



Adsorptive eradication of tartrazine from aqueous solutions onto doped polyaniline

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Abstract: A potential polymeric adsorbent, doped polyaniline (PANI) has been investigated for the eradication of the hazardous dye tartrazine from textile effluent. During the adsorption process, the influence of the acidic character of the adsorbate, pH, dose of the adsorbent, dye concentration and time of contact between the adsorbent and adsorbate were evaluated. The outcomes attained from batch experiments were applied to the Langmuir and the Freundlich isothermal models. Different error analysis techniques, such as mean square error, root mean square error, the Chi-square test (χ^2), sum of absolute errors and sum of squared errors, were determined for the doped polyaniline–tartrazine system. The Langmuir isotherm was established as the best-fit isothermal model, with minimum errors and high regression values. About 90–97 % removal was achieved in the first 70 min. A positive enthalpy value implied the adsorption process was endothermic. The energy of activation for the dye adsorbent system was found to be 28.9 kJ mol⁻¹, which is in line with physisorption.

Keywords: adsorption; doped polyaniline; endothermic; entropy; error analysis; tartrazine.

INTRODUCTION

Massive demand for synthetic dyes in various industries, such as the food, pharmaceutical and textile industries, has resulted in colossal amounts of wastewater release, damaging receiving water bodies and intensifying water pollution.^{1,2} Among the different types of dyes, azo dyes are associated with several toxic and mutagenic effects.^{3,4} The azo bond (–N=N–) and associated chromophores are responsible for the colour imparted by these dyes. The complexity in the elimination of these dyes is mainly because of their aromatic structures. Tar-

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tartrazine, an azo dye, is used widely in cosmetics, medicines and various food materials.⁵ Its health hazards are reported to be related to the respiratory tract,⁶ carcinogenicity and mutagenicity,⁷ allergic reactions,⁸ migraines and lumps,⁹ and dermal sensitivity.¹⁰ Therefore, it has become essential to develop treatment methods for textile wastewater, especially those contaminated with tartrazine dye, before it is let into the aquatic ecosystem. Several methods, such as chemical, biological and physicochemical methods, have been explored to treat textile effluent. The technique of adsorption has proved to be more promising than other wastewater treatment methods.¹¹ To date, many adsorbents have been explored for wastewater purification. Due to high stability, easy synthesis and regeneration possibility, polymers, such as polyaniline, polystyrene and their derivatives, have gathered enormous attention in recent years as adsorbents.^{12–15} They are being extensively employed as alternatives for conventional adsorbents and activated carbon, for exclusion of colour and toxicants from wastewater. Acid doped polyaniline (PANI) was successfully used by researchers for the removal of anionic dyes.¹⁶ In the present study, an oxalic acid (OA) doped polyaniline (PANI) was been utilized for the eradication of tartrazine (toxic dye) from aqueous solutions. The current investigations determine the potential of doped PANI for the removal of tartrazine and help in the determination of optimum experimental conditions. The investigation also incorporates the study of the adsorption behaviour and thermodynamic studies. Doped PANI was used as an adsorbent over the conventionally used and expensive activated carbon for the removal of the toxic anionic dye from wastewater.

EXPERIMENTAL

Characterization of the adsorbent

Numerous techniques, such as energy dispersive X-ray spectroscopy (EDS), implanted with field emission scanning electron microscopy (FESEM) and X-ray diffraction crystallography (XRD), were used for the analysis of elements and to study the nature and surface morphology of the PANI.

Adsorbate and adsorbent

Tartrazine is an anionic sulphonated dye (Fig. 1) containing an azo group ($-N=N-$), with FW = 534.4 and chemical formula $C_{16}H_9N_4Na_3O_9S_2$. The dye was procured from M/s Loba Chemicals.

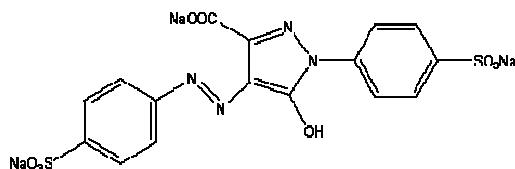


Fig. 1. Structure of tartrazine.

All the reagents employed during this study were of analytical reagent (A.R.) grade. A stock solution of tartrazine having concentration 10^{-3} M was prepared and used for further experimentation after dilution. OA doped PANI was chemically synthesized in three-neck flask by oxidative polymerization of aniline (Qualigen, A. R. Grade), using oxidizing agent ammonium persulphate (Loba) and oxalic acid (OA, Qualigen) as dopants. Continuous stirring was carried out using a magnetic stirrer at 0 to 4 °C, for 8 h. A dark green coloured precipitate of PANI was obtained which was filtered off using a Whatman filter paper 42. This precipitate was exposed to several washings with distilled water, followed by drying at 60 °C in an oven for 24 h. This mass was kept sealed in a container for further use.

Batch studies

Batch experiments were performed by adding 0.01 g of PANI to 25 ml of each dye solution, in 100 mL volumetric flasks for the study of vital parameters such as pH, amount of adsorbent, dye concentration and contact time. The concentration of solutions was kept at 9×10^{-5} M and investigations were performed at 30, 40 and 50 °C. The solutions were thoroughly shaken in a rotary shaker at 100 rpm. Hydrochloric acid and sodium hydroxide were employed to alter the pH of the test solution. After reaching equilibrium, the solutions were strained through Whatman filter paper number 42 and the dye uptake by the adsorbent was investigated using a spectrophotometer at λ_{max} 426 nm. By changing adsorbent doses and dye concentration, the quantity of dye adsorbed was analyzed. The dye adsorbed, q_e , and percentage removal were calculated using Eqs. (1) and (2):

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

$$\text{Removal, \%} = 100 \frac{C_0 - C_e}{C_0} \quad (2)$$

The initial and equilibrium concentrations of tartrazine are given by C_0 and C_e in mol L⁻¹, V is the volume of the solution in L, and m is the amount of the adsorbent in g.

Isothermal studies

The adsorbent surface is homogeneous as presumed by Langmuir (1918),¹⁷ whereas Freundlich advocated the surface of an adsorbent to be heterogeneous, containing irregular sites having diverse energies of adsorption.¹⁸ Langmuir isotherm and its vital feature, dimensionless separation factors (R_L) were computed by Eqs. (3) and (4) whereas Freundlich isotherm by Eq. (5):

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0C_e} \quad (3)$$

$$R_L = \frac{1}{1+bC_0} \quad (4)$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (5)$$

In the above equations, Q_0 is the adsorption capacity in mol L⁻¹, b is the Langmuir constant in L mol⁻¹, and K_f and n are Freundlich constants related to the capacity of adsorption and intensity.

Thermodynamic and kinetic studies

Kinetic studies play a vital role and help illustrate the rate of reaction throughout the process. During the conducted experiment, Lagergren Pseudo 1st order and pseudo 2nd order kinetic models were evaluated by Eqs. (6) and (7):

$$\log(q_e - q_t) = \log q_e - \frac{k_{\text{ads}}}{2.303} t \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

In the above equation, q_e , is the dye adsorbed at equilibrium in mg g⁻¹, q_t , gives the dye concentration at any time t in mg g⁻¹, k_{ads} is the pseudo 1st order rate constant in min⁻¹, and k_2 is the pseudo 2nd order rate constant of adsorption in g mg⁻¹ min⁻¹. Gibbs energy change (ΔG), the enthalpy change (ΔH) and entropy change (ΔS) were determined to ascertain the spontaneity, feasibility and disorder in the molecules.¹⁹ These factors were evaluated using Eqs. (8) to (10):

$$\Delta G = -RT \ln b \quad (8)$$

$$\Delta H = -R \left(\frac{T_2 T_1}{T_2 - T_1} \right) \ln \left(\frac{b_2}{b_1} \right) \quad (9)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (10)$$

where T implies temperature in Kelvin, R is the gas constant (8.314 kJ mol⁻¹) and b gives the Langmuir constant.

Mathematical investigation

Mathematical studies were applied to compute the difference between the experimental data and predicted data in various systems. The most suitable error function for the system was recognized after comparison of the outcomes achieved by adsorption studies, by different error methods, such as mean squared error (MSE), root mean square error ($RMSE$),²⁰ chi-squared test (χ^2), sum of absolute errors (SAE) and sum of squared errors (SSE).²¹⁻²³ These statistical error functions were evaluated by Eqs. (11) to (15):

$$RMSE = \sqrt{\frac{1}{N-2} \sum_{i=1}^N (q_{e\text{exp}} - q_{e\text{model}})^2} \quad (11)$$

$$MSE = \frac{\sum_{i=1}^N (q_{e\text{exp}} - q_{e\text{model}})^2}{n} \quad (12)$$

$$\chi^2 = \frac{\sum_{i=1}^N (q_{e\text{exp}} - q_{e\text{model}})^2}{q_{e\text{exp}}} \quad (13)$$

$$SSE = \sum_{i=1}^n (q_{e\text{model}} - q_{e\text{exp}})^2 \quad (14)$$

$$SAE = \sum_{i=1}^n |q_{e_{\text{model}}} - q_{e_{\text{exp}}}| \quad (15)$$

where $q_{e_{\text{exp}}}$ and $q_{e_{\text{model}}}$ are the perceived adsorption capacities from experimental statistics and the theoretical model (mol g^{-1}), respectively. The smallest values of MSE , SSE , SAE , χ^2 and $RMSE$, along with maximum R^2 value represent the best-fit isothermal model.

RESULTS AND DISCUSSION

Characterization of the adsorbent (PANI)

Images (Fig. 2a) obtained by FE-SEM revealed the surface of PANI to be rough distorted with spherical flakes, which smoothen after adsorption owing to agglomeration of dye molecules on the adsorbent surface. The XRD spectra (Fig. 2b) of unloaded and dye-loaded adsorbent ($\lambda = 0.1506 \text{ nm}$) were scanned in the 2θ range of $10\text{--}70^\circ$.

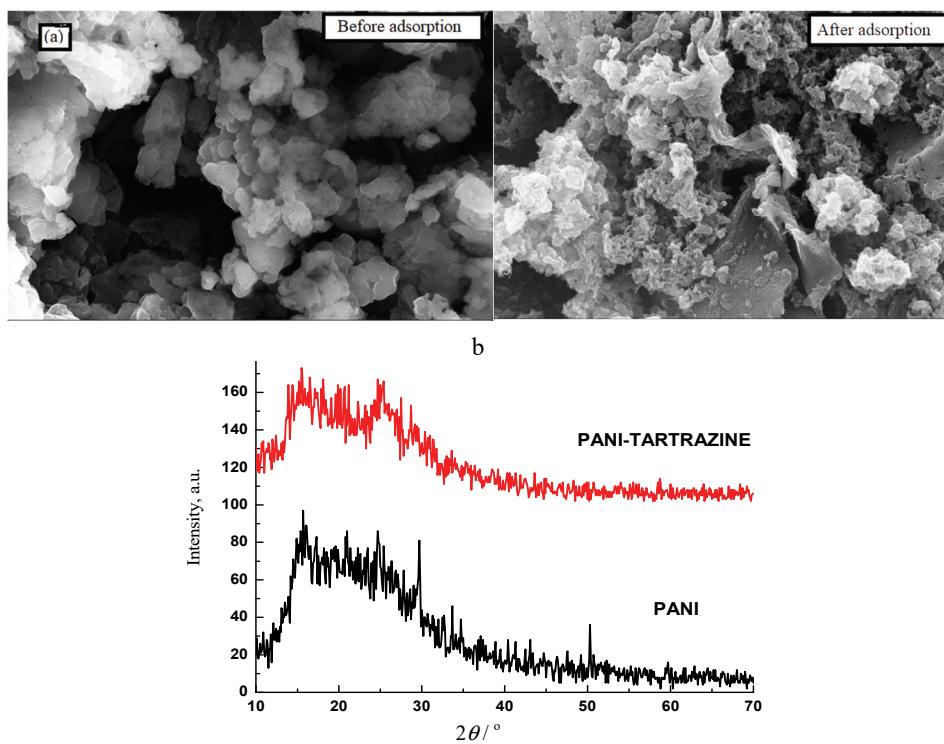


Fig. 2. a) SEM and b) XRD analysis of PANI before and after adsorption of tartrazine.

The XRD spectra show 2θ values at 16 , 21 , 25 and 30° . The peaks at 20.1 and 25.5° were attributed to the periodic vertical and parallel structure of the polymer linkage in PANI.^{24–26} No noteworthy changes were observed in the XRD pattern of doped PANI before and after adsorption of the dye. Hence, it was

concluded that the adsorption of tartrazine does not affect the crystallinity of the doped adsorbent.

A semi-crystalline nature was revealed owing to the existence of groups such as imine and amine, which were formed by intra and intermolecular H-bonding in the doped PANI. Analogous outcomes were recorded by various investigators.^{27,28} EDS investigation of PANI after adsorption of dye demonstrated bands corresponding to carbon (73.92 %), nitrogen (15.68 %), oxygen (9.42 %) and sulphur (0.91 %), with a small amount of sodium (0.07 %).

Batch studies

Effect of pH. In adsorption studies, the pH of the adsorbate plays a vital role in the removal process. The uptake of the dye was investigated within the pH range of 1–10. The results obtained in the pH studies indicated that maximum removal percentage (94 %) occurred at pH 2, owing to the electrostatic attraction between PANI and the dye. However, at higher pH values the adsorption decreased (Fig. 3a) owing to a reduction of active sites in PANI as a result of the deprotonation of the amino groups. Analogous results were revealed by Janaki *et al.*²⁹ Therefore, pH 2 was chosen for further batch studies.

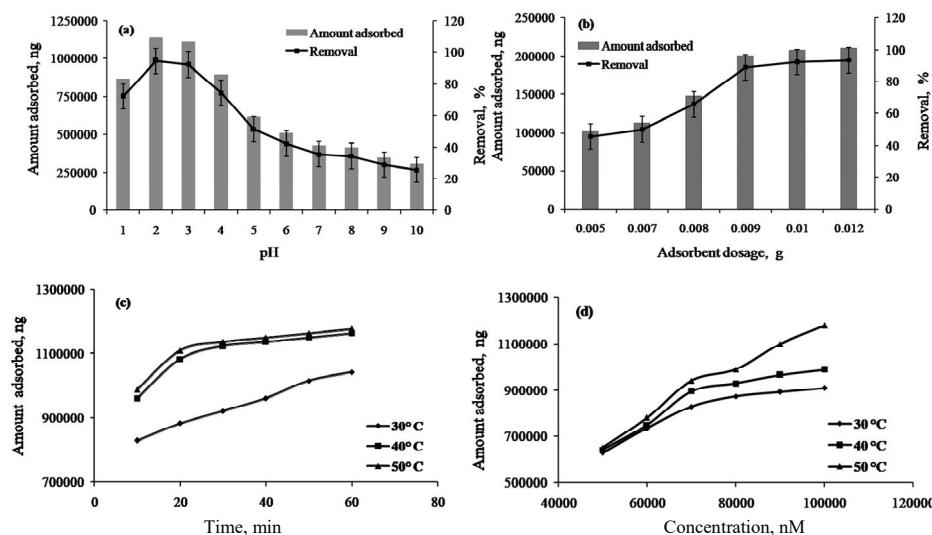


Fig. 3. Effect of a) pH (30 °C), b) amount of adsorbent (30 °C), c) contact time and d) dye concentration.

Effect of adsorbent dosage. The adsorption of tartrazine dye onto PANI was studied at 30 °C with an adsorbent dosage of 0.005 to 0.012 g and a dye concentration of 9×10^{-5} M at pH 2. The variation in dye uptake with variation in the amount adsorbent at 30 °C is shown in Fig. 3b. The maximum amount of dye adsorbed ranged from 110.8×10^{-5} to 164.1×10^{-5} g in moving from 30 to 50 °C with

0.01 g adsorbent dosage. An increase in the amount adsorbed was registered with increasing adsorbent dosage since more active sites were available with an augmented surface area. During the study, adsorption was found to increase with elevation of temperature for all adsorbent doses. However, there was no remarkable change noted in the amount adsorbed from 0.01 to 0.012 g adsorbent. Therefore, 0.01 g was taken as the optimum dosage for further studies.

Effect of contact time. These studies were executed using 0.01 g adsorbent dosage at pH 2 and dye concentration of 9×10^{-5} M, at temperatures 30 to 50 °C. The dye uptake was assessed at a fixed interval of 10 min. Investigations revealed an increase in the dye uptake with increasing temperature and time. From Fig. 3c, it is clear that equilibrium was accomplished within 70 min of contact. As the temperature was elevated from 30 to 50 °C, the removal percentage was found to increase from 68 to 97 %, signifying the process was endothermic. An analogous study was reported by Doğan *et al.* in 2004, in which the removal of methylene blue dye was examined using perlite.³⁰

Effect of dye concentration. Experimental studies were performed with dye concentrations ranging from $5\text{--}10 \times 10^{-5}$ M using the optimal adsorbent dosage (0.01 g) at 30, 40 and 50 °C. It was noticed that the interaction of doped PANI with dye molecules increased with increasing dye concentration. The results signified that dye adsorption increased from 62.79, 64.12, 65.5 to 90, 98.8 and 118×10^{-5} g within the concentration range of $5\text{--}10 \times 10^{-5}$ M dye at the studied temperatures (Fig. 3d).

Adsorption isotherms

Studies were carried out using the Langmuir and the Freundlich isotherms to understand the equilibrium correlation between the dye tartrazine and the adsorbent.

Langmuir adsorption isotherm. Langmuir constants related to adsorption intensity were calculated to be 7.1, 10.9 and 15.7×10^5 L mol⁻¹, at temperatures 30, 40 and 50 °C, respectively. It is apparent from Table I that the maximum adsorption capacity (Q_0) of doped PANI proved its worth over the other adsorbents. The separation factor, R_L , ranged from 0.03 to 0.01 in temperature range of 30–50 °C. The determined values of R_L were < 1 and > 0, indicating the favourability of this model for the studied system.³¹

Freundlich adsorption isotherm. As for Freundlich studies, the values of K_F allied with adsorption intensity, procured from the slope of the plot $\log C_e$ vs. $\log q_e$, were 0.0006, 0.0008 and 0.0031 at temperature from 30 to 50 °C. This increase with temperature signifies that the process was favoured at higher temperature. The value of Freundlich constant, n , obtained from intercept, were in the range 1–10 at studied temperatures, which are indicative of favourable adsorption of tartrazine dye on doped PANI. The plots for Langmuir and Freundlich iso-

therms for adsorbate–adsorbent system are illustrated in Fig. 4a and b, respectively.

TABLE I. Comparison of adsorption capacity of tartrazine on doped PANI with other adsorbents

Adsorbent	$Q_0 / \text{mol g}^{-1}$	Reference
Bottom ash	2.358×10^{-5}	9
De-oiled soya	4.608×10^{-5}	9
Hen Feather	1.40×10^{-4}	32
Commercial activated carbon	8.39×10^{-6}	33
Apricot stone based Activated carbon	1.42×10^{-4}	34
Activated carbon of Lantana Camara	4.62×10^{-6}	35
Polyaniline nanolayer composite	4.62×10^{-6}	36
Polyaniline/chitosan	1.09×10^{-3}	37
Sawdust	8.81×10^{-6}	38
OA doped PANI	2.12×10^{-4}	This study

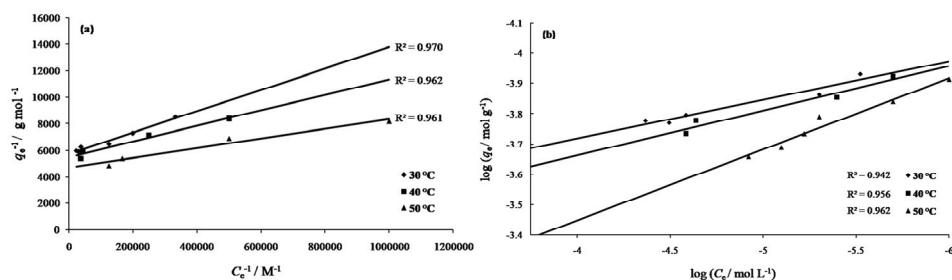


Fig. 4. Adsorption isotherm models; a) Langmuir, b) Freundlich for tartrazine–PANI system (adsorbent dose 0.01 g, pH 2.0).

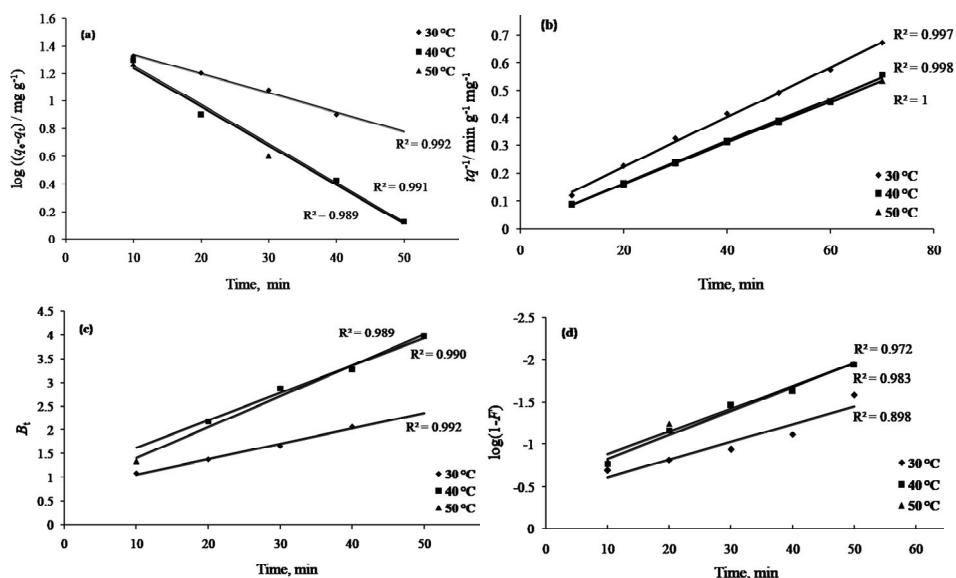
As indicated by the correlation coefficient (R^2) values, the Langmuir isotherm was better applicable for the adsorption data in comparison to the Freundlich isotherm. The different error functions (Table II), *i.e.*, MSE , $RMSE$, χ^2 , SSE and SAE computed for the Langmuir isotherm showed smaller values in comparison to the Freundlich isotherm, verifying the better applicability of the Langmuir model and suggesting monolayer adsorption of tartrazine onto homogeneous active sites of doped PANI.

Adsorption kinetics

Pseudo 1st order and 2nd order kinetic studies were performed. Rate constants k_1 , obtained from the slopes of Fig. 5a, were found to be 3.22×10^{-2} , 6.51×10^{-2} and $6.51 \times 10^{-2} \text{ min}^{-1}$ at 30, 40 and 50 °C, respectively. The values of the adsorption capacity, q_e , at equilibrium were obtained from the slope and rate constant k_2 , acquired from the intercept of graph q_t/t vs. time (Fig. 5b), were found to be 1.82×10^{-3} , 5.64×10^{-3} and $3.97 \times 10^{-3} \text{ g mg}^{-1} \text{ min}^{-1}$ at 30, 40 and 50 °C, respectively. R^2 values of the kinetic model were close to unity indicating that

TABLE II. Isothermal parameters and error analysis for tartrazine adsorption onto doped PANI at different temperatures

Model	Parameter	Temperature, °C		
		30	40	50
Langmuir isotherm	$Q_0 / \text{mol g}^{-1}$	1.75×10^{-4}	1.80×10^{-4}	2.12×10^{-4}
	$b / \text{L mol}^{-1}$	7.1×10^5	10.9×10^5	15.7×10^5
	R^2	0.970	0.962	0.961
	$RMSE$	0.072×10^{-4}	0.34×10^{-4}	0.18×10^{-4}
	MSE	0.0051×10^{-8}	0.12×10^{-8}	0.03×10^{-4}
	χ^2	0.012×10^{-4}	0.28×10^{-4}	0.08×10^{-4}
	SSE	0.021×10^{-8}	0.46×10^{-8}	0.13×10^{-8}
	SAE	0.28×10^{-4}	1.28×10^{-4}	0.8×10^{-4}
	K_F	0.0006	0.0008	0.0031
	$1/n$	7.87	6.85	4.3
Freundlich isotherm	R^2	0.942	0.956	0.962
	$RMSE$	1.88×10^{-4}	1.99×10^{-4}	2.16×10^{-4}
	MSE	3.5×10^{-8}	3.97×10^{-8}	4.68×10^{-8}
	χ^2	9.13×10^{-4}	9.65×10^{-4}	10.4×10^{-4}
	SSE	14.1×10^{-8}	15.9×10^{-8}	18.7×10^{-8}
	SAE	9.14×10^{-4}	9.66×10^{-4}	10.4×10^{-4}

Fig. 5. Kinetic study; plot of: a) $\log q_e - q_t$ vs. time for the pseudo-first-order model, b) t/q_t vs. time for the pseudo-second-order model, c) discriminate between film and particle diffusion through B_t vs. time and d) McKay graph, $\log(1-F)$ vs. time.

the pseudo 2nd order model was appropriate for the studied PANI–tartrazine system. Studies were performed to study the diffusion mechanisms proposed by

Boyd *et al.*³⁹ A plot of B_t vs. time (Fig. 5c) gave a straight line, implying that the current system proceeds *via* the film diffusion mechanism. The B_t values can be derived from fractional attainment values using the Reichenberg Table. The fractional attainment (F) of equilibrium is the ratio of the amount adsorbed at time t to that amount adsorbed at equilibrium.

The values of diffusion coefficient, D_i , obtained from the slope of B_t vs. time were found to increase from 3.25 to $6.59 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$ with an increase in temperature from 30 to 50°C , asserting that the mobility of the ions increased at elevated temperature.⁴⁰ The pre-exponential factor D_0 ($3.49 \times 10^{-2} \text{ cm}^2 \text{ min}^{-1}$), obtained from the intercept of the plot $\log D_i$ vs. $1/T$, was used to calculate the energy of activation ($E_a = 28.9 \text{ kJ mol}^{-1}$). The process followed physisorption as the energy of activation (E_a) value was less than 40 kJ mol^{-1} mentioned by Ahmad *et al.* in 2014.⁴¹ No substantial change occurred in the internal structure of PANI as indicated by a negative value of entropy ($\Delta S^\# = -231.72 \text{ J K mol}^{-1}$). A plot of $\log(1-F)$ vs. time (McKay graph, Fig. 5d) gave a straight line, additionally supporting external transport of the adsorbate onto the doped PANI surface signifying that the adsorption process followed the film diffusion mechanism.⁴²

Adsorption thermodynamics

The imperative parameters were determined by Eqs. (6)–(8). The value of the obtained Gibbs energy change, ΔG , was $-36.16 \text{ KJ mol}^{-1}$, suggesting the adsorption process to be viable and spontaneous, while the positive enthalpy change ($\Delta H = 506 \text{ J mol}^{-1}$) indicated the ongoing process to be endothermic. The positive entropy change ($\Delta S = 117 \text{ J mol}^{-1} \text{ K}^{-1}$) of the system indicated an increase in randomness throughout the adsorption process.⁴³

CONCLUSIONS

The removal of tartrazine by PANI was enhanced with elevation in temperature and contact time. Almost 97 % adsorption was accomplished in 70 min with 0.01 g of adsorbent at pH 2. The Langmuir isotherm was suitable, and hence was further analysed for assorted error study functions in conjunction with R^2 values. The Langmuir model was established as the best fit for the current system with $R^2 > 0.96$, and error functions with lower values at the studied temperatures. Kinetic experiments indicated that ongoing adsorption was a pseudo second-order reaction. The computed energy of activation (E_a) was 28.9 kJ mol^{-1} . The adsorption of toxic tartrazine dye onto doped PANI, therefore, demonstrated an efficient method in wastewater treatment.

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ИЗВОД

УКЛАЊАЊЕ ТАРТАЗИНА ИЗ ВОДЕНИХ РАСТВОРА АДСОРПЦИЈОМ НА ДОПИРАНОМ
ПОЛИАНИЛИНУ

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Испитан је допирани полианилин (ПАНИ) као потенцијални полимерни адсорбент за уклањање опасне боје тартазина из ефлумента текстилне индустрије. Измерен је утицај киселог карактера адсорбата, pH, дозирања адсорбента, концентрације боје и времена контакта између адсорбента и адсорбата, у току процеса адсорпције. Добијени резултати су испитани Лангмировим и Фројндлиховим изотермама. Примењено је неколико анализа грешке као што су средња квадратна, корен средње квадратне, хи-квадрат (χ^2), збир апсолутних грешака и збир квадратних грешака на систем допираних тартазина полианилином. Утврђено је да Лангмирова изотерма најбоље описује систем, са најмањим грешкама и високим вредностима регресије. Постигнуто је око 90–97 % уклањања у првих 70 min. Позитивна вредност промене енталпије је указала на ендотермност адсорpcionог процеса. За енергију активације овог система добијена је вредност од 28.9 kJ mol⁻¹, што је сагласно физисорпцији.

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