Chemical Engineering Research Bulletin 24 (2024) 95-104
Available online at http://banglajol.info/index.php/CERB
DOI: https://doi.org/10.3329/cerb.v24i1.78489

Competitive Adsorption of Crystal Violet and Safranin onto Black Tea Waste for Wastewater Treatment

Sagar Das Gupta*, Masum Ahmed, Md. Akhtarul Islam

Department of Chemical Engineering and Polymer Science, Shahjalal University of Science and Technology, Kumargaon, Sylhet-3114, Bangladesh

*Correspondance: sagardasgupta99@gmail.com

Abstract

Black tea waste (BTW) has been studied as a low-cost adsorbent for the removal of a binary mixture of dyes (Crystal Violet (CV) & Safranin (SF)) from an aqueous solution by batch adsorption mode. The study has been performed at 25°C. Adsorption isotherm has been determined separately for CV and SF. Langmuir isotherm fits very well with experimental data for both SF and CR with R2 value, 0.999. The Langmuir parameters are determined for individual dyes. The maximum adsorption capacities of BTW for CV and SF in a single solution system are found to be 147.06 mg/g and 128.20 mg/g respectively. Equilibrium adsorption for the binary mixture of dyes is analyzed by extended Langmuir model, and this model is found to describe the adsorption behavior of the binary mixture satisfactorily. The adsorbent is characterized by Brunauer-Emmett-Teller (BET) analysis which gives an external surface area of 3.0744 m2/g.

Keywords: Black tea waste, Crystal Violet, Safranin, Single isotherm, Binary isotherm.

1. Introduction

Most industries throughout the world utilize copious amounts of dyes to color their products. During the dyeing process, a portion of the dyes cannot bind with the textiles and continuously produces waste coloring components [1]. These industries release between 10 and 15 percent of all effluents [2]. As a result, dyes prevent sunlight from penetrating the water, which could eventually reduce the stream's quality of life [3]. Additionally, dyes have been found to have significant genotoxic and carcinogenetic impacts on our lives [4]. SF and CV dyes are both cationic salts in nature. They have been used for coloring, as well as other things like staining, detecting microorganisms and membrane potentials, food packaging, etc., particularly in the textile sector [5]. SF and CV have complicated structures, and their long-term stability provides challenges for biodegradation [6]. These colors have the ability to mutate and carcinogenically destroy the nucleic acids of microorganisms. In order to maintain environmental sustainability, it is important to conduct research on their elimination. It is difficult to remove dyes from effluents or aqueous solutions using microorganisms [7]. SF and CV dye exposure, whether short-term or long-term, may result in several negative health effects, including itching and redness of the skin as well as irritation of the eyes, lips, tongue, and stomach.

Nausea, vomiting, and diarrhea are additional effects of exposure to these dyes [8]. Wastewater treatment techniques such as membrane filtration, coagulation, and precipitation, oxidation with ozone, advanced oxidation processes with H2O2/UV and H2O2/Fe2+, enzymatic degradation, adsorption, etc. are used to remove toxins. However, these techniques are very expensive to use and produce a significant amount of harmful sludges [9,10]. An advantageous alternative approach for the adsorption of agricultural waste exists [11-13]. In the present study, an experimental investigation has been conducted to remove SF and CV from an aqueous medium using black tea waste.

Tea leaves, a biomass material have attracted the attention of researchers for their high sorption capability, low-cost, and straightforwardness in recovering the adsorbate from tea leaves [14]. In the present work, batch sorption experiments were performed on black tea waste for the removal of CV and SF from their solution and the Langmuir parameters obtained from the equilibrium study of a single dye were utilized to predict the binary sorption behavior of the dyes.

2. Materials

2.1 Black Tea waste

Fresh tea leaves are collected from a local shop. They were boiled in distilled water for 72 hours to extract all the colored ingredients, such as caffeine, catechins, and theanine. Then the tea waste was washed with distilled water several times and subsequently dried in an oven at 105°C for two days so that the moisture can be removed totally from the adsorbent. With a grinding machine, the dried mass (adsorbent) was crushed and sieved in a sieve shaker to get particles with particular size of around 0.25 nm. The adsorbent was then kept in a tightly closed plastic container.

2.2 Dyes

Safranin (MW: 350.85 g/mol) is a water-soluble cationic dye widely used in textile, paper, and pharmaceutical industries.

Crystal Violet (MW: 407.97 g/mol) is a cationic water-soluble dye and is widely used as a textile and paper dye. It is sometimes used to colorize diverse products such as fertilizers, anti-freeze, detergent, and leather. Both the dyes were collected from a local market and used as obtained without purification.

3. Methodology

3.1 Preparation of dyes solutions

Two stock solutions of SF and CV were prepared by dissolving 0.1 g dye in 1L doubled distilled water. Desired concentration of working solutions were achieved by dilution. The pH of the solution is adjusted to the required value with the addition of 0.1 N HCl and 0.1 N NaOH solutions dropwise.

3.2 Study of batch adsorption isotherm for single dyes

Equilibrium studies for single dyes (CV & SF) were carried out by contacting tea waste with 200 ml of dye solution of different initial concentrations (30, 40, 50, 100, 150, 200, 250, &300 mg/L) in 250 ml stopper conical flasks. The samples were then shaken at a constant oscillation of 400 osc/min for 4 h. After equilibrium, the samples were centrifuged at 4000 rpm/min for 30 minutes for the dispersed particles of adsorbent to settle down and the concentration in the supernatant solution was analyzed. Each experiment was duplicated under identical conditions. The amount of adsorption at equilibrium qe (mg/g) was calculated by the following equations:

$$q_e = \frac{V(C_0 - C_e)}{W} \quad (1)$$

Where, Co and Ce (mg/L) are the liquid-phase concentrations of the dye initially and at equilibrium, respectively. V is the volume of the solution (L) and W is the mass of the dry adsorbent used (g).

3.3 Study of batch adsorption isotherm for a mixture of dyes

Equilibrium studies for a mixture of dyes (CV & SF) were carried out by contacting 0.2 g tea waste with 200 ml of dye solution having different ratios of initial concentrations (3:1, 2:1, 3:2 and 4:3 in mg/L) of CV and SF respectively in 250 ml stopper conical flasks. The procedure is the same as that of the adsorption study with single dye solution described in the previous section.

4. Results and Discussions

4.1 Determination of λ_{max} of absorption

Figures 1, 2, and 3 show absorbance vs wavelength relation for SF, CV, and their binary mixture in the λ-range of 400-700nm.

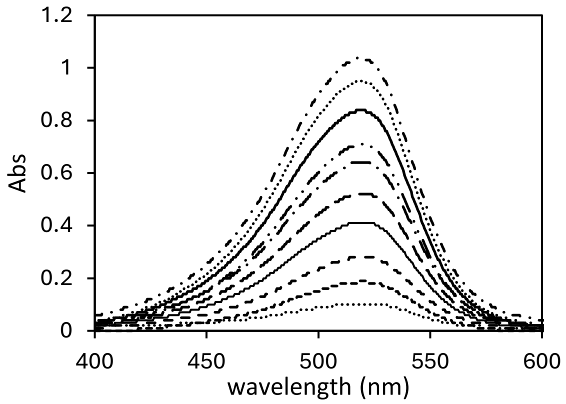

Figure 1: Absorption vs wavelength relation for SF in the concentration range of 1- 10 mg/L arranged in the order 'from bottom to top'

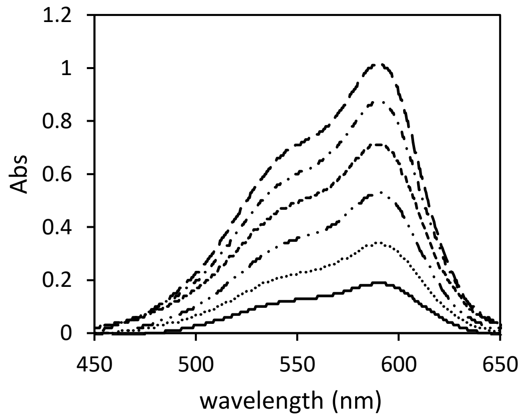

Figure 2: Absorption vs wavelength relation for CV in the concentration range of 1-6 mg/L arranged in the order 'from bottom to top'

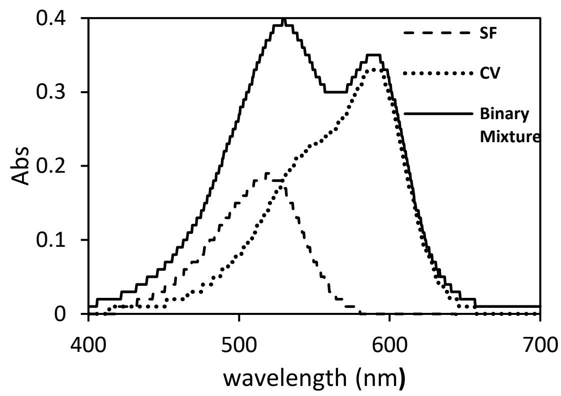

Figure 3: Absorption vs wavelength relation for single and binary mixture of SF and CV with each at 2 mg/L

Figure 1 represents absorbance vs wavelength for Safranin at different concentrations. As seen in the figure, the highest response is observed at 519.5 which is the characteristic wavelength (λ_{max}) of safranin. Similarly, in Fig 2, the maximum absorbance peak (λ_{max}) is observed at 590 nm. Figure 3 shows two distinct peaks at 519.5 nm and 590 nm for the binary mixture. It is also observed that while at 590 nm, SF shows insignificant absorbance, at 519.5 nm the response of CV is high enough to be counted along with that of the SF. The absorbance of the two dyes is additive in binary mixture.

4.2 Calibration curve for SF and CV

Figure 4, presents the concentration calibration plot for Safranin at λ_1 =519.5 nm and those of CV at λ_1 =519.5 and λ_2 =590 nm. The absorbance coefficient of SF at 519.5 is k_{11}= 0.1034, while those of CV at 519.5 and 590 are k_{12} =0.0745 and k_{22}= 0.1717, respectively. As was seen in Figure 3 earlier, the absorbance of SF at 590 nm was negligible, and for that reason, concentration plot of SF at 590 nm is missing in Figure 4, and the corresponding absorbance coefficient k_{21}=0.

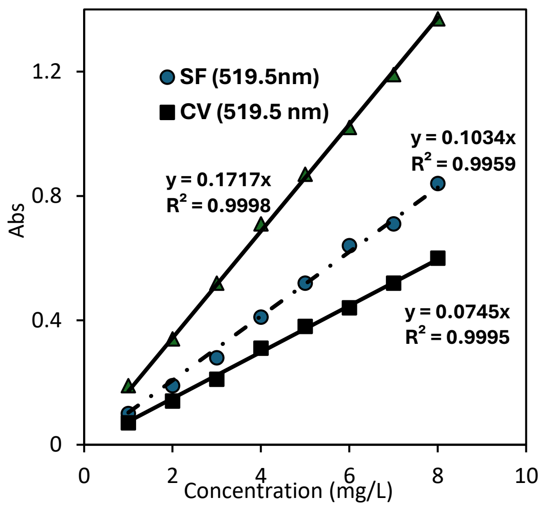

Figure 4: Calibration curve for SF at 519.5 nm, and those of CV dyes at 519.5 nm & 590 nm

4.3 Adsorption isotherm for SF & CV in single solution

Figure 5 shows that qe increases with an increase in Ce up to 100 ppm of SF due to adequate number of free available active sites on the adsorbent surface. Beyond this equilibrium concentration, the equilibrium adsorption density of the adsorbent approaches a limited value demonstrating that the surface is becoming gradually saturated with the dye.

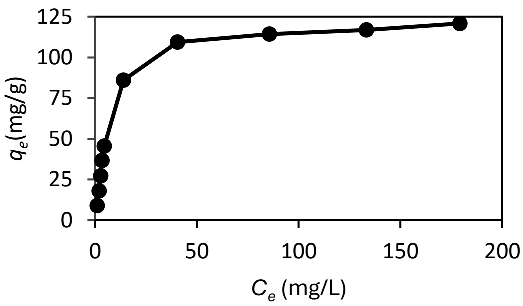

Figure 5: Adsorption isotherm for SF

Fig 6 shows similar behavior of the isotherm for CV. qe increases with an increase in dye equilibrium concentration up to 60 ppm and then gradually approaches to a limiting value.

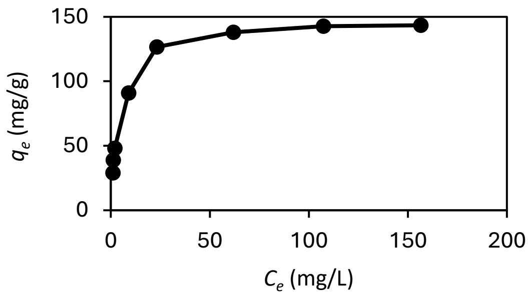

Figure 6: Adsorption isotherm for CV

4.4 Langmuir isotherm model

The Langmuir isotherm model assumes that once an adsorption site is occupied by a molecule of dye, no further molecule can be adsorbed at that site [15] indicating maximum of dyes on the (BTW) surface is achieved when the surface becomes saturated. The Langmuir isotherm model is expressed as [16]

$$q_e = q_{max} \frac{K_L C_e}{1 + K_L C_e} \tag{2}$$

In linearized form, the model assumes the form as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \tag{3}$$

Where, K_L (L/mg) and q_{max} (mg/g adsorbent) are Langmuir constants. The slope and intercept of a C_e/q_e vs. C_e plot Eq. (3) will give the fitted values of the parameters.

The adsorption data from the Figures 5 & 6 have been fitted to the Eq. (3) in Figures 7 & 8. As seen in the Figures 7 & 8, the Langmuir model excellently describes the adsorption data of SF and CV independently.

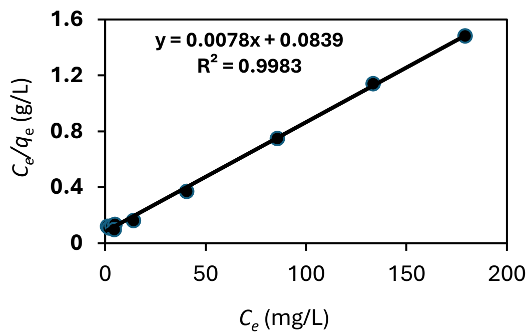

Figure 7: SF adsorption data fitted Langmuir model in linearized form (Eq. (3))

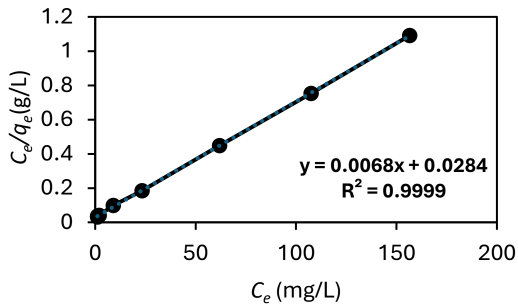

Figure 8: CV adsorption data fitted Langmuir model in linearized form (Eq. (3))

Table 1: Langmuir parameters of BTW for Safranin and Crystal Violet

Dyes	Parameters		
	q_{max} (mg/g)	K_L(L/mg)	R^2
Safranin	128.20	0.093	0.9983
Crystal Violet	147.06	0.28	0.9996

5. Determination of dye concentration in multi-component solution

UV-spectrophotometer method is the common procedure for determination of the dye concentration in their mixture. To achieve that, a linear relation between absorbance (A) and concentration of dye (C) (mg/L) which was given by Beer-Lambert law in (5) was applied [17].

$$A=KC \tag{5}$$

Where A is the absorbance of light at the wavelength, λ_{max}, of maximum response; K is the absorbance coefficient; and C is the concentration of the dye in solution (mg/L).

For binary mixture, the total absorbance A_1 at λ_{1max} of dye 1 will be the sum of the absorbance of the individual dye components, CV and safranin SF. Similarly, A_2 is the total absorbance of the binary mixture measured at λ_{2max} of the dye 2. Thus,

$$A_1=K_{11}\, C_1+K_{12}\, C_2 \tag{6}$$

$$A_2=K_{21}\, C_1+K_{22}\, C_2 \tag{7}$$

Where K_{11} & K_{21}, and K_{12} & K_{22} represent the absorbance coefficients for dyes SF and CV at the wavelengths 519.5 nm and 590 nm respectively.

5.1 Validation of extended Langmuir model for binary mixture

Langmuir model can be extended for binary dye system and the assumptions for the extension of this model are [18]

i) All the sites are equivalent

ii) Each site can hold at most one molecule of dye 1 or one molecule of dye 2 but not both

iii) There is no interaction between adsorbate molecules on adjacent sites

The extended Langmuir model for binary dyes, A & B, is presented by a pair of equations (Eqs. 8,9).

$$q_{A,e} = q_{A,max} \frac{K_{A,L}C_{A,e}}{1 + K_{A,L}C_{A,e} + K_{B,L}C_{B,e}} \quad (8)$$

$$q_{B,e} = q_{B,max} \frac{K_{B,L}C_{B,e}}{1 + K_{A,L}C_{A,e} + K_{B,L}C_{B,e}} \quad (9)$$

Figure 10 presents binary SF-CV adsorption data as required by the Eq. (10). As seen in the Figure, the model satisfactorily describes the binary dye adsorption.

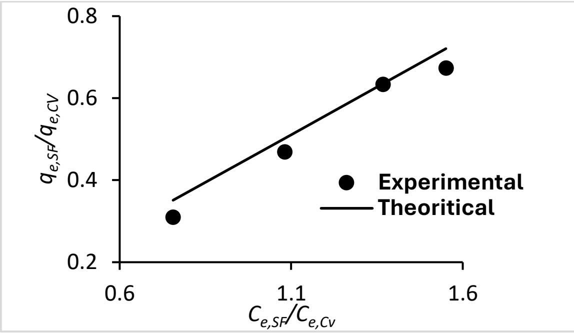

Figure 9: Validation of Extended Langmuir model with SF & CV adsorption data

6. Conclusion

Adsorption study has been performed with Safranin and Crystal Violet onto black tea waste as single and binary dye composition. Langmuir model has satisfactorily described the adsorption of single dye and the extended Langmuir model describes the adsorption of the binary dye mixtures. The active sites on the black tea waste surface or pores are equally accessible to safranin and crystal violet, and both of them are adsorbed on the competitive basis.

Acknowledgment

The financial support from the University Grants Commission, Bangladesh with Grant No 37.01.0000.073.11.001.23.341 Dated: April 16, 2023 for conducting this research work is highly appreciated.

7. References

[1] Weber, E. J.; Adams, R. L. Chemical-and sediment-mediated reduction of the azo dye disperse blue 79. Environmental science & technology. 1995, 29(5), 1163-1170.

[2] Adegoke, K. A.; Bello, O. S. Dye sequestration using agricultural wastes as adsorbents. Water resources and industry. 2015, 12, 8-24.

[3] Padmesh, T. V. N.; Vijayaraghavan, K.; Sekaran, G.; Velan, M. Biosorption of Acid Blue 15 using fresh water macroalga Azolla filiculoides: Batch and column studies. Dyes and Pigments. 2006. 71(2), 77-82.

[4] Daneshvar, N.; Ayazloo, M.; Khataee, A. R.; Pourhassan, M. J. B. T. Biological decolorization of dye solution containing Malachite Green by microalgae Cosmarium sp. Bioresource technology. 2007, 98(6), 1176-1182.

[5] Danesh, S. M. S.; Faghihian, H.; ; Shariati, S. Sulfonic acid functionalized SBA-3 silica mesoporous magnetite nanocomposite for safranin O dye removal. Silicon. 2019, 11, 1817-1827.

[6] Kumar, K. V. Pseudo-second order models for the adsorption of safranin onto activated carbon: comparison of linear and non-linear regression methods. Journal of hazardous materials.2007,142(1-2), 564-567.

[7] Sabnis, R. W. Handbook of biological dyes and stains: synthesis and industrial applications. John Wiley & Sons. 2010.

[8] Rejniak, L.; Piotrowska, H. Effect of malachite green, Congo red and safranin on cell division in gemmae of Allium cepa. Nature.1966, 209 (5022), 517-518.

[9] Anjaneyulu, Y.; Sreedhara C. N.; Samuel S.; Raj, D. Decolorization of industrial effluents–available methods and emerging technologies–a review. Reviews in Environmental Science and Bio/Technology. 2005, 4, 245-273.

[10] Forgacs, E.; Cserháti, T.; Oros, G. Removal of synthetic dyes from wastewaters: a review. Environment international. 2004, 30(7), 953-971.

[11] Malekbala, M. R.; Soltani, S. M.; Yazdi, S. K.; Hosseini, S. Equilibrium and kinetic studies of safranine

adsorption on alkali-treated mango seed integuments. Int. J. Chem. Eng. Appl, 2012, 3(3), 160-166

[12] Farahani, M.; Kashisaz, M.; l Abdullah, S. R. S. Adsorption of safranin O from aqueous phase using sugarcane Bagasse. Int J Ecol Sci Environ Eng. 2015, 2, 17-29.

[13] Mullerova, S.; Baldikova, E.; Prochazkova, J.; Pospiskova, K.; Safarik, I. Magnetically modified macroalgae Cymopolia barbata biomass as anadsorbent for safranin O removal. Materials Chemistry and Physics. 2019, 225, 174-180.

[14] Hossain, M. A. Study on process development for removal of Cr (6) from wastewater by sorption on used black tea leaves. Doctoral dissertation, Kanazawa University, 2007

[15] Allen, S. J.; Mckay, G.; Porter, J. F. Adsorption isotherm models for basic dye adsorption by peat in single and binary component systems. Journal of colloid and interface science.2004, 280(2), 322-333.

[16] Langmuir, I. The adsorption of gases on plane surfaces of glass, mica and platinum. Journal of the American Chemical society. 1918, 40(9), 1361-1403

[17] Dalai, C.; Jha, R.; Desai, V. R. Rice husk and sugarcane baggase-based activated carbon for iron and manganese removal. Aquatic procedia, 2015, 4, 1126-1133

[18] Butler, J. A. V.; Ockrent, C. Studies in electrocapillarity. J. Phys. Chem. III. 1930, 34(12), 2841-2859