**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 to eradicate of 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 has been evaluated. The outcomes attained from batch experiments have been applied to Langmuir and Freundlich isothermal models. Different error analysis techniques like mean square error, root mean square error, Chi-square test (*χ****2***), sum of absolute errors and sum of squared errors have been determined for the doped polyaniline- tartrazine system. Langmuir isotherm has been 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 to be endothermic. The energy of activation for the dye adsorbent system was found to be 28.9 *kJ* mol-1 which was in line with physisorption.

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

RUNNING TITLE: ERADICATION OF TARTRAZINE BY DOPED PANI

INTRODUCTION

Massive demand for synthetic dyes in various industries like food, pharmaceutical, textile 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 color imparted by these dyes. The complexity in the elimination of these dyes is mainly because of their aromatic structures. Tartrazine, an azo dye, is used widely in cosmetics, medicines and various food materials5. Its health hazards are reported to be related to the respiratory tract,6 carcinogenicity and mutagenicity,7 allergic reactions,8 migraines and lumps,9 dermal sensitivity.10 Therefore, it becomes essential to develop treatment methods for textile wastewater, especially 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 Many adsorbents have been explored for wastewater purification to date. Due to high stability, easy synthesis and regeneration ability, polymers like 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), has been utilized for the eradication of tartrazine (toxic dye) from aqueous solutions. The current investigations determine the potential of PANI for the removal of tatrazine and help in the determination of optimum experimental conditions. The investigation also incorporates the study of the adsorption behavior and thermodynamic studies. Doped PANI has been used as an adsorbent over the conventionally used and expensive activated carbon, for the removal of toxic anionic dye from wastewater.

EXPERIMENTAL

*Characterization of the adsorbent*

Numerous techniques like 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, to study nature and surface morphology of the PANI.

*Adsorbate and adsorbent*

Tartrazine is an anionic sulfonated dye (Fig.1) containing azo group (-N=N-), with M.W. = 534.4 and chemical formula C16H9N4Na3O9S2. The dye was procured from M/s Loba chemicals. All the reagents employed during this study were of A.R. grade. A stock solution of tartrazine having concentration 10-3M 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 hours. A dark green colour precipitate of PANI was obtained which was segregated through 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 (hours). This mass was kept sealed in a container for further use.

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Fig.1. Structure of Tartrazine

*Batch studies*

Batch experiments were performed by adding 0.01 g of PANI in 25 ml of dye solutions, in 100 mL volumetric flasks, for the study of vital parameters like pH, amount of adsorbent, dye concentration and contact time. The concentration of solutions was kept at 910-5 M and investigations were carried out at 30, 40, and 50 °C. The solutions were thoroughly shaken in a rotary shaker at 100rpm. Hydrochloric acid and sodium hydroxide were employed to alter the pH of the test solution. After the accomplishment of equilibrium, the solutions were strained with Whatman filter paper number 42 and the dye uptake by the adsorbent was investigated using 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 by using Eq.1 and 2.

 (1)

 (2)

The initial and equilibrium concentrations of tartrazine are given by *C*o 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 advocates the surface of adsorbent 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.

 (3)

 (4)

 (5)

In the above eqs. *Q*0 is the adsorption capacity in mol L-1, b is Langmuir constant in *L* mol-1, *K*f and n are Freundlich constants related to 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.

 (6)

 (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 pseudo 2nd order rate constant of adsorption in g mg-1min-1. Gibb’s energy (Δ*G*°), the heat of the reaction (Δ*H*°) and randomness (Δ*S*°) were found out to ascertain the spontaneity, feasibility, and disorder in the molecules.19 These factors were evaluated using Eqs. 8 to 10.

 (8)

 (9)

 (10)

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

*Mathematical investigation*

Mathematical studies are applied to compute the difference between 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 like mean squared error (MSE), root mean square error (RMSE),20 Chi-square 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.

 (11)

 (12)

 (13)

 (14)

 (15)

In previous eqs,  and are the perceived adsorption capacities from experimental statistics and theoretical model (mol g-1) respectively. The smallest values of MSE, SSE, SAE, *χ*2, and RMSE, along with maximum R2 value represent the best fit isothermal model.

RESULT AND DISCUSSION

*Characterization of the adsorbent (PANI)*

Images (Fig. 2a) by FE-SEM revealed the surface of PANI to be rough distorted with spherical flakes, which smoothen after adsorption, owing to agglomeration dye molecule on the adsorbent surface. The XRD spectra (Fig.2b) of unloaded and dye loaded adsorbent (*λ*=1.506A°) were scanned in 2*θ* the range of 10-70 °. The figure shows 2*θ* values as 16 °, 21 °, 25 ° and 30 °. Two 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 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 doped PANI. Analogous outcomes have been recorded by various investigators.27, 28 EDS investigation of PANI after adsorption of dye demonstrated bands corresponding to the carbon (73.92 %), nitrogen (15.68 %), oxygen (9.42 %) and sulphur (0.91 %), with a small amount of sodium (0.07 %).

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**(a)**

After Adsorption

Before Adsorption



**(b)**

Fig.2. (a) SEM, (b) XRD analysis of PANI before and after adsorption of Tartrazine

*Batch studies*

*Effect of pH*

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

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

*Effect of adsorbent dosage*

The adsorption of tartrazine dye onto PANI was studied at 30 °C with adsorbent dosage 0.005 to 0.012 g with the dye concentration of 9  10-5 M at pH 2. Fig.3b shows the variation in the amount of dye uptake with a variation in the amount of adsorbent at 30 °C. The maximum amount of dye adsorbed ranged from 110.8 to 164.1 10-5 g in moving from 30 to 50 °C with 0.01 g adsorbent dosage. An increase in adsorption was noticed with a rise in adsorbent dosages since more number of active sites was 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 an optimum dosage for further studies.

*Effect of contact time*

(a) a)aaaaa

These studies were executed using 0.01 g adsorbent dosage at pH 2 and dye concentration of 9 10-5M, 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 an increase in temperature and time. From Fig. 3c it was clear that equilibrium was accomplished within 70 min of contact time. As temperature elevated from 30 to 50 °C 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, where the removal of methylene blue dye was carried out using perlite.30

*Effect of dye concentration*

Experimental studies were performed with a change in dye concentration from 5-10 10-5 M with opted 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 an increase in dye concentration. Results signified that dye adsorption increased from 62.79, 64.12, 65.5 to 90, 98.8 and 118 10-5 g with a concentration range of 5-10 10-5 M dye at studied temperatures (Fig 3d).

*Adsorption isotherms*

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

*Langmuir adsorption isotherm*

Langmuir constants related to adsorption intensity (b) were calculated to be 7.1, 10.9 and 15.7  105 *L* mol-1, at temperatures 30, 40 and 50 °C.  It was apparent from Table I that the maximum adsorption capacity (Q0)of doped PANI proved its worth over the other adsorbents. The separation factor, *R*L, ranged from 0.03 to 0.01 at 30 to 50 °C. The determined values of *R*L were < 1 and > than zero indicating favorability of the 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 plot log *C*e versus log *q*e were 0.0006, 0.0008, and 0.0031, which increased with temperature from 30 to 50 °C, signifying that the process was favored at higher temperature. The value of Freundlich constant ‘n’ obtained from intercept were in the range 1-10 at studied temperatures, indicative of favourable adsorption of tartrazine dye on doped PANI. Fig. 4a and 4b illustrate the plots for Langmuir and Freundlich isotherms for adsorbate-adsorbent system respectively.

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

|  |  |  |
| --- | --- | --- |
| Adsorbent | *(Q0 /* 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 |

As indicated by the correlation coefficient (R2) values, Langmuir isotherm was better applicable for the adsorption data in comparison to Freundlich isotherm. The different error functions (Table II) i.e. MSE, RMSE, *χ*2, SSE and, SAE computed for Langmuir, showed smaller values in comparison to Freundlich, verifying the better applicability of the Langmuir model and suggesting monolayer adsorption on homogeneous active site of tartrazine onto doped PANI.

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

TABLE II.Isothermal Parameters and Error analysis for tartrazine adsorption onto doped PANI at different temperatures

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Models** | ***Parameters*** | **Temperature** | | |
| 30 °C | 40 °C | 50 °C |
| Langmuir isotherm | *Q0* /mol g-1 | 1.75  10-4 | 1.80  10-4 | 2.12  10-4 |
| *b* /Lmol-1 | 7.1 105 | 10.9 105 | 15.7 105 |
| *R2* | 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 |
| *χ2* | 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 |
| *MAD* | 0.046 10-4 | 0.21 10-4 | 0.1310-4 |
| Freundlich isotherm | *KF* | 0.0006 | 0.0008 | 0.0031 |
| *1/n* | 7.87 | 6.85 | 4.3 |
| *R2* | 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 |
| *χ2* | 9.13 10-4 | 9.6510-4 | 10.4 10-4 |
| *SSE* | 14.1 10-8 | 15.9 10-8 | 18.710-8 |
| *SAE* | 9.14 10-4 | 9.66 10-4 | 10.4 10-4 |
| *MAD* | 1.5210-4 | 1.6110-4 | 1.7310-4 |

*Adsorption kinetics*

Pseudo 1st order and 2nd order kinetic studies were carried out. Rate constants *k*1 obtained from the slope of Fig.5a and were found to be [1.4 10-2, 2.8 10-2 and 2.8 10-2](javascript:openDSC(972249,%2037,%20'31476');) min-1 at 30, 40 and 50 °C respectively. The value of adsorption capacity, *q*e, at equilibrium obtained by slope and rate constant *k*2, acquired by intercept of graph *q*t/t vs time (Fig.5b), was found to be 4.4 10-2, 1.0 10-2, 1.3 10-2 g mg-1 min-1 at 30, 40 and 50 °C respectively. R2 values of the kinetic model were close to unity asserting that the pseudo 2nd order model was appropriate for the studied PANI -Tartrazine system. Studies were carried out for studying diffusion mechanisms proposed by Boyd *et al*. (1947).39 Plot of *B*t vs time (Fig.5c) gave a straight line implying that the current system proceeds via film diffusion mechanism.

The values of diffusion coefficient *D*i obtained by the slope of *B*t versus time were found to increase from 3.25 to 6.59  10-7cm2 min-1, with an increase in temperature from 30 to 50 °C, asserting that the mobility of ions increased at elevated temperature.40 The pre-exponential factor *D*o (3.49  10-2 cm2min-1) obtained from the intercept of plot log *D*i versus 1/T was used to calculate the energy of activation (*E*a= 28.9 *kJ* mol-1). The process followed physisorption as energy of activation (*E*a) value was lesser than 40 *kJ* mol-1mentioned by Ahmad *et al*. in 2014.41 No substantial change took place in the internal structure of PANI as indicated by a negative value of entropy (Δ*S*#= -231.72 *J K* mol-1). Plot of log (1-F) vs time (McKay’s graph) (Fig.5d) gave a straight line additionally supporting external transport of adsorbate onto doped PANI surface, and signified that the adsorption process followed film diffusion mechanism.42

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Fig.5. Kinetic study, Plot of (a) log qe-qt versus time for pseudo-first-order model, (b)t/qt versus time for pseudo-second-order model, (c) discriminate between film and particle diffusion through Bt versus time, (d)McKay’s graph Log (1-F) versus time

*Adsorption thermodynamics*

Imperative parameters were determined by Eqs. 6*-*8. The value of free energy (Δ*G*°) obtained was -36.16 *KJ* mol-1 suggesting the adsorption process to be viable and spontaneous, while positive enthalpy (Δ*H*° =506 *J* mol-1) indicated the ongoing process to be endothermic. The positive entropy (Δ*S*° =117 *J* mol-1 K-1) of the system indicated an increase in randomness throughout the adsorption process.43

CONCLUSIONS

The removal of tartrazine by PANI 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 most suitable isotherm was Langmuir which was further analyzed for assorted error study functions in conjunction with R2 values. Langmuir model was established as the best fit for the current system with R2 > 0.96, and error functions with lower values at 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 PANI, therefore, demonstrated an efficient method in wastewater treatment.

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*Conflict of interest*

The authors declare that they have no conflict of interest.

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