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## Original Research Article

# Synthesis of tannic acid doped polyaniline (TPAni) for the removal of crystal violet dye by adsorption process

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### ABSTRACT

This research paper shows the adsorption proficiency of Tannic acid doped with polyaniline (TPAni) to remove crystal violet dye from its dilute solution. TPAni was characterized using FTIR, FE-SEM, TEM technology. Batch mode experiments were then employed to adsorb the aqueous solution of crystal violet (CV) dye. TPAni is relevant for the adsorption of cationic dyes like crystal violet (CV) because of their negatively charged backbone. The adsorption data was described in various kinetic models in order to find the kinetics of the adsorption process: both the pseudo-first and pseudo-second order models. The kinetic study's findings showed that chemisorption was the method of adsorption and that the pseudo-second-order model best matched the data. The Freundlich isotherm model was found to fit the process's adsorption data the best, according to isotherm studies utilizing the Freundlich and Langmuir models. Additionally, the effects of temperature, pH, contact time, and initial concentration of CV were examined and optimized to 35°C, 9,70 minutes, 7mg/L, and, respectively. For the treatment of wastewater, polyaniline surface modification or doping gives an alternative and efficient modified adsorbent.

## 1. Introduction

Water pollution is one of the most critical environmental challenges worldwide, arising from the continuous discharge of untreated or partially treated industrial, agricultural, and domestic wastes into natural water bodies. Rapid industrialization and urbanization have significantly increased the release of toxic contaminants such as heavy metals, pesticides, pharmaceuticals, and synthetic dyes into aquatic environments. These pollutants degrade water quality, disturb ecological balance, and pose serious risks to both aquatic life and human health. Water pollution caused by synthetic dyes has become a major environmental concern, particularly due to the rapid growth of textile, paper, leather, and pharmaceutical industries. Among these dyes, crystal violet is a widely used cationic triphenylmethane dye known for its intense colour, high solubility, and chemical stability, widely used in textile dyeing, paper printing, biological staining, and as an antimicrobial agent. Large volume of crystal violet-containing wastewater are often discharged into natural water bodies with insufficient treatment, leading to serious environmental pollution. Composite prepared by using biological moieties and peanuts hull waste biomass used for adsorption of crystal violet dye [1]. Crystal Violet (CV) Dye removed by adsorption using Polyacrylonitrile-based beads (PAN) as an adsorbent [2]. Multi-walled carbon nanotube coupled  $\beta$ -Cyclodextrin/PANI hybrid photocatalyst used for advance oxidative degradation of crystal violet [3]. Copolymer adsorbent was proficient to eliminate crystal violet dye at various temperature and time [4].

Bio-compost, derived from the decomposition of organic wastes such as agricultural residues, food waste, and plant biomass, is rich in functional groups ( $-\text{OH}$ ,  $-\text{COOH}$ ,  $-\text{NH}_2$ ) and possesses a porous structure, which enhances its adsorption capacity. These surface characteristics enable strong electrostatic interactions and hydrogen bonding with cationic dyes like crystal violet. The modified rice bran (MRB) was used for the elimination of crystal violet (CV) from polluted effluent. In this research, rice bran (RB) doped by chlorosulfonic acid [5]. Polyacrylamide-Grafted *Actinidia deliciosa* peels powder (PGADP) for the sequestration of crystal violet dye and study isotherms, kinetics and thermodynamic entity [6]. Increasing need for clean water due to pollution from industrial dyes emphasizes waste water treatment. A novel electrochemical sensing approach using polymer composite base on polyaniline and graphene oxide to detect hazardous dye at ppm-ppb levels. This composite has higher sensitivity toward cationic dye removal as compared to anionic dye [7]. The research focuses on synthesizing a montmorillonite nanosheet-based poly(acrylamide-co-2-acrylamide-2-methylpropane sulfonic acid) hydrogel composite using ultrasound-assisted dye adsorption. The nanosheets form a 3D network through hydrogen bonding and ionic interactions, enabling rapid dye uptake [8]. Biosorbent like rice husk obtained from agriculture waste materials act as best adsorbent for the removal of CV dye from polluted water [9]. Some bio waste materials also use to modified with



polymers for better removal of dye. Potato peel (PP) modified with polyaniline to increase adsorbanceability to remove multiple synthetic dye (Basic Fuchsin (BF), Methylene Blue (MB), Malachite Green (MG), Rhodamine B (RhB), Congo Red (CR), and Bordeaux B (BB)) [10]. The development of effective, low-cost, and environmentally friendly adsorbents for the removal of crystal violet from aqueous solutions has become an important area of research. This study focuses on the removal behaviour of crystal violet dye under various experimental conditions, aiming to contribute to sustainable wastewater treatment strategies.

## 2. Materials and methods

The chemicals used in this research were AR quality. (Sigma Aldrich) Aniline was initially used before the polymerization process. Tannic acid (TA), crystal violet, double-distilled water and ammonium persulfate (APS)  $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$  (Sigma Aldrich) were all used accurately as given.

The procedure of polymerization is used to create tannic acid doped with polyaniline. First, 20 millilitres of distilled water are combined with 4.6 millilitres of 50% tannic acid and 4.6 millilitres of aniline in a single beaker. In a separate beaker, 2.85 g of ammonium per sulphate (APS) was dissolved in 10 mL of distilled water. In less than a minute, the APS solution is combined with another beaker solution. For 23 hours, keep the reaction mixture undisturbed at 4 degrees Celsius. Studies in the literature indicate that aniline polymerization took place at the point of contact [11]. Following that, the bottom aqueous mixture was thoroughly filtered to remove the reaction mixture.

### Adsorption experiments

A stock solution of crystal violet dye was prepared in double-distilled water and diluted to obtain different concentrations. In batch adsorption experiments, a fixed amount of adsorbent (3 mg) was shaken with the dye solution at 250 rpm. After a set contact time, the mixture was centrifuged at 6000 rpm for 15 minutes. The remaining dye concentration in the supernatant was measured at 590 nm using a UV-Visible spectrophotometer, which was calibrated with standard crystal violet solutions. A linear calibration curve was obtained from the absorbance-concentration relationship.

## 3. Results and discussion

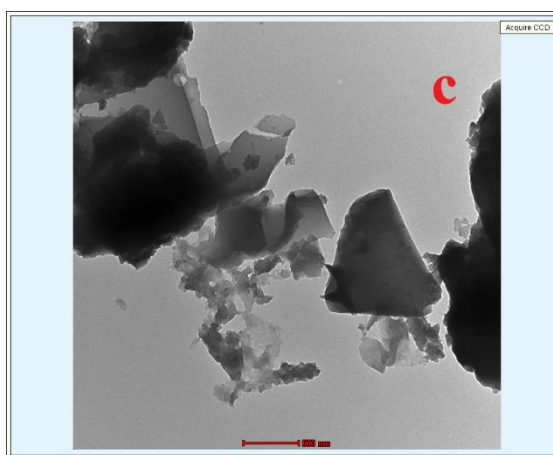
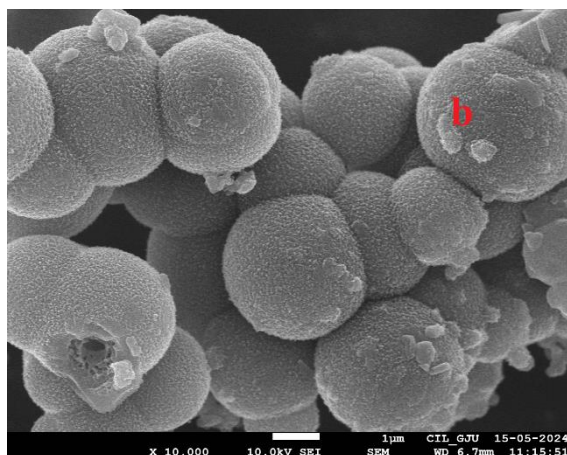


Figure 1: (b) SEM of TPAni; (c) TEM of TPAni.

### 3.1 Structural characterization of tannic acid-doped polymer

FTIR of TPAni (figure 1(a)) shows a peak at  $3235\text{ cm}^{-1}$  representing the structure's N-H stretching. The absorption band at  $2165\text{ cm}^{-1}$  is due to the asymmetric stretching mode of the C-H aromatic bond [12]. The sample's quinoid and benzenoid ring structures are what cause the peaks at  $1561\text{ cm}^{-1}$  and  $1485\text{ cm}^{-1}$ . The signal at  $1306\text{ cm}^{-1}$  indicates that secondary amines are stretched. At  $1073\text{ cm}^{-1}$ , the C-H bending vibration produces an absorption band.

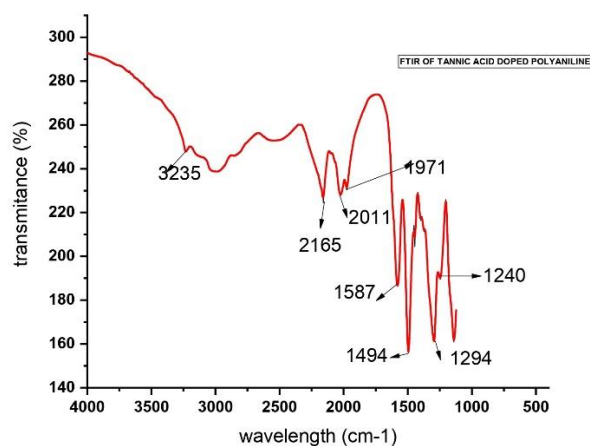


Figure 1: (a) FTIR of TPAni.

(SEM) data show the surface morphology of tannic acid doped polyaniline produced by polymerization in figure 1(b) having a globular structure and figure 1(c) shows an HRTEM image of TPAni showing irregular dark and light regions representing the internal structure of TPAni.

### 3.2 Adsorption studies

#### Contact time's effect on CV removal

The study examined how contact time affects the removal of crystal violet (CV) dye using tannic acid-doped polyaniline. Batch adsorption experiments were conducted by mixing 50 mL of CV solution (7 mg/L) with 0.003 g of the adsorbent at pH 9,  $35\text{ }^\circ\text{C}$ , and 250 rpm. Dye removal increased with contact time, with about 90% adsorption occurring within the first 30 minutes (figure 2a). Equilibrium was reached after 70 minutes, achieving approximately 95% dye removal, which was identified as the optimal contact time for the process.

### Impact of initial dye concentration on elimination of CV

The significance of initial dye concentration on adsorption is visible in (Fig. 2b). This is accomplished by varying the initial concentration of CV dye (2–10 mg/L) while keeping the values of all other parameters (pH-9, dose 0.003 g, temperature – 35°C, and contact duration = 70 min) constant. The figure display that adsorption percentage decreases as the original dye concentration rises. This is due to the fact that there are more empty active sites on the adsorbent's surface when the initial dye concentration is lower. The amount of dye adsorption at equilibrium increases with the initial dye concentration. The forces that propel the supply of dye molecules to get past the obstacle to mass transfer (dye molecules) between the aqueous and solid phases can explain this. In addition, as the initial dye concentration rises, there appears to be a greater interaction between the adsorbent and the dye molecules. There hasn't been any discernible alteration in CV adsorption after a particular initial dye concentration, such as 7 mg/L. Therefore, the concentration at equilibrium for the current study is 7mg/L.

### Impact of pH on the adsorption of CV

To determine the effect of changes pH on CV removal by TPAni was taking different solution having pH values ranging from 2 to 11 (Fig. 2c). Tannic acid-doped polyaniline's tannic acid hydroxyl groups were deprotonated according to the pH of the reaction solution. Higher pH levels therefore cause greater CV adsorption, and pH-9 is the final pH at equilibrium.

### Adsorbent dosage impact on CV dye uptake

Another important parameter in adsorption experiments is the dose (amount) of adsorbent used. Effect of dose of doped polyaniline on the adsorption of CV dye, taking it value varying from 0.01 to 0.1 g while all other parameters remained constant (fig. 2d). As the amount of doped polyaniline increases from 0.01 to 0.1 g, the percentage of dye adsorption rises rapidly due to the greater availability of surface area and active sites. However, beyond an optimum dose (about 0.03 g for 20 mL dye solution), further increase in adsorbent does not result in appreciable improvement in adsorption. Therefore, 0.03 g was identified as the ideal adsorbent dosage for effective CV dye removal in this study.

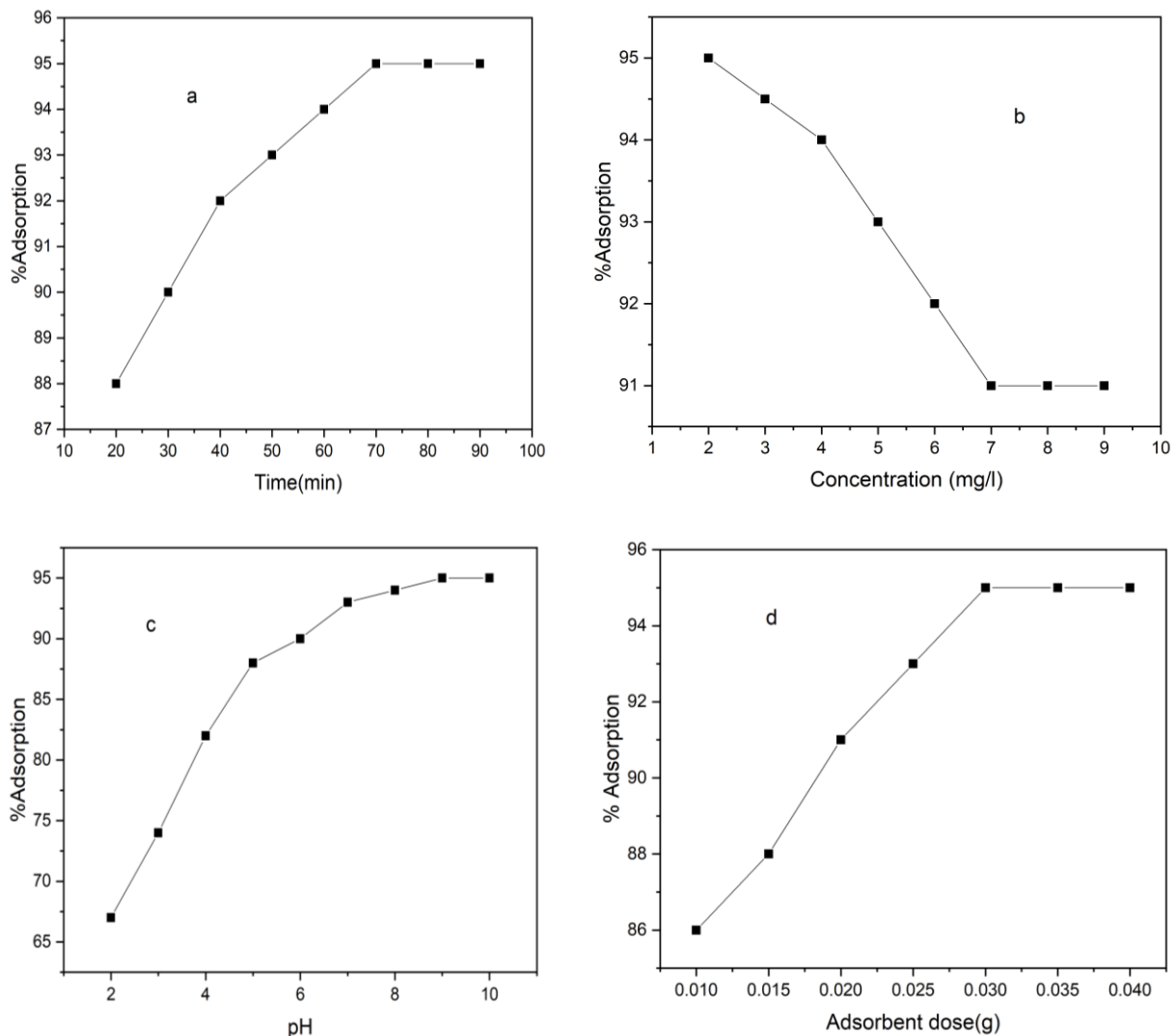


Figure 2: (a), (b), (c), (d) represent the effect of time, initial concentration, pH, and adsorbent dose, respectively.

### Kinetic study of CV adsorption onto TPAni

Kinetic research of adsorption-based dye removal is significant because it controls the equilibrium duration and adsorption efficiency [13]. It described the mechanisms of adsorption. Dye uptake and its rate on modified polyaniline with tannic acid show two distinct kinetic models were employed: the model of pseudo-first order and the pseudo-second-order model. The pseudo-first-order model is represented by the following equation:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (1)$$

A graph between  $\log(q_e - q_t)$  vs. time shown in Figure 3(a), project the analysis of pseudo-first order model to the adsorption data.  $q_e$  and  $q_t$  represent the CV dye amount that was adsorbed on polyaniline modified with tannic acid at equilibrium and time  $t$  (min), respectively. The pseudo-first-order model's adsorption constant is  $K_1$  (l/min). The values of  $K_1$  and  $q_e$  were taken from the graph's slope and intercept (Fig. 3a) correspondingly. Table 1 provides the adsorption

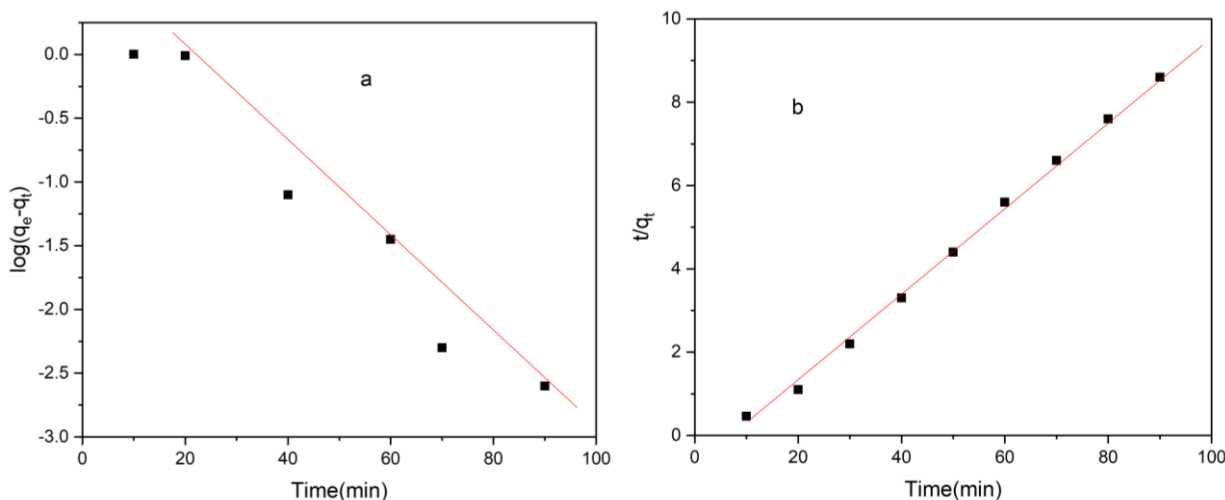
parameters' values preceding earlier. It shows that this adsorption system does not adhere to this specific model. The pseudo-second-order model, which considers the quantity of dye adsorbed on the polyaniline surface and at equilibrium, is an adsorption model examined for CV adsorption on polyaniline modified with tannic acid. The model's pseudo-second-order linearized form can be seen in the following expression:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

The pseudo-second-order model's rate constant is  $k_2$  (g/mg min), and  $t/q_t$  vs.  $t$  is plotted as a straight-line curve. As it can be evident that the experimental  $q_e$  exp. (2.85) and computed cal. (2.96) values close with one another, and the value of  $R^2$  is probably equal to 0.98. Thus, given observed data, it is presumed that this model best fits the adsorption data for CV onto TPAni. Additionally, adsorption data suggests that chemisorption was a major factor in this experiment.

**Table 1:** Rate constant values for CV adsorption showing kinetic models on tannic acid-doped polyaniline.

Kinetic models	Parameters	R <sup>2</sup> value
Pseudo first order	K <sub>1</sub> =0.049(min) <sup>-1</sup> Exp q <sub>e</sub> (mg g <sup>-1</sup> ) 2.85 Cal q <sub>e</sub> (mg g <sup>-1</sup> ) 0.28	0.91
Pseudo-second-order	K <sub>2</sub> 0.070 (g mg <sup>-1</sup> min <sup>-1</sup> ) cal q <sub>e</sub> (mg g <sup>-1</sup> ) 2.96	0.97



**Figure 3:** Kinetic studies (a) pseudo first order modal and (b) pseudo second order modal.

### 3.3 Adsorption isotherm

The result of adsorption of CV dye on TPAni showed a variety of adsorption isotherm modal include Freundlich and Langmuir isotherm modal. Adsorption research involved relationship between amount of dye adsorbed at equilibrium and its concentration in solution help in optimize adsorption system [14]. The Langmuir isotherm model's equation is as follows:

$$\frac{C_e}{q_e} = \frac{1}{b q_m} + \frac{1}{q_m} C_e \quad (3)$$

$C_e$  and  $q_e$  in the above equation, stand for dye adsorbed concentration and quantity at equilibrium, respectively. The Langmuir constant  $b$  and the Langmuir monolayer adsorption of dye are denoted by  $q_m$ . Plotting  $C_e/q_e$  vs.  $C_e$  determine

whether the experimental data is suitable for this model. The straight line shows best results in Figure 4(a). The straight line's slope and intercept yield the values of  $q_m$  and  $b$ , respectively. Table 2 display the values of all the parameters that were obtained. The separation factor  $R_L$  is used to predict the adsorption efficiency. The expression (Eq. 4) for the dimensionless separation factor ( $R_L$ ) is as follows:

$$R_L = \frac{1}{1 + b C_0} \quad (4)$$

where the starting dye concentration is denoted by  $C_0$ .  $R_L$  and  $q_m$  have respective values of 0.0045 and 41.5 mg g<sup>-1</sup>. The Langmuir isotherm modal show monolayer process occurring on surface.

**Table 2:** Crystal violet dye (CV)adsorption isotherm parameter on TPAni.

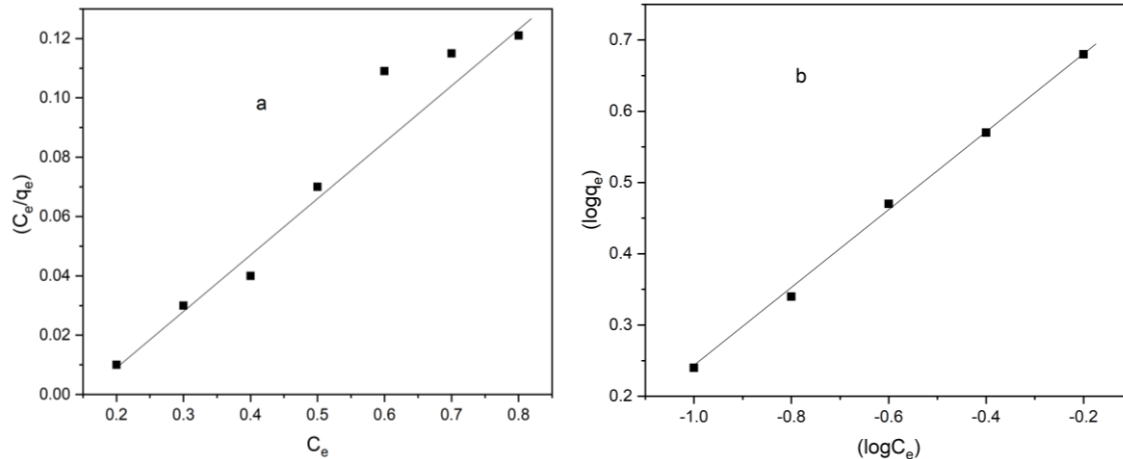
Isotherms	Isotherm constant	R <sup>2</sup> value
Langmuir	$q_m = 41.5, b = 0.23, R_L = 0.0045$	0.616
Freundlich	$K_f = 10.48, n_h = 0.96$	0.96

**Freundlich Isotherm**

The Freundlich adsorption isotherm model describe adsorption on heterogenous surface and assume multilayer adsorption adsorption of CV dye on modified polyaniline. The model's linear correlation coefficient (R<sub>2</sub>) was high (0.96), imply that it can partially explain equilibrium adsorption. Equation 5 is the linearized version of the Freundlich isotherm:

$$\log q_e = \log k_f + n_h \log C_e \tag{5}$$

where the Freundlich coefficients are denoted by  $K_f$  and  $n_h$ . Plotting  $\log q_e$  vs.  $\log C_e$  produced the straight line that fits the data the best (Figure 4b) and the values of  $K_f$  and  $n_h$  were obtained from the intercept and slope., respectively. Table 2 provides the R<sup>2</sup>,  $K_f$ , and  $n_h$  values. With a regression coefficient of R<sup>2</sup> = 0.96, it shows that the data best-fit in Freundlich isotherm model. Thus, it can be said that during this adsorption experiment, multilayer adsorption occurred on the surface that is heterogeneous of doped polyaniline.



**Figure 4:** Isotherm model representations of (a) Langmuir model (b) Freundlich model.

**4. Mechanism**

Crystal violet dye when dissolve in water give cationic ion  $[C_{25}H_{30}N_3]^+$  and chloride anions dye adsorption on TPAni involve electrostatic interaction,  $\pi$ - $\pi$ staking and hydrogen bonding TAPni has large amount of (OH)has efficiently remove the CV dye from polluted water. This method of using TPAni as adsorbent is more economical reusable, desorption research was conducted. In order to regenerate the depleted adsorbent, the CV dye filled with modified polyaniline was given treatment in several solvents in this study, including 95% ethanol, water, 0.1 M NaOH, and 0.1 M HCl. It is found that ethanol (95%) was the most efficient of the preceding solvents and that over 65% of the dye was re capture from the adsorbent's pores.

**5. Conclusions**

Tannic acid doped polyaniline shows excellent ability to remove crystal violet dye because TPAni has higher number of negatively charged backbone which bind with positively charged cationic dye. The reaction follows pseudo second order kinetic studies and Freundlich adsorption isotherm.

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**Authors' contributions**

Meena performed the experiments and drafted the manuscript. Monika Duhan carried out material characterization and data interpretation. Manju Bala analyzed the kinetic and isotherm models. Arpna assisted in experimental design and manuscript revision. All authors approved the final manuscript.

**Conflicts of interest**

The author declares no conflict of interest.

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**Data availability**

No new data were created.

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