Phenomena of Removal of Crystal Violet from Wastewater Using Khulays Natural Bentonite

Saad Al-Shahrani

Department of Chemical and Material Engineering, King Abdulaziz University, Jeddah, Saudi Arabia

Correspondence should be addressed to Saad Al-Shahrani; ssaalshahrani@kau.edu.sa

Received 9 October 2019; Revised 14 January 2020; Accepted 21 February 2020; Published 21 March 2020

1. Introduction

Pollution accounts for substantial threats globally for both living organisms and the environment [1]. Majorly, a substantial impact of dyes is observed in the changing environment due to its significant production of several goods, notably, papers, textiles, plastics, leather, rubber, cosmetics, and food [2]. The textile industry alone is estimated to produce 7x metric tons of dye on an annual basis [3]. The widespread of these dyes and immense utilization increasingly contribute to the wastewater, causing a detrimental effect on the environment. Along with it, the colour effluents present in the dyes negatively impact the penetration capacity of the sunlight, detrimental to the aquatic environment. Studies reveals that dyes constitute synthetic origin as well as complicated aromatic structures, which improves their stability with light, heat as well as an oxidizing agent [1, 4]. Most studies confirm that throughout the dying process, 2 to 20 percent of aqueous effluents are discharged in the environment [3, 5].

Primarily, the dye effluents discharge in the water leads to adverse outcome not only because of its colour but also due to its release as well as a breakdown of products including toxic, mutagenic, or carcinogenic components to other living organisms including compounds such as benzidine, naphthalene, and another aromatic element [6]. The absence of adequate treatment for the removal of these is likely to affect the environment in the long-run. For example, the hydrolyzed Reactive Blue 19’s half-life is almost 46 years with a pH value of 7 at 25°C.

The use of water across different disciplines, including domestic, agriculture, and industrial impact, pose adverse and undesirable pollutants, which can become toxic. Efforts are needed for the protection of the water resources [7–9]. One specific agent which is immensely used in the printing of papers, dying of textile, the colouring of leather, and sometimes as a dermatological agent is crystal violet, also recognized as gentian violet [10]. The dye becomes toxic and can be the cause of irritation on the skin when inhaled or ingested [11]. Numerous procedures are used for the
treatment of the water waters comprising coagulation, reverse osmosis, flocculation, biological methods, and more. Several of these methods constitute one or more limitations and cannot completely clear the water of any dye [12]. In contrast, the process of adsorption stands strong for the treatment of the wastewater concerning its design, cost, functionality, as well as insensitivity to the formed toxic sludge [13].

For the adsorption process, the use of bentonite has significantly increased in various disciplines, such as the treatment of the contaminated water comprising heavy metals, dyes, and phenols. Realizing the impact caused by the dyes, efforts are being made at the global level to overcome the environmental hazards using adsorbent that is economical and easily available from the agricultural waste [14]. The developing countries such as Saudi Arabia are also making efforts to set the base for new industries by utilizing natural resources, also aimed at the achievement of its Saudi Vision 2030. Considering the global scenario, the study assesses the feasibility of treating the wastewater, which is achieved upon the utilization of the Khulays natural bentonite for clearing it off the crystal violet. The increased availability, as well as the cost-effectiveness associated with Khulays natural bentonite, made its selection all more preferable.

2. Materials and Methods

2.1. Chemicals and Reagents. In the present study, the crystal violet (CV) was obtained from Loba Chemie, a chemical manufacturer. The obtained crystal violet was used as it is without undergoing the purification process. The molecular weight of it is C₃₅H₇₀N₅Cl, with a number of CAS as 548-62-9 and a molecular weight of 407.98; the maximum adsorption was found at 590 nm [10]. Figure 1 represents the CV molecular structure. The CV stock solution (1000 mg/L) was prepared by dissolving a known quantity of CV in distilled water. The preparation of various solutions with the preferred concentration was done by diluting a proper amount of stock solution with distilled water.

2.2. Adsorbent. The samples of the bentonite were gathered from Khulays, which is situated in the north of Jeddah at 95 km in Saudi Arabia. The samples were collected in the form of ungrounded rocks, which further underwent the process of drying and grinding for the reduction of their size, as per the requirement. After the grinding process, bentonite samples were sieved with 200 mesh sieving trays. The suspended clay residue was sent back to the ceramic ball grinding machine, and the passed bentonite was used in the adsorption process without any treatment. Table 1 demonstrates the chemical composition of the Khulays natural bentonite [14]. The measurement of the surface area was 64.5 m²/g computed using the computer-generated program based on BET. The image scanning electron microscopy (SEM) of the natural Khulays natural bentonite is shown in Figure 2. The image shows spherical shape surfaces with semiflowered structure, with high pores on the bentonite surface, which give a good indication for Khulays bentonite to be a good adsorbent.

2.3. Characterization of the Bentonite Absorbent. FTIR spectroscopy (Thermo Nicolet NEXUS 670 Spectrophotometer) and XRD (Philips X’Pert Pro) was used for the characterization of the activated bentonite. Figures 3 and 4 presents the FTIR and XRD analysis, which shows that the activated bentonite ranges from 600 to 3800 cm⁻¹. It shows that FTIR spectra are substantially sensitive to the bentonite structure modification when treated with acid. Concerning the XRD analysis, the decline in the intensity, as well as the upsurge in the peak width, shows that acid activation affects the bentonite crystallinity. It also shows the decomposition of the crystalline bentonite structure, which shows the appearance of the amorphous phase. Overall, the findings showed similar chemical nature, though the physical and morphological properties were found to be highly variable. Previous results show similar statistics, as observed in the study of Ajemba [15].

2.4. Experiments for Adsorption. In the study, the batch method was used for all the performed adsorption experiments. The solution was prepared by mixing the adequate amount of Khulays natural Bentonite and CV (50 ml) in the conical flasks (100 ml). Following it, the conical flask was placed in a water bath with a horizontal shaker (JULABO SW 22) at a temperature of 25°C at 200 rpm. Preparation of the CV stock solution took place by dissolving the definite CV quantity in the distilled water. The stock solution was diluted according to the requirement, needed for various standards solutions containing CV in the 50–300 mg/L amount. The exploration of the effects such as pH of a solution, time for shaking, the concentration of CV, and dosage of adsorbent took place by performing the experiments for adsorption. After shaking, the shaker was then emptied of the samples at regular intervals for contact time, which were separated at 4000 rpm by centrifuging for fifteen minutes with the utilization of the ROTOFIX 321 model (Hettich Zentrifugen). The measurement of the CV concentration took place following every run in the solution,
with the use of a UV-visible spectrophotometer in the PD-303 UV (Apel) model. These were used for the calculation of the adsorbent when the wavelength is maximum, that is, 590 nm [16]. The calculation of the collected data for the adsorbed quantity of CV \( q_e \) (mg/g) was done, as per the given equation.

\[
q_e = \frac{V \left(C_o - C_e\right)}{m},
\]

(1)

where \( q_e \) = adsorbed amount of CV at equilibrium (mg/g), \( C_o \) = initial CV concentration in the aqueous solution (mg/L), \( C_e \) = aqueous solution equilibrium concentration of CV (mg/L), \( V \) = solution volume (L), and \( m \) = mixture bentonite amount (g).

The percentage calculation for the removal was done using the given equation:

\[
\% \text{ CV Removal} = \frac{V \left(C_o - C_t\right)}{C_o} \times 100,
\]

(2)

where \( C_t \) = concentration of CV concentration in "t" time (mg/L).

### 3. Results and Discussion

#### 3.1. Outcomes of the Time for Shaking and the Starting Concentration of the Solution.

The impact of the shaking time was evaluated at various concentration levels with the use of Khulays natural bentonite. This evaluation was centred on the exploration of the CV removal, where the concentration level lies in the range from 50 to 300 mg/L. The bentonite dosage was 0.025 g/50 ml. The pH value of the solution was not changed throughout the process. Figure 5 highlights that an increased rate of CV removal, at the start, gradually reduced until it reached the equilibrium point. The CV adsorption on the natural bentonite Khulays was comparatively swift as the equilibrium point was reached in 40 minutes. Furthermore, the percentage of the removal declined as a result of the initial increase in the concentration of CV because of the saturation of active sites on the adsorbent. Similar observations were reported by other researchers [17–19], which showed the increase in an absorbent dose reduces the amount of adsorbed dye per unit mass. It is because, in it, the equilibrium time is considered fast compared to what was reported before [17].

#### 3.2. Effect of pH.

One factor that is significantly associated with the adsorption of dye is the pH of the solution. Additionally, the absorbent surface change is also immensely affected by the pH value of the solution [20–22]. The initial effect caused by the initial solution pH was explored, which was found to range from 3 to more than 11. In addition, the change is no longer significant from 7 to 8 and not 11. The equilibrium was reached after 40 minutes of contact time. The CV was 150 mg/L, while the constant dosage of bentonite was 0.025/50 ml in the dye solution, with 200 rpm of shaking time at 25°C. In the beginning, the solution pH was controlled using 1N HCl and 1N NaOH.

The percentage of a CV that was removed at various initial solution pH is demonstrated in Figure 6. The removal percentage of CV by Khulays natural bentonite increased gradually with the increase in initial solution pH up to pH 5, where about 85% of CV was removed from the solution. No significant results were found by increasing the pH of the solution up to 10. The enhancement of the pH value drives the positive surface charge low while simultaneously increasing the negative charge, given that the ions of hydrogen compete with the cations present in the dye [23].

The increase of the site negative charge on the clay increases the cationic dye adsorption, which results due to increased electrostatic attraction. Previous studies have established that the increase in the solution pH improves the sorption of the cationic dye at an increasing pH level [24]. This behaviour reflects the positive charges on bentonite surface decline with the rise in solution pH, increasing the negatively charged number on the bentonite sites. On acidic
medium, the Khulays natural bentonite negative charge decreases when the increase of the positive charge number takes place. Accordingly, the removal efficiency is impacted by the electrostatic impulsion existing between the surface that is positively charged and the CV [25].

3.3. Effect of Adsorbent Dosage. In the provided operational condition, the dosage adsorbent procedure assists in the evaluation of the adsorbent capacity. For this, the Khulays natural bentonite quantity was investigated for the elimination of the CV when the 50 ml solution of the CV was shaken with constant dye concentration value at 150 mg/L. In it, the dosage of bentonite ranges from 0.005 to 0.125 g/50 mL (given the results in Figure 7). It also had 40 minutes for contact, with a pH value of 5.3 (given the results in 6) and a temperature of 25°C. The results in Figure 7 show that increased dosage leads to increased removal of a dye, such as at 0.005 g, the removal percentage was 15%, while at 0.075 g, it was about 99.9%. Following it, the removal percentage of CV was kept above 99 with the increase of the clay dosage, that is, 0.125. Consequently, the Khulays natural bentonite amount of 0.075 was considered adequate for the CV removal from a CV solution of 150 mg/L, in the presence of the mentioned conditions. The results predict that the increase in bentonite dosage quantity causes increased absorption at sites, which increases CV absorption. This is observed from the use of 0.075 g of Khulays natural bentonite, which removed better absorption capacity for the active bentonite surfaces.

3.4. Adsorption Isotherms. Adsorption isotherms are used to describe the equilibrium relationships between adsorbent and adsorbate. In this study, two different adsorption isotherm models, the Langmuir [26] and Freundlich [27] isotherm equations were used to fit the experimental data obtained from this study. These two models were tested to find out the sorption capacity of crystal violet using Khulays natural bentonite. The best-fitting model is estimated by using the correlation coefficient for the regression ($R^2$), where the isotherm giving an $R^2$ value closest to unity is considered to give the best fit [28].
The adsorption isotherms for CV removal were carried out by initially utilizing multiple concentrations of dye (i.e., 50–300 mg/L), the constant adsorbent mass of 0.025 g, constant temperature (25°C), and solution pH at 5.3. Afterward, the experimental data were fitted to the Langmuir and Freundlich equations.

The Langmuir sorption isotherm is based on the assumption that when the adsorbate occupies a bentonite site, no further sorption can take place at that site [29]. It is used to evaluate maximum dye adsorption capacity and can be explained by the following equation:

\[
\frac{C_e}{q_e} = \frac{1}{bq_{\text{max}}} + \frac{C_e}{q_{\text{max}}},
\tag{3}
\]

where \( C_e \) is the equilibrium concentration of CV (mg/L), \( q_e \) is the amount of CV adsorbed per unit weight of bentonite (mg/g), \( q_{\text{max}} \) is the amount of maximum adsorption capacity (mg/g), and \( b \) is the Langmuir constant (L/mg).

The data obtained from the linear Langmuir isotherm plot for the adsorption of CV onto Khulays natural bentonite are shown in Table 2 and plotted in Figure 6, where the model gives the best fit for the experimental data. The maximum adsorption \( q_{\text{max}} \) (monolayer coverage) for CV on Khulays natural bentonite equals to 263 mg/g.

Freundlich isotherm is an empirical equation used to describe the adsorption process on heterogeneous surfaces and is expressed by the following equation [30]:

\[
\log q_e = \log K + \frac{1}{n} \log C_e,
\tag{4}
\]

where \( K \) and \( n \) are the systems Freundlich isotherm constant. Table 2 provides a brief on the best predictable values for the overall equation parameters (see Figure 8).

![Figure 7: Effect of bentonite dosage on the removal of CV.](image)

![Figure 8: Langmuir adsorption isotherm of CV onto Khulays' natural bentonite.](image)

![Figure 9: CV Freundlich adsorption isotherm using Khulays natural bentonite.](image)

The data obtained from the linear Freundlich isotherm plot for the adsorption of CV onto Khulays natural bentonite is shown in Table 2 and plotted in Figure 9. The Freundlich isotherm model showed an excellent fit for the adsorption data of CV. The value of Freundlich constant lies between 1 and 10, which means good adsorption of crystal violet on Khulays natural bentonite [31].

### Table 2: Langmuir and Freundlich constant calculated from adsorption isotherm data of CV onto Khulays natural bentonite.

| Isotherm parameters | Values  |
|--------------------|---------|
| Langmuir           |         |
| \( q_{\text{max}} \) (mg/g) | 263     |
| \( b \) (L/mg)      | 0.57    |
| \( R^2 \)           | 0.999   |
| Freundlich         |         |
| \( K \) (mg/g)      | 139     |
| \( N \)             | 7.5     |
| \( R^2 \)           | 0.983   |

3.5. **Adsorption Kinetic.** For evaluating the effective process for utilization of the kinetic model, the adsorption of the kinetic onto Khulays’ natural bentonite concerning the crystal violet was explored. The kinetic model utilization is done for designing and modeling the system of adsorption. Pseudo-first-order and pseudo-second-order models were used to determine which mechanism is controlling the process of adsorption like a chemical reaction, mass transfer as well as diffusion controlled.
Lagergren provided the framework for the pseudo-first-order kinetic. The following is its equation [32]:

\[
\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t,
\]

where \( K_1 \) = constant for pseudo-first-order rate (min \(^{-1}\)), \( q_e \) = bentonite adsorbed dye quantity at equilibrium (mg/g), and \( q_t \) = quantity of adsorbed CV (mg/g). \( t \) = time (min).

The framework of pseudo-second-order kinetics is as follows [33]:

\[
t = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t,
\]

where \( K_2 \) = constant for pseudo-second-order (g/(mg/min)), \( q_e \) = bentonite adsorbed dye quantity at equilibrium (mg/g), and \( q_t \) = quantity of adsorbed CV (mg/g) at \( t \). \( t \) = Time (min).

The batch method was used for the exploration of the kinetic parameters part of the adsorption process with a 25°C room temperature. The CV concentration was 300 mg/L initially, 0.025 g/50 ml was the dosage of bentonite in the solution of CV, with a shaking speed of 200 rpm.

Both models, such as pseudo-first-order and pseudo-second-order, were evaluated for the experimental data, as plotted in Figures 10 and 11. The results exhibit a good consensus between the Pseudo-second order kinetic model and experimental data. The achieved value for the regression coefficients \((R^2)\) was 0.72 for pseudo-first-order and 1 for the pseudo-second-order model, which were obtained by inputting the experimental data. Thus, it can be reflected that pseudo-second-order rate kinetics controls the CV removal through adsorption using Khulays natural bentonite.

3.6. Thermodynamic Study. The temperature affects the adsorption process when there is an increase in the diffusion rate of the adsorbent. In contrast, the change in temperature affects the adsorbent capacity at equilibrium [34]. The mentioned equation below is used for the calculation of the parameters for thermodynamic [35].

\[
\Delta G = -RT \ln K, \quad \ln K = \frac{\Delta S}{R} - \left( \frac{\Delta H}{R} \right) \frac{1}{T},
\]

where \( G \) = Gibbs free energy alteration (kJ/mol), \( S \) = change in entropy (J/mol K), \( H \) = change in enthalpy (kJ/mol), \( T \) = temperature (Kelvin), \( R \) = gas constant (8.314 J/mol K), and \( K \) = coefficient for distribution which is measured using the given equation [35]:

\[
K = \frac{q_e}{C_e},
\]

The experiments for thermodynamics were performed at a different temperature such as 25, 35, and 45°C, where the CV concentration of 150 ml/l was used. The bentonite amount used was 0.075 g for shaking for 40 minutes with a CV solution of 50 ml. Figure 12 shows that the temperature increases, such as 25 to 45, led to the percentage increase of removal at equilibrium, such as 62 to 69%. The plot of Van’t Hoff of LnK to1/T is shown in Figure 13, where the value assessment of the \( \Delta H \) and \( \Delta S \) is done at the straight-line slope as well as intercept. The \( \Delta G \) negative value is observed, which signifies the spontaneous processing of adsorption;
along with it, the ΔH positive value, that is, 6.7 kJ/mol, highlights the endothermic nature of the adsorption process. The ΔS positive value (57.3 J/mol K) highlights that CV adsorption in Khulays natural bentonite improves the randomness at the interface of the bentonite or dye solution [36]. Bendaho et al. [37] also found similar results for the adsorption of acid dye onto activated Algerian clay. Sari and İpşıldak [38] study on the stearic acid onto untreated kaolinite also found the ΔS positive value at the solid. Liquid interface leads to an increase in the process of adsorption (see Table 3).

### 4. Conclusion

The present study investigated the treatment of water for CV removal with the use of Khulays natural bentonite following multivariate conditions. The crystal violet sorption onto Khulays’ natural bentonite was comparatively swift such as at 40 minutes, the acquisition of equilibrium was made possible. Moreover, CV concentration enhancement at the initial stages reduces the percentage for removal as a result of the active adsorbent site saturation. The improved pH of the solution served as a stimulant for the advancing percentage of CV removal using the Khulays natural bentonite. CV absorbance increased with the increase in the dosage of bentonite, which improves the absorbents site number. The data for the adsorption isotherm is adequate for the both models, that is, Langmuir and Freundlich, where the maximum capacity of the Khulays natural bentonite adsorption was achieved 263 mg/g. In the experiments, adsorption kinetic exhibits that the adsorption of CV against Khulays natural bentonite is regulated using pseudo-second-order rate kinetics. The findings of the research determine that the established thermodynamic process of adsorption is spontaneous and is endothermic. The study positions Khulays’ natural bentonite as a promising adsorbent for the treatment of water for the removal of the basic dyes. However, the findings of the study are limited, given its limited characterization, where the use of $pH_{pzc}$ could have expanded the research findings and provided better interpretation. Given this, the present study recommends future studies to perform a comparison of similar natural materials and their regeneration capacity (recycling) for improving the research scope. This would also assist in evaluating the reproducibility of the found results.

### Data Availability

The datasets used and analysed during the current study are available from the author upon reasonable request.

### Conflicts of Interest

The author declares that there are no conflicts of interest regarding the publication of this paper.

### Acknowledgments

The author is very thankful to all the associated personnel in any reference that contributed to the purpose of this research.

### References

[1] F. A. Awadallah and S. A. Al-Muhtaseb, “Removal of crystal violet from wastewater using resorcinol-formaldehyde carbon xerogels,” *Separation Science and Technology*, vol. 51, no. 3, pp. 403–415, 2016.

[2] L. Akinola and A. Umar, “Adsorption of crystal violet onto adsorbents derived from agricultural wastes: kinetic and equilibrium studies,” *Journal of Applied Sciences and Environmental Management*, vol. 19, no. 2, p. 279, 2015.

[3] Z. Carmen and S. Daniel, “Textile organic dyes—characteristics, polluting effects and separation/elimination procedures from industrial effluents—a critical overview,” *Organic Pollutants Ten Years After the Stockholm Convention - Environmental and Analytical Update*, IntechOpen, London, UK, 2012.

[4] R. D. Saini, “Synthetic textile dyes: constitution, dying process and environmental impacts,” *Asian Journal of Research in Chemistry*, vol. 11, no. 1, p. 206, 2018.

[5] I. A. Aneyo, F. V. Doherty, O. A. Adebesin, and M. O. Hammed, “Biodegradation of pollutants in waste water from pharmaceutical, textile and local dye effluent in lagos, Nigeria,” *Journal of Health and Pollution*, vol. 6, no. 12, pp. 34–42, 2016.

[6] G. Crini and E. Lichtfouse, “Advantages and disadvantages of techniques used for wastewater treatment,” *Environmental Chemistry Letters*, vol. 17, no. 1, pp. 145–155, 2018.

[7] M. N. Khalaf, *Green Polymers and Environmental Pollution Control*, Apple Academic Press, New York, NY, USA, 2016.

[8] K. Rathoure and V. K. Dhatwalia, Eds., “Toxicity and waste management using bioremediation,” *Advances in Environmental Engineering and Green Technologies*, IGI Global, Hershey PA, USA, 2016.
8 Journal of Chemistry

[9] N. Morin-Crini, G. Crini, and L. Roy, *Eaux Industrielles Contaminées*, PUF, Besançon, France, 2017.

[10] D. Jaynes, R. Tamilarasan, M. Kumar, M. Murugavelu, and V. Sivakumar, "Equilibrium and Modelling Studies for the Removal of Crystal Violet Dye from aqueous solution using eco-friendly activated carbon prepared from Sargassum wightii seaweeds," *Journal of Materials and Environmental Sciences*, vol. 8, no. 4, pp. 1508–1517, 2017.

[11] M. Kumar and R. Tamilarasan, "Modeling of experimental data for the adsorption of methyl orange from aqueous solution using a low cost activated carbon prepared from Prospopis juliflora," *Polish Journal of Chemical Technology*, vol. 15, no. 2, pp. 29–39, 2013.

[12] G. Vijayakumar, R. Tamilarasan, and M. Dharmendirakumar, "Adsorption, Kinetic, Equilibrium and Thermodynamic studies on the removal of basic dye Rhodamine-B from aqueous solution by the use of natural adsorbent perlite," *Journal of Materials and Environmental Sciences*, vol. 3, pp. 157–170, 2012.

[13] M. Nageeb, "Adsorption technique for the removal of organic pollutants from water and wastewater," *Organic Pollutants—Monitoring, Risk and Treatment*, IntechOpen, London, UK, 2013.

[14] Saad Al-Shahrani, "Treatment of wastewater contaminated with cobalt using Saudi activated bentonite," *Alexandria Engineering Journal*, vol. 53, no. 1, pp. 205–211, 2014.

[15] R. Ajemba, "Enhancement of physicochemical properties of nteje clay to increase its bleaching performance using acid activation," *International Journal of Engineering Research and Applications (IJERA)*, vol. 2, no. 4, pp. 281–288, 2012.

[16] F. H. Kamar, F. E. Niamat, A. A. H. Faisal, A. A. Mohammed, A. C. Nechifor, and G. Nechifor, "Use of artificial neural network for modeling and prediction of reactive red dye removal from wastewater using banana peels bio-sorbent," *Revista de Chimie*, vol. 69, no. 8, pp. 1919–1926, 2018.

[17] A. R. Obiageli, "Adsorption of cationic dye onto low-cost adsorbent synthesized from bentonite clay part I. Kinetic and thermodynamic studies," *Journal of Chemical Technology & Metallurgy*, vol. 52, 2017.

[18] G. K. Cheruiyot, W. C. Wanyonyi, J. J. Kiplimo, and E. N. Maina, "Adsorption of toxic crystal violet dye using coffee husks: equilibrium, kinetics and thermodynamics study," *Scientific African*, vol. 5, Article ID e00116, 2019.

[19] K. S. Bharathi and S. T. Ramesh, "Removal of dyes using agricultural waste as low-cost adsorbent: a review," *Applied Water Science*, vol. 3, no. 4, pp. 773–790, 2013.

[20] M. Alshabanat, G. Alseneini, and R. Almufarrij, "Removal of crystal violet dye from aqueous solutions onto date palm fiber by adsorption technique," *Journal of Chemistry*, vol. 2013, Article ID 210239, pp. 1–6, 2013.

[21] W. Zou, K. Li, H. Bai, X. Shi, and R. Han, "Enhanced cationic dyes removal from aqueous solution by oxalic acid modified rice husk," *Journal of Chemical & Engineering Data*, vol. 56, no. 5, pp. 1882–1891, 2011.

[22] K. Al-Essa, "Adsorption of humic acid onto Jordanian kaolinite clay: effects of humic acid concentration, pH, and temperature," *Science Journal of Chemistry*, vol. 6, no. 1, pp. 1–10, 2018.

[23] M. T. Yagub, T. K. Sen, S. Afroze, and H. M. Ang, "Dye and its removal from aqueous solution by adsorption: a review," *Advances in Colloid and Interface Science*, vol. 209, pp. 172–184, 2014.

[24] H. H. A. Ghafar, T. Salem, E. K. Radwan, A. A. El-Sayed, M. A. Embaby, and M. Salama, "Modification of waste wool fiber as low cost adsorbent for the removal of methylene blue from aqueous solution," *Egyptian Journal of Chemistry*, vol. 60, pp. 395–406, 2017.

[25] E. G. Sogut and N. Caliskan, "Isotherm and kinetic studies of Pb (II) adsorption on raw and modified diatomite by using non-linear regression method," *Presentis Environmental Bulletin*, vol. 26, pp. 2720–2728, 2017.

[26] I. Langmuir, "The adsorption of gases on plane surfaces of glass, mica and platinum," *Journal of the American Chemical Society*, vol. 40, no. 9, pp. 1361–1403, 1918.

[27] H. Freundlich, *Colloid & Capillary Chemistry*, Methuen & Co. Ltd, London, UK, 1926.

[28] H. Singh and F. Javadpour, "Langmuir slip-Langmuir sorption permeability model of shale," *Fuel*, vol. 164, pp. 28–37, 2016.

[29] X. Chen, "Modeling of experimental adsorption isotherm data," *Information*, vol. 6, no. 1, pp. 14–22, 2015.

[30] N. Laskar and U. Kumar, "Adsorption of crystal violet from wastewater by modified bambusa tulta," *KSCJE Journal of Civil Engineering*, vol. 22, no. 8, pp. 2755–2763, 2017.

[31] V. O. Shikuku, F. F. Donato, C. O. Kowenje, R. Zanella, and O. D. Prestes, "A comparison of adsorption equilibrium, kinetics and thermodynamics of aqueous phase clomazone between faujasite X and a natural zeolite from Kenya," *South African Journal of Chemistry*, vol. 68, pp. 245–252, 2015.

[32] J.-P. Simonin, "On the comparison of pseudo-first order and pseudo-second order rate laws in the modeling of adsorption kinetics," *Chemical Engineering Journal*, vol. 300, pp. 254–263, 2016.

[33] M. B. Ahmed, J. L. Zhou, H. H. Ngo, W. Guo, and M. Chen, "Progress in the preparation and application of modified biochar for improved contaminant removal from water and wastewater," *Bioresources Technology*, vol. 214, pp. 836–851, 2016.

[34] U. Pathak, P. Das, P. Banerjee, and S. Datta, "Treatment of wastewater from a dairy industry using rice husk as adsorbent: treatment efficiency, isotherm, thermodynamics, and kinetics modelling," *Journal of Thermodynamics*, vol. 2016, Article ID 3746316, 7 pages, 2016.

[35] D. C. d. Santos, M. A. Adebayo, E. C. Lima et al., "Application of carbon composite adsorbents prepared from coffee waste and clay for the removal of reactive dyes from aqueous solutions," *Journal of the Brazilian Chemical Society*, vol. 26, no. 5, pp. 924–938, 2015.

[36] A. Mittal, J. Mittal, A. Malviya, D. Kaur, and V. K. Gupta, "Adsorption of hazardous dye crystal violet from wastewater by waste materials," *Journal of Colloid and Interface Science*, vol. 343, no. 2, pp. 463–473, 2010.

[37] D. Bendaho, T. A. Driss, and D. Bassou, "Adsorption of acid dye onto activated Algerian clay," *Bulletin of the Chemical Society of Ethiopia*, vol. 31, no. 1, p. 51, 2017.

[38] A. Sari and O. İlyldak, "Adsorption properties of stearic acid onto untreated kaolinite," *Bulletin of the Chemical Society of Ethiopia*, vol. 20, no. 2, 2006.