mg/g)	1/n	R^2
Acid Orange 2	SD	0.457	0.542	0.925
	TEASD	0.537	0.510	0.936
	CTABSD	8.13	0.232	0.946

The results show (Table 3) that surfactant-treated sawdust has a relatively high adsorption capacity, suggesting it is a promising material for removing Acid Orange 2 dyes from aqueous solutions. The R^2 values, ranging from 0.98 to 0.998, confirm that the adsorption data for Acid Orange 2 on both untreated and surfactant-treated sawdust fit well with the Langmuir isotherm. The higher value of Q_0 for TEA SD and CTA SD for the removal of dyes confirms synergistic effect the effect of increase in chain length of alkyl group of surfactant used for the treatment of sawdust has on removal of dyes.

Conclusion

The present study demonstrated that sawdust can be effectively used as an adsorbent for removing Acid Orange 2 from aqueous solutions when modified with a cationic surfactant. The chain length of the alkyl group in the surfactant molecule plays a crucial role in enhancing the adsorption capacity of sawdust. Sawdust modified with long-chain quaternary ammonium cations, which have large alkyl groups, primarily exhibits hydrophobic characteristics and partition behavior. The results show that as the chain length of the cationic surfactant increases from TEA SD to CTA SD, the adsorption of dyes on sawdust also increases. The equilibrium data fit well with the Langmuir adsorption isotherm equation, indicating a higher adsorption capacity for surfactant-treated sawdust. Therefore, it can be concluded that surfactant-treated sawdust is an efficient adsorbent for the removal of anionic dyes.

References

[1]. Husain Q. Potential Applications of the Oxidoreductive Enzymes in the Decolorization and Detoxification of Textile and Other Synthetic Dyes from Polluted Water: A Review. Crit. Rev. Biotechnol. 2006;26:201–221. doi: 10.1080/07388550600969936.

[2]. Bruno Lellis, Címtia Zani Fávaro-Polonio, João Alencar Pamphile, Julio Cesar Polonio. (2019).Effects of textile dyes on health and the environment and bioremediation potential of living organisms, Biotechnology Research and Innovation3(2), 275-290, doi: 10.1016/j.biori.2019.09.001

[3]. Khatri, J., Nidheesh, P. v., Anantha Singh, T. S., & Suresh Kumar, M. (2018). Advanced oxidation processes based on zero-valent aluminium for treating textile wastewater. Chemical Engineering Journal, 348, 67–73. https://doi.org/10.1016/J.CEJ.2018.04.074

[4]. Kapoor, R. T., Danish, M., Singh, R. S., Rafatullah, M., & Abdul, A. K. (2021). Exploiting microbial biomass in treating azo dyes contaminated wastewater: Mechanism of degradation and factors affecting microbial efficiency. In Journal of Water Process

International Research Journal on Advanced Engineering and Management
https://goldncloudpublications.com
https://doi.org/10.47392/IRJAEM.2024.0280
e ISSN: 2584-2854
Volume: 02
Issue: 06 June 2024
Page No: 1885-1892

Engineering (43).doi.org/10.1016/j.jwpe.2021.102255

[5]. Mahalakshmi, M., & Saranaathan, S. E. (2019). Film-pore diffusion modeling for the adsorption of aqueous dye solution onto acid-treated sugarcane bagasse. Desalination and Water Treatment, 168, 324–339. https://doi.org/10.5004/dwt.2019.24645F Razak, S. Krishnan, A.W. Zularisam, M. Nas rullah Phys. Chem. Earth Parts A/B/C, 128 (2022), 103267, 10.1016/J.PCE.2022.103267

[6]. Veli, S., & Fatullayev, A. G. (n.d.). (2006) Application of Diffusion Model for Adsorption of Azo Reactive Dye on Pumice. Polish J. Environ. Stud. 15(2), 347-353/242079443

[7]. Sahoo, T. R., & Prelot, B. (2020). Adsorption processes for the removal of contaminants from wastewater: The perspective role of nanomaterials and nanotechnology. In Nanomaterials for the Detection and Removal of Wastewater Pollutants (pp. 161–222). Elsevier. doi.:10.1016/B978-0-12-818489-9.00007-4

[8]. Amalina, F., Razak, A. S. A., Krishnan, S., Sulaiman, H., Zularisam, A. W., & Nasrullah, M. (2022). Biochar production techniques utilizing biomass waste-derived materials and environmental applications – A review. In Journal of Hazardous Materials Advances (Vol. 7). Elsevier B.V. doi.: 10.1016/j.hazadv.2022.100134

[9]. Husien, S., El-taweel, R. M., Salim, A. I., Fahim, I. S., Said, L. A., & Radwan, A. G. (2022). Review of activated carbon adsorbent material for textile dyes removal: Preparation, and modelling. Current Research in Green and Sustainable Chemistry, 5, 100325. doi.:10.1016/J.CRGSC.2022.100325

[10]. C. Namasivayam, D. Kavitha (2002) Dyes and Pigments 54 , 47–58

[11]. M. Nasrullah. 2019 Chin. J. Chem. Eng., 27 (1) (2019), pp. 208-217, 10.1016/j.cjche.2018.07.021)

[12]. Adegoke, K. A., Adesina, O. O., Okon-Akan, O. A., Adegoke, O. R., Olabintan, A. B., Ajala, O. A., Olagoke, H., Maxakato, N. W., & Bello, O. S. (2022). Sawdust-biomass based materials for sequestration of organic and inorganic pollutants and potential for engineering applications. Current Research in Green and Sustainable Chemistry, 5, 100274. doi.:10.1016/J.CRGSC.2022.100274

[13]. Bajpai, S. K., Bajpai, M., & Rai, N. (2012). Sorptive removal of ciprofoxacin hydrochloride from simulated wastewater using sawdust: Kinetic study and effect of pH. Water SA, 38(5), 673–682. doi.:10.4314/wsa.v38i5.4

[14]. Rahman, N. U., Ullah, I., Alam, S., Khan, M. S., Shah, L. A., Zekker, I., Burlakovs, J., Kallistova, A., Pimenov, N., Vincevica-Gaile, Z., Jani, Y., & Zahoor, M. (2021). Activated ailanthus altissima sawdust as adsorbent for removal of acid yellow 29 from wastewater: Kinetics approach. Water, 13(15). doi.:10.3390/w13152136

[15]. Maria Jokova, Ognian Kostov, Ostawald Van Cleemput, Biological Agricultural and Horticultura,14(3):187-197 1997, 14(3), 187-197 10.1080/01448765.1997.9754809

[16]. P. B Rai, S.S. Banerjee, R V Jayaram, (2007), Removal of Disperse Dyes from Aqueous Solution Using Sawdust and BDTDA-Sawdust. Journal of Dispersion Science and Technology, 28, 1066–1071, doi:10.1080/01932690701524752

[17]. Qian Li a b, Qin-Yan Yue a, Hong-Jian Sun b, Yuan Su c, Bao-Yu Gao (2010) A comparative study on the properties, mechanisms and process designs for the adsorption of non-ionic or anionic dyes onto cationic-polymer/bentonite, Journal of Environmental Management 91(7), 1601-1611 doi:10.1016/j.jenvman.2010.03.001

[18]. Budnyak, T. M., Błachnio, M., Slabon, A., Jaworski, A., Tertykh, V. A., Deryło-Marczewska, A., & Marczewski, A. W. (2020). Chitosan Deposited onto Fumed Silica Surface as Sustainable Hybrid

e ISSN: 2584-2854
Volume: 02
Issue: 06 June 2024
Page No: 1885-1892

Biosorbent for Acid Orange 8 Dye Capture: Effect of Temperature in Adsorption Equilibrium and Kinetics. Journal of Physical Chemistry C, 124(28), 15312–15323. doi.:10.1021/acs.jpcc.0c04205

[19]. Langmuir, I. (1916) The constitution and fundamental properties of solid and liquid. J. Am. Chem. Soc., 38 (11): 2221– 2295

[20]. Freundlich, H.M.F. (1906) Uber die adsorption losungen zets chrift fur physikalische chemie. J. Phys. Chem., 57: 385– 47