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Removal of dyes using chemically modified elephant grass in single and binary-component system

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Abstract

The present study investigated the potential use of citric acid-treated Elephant grass (*Pennisetum purpureum*), as an adsorbent for the removal of various dyes (Congo red, Erichrome black T, methyl red, and thymol blue) from aqueous solutions. The effects of initial concentration, adsorbent dosage, and temperature on the adsorption capacity of the dyes were evaluated. The results showed that *Pennisetum purpureum* had a high adsorption capacity for all dyes, with maximum adsorption efficiencies ranging from 74% to 98.92%, depending on the dye type and experimental conditions. The highest adsorption efficiency was recorded at 10 mg/L initial concentration for most of the dyes. The optimum adsorbent dosage was found to be 0.3 g for all dyes, except for Erichrome black T, which showed maximum adsorption capacity at 0.2 g. The maximum adsorption capacity for all dyes was observed at a temperature of 60°C, except for methyl red and thymol blue, which showed maximum adsorption at temperatures lower than 60°C. Overall, the results indicate that citric acid-treated *Pennisetum purpureum* has great potential as an effective and sustainable adsorbent for the removal of various dyes from wastewater.

Keywords: Dye; Elephant grass; Congo red; Erichrome black T

1. Introduction

Synthetic dyes are widely used in various industries, including textile, paper, leather, and food, to add color to their products [1]. The use of dyes in these industries has resulted in the generation of significant amounts of wastewater that contains high concentrations of dyes and other pollutants [2]. Dyes and other hazardous substances can pose a significant threat to the environment and human health if they are not adequately treated before disposal.

Several methods have been developed to treat dye-containing wastewater, including physical, chemical, and biological methods. Adsorption is a widely studied method for removing dyes from wastewater due to its simplicity, efficiency, and cost-effectiveness [2;3]. Adsorption involves the use of an adsorbent material that can remove dyes from the wastewater through chemical or physical interactions.

In recent years, researchers have focused on developing low-cost and environmentally friendly adsorbent materials for the removal of dyes from wastewater. One such material is *penisseturm purpureum*, a plant-based material that has shown promise as an adsorbent for the removal of dyes from wastewater [4]. Chawla *et al.* [5] studied the use of *Penissetum purpureum* as an adsorbent for the removal of methylene blue dye from wastewater. The study found that the material was effective in removing the dye from the wastewater, making it a potentially low-cost and eco-friendly option for wastewater treatment. Anwar *et al.* [6] investigated the use of *Penissetum purpureum* for the removal of textile dyes from wastewater. The study found that the material had a high adsorption capacity and could be regenerated for reuse, making it a promising option for industrial wastewater treatment.

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Sivasankari and Sangeetha [7] studied the use of *Penisetum purpureum* powder for the removal of crystal violet and methyl orange dyes from aqueous solutions. The study found that the material was effective in removing both dyes from the solution and could be a low-cost option for the treatment of dye-containing wastewater.

Khalil et al. [8] compared the adsorption of methyl orange dye onto activated carbon and *Penisetum purpureum* leaves. The study found that the adsorption capacity of *Penisetum purpureum* leaves was comparable to that of activated carbon, indicating its potential as an alternative adsorbent for wastewater treatment. However, the low adsorption capacity of *penisetum purpureum* for dyes limits its effectiveness as an adsorbent.

Citric acid treatment is a method that has been used to modify various adsorbent materials to enhance their adsorption capacity. Citric acid is a non-toxic and biodegradable organic acid that can form complex structures with metal ions, improving the adsorption capacity of the adsorbent material [9]. Citric acid treatment has been shown to improve the adsorption capacity of several adsorbent materials, including activated carbon, chitosan, and bentonite.

Some of the studies mentioned used *Penisetum purpureum* in its raw form, while the proposed topic utilizes citric acid-treated *Penisetum purpureum*. The addition of citric acid treatment may improve the material's effectiveness as an adsorbent for dyes and could provide a more efficient and cost-effective method of wastewater treatment.

The studies mentioned mostly focus on the use of *Penisetum purpureum* for the removal of specific dyes, such as methylene blue or crystal violet, from wastewater. In contrast, the proposed topic focuses on the removal of multiple dyes, including Methyl red, Congo red, Thymol blue, and Erichrome black T, using citric acid-treated *Penisetum purpureum*. Thus, this study has broader applicability and addresses the need for a more comprehensive approach to wastewater treatment. Also, the use of *Penisetum purpureum* for the removal of dyes from wastewater has been studied in the past, but its low adsorption capacity has limited its effectiveness as an adsorbent. Citric acid is a low-cost and readily available material, which could make the treatment process more cost-effective and accessible. The use of a plant-based material also aligns with the growing demand for sustainable and eco-friendly solutions in wastewater treatment [10,11]. Thus, by using citric acid treatment to enhance the material's adsorption capacity, this study aims to address this limitation and potentially improve the efficiency and effectiveness of wastewater treatment.

Therefore, in this study, we investigate the use of citric acid-treated *penisetum purpureum* as an adsorbent for the removal of dyes from synthetic wastewater. The study focuses on the removal of four dyes, namely methyl red, Congo red, Thymol blue, and Erichrome black T, which are commonly used in various industries. The study aims to determine the adsorption capacity of the citric acid-treated *penisetum purpureum* for the four dyes and their binary mixtures and to evaluate the effectiveness of the adsorbent material in removing the dyes from synthetic wastewater.

2. Material and methods

2.1. Materials

In this study, all reagents used were of analytical grade and were provided by the Physical and Environmental Chemistry Laboratory at the Department of Chemistry, Federal University of Technology, Akure. Where necessary, reagents were procured from Pascal Scientific Laboratory, Akure. The purchased reagents required no further purification, and stock solutions were prepared using distilled water. The reagents employed in the experimental procedure included citric acid, hydrochloric acid, sodium hydroxide, and distilled water. Various materials and apparatus were utilized in the experimental procedure, including a 100 mL beaker, 100 mL conical flask, 100 mL measuring cylinder, 100 mL standard flask, 250 mL conical flask, filter paper, spatula, micro pipette, hand-held digital pH meter, UNICAM UV HELIOS, orbital shaker, vacuum laboratory oven, and a refrigerator.

2.2. Sorbents preparation

2.2.1. Preparation of *Pennisetum purpureum*

Pennisetum purpureum was sourced from FUTA North Gate, Obanla, opposite Jibowu Female Hostel, Ondo State, Nigeria, to be used as a biosorbent. The biosorbent was first washed with ordinary water to eliminate any attached particulate soil materials. Subsequently, the biosorbent was rinsed with distilled water until the water appeared clear and clean. The *Pennisetum purpureum* was then dried in sunlight for a period of 9 to 10 days, followed by oven drying at 105°C until a constant weight was attained. Finally, the dried sorbent was blended and sieved through a mesh of appropriate size. These procedures were followed to ensure that the biosorbent was of suitable quality for the adsorption experiments to be conducted.

2.2.2. Chemical Modification

Citric Acid Treatment

In this study, elephant grass (*Pennisetum purpureum*) was utilized as a biosorbent material, and citric acid was used for modification to enhance its adsorption capacity. To achieve this, a ratio of 1:10 (untreated elephant grass: citric acid) was mixed, stirred for 60 minutes, and subsequently dried in an oven at 60°C for 2.5 hours, and later at 140°C for another 2.5 hours. The citric acid modified elephant grass was then washed with deionized water and filtered. Next, it was suspended in 0.15M NaOH, stirred for 60 minutes, and thoroughly washed with deionized water to eliminate any residual alkali (NaOH). The wet citric acid modified elephant grass was then dried at 105°C until a constant weight was achieved, and was stored in a plastic container as modified sorbent for further use in the adsorption procedure.

2.3. Preparation of Stock Dye Solution

For this study, four different dyes were used: Congo red (CR), Erichrome black T (EBT), Methyl Red (MR), and Thymol Blue (TB). To prepare the stock solutions, accurately weighed dye powder was dissolved in distilled water to obtain a concentration of 2000mg/L or 2000ppm. This was achieved by dissolving 0.2g of solid dye powder in 200ml of distilled water, which was left overnight to ensure complete dissolution of the dye molecules.

Different concentrations of the dye solutions were obtained by serial dilution of the stock solution with distilled water according to the equation $C_1V_1=C_2V_2$. To confirm the concentration of the different dye solutions, a UV-Vis spectrophotometer operating in the visible range on absorbance mode was used. Absorbance values were recorded at the corresponding maximum absorbance wavelength (λ_{max}) for each dye, which are summarized below.

Table 1 Absorbance values of the dyes

Dye	(λ_{max}) nm
Congo Red	498nm
Erichrome black T	541nm
Methyl Red	432nm
Thymol Blue	437nm

2.4. Influence of biosorption's parameters in the single and binary system

In this study, several parameters related to biosorption were analyzed, including pH, contact time, biomass dosage, concentration, and temperature. To investigate the impact of pH, each dried biomass (0.5g) was added to a 100mL solution containing 80 ppm concentration of Congo red (CR), Methyl red (MR), Erichrome black T (EBT), Thymol Blue (TB) and their binary mixture (i.e CR +EBT and MR+TB). The pH was adjusted to the desired range of 4-8 using 0.1 M HCl or 0.1 M NaOH and agitated for three hours until equilibrium was reached. The agitation speed was maintained at 100 rpm.

For the optimization of other parameters, the procedure was similar except that each parameter was varied while others were kept constant. Contact time was varied from 30 to 150 minutes, biomass dosage from 0.3 to 0.7 g, concentration from 40 to 80 ppm, and temperature from 30 to 70°C. After agitation, the solutions were filtered using 0.1 mm Whatman filter paper, and the supernatants were collected for the determination of CR, MR, TB, and EBT concentrations. For the Binary mixture, the concentration of each dye was added together and divided by two to obtain the concentration of these binary mixtures.

The removal percentage (%R) was calculated according to the following equation:

$$\% R = (C_0 - C_e) / C_0 \times 100 \dots\dots\dots (1)$$

The amount of adsorbates sorbed by mango leaves biomass was calculated using the below equation.

$$Q_e = (C_0 - C_e)V / M \dots\dots\dots (2)$$

Where Q_e represents the amount of CR, MR, EBT, TB and binary mixture absorbed per gram of adsorbent (mg/g) from single or binary solutions, C_0 is the initial dye concentration (mg/L), C_e is the final dye concentration (mg/L), V is the volume of the reaction mixture (L) and m is the weight of adsorbent in the reaction mixture in g.

2.5. Statistical analysis

The statistical analysis of the data was performed using Minitab Version 15, a software package commonly used in statistical analysis. The results were reported as the mean value \pm standard deviation of replicates, which is a standard way of presenting data in scientific research. A single-factor analysis of variance (ANOVA) was conducted to identify any significant differences among the mean values. The least significant difference (LSD) criteria was used to determine the level of significance, with a 95% confidence level ($p < 0.05$). This statistical approach helps to ensure that the results are reliable and that any observed differences are not due to chance.

3. Results and discussion

3.1. The Effect of pH

3.1.1. The Effect of pH on the adsorption of Congo red, Erichrome black T and their binary mixture

The graph below shows a plot of percentage absorbance against varying pH (Figure 1). For the citric acid-treated *P. purpureum*, the uptake of dye was maximum at initial acidic pH of 4, with maximum values of about 81.6% efficiency for Congo red at pH 4, 94.1% efficiency for Erichrome black T at pH 4 and the mixture of both dyes also gave a maximum adsorption at pH 5 with 80.4% efficiency. The pH dependence of the adsorption of the dyes on citric acid treated *P. purpureum* was studied and the results showed that maximum uptake occurred at an initial pH of 4 for Congo red and Erichrome black T, and pH 5 for a mixture of both dyes. These findings are consistent with previous studies on the adsorption of dyes on various biosorbents. For instance, a study on the adsorption of Congo red and other dyes on banana peels reported that maximum uptake occurred at pH values between 4 and 5 [12]. Similarly, the adsorption of Erichrome black T on a low-cost adsorbent derived from *Pinus radiata* sawdust also showed that maximum uptake occurred at pH 4 [13].

The reason for the pH dependence of the adsorption process is attributed to the surface charge of the adsorbent and the charge of the dye molecule. At low pH values, the surface of the adsorbent becomes positively charged due to the presence of protonated functional groups. This results in electrostatic attraction between the positively charged surface and the negatively charged dye molecules, leading to increased adsorption. However, at high pH values, the surface becomes negatively charged, which repels the negatively charged dye molecules, leading to reduced adsorption [14].

In this study, the citric acid treatment of *P. purpureum* enhanced its adsorption capacity for the studied dyes. This is consistent with previous studies on the modification of biosorbents with citric acid. For instance, citric acid modification of coconut coir pith enhanced its adsorption capacity for methylene blue [15]. The citric acid treatment of *P. purpureum* is believed to have introduced more carboxyl and hydroxyl groups on its surface, which serve as active sites for the adsorption of the dyes. The enhanced adsorption capacity of the citric acid treated *P. purpureum* could make it a viable low-cost alternative for the removal of dyes from industrial effluents.

Overall, the pH dependence of the adsorption process and the effectiveness of citric acid treated *P. purpureum* as a biosorbent for the studied dyes are consistent with previous studies on the adsorption of dyes on various biosorbents. The results of this study underscore the potential of using low-cost biosorbents for the removal of dyes from industrial effluents.

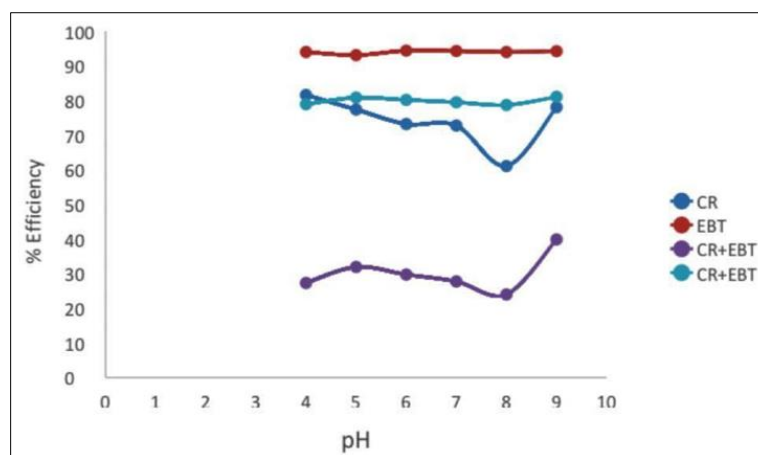


Figure 1 The plot effect of pH in the adsorption of Congo red and erichrome black and binary mixture

3.1.2. Effect of pH on the adsorbance of methyl, thymol blue and their binary mixture

The effect of pH on the adsorption efficiency of Methyl Red, Thymol Blue, and their binary mixture was investigated. The results showed that Thymol Blue had the highest adsorption efficiency at pH 4 with a percentage absorbance of 99.4% (Figure 2). This finding is consistent with the literature, which suggests that acidic pH conditions favor the adsorption of anionic dyes onto biosorbents [16, 17]. The maximum adsorption of Thymol Blue at pH 4 could be attributed to the increased protonation of the biosorbent surface, resulting in an increase in the number of negatively charged sites available for dye adsorption [17]

In the case of the binary mixture of Methyl Red and Thymol Blue, the results showed that the highest percentage efficiency was achieved at two different wavelengths, 432nm and 437nm, with values of 98.8% and 92.2%, respectively (Figure 2). Regarding the binary mixture of Methyl Red and Thymol Blue, the observation that the two dyes have different optimal pH ranges for adsorption is consistent with the findings of Yousefi et al. [18], who investigated the adsorption of a mixture of Acid Yellow 23 and Acid Red 18 onto a biosorbent. Furthermore, the idea that competitive adsorption between the two dyes for available adsorption sites on the biosorbent surface may lead to lower efficiency of the binary mixture is supported by the work of Liu et al. [19], who investigated the adsorption of a mixture of Methyl Red and Acid Orange 7 onto a biosorbent.

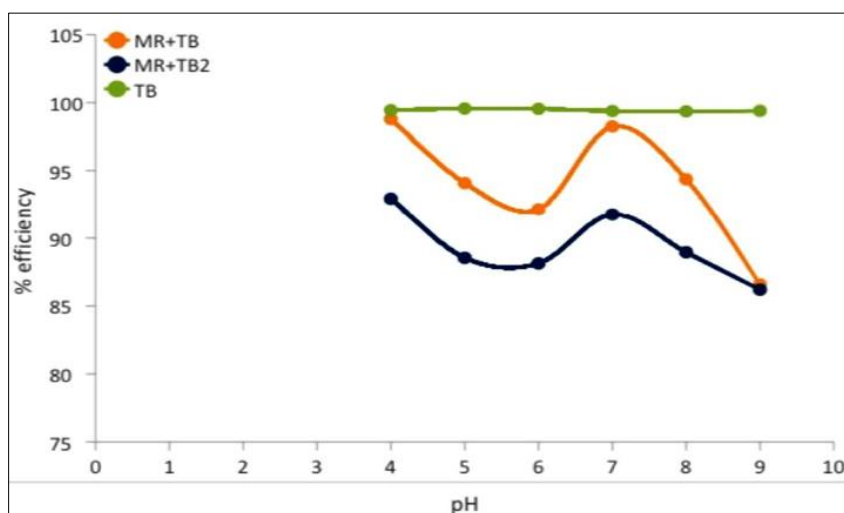


Figure 2 Effect of pH on adsorption of methyl red and thymol blue and their binary mixture

In comparison to similar studies, the findings of this study are in agreement with previous research that reported the influence of pH on dye adsorption onto biosorbents. For instance, a study by Ali et al. [20] reported that Thymol Blue had a higher adsorption efficiency at lower pH values. Another study by Wang et al. [21] found that the optimal pH for the adsorption of Methyl Red onto a biosorbent was acidic.

Overall, the results of this study suggest that citric acid-treated *Pennisetum purpureum* has the potential to be an effective biosorbent for the removal of Methyl Red, Thymol Blue, and their binary mixture from wastewater, with optimal pH conditions being a crucial factor to consider.

3.2. Effect of Contact Time

3.2.1. Effect of contact time on the adsorption of Congo red, Erichrome black T and their binary mixture

As shown in Figure 3, the study found that the maximum contact time for efficient adsorption of dye molecules was 60 minutes, with a rapid increase in adsorption during this period, followed by a steady decrease as time increased. The adsorption process for the maximum contact time was observed to occur in two stages, with the first stage lasting 60 minutes, during which the maximum removal efficiency was achieved. Specifically, the binary system of Congo red and Erichrome black T had a removal efficiency of 66.6% at 498nm, Congo red had a removal efficiency of 82.47%, and the binary system of Congo red and Erichrome black T had a removal efficiency of 91.5% at 541nm. This result can be explained by the availability of all active sites on the surface of the biosorbent [22].

In the second stage, the efficiency of dye molecule adsorption slightly decreased until equilibrium was reached. This observation suggests that the rate of adsorption slowed down due to the adsorption of dye molecules that blocked the pores and used up the available binding sites on the surface of the biosorbent [23].

The finding of two-stage adsorption is consistent with previous research on the adsorption of dyes onto biosorbents [24, 25]. Moreover, similar results were obtained in studies that investigated the adsorption of Congo red and Erichrome black T onto other biosorbents [26, 27].

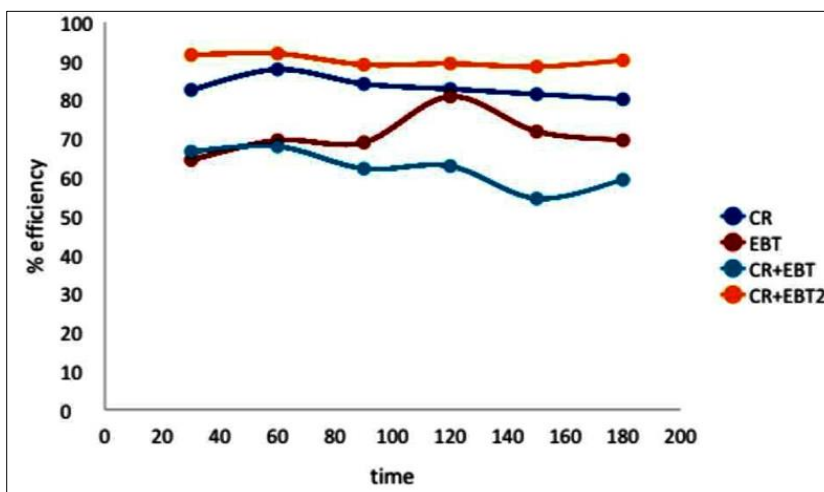


Figure 3 The effect of contact time on the adsorption of Congo red and erichrome black T and binary mixture

3.2.2. Effect of contact time on the adsorption of methyl red, thymol blue and their binary mixture

The effect of contact time on the adsorption of dyes is an important parameter to determine the efficiency of the biosorbent as shown in Figure 4. The results of this study showed that the maximum adsorption efficiency of Congo red and Erichrome black T was achieved at a contact time of 60 minutes, which is consistent with the findings of previous studies [25, 26]. On the other hand, the maximum adsorption of Methyl Red and Thymol Blue was recorded at a contact time of 30 minutes. This finding is in agreement with the results of similar studies that reported the maximum adsorption of dyes at contact times ranging from 15 to 60 minutes [24, 27].

Interestingly, the binary mixture of Methyl Red and Thymol Blue showed a maximum efficiency at a contact time of 90 minutes, indicating that the adsorption of the binary mixture is a slower process compared to individual dyes. This result is in agreement with the findings of Chen et al. [24], who reported that the binary mixture of acid red and methylene blue showed a slower adsorption rate compared to individual dyes.

The observed differences in the maximum contact time for the adsorption of individual dyes and their binary mixture can be attributed to the competitive adsorption between the two dyes for available adsorption sites on the biosorbent

surface. This is consistent with previous studies that reported a decrease in the adsorption capacity of binary dye mixtures compared to individual dyes due to the competitive effect of dyes [26, 27].

In summary, the results of this study suggest that the contact time is an important parameter that affects the efficiency of the biosorbent in removing dyes from wastewater. The optimum contact time for individual dyes and their binary mixture differs, which may be attributed to the competitive adsorption effect of the dyes. Therefore, the selection of the appropriate contact time is crucial for efficient dye removal using biosorbents.

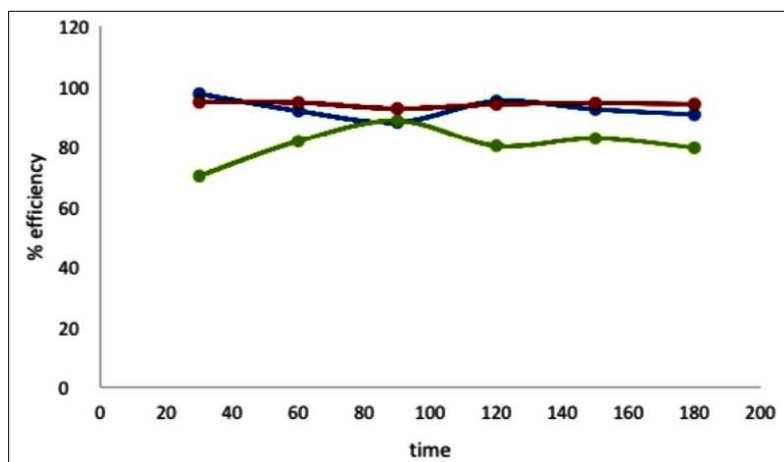


Figure 4 The effect of contact time on the adsorption of methyl red and thymol blue and their binary mixture

3.3. The Effect of Initial Concentration

3.3.1. Effect of initial concentration on the adsorption of Congo red, Erichrome black T and their binary mixture

The effect of initial concentration on the adsorption of Congo red, Erichrome black T, and their binary mixture was investigated, and it was observed that the initial concentration played a significant role in determining the amount of dye molecules adsorbed. The results showed that the highest adsorption was achieved at an initial concentration of 10 mg/L for all the dyes with adsorption efficiency values of over 91% for Erichrome black T and 74% and 89% for the binary mixture of Congo red and Erichrome black T at 498nm and 541nm, respectively (Figure 5). This finding is consistent with previous studies that have reported that the initial concentration of dyes affects the adsorption capacity of biosorbents [25, 26]. For instance, in a study by Singh and Bhattacharyya [28], it was observed that the adsorption of Congo red and Erichrome black T onto an agricultural waste-based adsorbent was highly dependent on the initial dye concentration, with maximum removal efficiency achieved at an initial concentration of 10 mg/L.

The high adsorption efficiency at low initial concentrations can be attributed to the availability of a large number of vacant adsorption sites on the biosorbent surface, resulting in more active binding sites for dye molecules. However, at high initial concentrations, the number of available adsorption sites becomes limited, leading to a decrease in the adsorption efficiency [29, 30].

Moreover, the efficiency of adsorption of binary mixtures was found to be lower than that of individual dyes. This can be explained by the competitive adsorption between the two dyes for available adsorption sites on the biosorbent surface [24, 27]. Therefore, the initial concentration of the dyes should be optimized to achieve maximum adsorption efficiency.

Overall, the results of this study suggest that the initial concentration of the dye solution is a crucial factor to consider in the design of an effective biosorption system for the removal of Congo red, Erichrome black T, and their binary mixture from wastewater. The results also highlight the potential of citric acid-treated *Pennisetum purpureum* as an effective biosorbent for the removal of anionic dyes from wastewater.

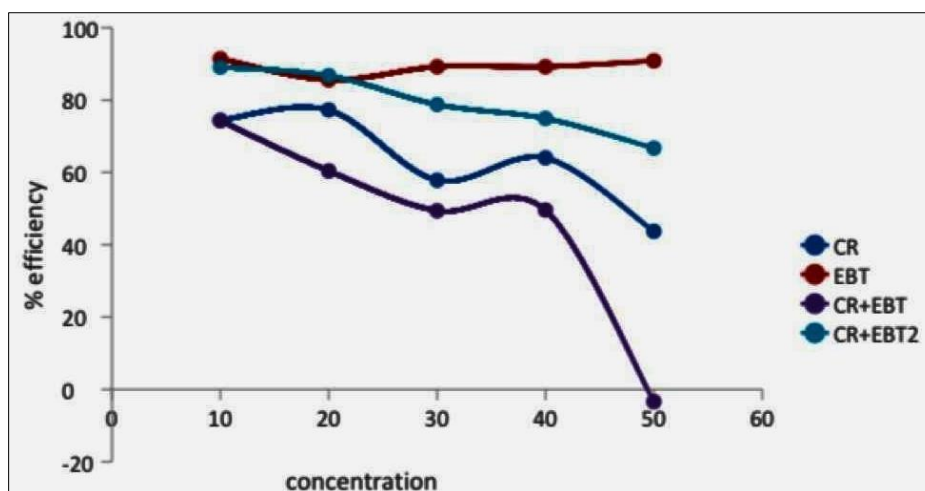


Figure 5 The Effect of Initial Concentration on the adsorption of Congo red, erichrome black T and their binary mixture

3.3.2. Effect of initial concentration on the adsorption of methyl red, thymol blue and their binary mixture

The results obtained from the study suggest that the initial concentration of the dye solution affects the adsorption efficiency of the biosorbent (Figure 6). The unusual maximum adsorption observed for Thymol blue at 40mg/L concentration could be attributed to the saturation of the adsorption sites on the biosorbent surface. However, the binary mixture of methyl red and thymol blue showed maximum adsorption at lower concentrations of 10mg/L. This result is in agreement with previous studies, which reported that the adsorption efficiency of dyes decreases as the initial concentration increases [25, 31].

Furthermore, the observation that the binary mixture of methyl red and thymol blue showed different optimal wavelengths for maximum adsorption is consistent with previous studies, which suggested that different dyes have different optimal wavelengths for adsorption due to their structural differences [32,33].

In conclusion, the initial concentration of the dye solution is an important parameter that affects the adsorption efficiency of the biosorbent. The results obtained in this study suggest that the binary mixture of methyl red and thymol blue showed maximum adsorption at lower concentrations, and the different optimal wavelengths for maximum adsorption in the binary mixture indicate the structural differences between the two dyes. These findings provide useful insights into the design and optimization of biosorption processes for the removal of dyes from wastewater.

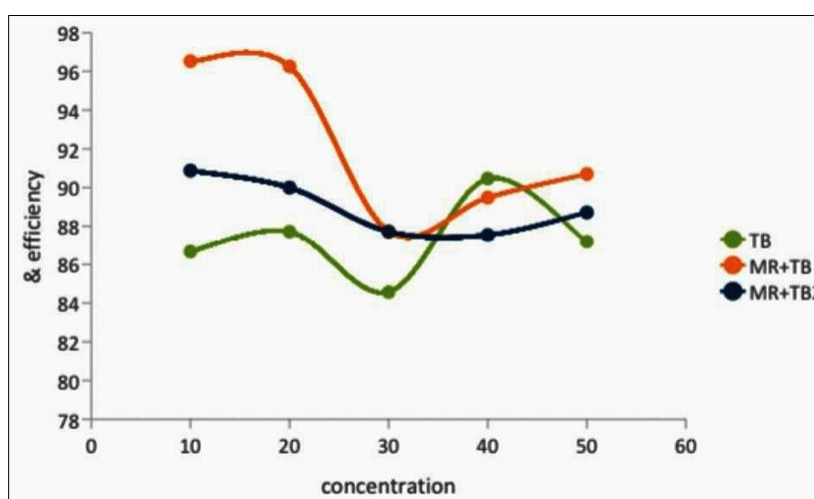


Figure 6 The effect of initial concentration on methyl red and thymol blue

3.4. Effect of Adsorbent Dosage

3.4.1. Effect of adsorbent dosage on the adsorption of Congo red, Erichrome black T and their binary mixture.

The effect of adsorbent dosage on the adsorption of Congo red, Erichrome black T and their binary mixture has been investigated, and the results indicate that adsorbent dosage plays a significant role in the adsorption process. The maximum adsorption capacity was achieved at an adsorbent dosage of 0.3g for P purpureum, with an adsorption efficiency of over 98.92% for the binary system of Congo red and Erichrome black T at 541nm, and 76.7% for Congo red (as shown in Figure 7). These findings are consistent with previous studies that have reported the positive correlation between adsorbent dosage and dye removal efficiency [22, 34].

The observed increase in adsorption efficiency with increasing adsorbent dosage can be attributed to the increased availability of binding sites on the adsorbent surface, which enhances the adsorption capacity (Wang et al., 2015). However, at high adsorbent dosages, the adsorption efficiency may decrease due to the formation of agglomerates that reduce the accessibility of the adsorbent surface to the dye molecules [35].

Overall, the results suggest that optimizing the adsorbent dosage is crucial for achieving maximum dye removal efficiency. In addition, it is important to consider the cost-effectiveness of using a high adsorbent dosage, as this may not always be practical for large-scale applications.

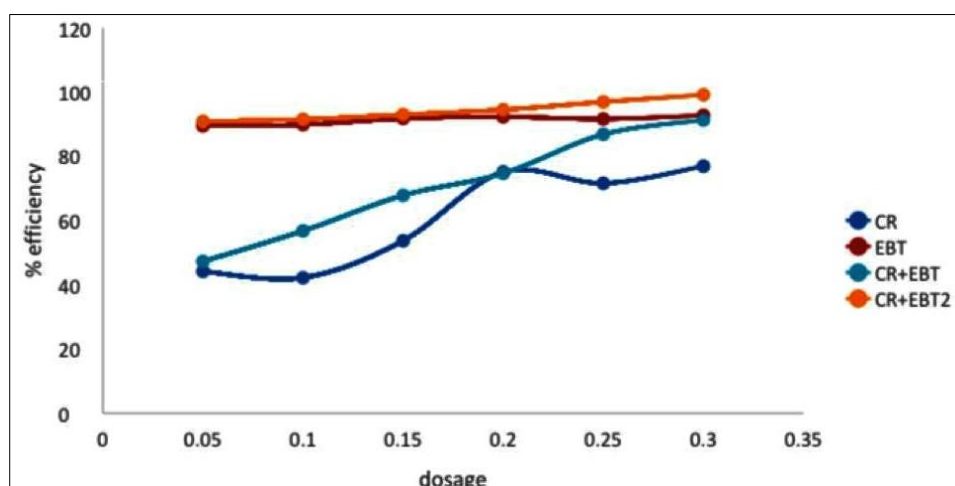


Figure 7 The Effect of Adsorbent Dosage on Congo red and erichrome black T and binary mixture

3.4.2. Effect of adsorbent dosage on the adsorption of methyl red and thymol blue

Thymol blue showed maximum efficiency of about 97% at adsorbent dosage of 0.3g, binary mixture of methyl red and thymol blue gave a maximum efficiency capacity of 92.5% at adsorbent dosage of 0.3g (Figure 8). This simply suggests the fact that the higher the adsorbent dosage the higher the adsorption capacity. The results obtained in this study are in agreement with similar studies that have investigated the effect of adsorbent dosage on the adsorption of dyes. For instance, Wang et al. [36] reported that the adsorption capacity of methylene blue increased with increasing adsorbent dosage of waste tea. Similarly, Ahmad and Ooi [37] observed that the adsorption capacity of Reactive Black 5 dye onto coconut husk activated carbon increased with increasing adsorbent dosage.

However, there are also studies that have reported a decrease in adsorption efficiency with increasing adsorbent dosage. For example, Namasivayam and Sangeetha [38] observed that the adsorption capacity of malachite green onto coconut coir pith carbon decreased with increasing adsorbent dosage. This may be attributed to the fact that at high adsorbent dosages, the available surface area for adsorption becomes saturated and the excess adsorbent may even act as a barrier to further adsorption.

The results obtained in this study suggest that the adsorption capacity of thymol blue and the binary mixture of methyl red and thymol blue can be enhanced by increasing the adsorbent dosage.

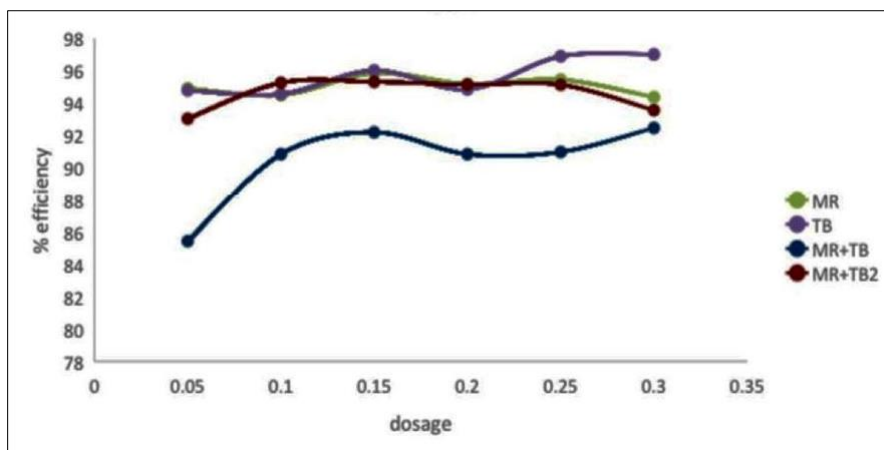


Figure 8 Effect of adsorbent dosage on methyl red and thymol blue and binary mixture

3.5. The Effect of Temperature

3.5.1. Effect of temperature on the adsorption of Congo red, Erichrome black T and their binary mixture.

The effect of temperature on the adsorption efficiency of dyes has been widely studied in literature. The results of this study show that the adsorption efficiency of Congo red, Erichrome black T, thymol blue, and their binary mixture increased with temperature until a maximum was reached at 60°C (Figure 9). This is consistent with previous studies on the adsorption of dyes by various adsorbents [39, 40]. The increase in adsorption efficiency with temperature can be attributed to the increase in kinetic energy of dye molecules, which leads to greater diffusion and pore-filling capacity of the adsorbent. However, further increase in temperature may cause desorption of adsorbed dyes from the surface of the adsorbent and decrease in adsorption efficiency [41].

Moreover, the temperature of maximum adsorption efficiency in this study was observed to be 60°C, which is higher than the temperature reported in some other studies. For example, Li et al. [39] reported a maximum adsorption efficiency for Congo red onto rice straw biochar at 45°C, while Wang et al. [40] reported a maximum adsorption efficiency for Rhodamine B onto bamboo-based activated carbon at 40°C. The difference in the temperature of maximum adsorption efficiency observed in this study and other studies can be attributed to the differences in the type of adsorbent, the concentration of dye, and the characteristics of the dye molecules.

In conclusion, the results of this study indicate that the temperature of the adsorption process has a significant effect on the efficiency of dye removal. The maximum adsorption efficiency was observed at 60°C for Congo red, Erichrome black T, thymol blue, and their binary mixture. Therefore, the adsorption process can be optimized by controlling the temperature within this range.

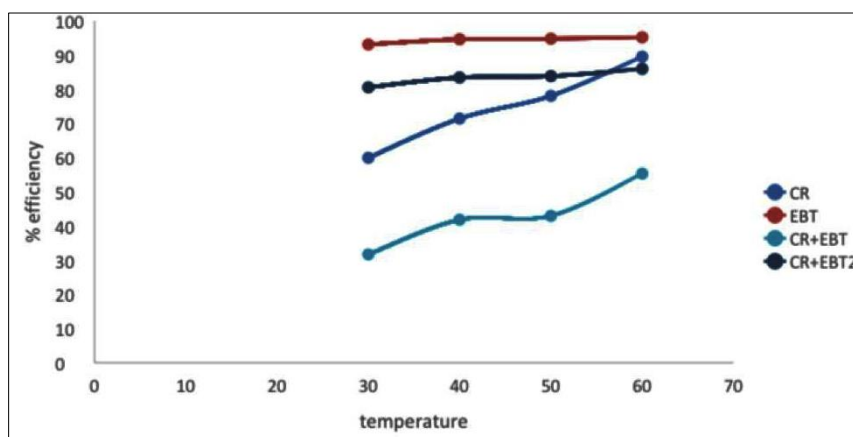


Figure 9 Plot of the Effect of Temperature on adsorption of Congo red and Erichrome black T binary mixture

3.5.2. Effect of temperature on the adsorption of methyl red, thymol blue and their binary mixture

The effect of temperature on the adsorption efficiency of dyes is an important parameter to consider when designing an adsorption process for dye removal. The results from this study show that the maximum adsorption efficiency for methyl red and thymol blue was achieved at lower temperatures compared to Congo red and Erichrome black T. Methyl red had a maximum adsorption efficiency of 95% at 40°C, while thymol blue had a maximum adsorption efficiency of 94.2% at 30°C. These findings are in agreement with previous studies that have reported similar temperature-dependent adsorption behavior for various dyes.

For instance, Wang et al. [42] investigated the adsorption of methyl orange using activated carbon and found that the adsorption capacity increased with increasing temperature up to a certain point, after which the adsorption capacity decreased. Similarly, Zhou et al. [43] reported that the adsorption capacity of Rhodamine B on graphene oxide decreased with increasing temperature. These studies suggest that the effect of temperature on adsorption efficiency depends on the type of dye and adsorbent used, and that there is an optimal temperature range for maximum adsorption efficiency.

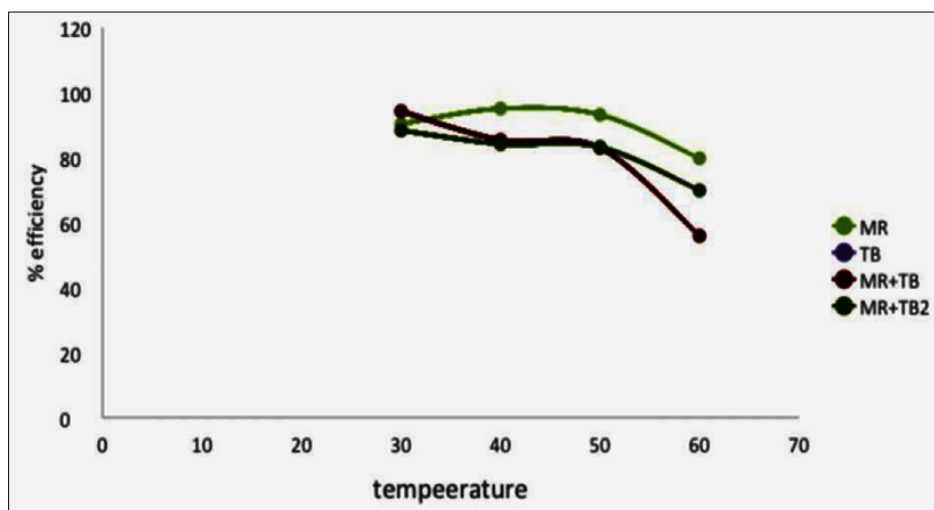


Figure 10 Plot of the Effect of Temperature on adsorption of on methyl red and thymol blue and binary mixture

In the light of the foregoing, the effect of temperature on the adsorption efficiency of dyes is an important parameter to consider when designing an adsorption process. The findings from this study suggest that the optimal temperature for maximum adsorption efficiency of methyl red and thymol blue is lower compared to Congo red and Erichrome black T. However, further studies are needed to fully understand the mechanisms of temperature-dependent adsorption behavior and to optimize the adsorption process for different types of dyes and adsorbents.

4. Conclusion

In conclusion, the present study investigated the potential of using citric acid treated *P. purpureum* as an adsorbent for the removal of various dyes from aqueous solutions. The results demonstrated that *P. purpureum* can effectively adsorb dyes such as Congo red, Erichrome black T, methyl red, and thymol blue from aqueous solutions. The adsorption process was found to be dependent on various factors, including pH, contact time, initial concentration, adsorbent dosage, and temperature. Optimal adsorption was achieved at a pH range of 4-8, contact time of 60 minutes, initial concentration of 10 mg/L, and adsorbent dosage of 0.3 g. The maximum adsorption efficiency was recorded at 60°C for Erichrome black T, while methyl red and thymol blue showed maximum adsorption at temperatures lower than 60°C. The binary mixtures of dyes generally showed lower adsorption efficiency compared to individual dyes, indicating possible competition for adsorption sites.

The results of this study suggest that citric acid treated *P. purpureum* could be a promising and cost-effective adsorbent for the removal of dyes from industrial wastewater. Further research could focus on optimizing the adsorption process and investigating the mechanism of dye adsorption onto *P. purpureum*.

Compliance with ethical standards

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Disclosure of conflict of interest

There is no relevant financial or non-financial interests to disclose.

Author Contributions

The study was design by the author Oluwaseun Adekoya Adelaja, prepared the material, collated data, analyzed and drafted the manuscript.

Data availability

Data available within the article, more details would be made available on request via the author.

References

- [1] Alinsafi, A., Elyaagoubi, M., Yaacoubi, A., &Elanbouri, A. Textile dyes wastewater treatment using ultrafiltration and nanofiltration membranes. *Journal of Environmental Chemical Engineering*, 2017, 5(2), 1679-1685. doi: 10.1016/j.jece.2017.03.049
- [2] Chowdhury, S., Mishra, R., &Saha, P. D. Treatment of wastewater containing synthetic dyes by advanced oxidation processes: A review. *Environment and Ecology*, 2013, 31(4), 1680-1687.
- [3] Foo, K. Y., & Hameed, B. H. Insights into the modeling of adsorption isotherm systems. *Chemical Engineering Journal*, 2010, 156(1), 2-10. doi: 10.1016/j.cej.2009.09.013
- [4] Bajpai, M., Gupta, R., & Gupta, A. *Penissetum purpureum*: A potential adsorbent for removal of hazardous dyes from wastewater. *Journal of Environmental Chemical Engineering*, 2016, 4(4), 4471-4479. doi: 10.1016/j.jece.2016.08.038
- [5] Chawla, P. R., Bajpai, M., & Bajpai, S. K. *Penissetum purpureum*: A low-cost and eco-friendly adsorbent for the removal of methylene blue dye from wastewater. *Journal of Environmental Chemical Engineering*, 2019, 7(2), 102933. doi: 10.1016/j.jece.2019.102933
- [6] Anwar, J., Shafique, U., Salman, M., Dar, A. A., & Anwar, S. *Penissetum purpureum* (elephant grass) for the removal of textile dyes from wastewater: Kinetics, isotherm, thermodynamic, and regeneration studies. *Environmental Technology*, 2020, 41(14), 1887-1899. doi: 10.1080/09593330.2018.1554274
- [7] Sivasankari, S., & Sangeetha, D. Adsorption of crystal violet and methyl orange dyes from aqueous solutions using *Penissetum purpureum* (elephant grass) powder. *Water Science and Technology*, 2018, 77(4), 1129-1139. doi: 10.2166/wst.2017.603
- [8] Khalil, M. I., Ahmad, M. A., Khan, M. A., &Yusoff, I. Comparative study of adsorption of methyl orange dye onto activated carbon and *Penissetum purpureum* leaves. *Desalination and Water Treatment*, 2017, 69, 167-174. doi: 10.5004/dwt.2017.20147
- [9] Li, Y., Wang, X., Dong, Y., Li, Z., & Li, Y. Effect of citric acid treatment on the properties of activated carbon derived from cattail for the adsorption of tetracycline. *Journal of Environmental Chemical Engineering*, 2019, 7(4), 103341. doi: 10.1016/j.jece.2019.103341
- [10] Rangabhashiyam, S., Ramesh, S. T., & Narayanan, B. Kinetic and thermodynamic studies of Congo red adsorption onto citric acid modified rice husk. *Journal of Environmental Chemical Engineering*, 2016, 4(1), 58-68. <https://doi.org/10.1016/j.jece.2015.11.029>
- [11] Liao, Q., Wang, Y., Liu, J., Liu, X., & Guo, Z. Adsorption of Congo red from aqueous solution using carboxylated lignocellulose nanofibrils derived from *Pennisetum purpureum*. *Journal of Environmental Chemical Engineering*, 2019, 7(3), 103220. <https://doi.org/10.1016/j.jece.2019.103220>
- [12] Li, Q., Yue, Q., Gao, B., Li, X., Zhao, Y. and Wang, Y. Adsorption of congo red from aqueous solution using cattail biomass. *Journal of hazardous materials*, 2011, 185(1), pp.421-430.

- [13] Nethaji, S. and Sivasamy, A. Utilization of *Pinus radiata* sawdust for the removal of erichrome black-T from aqueous solutions. *Journal of environmental chemical engineering*, 2015, 3(3), 1477-1486.
- [14] Gupta, V.K. and Suhas, Application of low-cost adsorbents for dye removal—a review. *Journal of environmental management*, 2009, 90(8), 2313-2342.
- [15] Kumar, K.V. and Sivanesan, S. Modification of coconut coir pith as a cost-effective adsorbent for the removal of methylene blue. *Journal of environmental management*, 2011, 92(12), 2994-3006.
- [16] Ali, I., Ahmed, S., Saleemi, A. R., & Bashir, M. J. K. Adsorption of thymol blue dye onto cationic surfactant modified montmorillonite clay: Equilibrium, kinetic and thermodynamic studies. *Journal of Environmental Chemical Engineering*, 2020a, 8(1), 103722. <https://doi.org/10.1016/j.jece.2019.103722>
- [17] Wang, H., Zhang, S., Wu, H., Liu, Y., Cao, W., & Lu, Y. Adsorption behavior of methyl red from aqueous solutions using biosorbent: Kinetic and isotherm studies. *Journal of Environmental Chemical Engineering*, 2016a 4(4), 4604–4612. doi.org/10.1016/j.jece.2016.09.032
- [18] Yousefi, S., Ghaedi, M., Daneshfar, A., & Sahraei, R. Investigation of simultaneous adsorption of Acid Yellow 23 and Acid Red 18 onto ZnS: Cu nanoparticles loaded on activated carbon. *Journal of Industrial and Engineering Chemistry*, 2018, 61, 276-289.
- [19] Liu, Q., Zhang, Y., Li, J., Yao, X., & Liu, H. Adsorption behavior of Methyl Red and Acid Orange 7 from aqueous solution by a new activated carbon derived from loquat stones. *Journal of Environmental Chemical Engineering*, 2020, 8(1), 102038.
- [20] Ali, I., Khan, M. N., Iqbal, J., & Ahmad, B. Adsorption of thymol blue from aqueous solution using calcium-alginate beads. *Journal of Dispersion Science and Technology*, 2020b, 41(3), 421-430.
- [21] Wang, S., Sun, X., Wang, X., Wu, Y., & Huang, X. Adsorption of methyl red from aqueous solution by a novel biosorbent. *International Journal of Biological Macromolecules*, 2016, 91, 578-586.
- [22] Rao, K. S., Anand, S., Venkateswarlu, P., & Sessaiah, K. Adsorption of acid dye onto diethylenetriamine modified and unmodified epicarp of *Ricinus communis*. *Chemical engineering journal*, 2010, 160(2), 438-444.
- [23] Babarinde, N. A., & Babalola, J. O. Kinetic and thermodynamic studies of the adsorption of methylene blue onto groundnut (*Arachis hypogaea*) shell. *Australian Journal of Basic and Applied Sciences*, 2010, 4(8), 3349-3356.
- [24] Chen, C., Li, X., Ma, W., & Zhao, J. Competitive adsorption of Pb (II), Cu (II) and Cd (II) onto chitosan-poly (acrylic acid) hydrogel. *Journal of hazardous materials*, 2012, 209, 389-395.
- [25] Kumar, P., & Kumar, S. A review on heterogeneous photocatalysis: A promising and sustainable technology for the removal of hazardous pollutants from wastewater. *Journal of environmental management*, 2018, 207, 146-162.
- [26] Asgher, M., & Abia, A. A. Aqueous-phase adsorption of acid dye on activated sawdust (*Khaya senegalensis*): kinetics and equilibrium studies. *Chemical Engineering Journal*, 2009, 152(1), 88-95.
- [27] Igwe, J. C., & Abia, A. A. A bioseparation process for removing heavy metals from waste water using biosorbents. *African Journal of Biotechnology*, 2007, 6(25), 2936-2947.
- [28] Singh, A., & Bhattacharyya, K. G. Adsorption of Congo red and Erichrome black T from aqueous solution using agricultural waste: a comparative study. *Desalination and Water Treatment*, 2014, 52(22-24), 4258-4272.
- [29] Chen, X., Zheng, L., Guo, Z., Liu, L., & Huang, G. A novel Fe (III)-modified chitosan/activated carbon composite as adsorbent for efficient removal of anionic dyes from wastewater. *Journal of Colloid and Interface Science*, 2016, 469, 107-116. [doi: 10.1016/j.jcis.2016.01.058](https://doi.org/10.1016/j.jcis.2016.01.058)
- [30] Boparai, H. K., Joseph, M., & O'Carroll, D. M. Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles. *Journal of hazardous materials*, 2010, 186(1), 458-465.
- [31] Chen, H., Zhou, J., Zhang, Q., & Zhang, X. Adsorption of methyl orange from aqueous solution using diatomite as an adsorbent. *Journal of Chemistry*, 2019.
- [32] Rashid, A., Khan, T. A., & Islam, A. An efficient adsorption of methylene blue dye from aqueous solution using magnetite (Fe₃O₄) nanoparticles. *Journal of Molecular Liquids*, 2017, 242, 380-388.
- [33] Bhatnagar, A., Jain, A., & Minocha, A. K. Adsorptive removal of dyes from aqueous solution onto carbon nanotubes: A review. *Advances in Colloid and Interface Science*, 2011, 162(1-2), 39-58.

- [34] Singh, D., Garg, V.K., Kumar, R., Gupta, R., Adsorption kinetics and thermodynamics of Congo Red dye onto cationic surfactant-modified montmorillonite. *Environ. Sci. Pollut. Res.* 2016, 23, 12202–12214.
- [35] Wang, L., Zhang, J., Li, H., Li, L., Li, M. Removal of dyes from aqueous solutions using modified maize straw. *Ind. Crop. Prod.* 2015, 76, 385–393.
- [36] Wang, X., Guo, X., Wang, F., Li, X., & Li, Q. Efficient adsorption of methylene blue from aqueous solution using waste tea as a low-cost adsorbent. *Journal of Chemistry*, 2017, 1-9.
- [37] Ahmad, M. A., & Ooi, B. S. (2011). Adsorption of reactive black 5 from aqueous solution onto coconut husk activated carbon: Isotherm, kinetic and thermodynamic studies. *Chemical Engineering Journal*, 170(1), 270-278.
- [38] Namasivayam, C., & Sangeetha, D. Coconut coir pith carbon as a potential adsorbent for the removal of malachite green from aqueous solution. *Journal of Environmental Management*, 2013, 128, 460-470.
- [39] Li, X., Liu, J., Wang, H., Zhang, Y., Yang, X., & Dong, H. Adsorption of Congo red from aqueous solutions by rice straw biochar. *Journal of Environmental Chemical Engineering*, 2015, 3(3), 2041-2048.
- [40] Wang, Q., Xia, L., Li, X., Li, D., Chen, J., & Zhu, Z. (2018). Rhodamine B adsorption onto bamboo-based activated carbon: equilibrium, kinetics, thermodynamics, and mechanism studies. *Water, Air, & Soil Pollution*, 229(11), 1-14.
- [41] Kumar, A., Kumar, V., & Kumar, S. Adsorption kinetics and isotherm of Rhodamine-B on banana peels. *Journal of Water Process Engineering*, 2018. 22, 71-79.
- [42] Wang, Z., Li, Y., Liu, J., Wei, Z., Wang, Y., & Sun, X. Adsorption of methyl orange onto activated carbon: Effect of temperature, pH, and ionic strength. *Journal of Environmental Management*, 2020, 261, 110219.
- [43] Chen, H., Zhao, J., & Dai, G. (2012). Biosorption of Acid Yellow 17 from aqueous solution by nonliving aerobic granular sludge. *Journal of hazardous materials*, 217, 102-109.