

Kinetic Study of Crystal Violet Dye Adsorption from Wastewater Using *Populus nigra* Leaf Powder

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Abstract

*This study investigates the potential of *Populus nigra* (black poplar) leaf powder as a low-cost, eco-friendly adsorbent for the removal of Crystal Violet dye from wastewater. Batch adsorption experiments were conducted to assess the effects of pH, contact time, adsorbent dosage, initial dye concentration, and temperature. Optimal removal conditions were observed at pH 10 and 15 °C, achieving an adsorption efficiency of 84%. The adsorption followed the Langmuir isotherm model ($R^2 = 0.9696$), indicating monolayer adsorption, and the kinetics fit the pseudo-second-order model ($R^2 = 1$), suggesting chemisorption as the rate-limiting step. These results highlight *Populus nigra* leaves as a sustainable biosorbent capable of reducing dye pollution in industrial effluents, offering a promising alternative to conventional treatment methods*

Keywords: Crystal violet, *Populus nigra*, Langmuir isotherm.

Introduction

Human beings and other living creatures cannot survive without water. Nevertheless, this issue of water pollution has increasingly posed a threat to the ecological balance. Industrial wastewater is harmful to the health of the people and aquatic life because it contains a large variety of toxic substances. With the current growth of urbanization and industrialization, the disposal of untreated wastewater into water bodies is one of the issues that have become critical worldwide. Thus, it is important to treat wastewater then discharge it into the environment. The wastewater management sector is changing at an accelerated pace due to the increased regulation and the necessity to treat new pollutants such as pharmaceuticals, personal care and even synthetic dyes. (Rehman & Majeed, 2022; Urooja, Javed, Taj, & Haider, 2023).

Crystal violet (violet de gentian or violet de leucipide) is an artificial stain, which is a triphenylmethane dye. Its deep violet coloration properties make it broadly used in a number of industries such as medical, veterinary, and textile. The compound

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(C₂₅NH₃₀Cl; molecular weight: 407.98 g/mol) is characterized by a high level of lipid components affinity, which causes a typical deep violet coloration (Elella, Sabaa, Abd ElHafeez, and Mohamed, 2019). Although, its intractability, toxicity and possible carcinogenicity are a major environmental issue, an effective, inexpensive and harmless way of eliminating it is required (Khanna, Ahmad, Shahb, & Farooqui, 2021; Zaidi, Lim, & Usman, 2018).

The given work analyzes the effectiveness of natural biomaterials in the form of *Populus nigra* leaves as biosorbents to remove crystal violet dye in aqueous solutions. The solution can be taken as an alternative to other conventional wastewater treatment techniques as it is sustainable and economically viable, reducing the negative effects of dye pollution on aquatic life. (Rehman & Majeed, 2022; Urooja et al., 2023).

Methodology

All reagents used were of analytical grade and obtained from Sigma-Aldrich. *Populus nigra* leaves were collected, washed thoroughly with tap and distilled water, air-dried, and oven-dried at 70 °C for 3 hours. The dried material was ground, sieved (30–100 mesh), and stored in airtight containers for subsequent experiments. The stock dye solution (1000 mg/L) of Crystal Violet was prepared using distilled water. The pH was adjusted using 0.1 M HCl or NaOH. UV–Vis spectrophotometer ($\lambda_{\text{max}} = 590$ nm) was used to measure residual dye concentrations. Each experiment was performed in triplicate under batch conditions. The adsorption capacity (q_e , mg/g) and percent removal (%) were calculated as:

$$q_e = (C_0 - C_e) \times V/m$$
$$\% \text{ Removal} = ((C_0 - C_e) / C_0) \times 100$$

where C_0 and C_e are the initial and equilibrium dye concentrations (mg/L), V is the volume of solution (L), and m is the mass of adsorbent (g).

The *Populus nigra* powder was made by a multi-step procedure. Fresh leaves were taken and sprayed with tap water and distilled water so that any dust, dirt and other surface impurities would be removed. The washed leaves were air dried in strong sunshine and reduced to fine particles. To be sure of the extraction of the soluble pigments and impurities, the leaves powder was washed with deionized water multiple times until the washings appeared colorless. The resulting powder was dried in an oven at 70 °C on a three hour basis to remove any moisture content. Last, the sieved material was dried through meshes of different sizes (30, 60, and 100) in order to get homogeneous fractions of particles that were used as the adsorbent material. Prior to

their subsequent application in the adsorption studies of crystal violet dye removal, these produced adsorbents were stored in dry, airtight containers.

Result and Discussion

Batch Adsorption Experiments

Using a batch adsorption experiment, the removal of crystal violet dye using powdered *Populus nigra* leaves was examined. The purpose of the experiment was to ascertain the effects of several parameters, including contact time, which was kept at 0 to 50 minutes, and adsorbent dosage, which was raised to 0.2 g and 1.0 g. Also, the effects of solution pH were studied at varying pH of 1-10 and the temperature dependent ones were conducted at varying temperature of 15 °C to 50 °C. These parameters were tested to decide what role they played in the removal of crystal violet dye by adsorbent.

Factors Influencing Adsorption

There are a number of important parameters that affect the efficiency of crystal violet dye removal by *Populus nigra* leaves powder of aqueous solutions such as dosage of adsorbent, dye concentration (initial), contact time, solution pH, and temperature. This paper also critically analyses the effect of these conditions on the adsorption performance and delivers a critical analysis of the effect of each of the factors on adsorption efficiency in the following sections.

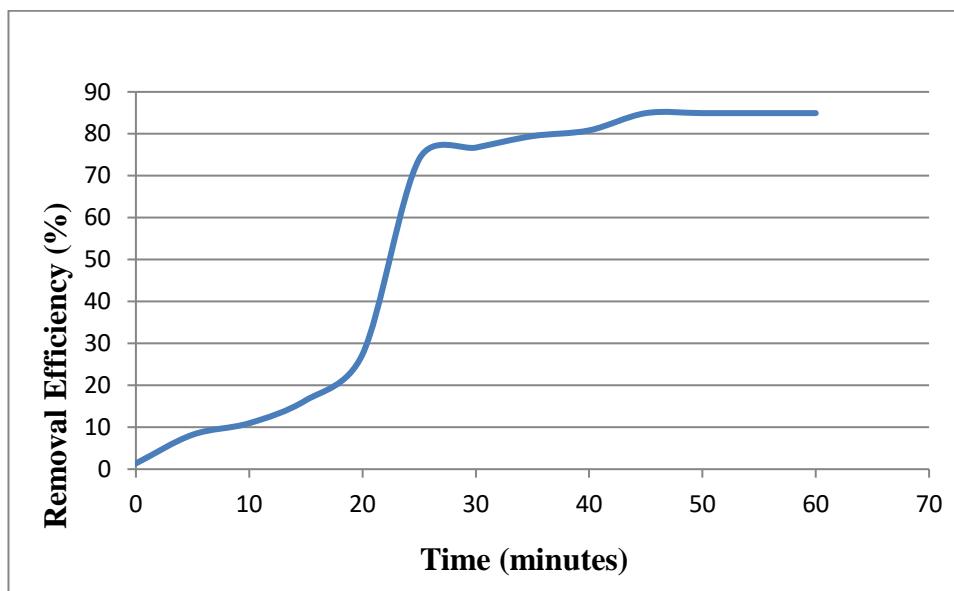
Effect of Time

The time of contact was systematically determined on adsorption of crystal violet dye on *Populus nigra* leaves powder. A 2 ppm dye solution was prepared and 0.1 g of adsorbent was added in the solution. Suspension was stirred with orbital shaker and aliquots were removed at certain time intervals between 5 to 50 minutes. The efficacy of adsorption with time was then assessable, by determining the remaining dye concentration in each of the samples, after filtration, using a UV-visible spectrophotometer.

The adsorption profile depicted a sharp rise of dye removal efficiency at the beginning, probably because the surface of adsorbent contains many active sites (Figure 1). The adsorption rate decreased with time to a near equilibrium using the occupied sites. This trend is common to adsorption processes and what is received at the beginning is a rapid uptake after which the plateau phase is subsequently experienced following a saturation of the sites (Ahmad, 2009; Rehman & Majeed, 2022). The equilibrium was achieved within the studied time, which means that the

Populus nigra leaves powder has a comparatively rapid adsorption ability towards crystal violet. The trends are consistent with literature in which natural adsorbents presented high adsorption efficiencies at short contact times and then equilibrium where the system reached maximum adsorption potential (Khanna, Ahmad, Shahb, & Farooqui, 2021; Urooja, Javed, Taj, & Haider, 2023).

Figure 1: Effect of Contact time on Removal of Dye



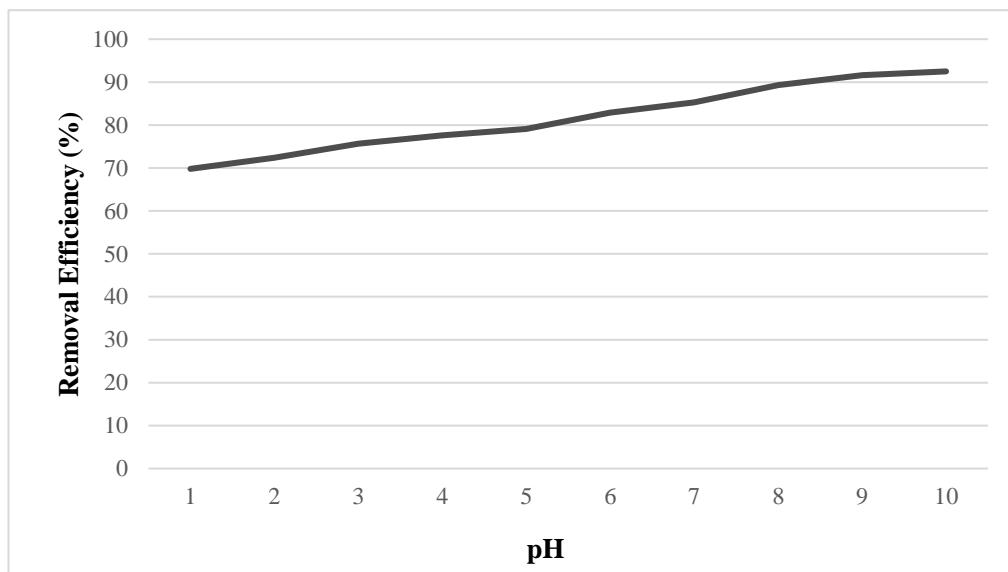
pH Effect

It is an important parameter in the adsorption of crystal violet dye since it has a direct impact on the adsorbent (surface charge) and the dye molecules (ionization character). The influence of pH on dye removal in this study was studied under controlled environment where the temperature was held at 15 °C, a contact time of 50 minutes, and dosage of adsorbent was 1 g. The pH level was regulated between 1 and 10 to determine the effect on adsorption process.

The results revealed that the removal efficiency of dye was increased with the rise in pH. At very low pH, the H⁺ ion interfered with the cationic dye molecule in adsorption sites, decreasing the efficiency. The removal of 92 % was achieved at pH=10 and compared to the work of Mokhtar et al., where 79.27 % was achieved. As the pH rises, the *Populus nigra* leaves surface is deprotonated, which augments the

number of negative sites, which attract the positively charged crystal violet dye molecules through electrostatic forces (Figure 2). This will lead to a better adsorption capacity because the contention with protons will be decreased and also there will be a greater level of electrostatic affinity between adsorbent and the dye. This behavior is related to the previous study results and shows that electrostatic interactions have an important part in the process of adsorption and it is pH-dependent phenomenon.

Figure 2: Effect of pH on Removal of Dye

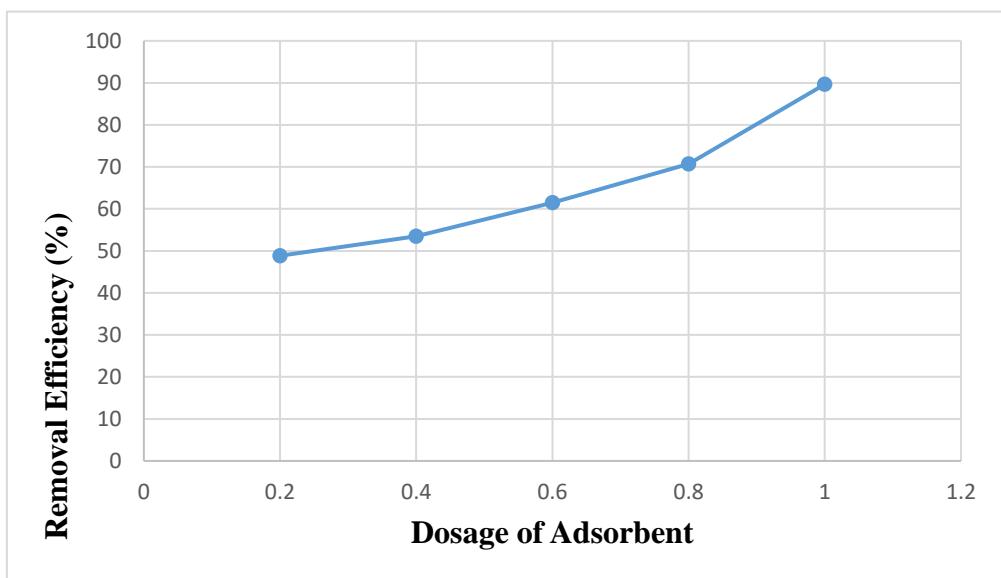


Adsorbent Dosage Effect

Adsorbent dosage effect on the dye removal capacity was examined by changing the *Populus nigra* leaves powder dosage to 0.2g -1.0 g at a constant dye concentration and with other conditions held constant. The maximum % removal was achieved at concentration of 1g. This enabled evaluation of the quantity of adsorbent on adsorption capacity and total dye removal efficiency. Percentage retention of crystal violet dye also increased with adsorbent dosage because more active binding sites and more surface areas were available to interact with dye molecules as the concentration of adsorbent increased. Such a tendency can also be explained by other researchers who reported that, with the rising adsorbent dosage, dye removal efficiency increased because the availability of adsorption sites increased as well, and,

therefore, the adsorbent and dye molecules could interact more effectively. The percent removal of dye with a higher dosage of adsorbent tended to increase, but the adsorption capacity in terms of unit mass of adsorbent might decrease with adsorbent dosage (Ahmad, 2009; Shojaeipoor, 2024). With the increase in amount of adsorbent dosage, the percent removal of dye increased, but higher dosages of adsorbent reduced adsorption capacity per unit mass of adsorbent. To explain this reduction, it can be explained by unsaturated adsorption sites and possible aggregation of particles, which lowers the effective surface area to adsorb, and in the end, the overall efficiency of the adsorption process. (Urooja, Javed, Taj, & Haider, 2023).

Figure 3: Effect of Adsorbent Concentration on Removal of Dye

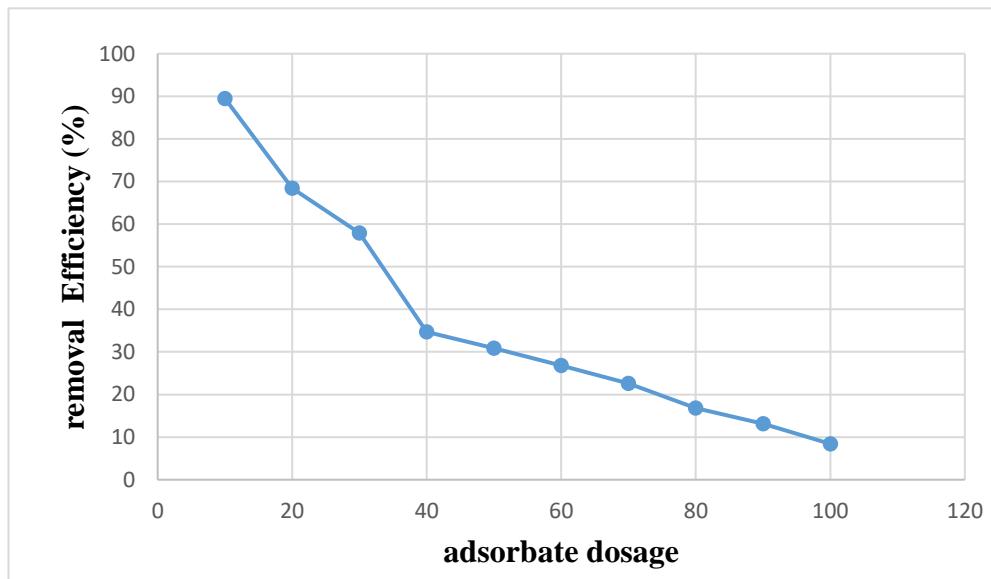


Adsorbate Concentration Effect

The effect of the initial concentration of dye on the removal of the crystal violet was examined with pH 10, and 1g/L of *Populus nigra* leaves powder at 15 °C (Figure 4). Being the force that fosters the movement of mass between the aqueous and solid adsorbent, the initial dye concentration is vital in adsorption efficiency and capacity. The findings indicated that the higher the concentration of the starting dye, the greater was the reduction in the efficiency of removal as adsorption sites available on the *Populus nigra* leaves powder surface were saturated. With low concentrations,

active sites were plenty thus being more effective at removing, but with high concentrations the few active sites would be ineffective since the concentration would not allow a great percentage to be removed. This pattern is also in agreement with the earlier works which note the effect of reduced binding sites with an enhanced competition among dye molecules and affects adsorption efficiency. Removal efficiency does decline as the dye concentration increases, but the adsorption capacity per unit mass of adsorbent (mg/g) can increase as a result of more effective use of the existing binding sites. The reason is that an increase in concentrations increases the driving force of mass transfer resulting in high uptake capacity, even though there is a reduction in percent removal. This tendency coincides with the results given by Shojaeipoor (2024).

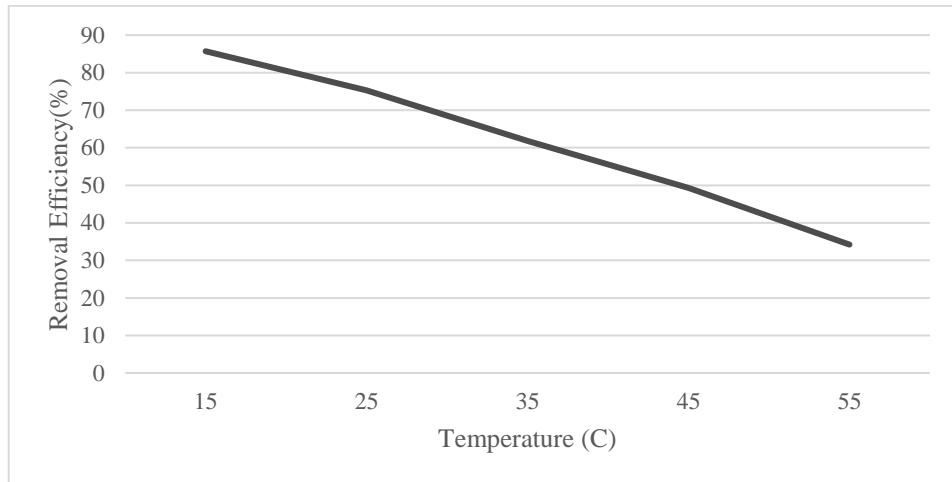
Figure 4: Effect of Adsorbate Concentration on Removal of Dye



Temperature Effect

Temperature was studied at 15°C, 25°C, 35°C, 45°C and 50 °C keeping all other parameters constant (Figure 5). The outcomes revealed that adsorbent capacity reduced with rise of temperature meaning that the adsorption process was exothermic. This indicates that crystal violet dye adsorption is more preferable in lower temperatures on *Populus nigra* leaves powder (Ahmad, 2009).

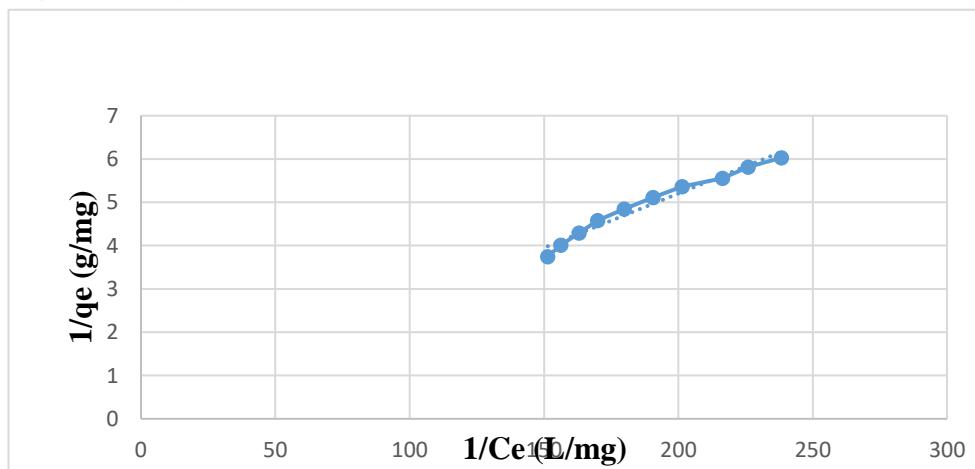
Figure 5: Effect of Temperature on Dye Removal



Adsorption Isotherm

The paper has investigated by the Langmuir and Freundlich adsorption isotherm models in order to learn how crystal violet dye adsorption on *Populus nigra* leaf powder behaves (Figure 6). Equilibrium data at different temperatures using these models and holding the concentration of the adsorbent constant at 1 g/L were used to understand the adsorption mechanism and adsorbent-dye interactions.

Figure 6: Langmuir Isotherm Model



The Langmuir isotherm model gave a superior fit to the experimental data ($R^2 = 0.9696$) than the Freundlich model ($R^2 = 0.0023$). This implies that crystal violet adsorption on the leaf powder of *P. nigra* is through monolayer adsorption on a uniform surface with finite binding sites which are energetically equivalent, which is in line with the assumption made of the Langmuir model.

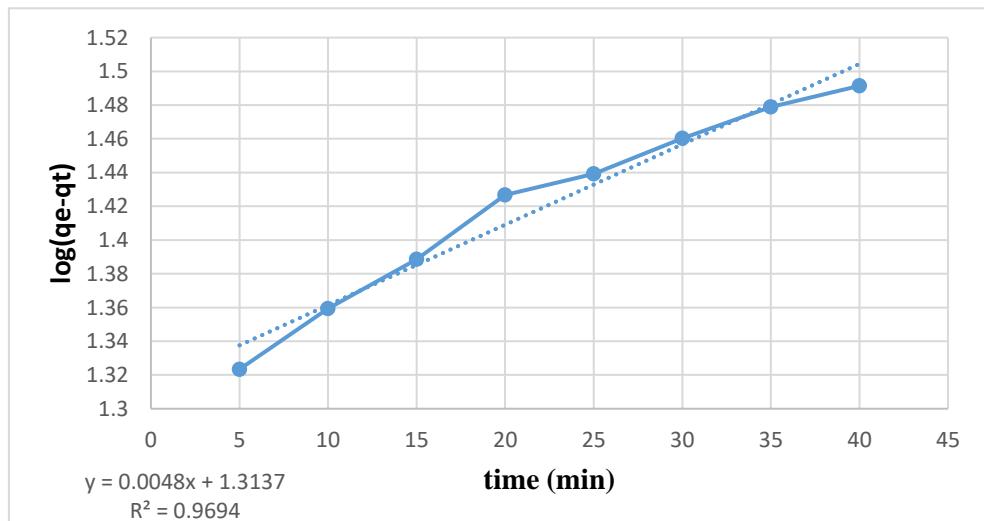
Adsorption kinetics

The pseudo-first-order and pseudo-second-order kinetic models were evaluated to determine the equilibrium adsorption capacity and rate constants at different temperatures.

Pseudo-first-order

The pseudo-first-order model, the rate constant (K_1) and equilibrium adsorption capacity (q_e) were obtained from the intercept and slope of the plot of $\log(q_e - q_t)$ versus time (Figure 7).

Figure 7: Pseudo-first-order Kinetic Model

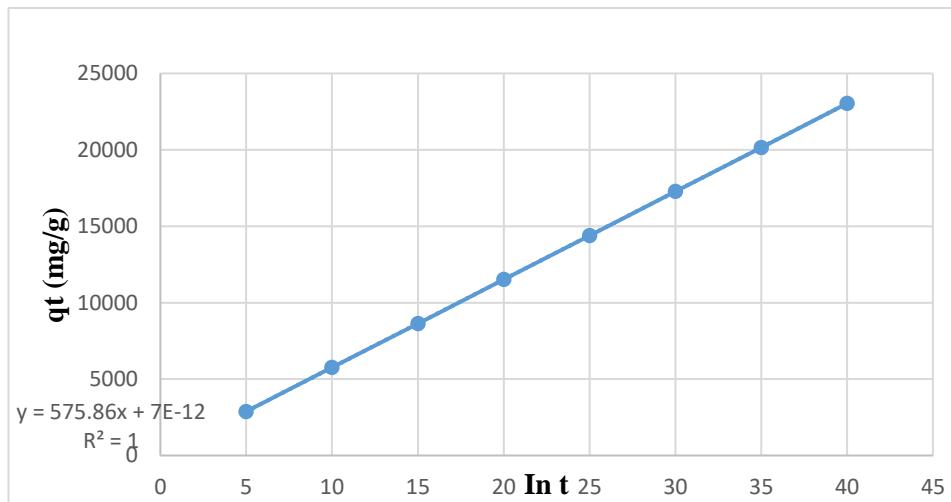


Pseudo-second-order

The pseudo-second-order model showed an excellent linear fit ($R^2 = 1$) when plotting t/qt versus time, indicating that the adsorption kinetics follow pseudo-second-order behavior. This suggests that chemisorption plays a significant role in the adsorption process, involving strong chemical interactions.

Between the adsorbent and adsorbate (Figure 8).

Figure 8: Pseudo-second-order Kinetic Model



Conclusion

The study highlights the potential of *P. nigra* leaves as a sustainable, low-cost adsorbent for removing crystal violet dye from aqueous solutions. Key operational parameters, including adsorbent dosage, initial dye concentration, pH, contact time, and temperature, significantly impacted adsorption performance, providing valuable insights for optimizing dye removal processes. The adsorption process reached equilibrium within 50 minutes, with optimal conditions identified at 15 °C and pH 10. The removal efficiency improved with increased adsorbent dosage due to the greater availability of active sites. In contrast, higher dye concentrations led to reduced removal efficiency due to site saturation. The adsorption was favored at higher pH values, likely due to stronger electrostatic interactions, and at lower temperatures, indicating exothermic behavior. These findings provide valuable insights into optimizing the use of *P. nigra* leaves as an effective adsorbent for crystal violet dye removal.

The optimization of parameters resulted in a maximum dye removal efficiency of approximately 84%, demonstrating the effectiveness of *P. nigra* leaves as a biosorbent for treating dye-contaminated wastewater. This eco-friendly approach offers a promising alternative to conventional methods, contributing to the growing

research on plant-based adsorbents for environmental remediation and paving the way for potential industrial wastewater treatment applications.

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