

# Determination of azine and triphenyl methane dye in wastewater using polyurethane foam functionalized with tannic acid

## Abstract

A simple and sensitive spectrophotometric method for the determination of azine (neutral red) and triphenyl methane (rosaniline) dye has been developed using tannic acid-polyurethane foam (TPF). TPF was prepared by coupling a polyhydroxypolyurethane foam matrix with tannic acid. TPF was characterized using a combination of analytical methods including IR and NMR spectroscopy, elemental analysis, density and  $pH_{zpc}$ . The qualitative and quantitative determination of dyes is based on its sorption on the surface of the TPF. The sorption behavior of dye onto the TPF was investigated by batch and dynamic processes. The maximum sorption of neutral red and rosaniline was in the pH range of 7-9. The kinetics of sorption of the dye by the TPF was found to be fast with average values of half-life of sorption of 1.2 min. The equilibrium process was well described by the Freundlich isotherm model. The visual detection limit of dye in aqueous solution is  $0.1 \mu\text{g mL}^{-1}$ . The Sandell's sensitivity is  $0.26 \text{ ng cm}^{-2}$  with molar absorptivity  $1.3 \times 10^6 \text{ L mol}^{-1} \text{ cm}^{-1}$ . The average sorption capacity of TPF and the recovery of dyes were  $0.47 \text{ mmol g}^{-1}$  and 96.4 % (RSD ~ 1.5%, n=7). The method has been applied to various wastewater samples.

## Keywords

Polyurethane foam • Tannic acid • Neutral red • Rosaniline • Dye removal

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## 1. Introduction

Many industries and laundry release wastewater containing dyes and thereby contaminate water resources. Basic dyes, such as azine and triphenyl methane, are considered as one of the more problematic classes of dye and are classified as toxic colorants [1,2]. The main problem lies in that the basic dyes cannot be detected visually in neutral and alkaline effluents.

To minimize the risk of the generated pollution, the dyes must first be detected and determined in the effluent, and then the effluent must be treated before discharge into the environment. Several methods including thin-layer chromatography [3], liquid chromatography [4-6], high performance liquid chromatography (HPLC) [7,8], pyrolysis gas chromatography [9] and capillary electrophoresis [10-15] have been used for the determination of basic dyes. Common detection techniques are UV [11,12], diode array detection [3,10], mass spectrometry [7,9] and electrochemical detection [13-15], all of which are limited by

a relatively high cost of the instrumentation required. Other techniques such as electrophoresis [16], fluorimetry [17] and voltammetry [18] have also been employed for the basic dye determination in different kinds of samples.

The colour of a dye solution is usually measured by spectrophotometric methods. High sensitivity dye detection can easily be achieved using the solid phase spectrophotometric method. This method is based on preconcentration of dye and detection using visual or UV-Vis spectrophotometer [19-21]. This adsorption method has a number of advantages including a high preconcentration factor, environmental safety and the possibility of carrying out on-site analyses.

Polyurethane foam (PUF) is an excellent sorbent. It has a high surface area, an extremely low cost, is stable in both acids and bases and stable up to 180 °C [22,23]. Thus, it is a very suitable material for batch and column extraction techniques. PUF is used for adsorption and recovery of organic and inorganic components from aqueous solutions [24-26]. Also, it is normally

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used for the detection and semiquantitative determination of different analytes in water [20,27,28].

The aim of this study is to highlight the approach of modification of polyurethane foam with tannic acid. Polyurethane foam functionalized with tannic acid (TPF) was prepared by coupling a polyhydroxy polyurethane foam matrix with tannic acid. The highly acidic character of TPF due to the large number of phenolic groups makes it suitable for adsorbing basic organic dyes from wastewater. Therefore, TPF could be used for detection and determination of trace amounts of neutral red and rosaniline dyes in wastewater. The sorption behavior of basic dyes onto TPF has been studied to optimize the conditions for removal of dyes from wastewater.

## 2. Experimental

### 2.1 Reagents and materials

All reagents were prepared from analytical reagent grade chemicals and distilled water. 1 mg mL<sup>-1</sup> stock solutions of neutral red (C<sub>15</sub>H<sub>17</sub>N<sub>4</sub>Cl, 288.8, 3-Amino-7-dimethylamino-2-methylphenazine hydrochloride, toluylene red, toluylene red, Basic Red 5, C.I. 50040, CAS 553-24-2) and rosaniline (C<sub>20</sub>H<sub>19</sub>N<sub>3</sub>HCl, 337.9, 4-[(4-Aminophenyl)-(4-imino-1-cyclohexa-2,5-dienylidene)methyl]aniline hydrochloride, basic violet 14, basic red 9, pararosaniline, CI 42500, CAS 632-99-5) dyes were prepared by dissolving 0.1 g of dye in 5 mL of ethanol and the solution was diluted to 100 mL with distilled water in a measuring flask. Commercial white sheets (Density ≈ 13.5 kg m<sup>-3</sup>) of open cell polyether type based polyurethane foam were used.

### 2.2 Synthesis of the PPF and TPF

Polyhydroxy polyurethane foam (PPF) was prepared by cutting of PUF into small cubes (~0.125 cm<sup>3</sup>). The cubes of PUF were washed by a 3 mol L<sup>-1</sup> solution of HCl, followed by distilled water and acetone and then left to dry at room temperature. 5 g of PUF cubes were soaked in a 3 mol L<sup>-1</sup> solution of HCl for 24 h to liberate the maximum number of free amino groups [22]. Then, the PUF was washed with water, placed into a 0.1 mol L<sup>-1</sup> HCl solution and cooled in an ice bath. The PUF was diazotized by the dropwise addition of 25 mL NaNO<sub>2</sub> (2 mol L<sup>-1</sup>) to the cold solution and stirred vigorously until the pale yellow color appeared due to the formation of diazonium chloride [29]. Next, the diazotized PUF was filtered, washed with water and boiled in 500 mL water for 2 h. The yellow PPF material was washed with distilled water followed by acetone and then dried at room temperature.

Tannic acid polyurethane foam (TPF) was prepared by mixing 5 g of PPF with 5 g tannic acid in 250 mL of 1 mol L<sup>-1</sup> HCl. The mixture was heated at 90 °C for 24 h with continuous stirring. Afterwards, the yellow-orange cubes of TPF were filtered, washed several times with ethanol and finally with water then dried at room temperature.

### 2.3 Apparatus

All spectrophotometric measurements were performed using spectro UV-Vis RS Digital spectrophotometer (Labomed, Inc).

The pH measurements were carried out using a pH meter from Microprocessor pH Meter (HANNA Instruments). The calibration of the pH meter was systematically carried out using suitable buffer solutions. Glass columns of about 25-cm long and 1.5 cm in diameter were employed in the chromatographic separation experiments.

### 2.4 Analytical procedures

The removal of neutral red and rosaniline dyes was carried out by a batch technique at 25°C. Adsorption experiments were carried out by agitating 0.1 g of TPF with 25 mL of dye solutions (5 mg mL<sup>-1</sup>) in a shaker adjusted to the desired shaking speed. After shaking for 30 minutes, the concentration of remaining dye in the supernatant solution was determined spectrophotometry. The following equations were used to calculate the removal percentage of dye (%E) and capacity of sorbents (Q, mg/g):

$$\%E = ((C_o - C)/C_o) \times 100 \quad (1)$$

$$Q = (C_o - C)V/m \quad (2)$$

where C<sub>o</sub> and C are the initial and remain concentrations of dyes in solution, respectively. V is the volume of solution and m is the mass of sorbent.

pH<sub>ZPC</sub> is the pH when the charge on the TPF surface is zero (zero point charge, pH in which the initial pH equals the final pH). To determine the pH<sub>ZPC</sub> of the TPF surface, we take 25 mL of solution in a series of 100 mL flasks whose pH in the range 1-13. The initial pH (pH<sub>i</sub>) of the solutions was determined and 0.1 g of the TPF was added to each flasks. After 24 h, the pH of these solutions (pH<sub>f</sub>) was measured. The ΔpH (difference between the initial and final pH values, ΔpH= pH<sub>f</sub> - pH<sub>i</sub>) was plotted against the pH<sub>i</sub> [30].

In the dynamic experiments, 1.0 g portions of TPF were packed into a column (25×1.5 cm). Neutral red and rosaniline solutions were passed through the TPF column (L= 12 cm) at flow rate 5 mL min<sup>-1</sup>. The stripping of the dye from the TPF column was carried out using (1:1) C<sub>2</sub>H<sub>5</sub>OH: H<sub>2</sub>O and the amount of the neutral red and rosaniline was measured.

For the solid phase spectrophotometric determination of tested dye, the thin film of TPF was separated from the sample solution (after shaking 5 minutes) and washed twice with distilled water. The absorbance of the TPF thin film was measured at appropriate wavelengths. For the semiquantitative determination of neutral red and rosaniline, the colour of TPF cubes after dye sorption were compared with a standard scale of dye concentrations in test tubes [27].

## 3. Results and discussion

### 3.1. Characterization of TPF

The elemental analysis of PUF and TPF showed that the percentage of carbon, hydrogen and nitrogen in TPF is less than in PUF because of the partial hydrolysis of urethane groups. Further, the percentage of oxygen in TPF is more than in PUF due to addition of tannic acid groups (Table 1).

Table 1. Comparison between the characterization of PUF and TPF.

Property	PUF	TPF
<b>IR spectra</b>		
ν NH, OH <sub>st</sub> (cm <sup>-1</sup> )	3509.8-3137.6	33683.4-3039.3
ν NCO (cm <sup>-1</sup> )	2308.4	Disappeared
ν CO, OH <sub>def</sub> (cm <sup>-1</sup> )	Nil	1727.9 and 1322.9
<b>Vis spectra</b>		
λ <sub>max</sub> (nm)	Nil	416
<b>NMR spectra</b>		
δ (ppm)	1.23, 1.49 and 5.28	1.23, 1.49, 5.28 and 7.28
Density (kg m <sup>-3</sup> )	13.5	21.3
Colour	White	Yellow-orange
<b>Elemental analysis</b>		
C, H, N and O %, respectively	64.0, 9.5, 7.2 and 18.8	61.7, 8.8, 6.0, and 23.1

The densities of PUF and TPF were 13.5 and 21.3 kg/m<sup>3</sup>, respectively. The higher density of the TPF could be attributed to the inter bonding between tannic acid molecules and the PUF groups.

The infrared spectra of PUF and TPF were acquired using the thin film technique. The results showed that the broadband at 3509.8-3137.6 cm<sup>-1</sup>, characteristic of O-H and N-H groups, was shifted to 33683.4-3039.3 cm<sup>-1</sup> after reaction with tannic acid. The band at 2308.4 cm<sup>-1</sup>, characteristic of isocyanate (-NCO) group of the PUF, disappears. On the other hand two new bands at 1727.9 and 1322.9 cm<sup>-1</sup>, characteristic of the C=O and O-H groups, appeared.

The pH<sub>ZPC</sub> value of TPF was approximately 4.4 (pH<sub>ZPC</sub> is the pH when the charge on the TPF surface is zero). Therefore, the surface of the TPF is positively charged at pH lower than 4.4 and negatively charged at pH greater than 4.4.

The spectral data from <sup>1</sup>H NMR is listed in Table 1. Three peaks were observed in the spectra of PUF and TPF at 1.23, 1.49 and 5.28 ppm, consistent with chemical shifts of H in aliphatic -CH and phenolic -OH environments. A single peak at 7.28 ppm in the spectra of TPF is due to the aryl protons (Ar-H) of tannic acid.

### 3.2. Optimum condition for removal of neutral red and rosaniline

The effect of initial pH on the sorption of neutral red and rosaniline dyes onto TPF was examined. Initial pH of the solutions was adjusted to between 1 and 13 by adding either HCl (1 mol L<sup>-1</sup>) or NaOH (1 mol L<sup>-1</sup>). The results show that the maximum sorption of neutral red and rosaniline onto TPF occurs in range of pH 7-9 (Figure 1). At pH between 1 and 4.4, electrostatic repulsion between the surface of TPF and the dye molecules occurs accounting for the decreased sorption of neutral red and rosaniline observed. The sorption of neutral red and rosaniline increased at pH values greater than 4.4 due to electrostatic attraction between the dye and surface functional groups of TPF.

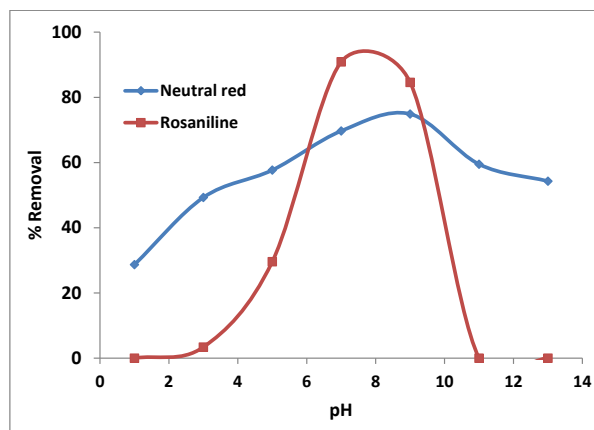


Figure 1. Effect of pH on the sorption of neutral red and rosaniline onto TPF.

Kinetic measurements were carried out using cubes of TPF (0.125 cm<sup>3</sup>) by a batch extraction mode at different time intervals. The required time for sorption equilibrium of neutral red and rosaniline onto TPF was found to be 8 and 5 minutes, respectively. The sorption rate of dye onto TPF is relatively fast as compared to the other sorbents [3,9].

The uptake of the neutral red and rosaniline onto TPF was determined as a function of dye concentration in the aqueous solution. The resultant isotherms show a good linear relationship. The average values of correlation coefficient (*R*<sup>2</sup>) and intercept were 0.992 and 7.9×10<sup>-5</sup>, respectively (Table 2). The average capacity (*Q*) of the TPF for neutral red and rosaniline was 0.47 mmol g<sup>-1</sup>. The *Q* value of TPF for neutral red is greater than for rosaniline, which depends on the molecular size of the dye.

The temperature dependence of sorption of neutral red and rosaniline onto TPF was studied and showed that maximum sorption occurs at low temperatures. Thermodynamic parameters for the sorption of tested dyes were calculated using the equations:

Table 2. Characteristics of the isotherm curves of the sorption of neutral red and rosaniline dye onto TPF.

Dye	Least square equation		correlation coefficient (r)	Capacity Q (mmol g <sup>-1</sup> )
	Slope	Intercept×10 <sup>-3</sup>		
Neutral red	0.87	0.000	1.000	0.69
Rosaniline	0.48	0.159	0.983	0.24

$$\ln K = -\Delta H/RT + \Delta S/R$$

$$K = ((C_o - C)/C)$$

$$\Delta G = \Delta H - T\Delta S$$

where  $K$  is the distribution coefficient for sorption. The linear plots of  $\ln Kc$  vs.  $1/T$  ( $R^2 = 0.889$ ) give the numerical values of enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) from the slope and the intercept, respectively. Values of  $\Delta G$  for neutral red and rosaniline are  $-5.0$  and  $-0.4$  kJ mol<sup>-1</sup>, respectively, suggesting that the adsorption of tested dye is spontaneous process. The values of  $\Delta H$  are  $-29.3$  and  $-60.7$  kJ mol<sup>-1</sup> indicating that the chemisorption of dye onto TPF is exothermic in nature. The negative values of entropy ( $-81.6$  and  $-202.3$  J K<sup>-1</sup> mol<sup>-1</sup>) could be interpreted as an indication that sorption of neutral red and rosaniline onto TPF is fast.

The effect of sample volume (10 – 100 mL) on the removal of rosaniline and neutral red was investigated. It was found that the maximum sorption of neutral red and rosaniline occurred in 10 – 25 mL of sample solution (Figure 2). The batch factor ( $V/m$ ) ranged from 100 to 250 where  $m$  is the mass of TPF. The sorption of the dye decreases with increased sample volume (from 82.5% to 66.4%) using a batch factor of 500. The average value of  $RSD$  was 3.8% ( $V/m = 250$ ,  $n = 5$ ).

The dependence of sorption of neutral red and rosaniline on the weight (0.02-0.2 g) and size (0.0625-1 cm<sup>3</sup>) of TPF was also examined. The results show that the maximum sorption of neutral red and rosaniline occurred by using 0.05-0.2 g and 0.125-1 cm<sup>3</sup> of TPF.

The effect of different salts on the removal of neutral red and rosaniline from wastewater was studied using a batch technique. It was found that 1 mol L<sup>-1</sup> of NaCl, KCl, NH<sub>4</sub>Cl, NaF, NaNO<sub>3</sub> or NaHCO<sub>3</sub> do not effect on the removal of dye. NaH<sub>2</sub>PO<sub>4</sub> and Na<sub>2</sub>CO<sub>3</sub> salts reduce the sorption of rosaniline. NaF and Na<sub>2</sub>CO<sub>3</sub> salts reduce the sorption of neutral red. Observed decreases in the percentage of dyes removed in the presence of NaF, NaH<sub>2</sub>PO<sub>4</sub> and Na<sub>2</sub>CO<sub>3</sub> salts are due to changes in the pH of dye solution.

### 3.3. Absorption Spectrum and Calibration Curve

A simple and sensitive spectrophotometric method for the determination of neutral red and rosaniline has been developed. The quantitative and semiquantitative determination of tested dyes is based on the colour of the TPF surface after the dye is sorbed. The colour of a thin film of TPF (0.1 cm) was changed from yellow-orange to red. The absorption spectra of dyed TPF (after absorbing the neutral red and rosaniline) are

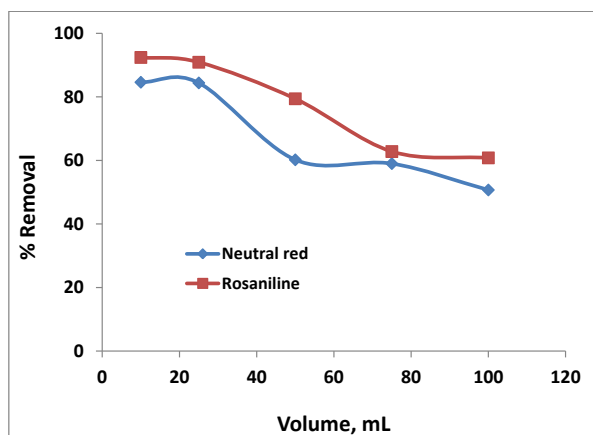


Figure 2. Effect of sample volume on the sorption of neutral red and rosaniline.

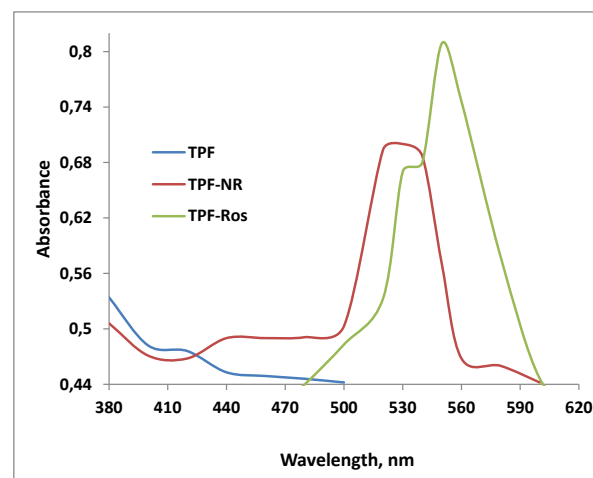


Figure 3. Spectra of TPF and TPF after sorption of neutral red and rosaniline.

compared with the spectrum of TPF in Figure 3. The spectra of the dyed TPF were red shifted from 415 nm to 528 and 551 nm after sorption of neutral red and rosaniline, respectively (Table 3).

The method obeyed Beer's law in the concentration range 0.01 – 1 and 0.01 – 3 µg mL<sup>-1</sup> for neutral red and rosaniline, respectively (Figure 4). A regression analysis of the calibration curve revealed a good correlation (Table 4,  $R^2 = 0.994$ ). The values of molar absorptivity ( $\epsilon$ ) are  $1.5 \times 10^5$  and  $6.8 \times 10^5$  L mol<sup>-1</sup> cm<sup>-1</sup> for neutral red and rosaniline, respectively.

**Table 3.** Detection limit (Sandell's sensitivity,  $S$  and semiquantitative determination,  $Se$ ), wavelength ( $\lambda_{max}$ ), and molar absorptivity ( $\epsilon$ ) for spectrophotometric measurements for basic dyes using TPF.

Dye	Sensitivity, LDL		$\lambda_{max}$ (nm)	$\epsilon$ L mol <sup>-1</sup> cm <sup>-1</sup>
	$S$ (ng cm <sup>-2</sup> )	$Se$ ( $\mu$ g mL <sup>-1</sup> )		
Neutral red	1.52	0.17	528	$1.5 \times 10^5$
Rosaniline	0.34	0.10	551	$6.8 \times 10^5$

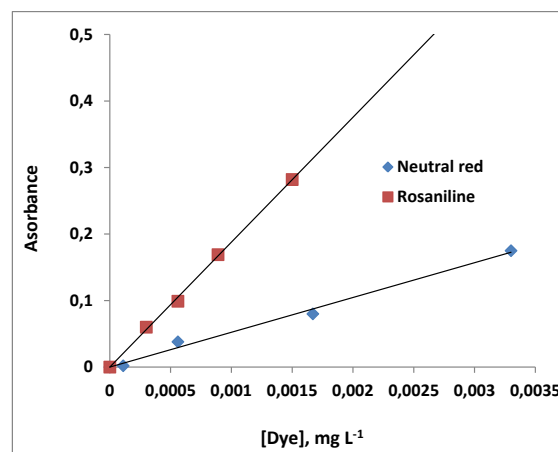
**Table 4.** Characteristics of the calibration curves of the solid phase spectrophotometric determination of neutral red and rosaniline dye using a thin layer of TPF.

Dye	Line equation		correlation coefficient, $R^2$	LOD $\mu$ g L <sup>-1</sup>	LOQ $\mu$ g L <sup>-1</sup>
	Slope	Intercept			
Neutral red	52.3	$-1 \times 10^{-5}$	0.992	0.01	0.03
Rosaniline	186.8	$-6 \times 10^{-5}$	0.996	0.01	0.04

The sensitivity sequence was in the order of rosaniline > neutral red, which has an average value of the lower detection limit (LDL) of Sandell's sensitivity of 0.93 ng cm<sup>-2</sup>,  $S = 0.001/a$  where "a" is specific absorptivity (Table 4). The results obtained show that the TPF method is more sensitive than the direct spectrophotometric method for the determination of neutral red and rosaniline. This result indicates that the proposed method is more sensitive and rapid than direct spectrophotometric methods for the determination of neutral red and rosaniline dye.

The LOD of neutral red and rosaniline were established by analyzing four blank solutions and defined as  $LOD = 3 \sigma$  equation, where  $\sigma$  is the standard deviation of blank determination. The LOD of rosaniline and neutral red were each found to be 0.01  $\mu$ g L<sup>-1</sup> and the limits of quantitation 0.04  $\mu$ g L<sup>-1</sup> ( $LOQ = 10 \sigma$ ) (Table 4). The lower limits of detection of neutral red and rosaniline with average value of RSD from 2.9 % ( $n = 4$ ), are suitable for the analysis of the tested dyes using TPF.

The absorbance of the TPF was measured after immersing the TPF cubes in different solvents (water, benzene, and chloroform) in a spectrophotometer cell. Considerable improvement in the absorbance values were noticed in benzene compared with the other solvents ( $\epsilon$ ,  $1.3 \times 10^6$ ). The sensitivity sequence was in order of  $C_6H_6 > H_2O > CHCl_3$ . The low relative standard deviation values (RSD = 0.46 %) for the analysis of four sample replicates of the neutral red and rosaniline indicates a good precision and accuracy of the proposed method. Finally, the color of the TPF after absorbance of neutral red and rosaniline was stable over 60 minutes while the intensity of the color of dye in aqueous solution decreased after 3 only minutes. As low as 0.1  $\mu$ g mL<sup>-1</sup> of neutral red and rosaniline were detected after shaking one cube (0.125 cm<sup>3</sup>) of the TPF with 2 mL of the solution of tested dye in test tube. The color intensity on the TPF was found to be proportional to the concentration of dyes in aqueous solution. Neutral red and rosaniline were determined semiquantitatively by a visual comparison of the color of the TPF cube with a standard scale of rosaniline and neutral red prepared under the same experimental conditions. The results obtained indicate that rosaniline could be more sensitively determined than neutral red.



**Figure 4.** Calibration curves for neutral red and rosaniline determination using TPF.

### 3.4. Dynamic technique

The sorption of neutral red and rosaniline onto TPF columns was studied at different sample solution flow rates. A set of solutions (25 mL) containing 100 mg of dye was passed through a TPF column at flow rates varying from 1 to 30 mL min<sup>-1</sup>. The dye was eluted by (1:1) C<sub>2</sub>H<sub>5</sub>OH:H<sub>2</sub>O solution. It was found that the optimum flow rate for sorption of neutral red and rosaniline was 1 – 10 and 1 – 15 mL min<sup>-1</sup>, respectively. The percentage uptake decreased with increasing flow rates from 15 to 45 mL min<sup>-1</sup>.

The elution of 4 mg of neutral red and rosaniline from the TPF column by using (1:1) C<sub>2</sub>H<sub>5</sub>OH:H<sub>2</sub>O solution was examined at different flow rates (3, 4, 6 and 8 mL min<sup>-1</sup>). The chromatograms indicate that neutral red and rosaniline could be completely eluted within the first 5 – 28 and 10 – 42 mL, respectively (Figure 5).

The height equivalent to a theoretical plate (HETP) is calculated from the elution curves using Glueckauf ( $HETP = LW^2/16V_R^2$ ) and Van Deemter ( $HETP = A + B/U + CU$ ) equations. Where  $V_R$  is volume of eluate at peak maximum,  $W$  is width of the peak,  $L$  is length of the foam bed,  $U$  is flow rate and

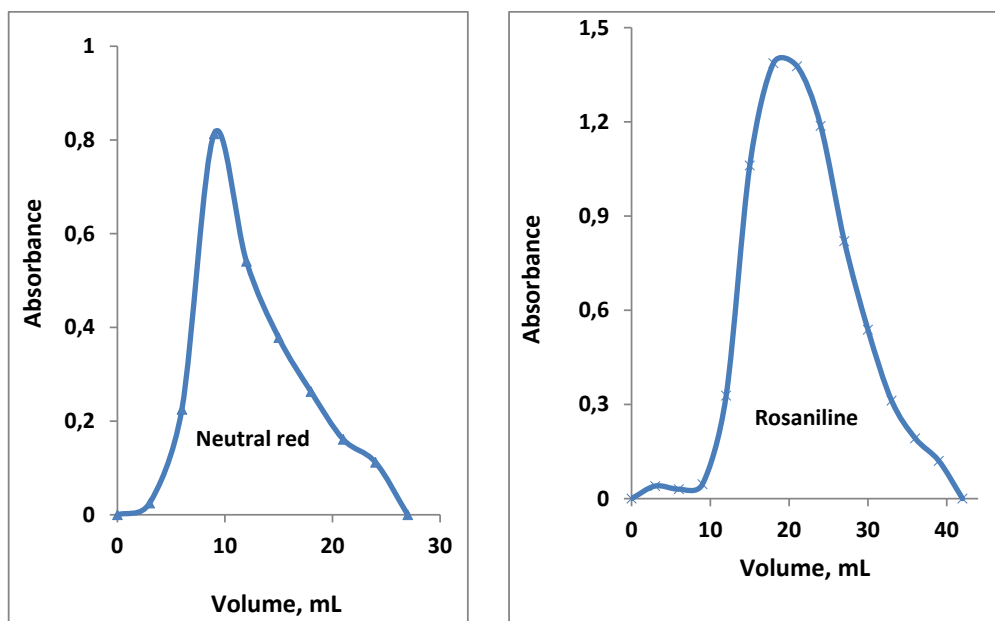


Figure 5. Elution chromatograms of neutral red and rosaniline using TPF column.

A, B, C are constants. The average values of HETP and number of theoretical plate ( $N = L/HETP$ ) were 0.52 mm and 162, respectively at flow rate  $4 \text{ mL min}^{-1}$  for the elution of dye. The ideal flow rate can be also calculated from the equation:  $U = \sqrt{B/C}$ , where B represents longitudinal or molecular diffusion of sample components and C represents the rate of mass transfer. The values of U obtained by these equations are 3.9 and  $3.3 \text{ mL min}^{-1}$  for neutral red and rosaniline, respectively. The HETP value is also calculated from the breakthrough curve (Figure 6) using the equation:  $HETP = L(V - \bar{V})/VV$  where V is the volume of effluent at the center of an S-shaped breakthrough where the concentration is one half the initial concentrations, and  $\bar{V}$  is the volume at which the effluent has a concentration of: 0.1587 of the initial concentration. The value of HETP obtained by this equation is 0.50 mm. The value of HETP is in a good agreement with those values obtained from the elution curves.

The effect of various eluting agents like 1 M HCl, 1 M NaOH, NaF,  $\text{NaNO}_3$ ,  $\text{NaH}_2\text{PO}_4$ ,  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{CH}_3\text{OCH}_3$ ,  $\text{CHCl}_3$  and  $\text{C}_6\text{H}_6$  on the stripping of the neutral red and rosaniline from TPF column matrix was studied. It was observed that the tested dyes could not be eluted with HCl, NaOH, NaF,  $\text{NaNO}_3$ ,  $\text{NaH}_2\text{PO}_4$ ,  $\text{CHCl}_3$  or  $\text{C}_6\text{H}_6$ .  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$  and  $\text{CH}_3\text{OCH}_3$  were able to completely elute the neutral red and rosaniline from TPF column.

The reusability of the TPF column was tested by running cycles of loading and stripping of dye from the TPF column with  $\text{C}_2\text{H}_5\text{OH}:\text{H}_2\text{O}$  (1:1). The results showed that the TPF column could extract more than  $96.44\% \pm 0.03\%$  of the neutral red or rosaniline dye from aqueous solution through more than 7 extraction cycles. The reusability of the TPF column indicates that the TPF sorbent is stable.

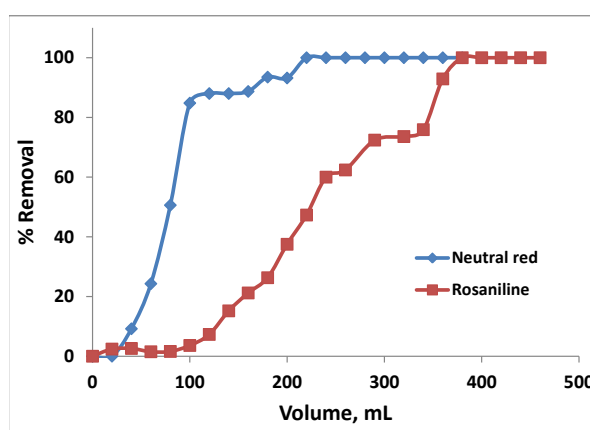


Figure 6. Breakthrough curve of TPF column for the removal of neutral red and rosaniline.

### 3.5 Sorption mechanism

There were many factors that may influence the sorption behavior, such as dye structure and size, sorbent surface properties, steric effect and hydrogen bonding and van der Waals forces [31]. The solvent extraction, ion association, surface adsorption and ion exchange are the most probable mechanisms of basic dye sorption onto TPF.

The pH of the dye solution is an important factor in the sorption of dye onto sorbent, which has an effect on the surface charge of sorbent material and the degree of ionization of the dye molecule [32]. The surface of TPF has negative charge at pH greater than 4.4 and the negative charge of TPF increases further at increasing pH values. At  $\text{pH} > 4.4$ , the electrostatic attraction between the basic dye and TPF surface took place and led to increase of the extraction of neutral red and rosaniline. This result

shows that ion association may be the principal mechanism for the sorption of tested dyes.

A decrease in pH leads to protonation of the oxygen atoms of the TPF and reduces dyes sorption. Increasing pH, decreases the electrostatic repulsion between the positively charged dye ions and the TPF surface, which led to an increase in dye sorption. Maximum sorption was achieved around pH 7-9. Since the dyes contain nitrogen atoms that are capable of hydrogen bonding with OH groups in TPF, they were extracted mainly in the neutral form by a solvent extraction at pH 7. The interaction between neutral red and rosaniline dyes with TPF may be taking place through either weak or strong bonds [31]. The weak bonds could occur due to van der Waals forces. Strong bonds could form through either hydrogen bonding interaction between the nitrogen containing amine groups of dye and TPF surface and/or electrostatic interactions between the cationic dye and negatively charged TPF surface [31]. Finally, one could reasonably suggest that the sorption of basic dyes onto TPF may proceed via a solvent extraction and ion association mechanism.

The sorption of neutral red and rosaniline onto TPF depends on three transport processes: bulk transport of solute in solution, film transfer involving diffusion of solute through a hypothetical film boundary layer and diffusion of the solute within the pore volumes of the sorbent and along pore-wall surfaces to active adsorption sites [33]. In this regard, The Bangham ( $\log \log(C_o/C_o - Q_t/m) = \log(k_o m/2.303V) + \alpha \log(t)$ ), Reichenberg ( $Q_t/Q_e = 1 - 6\pi^{-2}e^{-B}$  where  $B = \pi^2 r^{-2} D_i t$ ) and Morris-Weber ( $Q_t = k_i \sqrt{t}$ ) equations are applied to explain the diffusion mechanism of neutral red and rosaniline onto TPF. For the pore diffusion mechanism, the kinetic data for the sorption of dye onto TPF were analyzed by using the Bangham model. The linearity (Table 5,  $R^2 = 0.961$ ) of the double logarithmic plot for the Bangham equation shows that the diffusion of dye into pores of the TPF is rate the controlling step. The  $Q_t$  was plotted against the square root of time to test the applicability of the Weber–Morris equation. The results show the rate of diffusion is fast in the early stages of sorption and a linear relationship (Table 5,  $R^2 = 0.883$ ) was verified where the diffusion constant ( $k_i$ ) was found to be  $0.497 \mu\text{mol g}^{-1} \text{min}^{-1/2}$ . The sequence of  $k_i$  values was rosaniline > neutral red, which indicates that the  $k_i$  is independent on the molecular size of dye. For the film diffusion controlled kinetics, the expression developed by Boyd and improved by Reichenberg was applied. The plot of  $Bt$  versus  $t$  shows straight lines that do not pass through the origin. In addition, the values of the effective diffusion coefficient ( $D$ ) are increased with increasing molecular size of the dye (Table 5).

Table 5. Diffusion parameters for the sorption of basic dyes onto TPF.

Dye	Bangham model		Reichenberg model		Morris-Weber model	
	$\alpha$	$R^2$	$D_i \times 10^{-8}$	$R^2$	$k_i$	$R^2$
Neutral red	0.30	0.957	8.4	0.994	0.35	0.851
Rosaniline	0.14	0.964	8.7	0.904	0.65	0.914

The pseudo first order [ $\log(Q_e - Q_t) = (\log Q_e) - (k_1 t/2.303)$ ] and pseudo second order [ $t/Q_t = (1/k_2 Q_e^2) + (t/Q_e)$ ] kinetic model was found to fit the experimental data for the sorption of neutral red and rosaniline onto TPF. The  $R^2$  values for pseudo second order sorption model (0.999) are higher than the values of  $R^2$  (0.949) for pseudo first order kinetic. This suggests that the pseudo second order adsorption mechanism is predominant. The value of  $h$  (initial sorption rate constant,  $h = k_2 Q_e^2$ ) was calculated from Figure 7. The data obtained show that the rate of sorption is rapid and the values of  $h$  are 3.1 and 5.7  $\text{mmol g}^{-1} \text{min}^{-1}$  for the sorption of neutral red and rosaniline, respectively. The values for  $k_2$  are found to be 0.05 and 0.06  $\text{g mmol}^{-1} \text{min}^{-1}$ , respectively. The values of the initial sorption rate,  $h$ , for both dyes were much higher than the pseudo-second order rate constant,  $k_2$ , as predicted by the pseudo-second order kinetics [34]. The initial sorption rate,  $h$ , and pseudo-second order rate constants,  $k_2$ , for the rosaniline sorption were much higher than for neutral red sorption. This indicates that the rate of rosaniline removal is much faster than neutral red removal. These result indicate that the rate of sorption of dye onto TPF is independent on the size of the dye.

The Benesi-Hildebrand equation ( $C_1 C_2 / A = 1/K\varepsilon + (C_1 + C_2)/\varepsilon$ ) was used to calculate the amount of tannic acid present on the PUF matrix where the  $C_1$  and  $C_2$  are the concentration of sorbed dye and tannic acid, respectively. It is found that the amount of tannic acid on the PUF matrix is  $0.035 \text{ mmol g}^{-1}$  whereas the amounts of neutral red and rosaniline sorbed on TPF are 0.69 and  $0.24 \text{ mmol g}^{-1}$ , respectively. The corresponding molar ratios (Dye: TPF) for neutral red and rosaniline are 20:1 and 7:1, respectively.

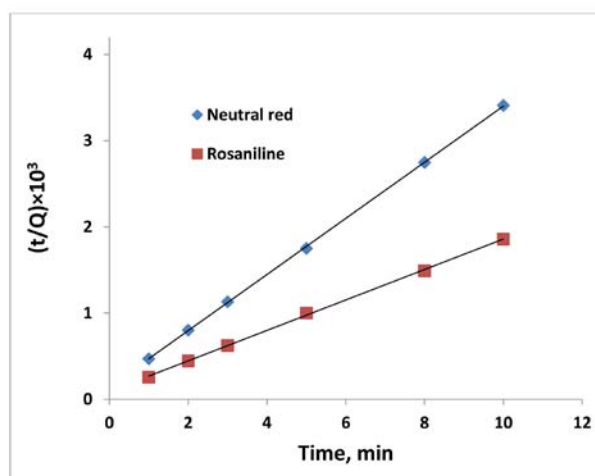


Figure 7. Pseudo-second-order plot for the sorption of neutral red and rosaniline by TPF.

The plot of  $Q_c/C_e$  vs.  $C_e$  for the experimental data according to the Langmuir model [ $C_e/Q_c = (1/K_L b) + (C_e/K_L)$ ] give a poor linear relationship ( $R^2 = 0.248$ ) for the sorption of neutral red and rosaniline onto TPF. This model suggests that the sorption of dye from aqueous solution to the solid is monolayer coverage. The plot of  $\log q_c$  vs.  $\log q_e$  from the Freundlich model ( $\log Q_c = \log K_F + \frac{1}{n} \log C_e$ ), where  $K_F$  is adsorption capacity of the TPF sorbent and the constant  $1/n$  is the intensity of the adsorption, was constructed. The average value of  $R^2$  was 0.911, which indicates that the surface structure of TPF is heterogeneous. The slopes ( $1/n$ ) of the Freundlich plot are 0.91 and 0.99 for sorbed neutral red and rosaniline, respectively. Values of  $1/n$  ranging between 0 and 1 represent favorable adsorption conditions [35].

The Dubinin Radushkevich equation ( $\ln Q_c = \ln k_{dr} - \beta \epsilon^2$  &  $\epsilon = RT \ln[1 + (1/Q_c)]$ ) for non-gaseous application [36] was used to calculate the activation energy ( $\Delta E$ ) and determine the sorption mechanism. In this equation,  $K_{DR}$  is the maximum amount of dye sorbed onto TPF,  $\beta$  is a constant related to the transfer energy of dye from the bulk solution TPF sorbent and  $\epsilon$  is the Polanyi potential. The values of  $b$  for the sorption of neutral red and rosaniline onto TPF are -0.006 and -0.004, respectively (Figure 8). The values of sorption energy or activation energy ( $\Delta E$ ) were correlated to  $b$  ( $E = 1/\sqrt{-2\beta}$ ). The values of ( $E$ ) were 9.1 and 11.2 kJ mol<sup>-1</sup> for sorption of neutral red and rosaniline, respectively. Solvent extraction, weak-base anion exchange and surface adsorption are the most probable mechanisms for dye uptake by TPF [37].

The average values of  $DH$  and  $DG$  were -45.0 and -2.7 kJ mol<sup>-1</sup>, respectively. The negative values of  $DH$  indicate that the chemisorption of dye is an exothermic process. The negative values of  $DG$  indicate that the process is spontaneous in nature without an induction period [38]. The lower values of  $DE$  than those of  $DH$  indicate the strong attraction between the tested dyes and the sorbent and that the extraction process occurs even under normal conditions [30]. The average value of  $DS$  was -142.0 J K<sup>-1</sup> mol<sup>-1</sup>; the negative value of the entropy indicates that the rate of sorption of neutral red and rosaniline onto TPF is fast.

#### 4. Analytical Applications

A validation of the proposed procedure for the spectrophotometric determination of neutral red and rosaniline using TPF was carried out. Also, the validity and accuracy of the method for the removal of neutral red and rosaniline from the two environmental samples, laundry water and industrial wastewater, was evaluated.

Table 6. Determination of neutral red and rosaniline in wastewater.

Dye	Solid-phase spectrophotometer	Visual	Direct spectrophotometer
Neutral red, µg mL <sup>-1</sup>	0.17	0.1	0.18
Rosaniline, µg mL <sup>-1</sup>	0.43	0.5	0.53

Neutral red and rosaniline in wastewater were determined using solid-phase spectrophotometric and visual techniques. A 0.1 cm thin film of the TPF was mixed with a 2 mL of wastewater spiked with 5 and 10 mg of dye. The concentration of neutral red and rosaniline after sorption onto TPF was determined spectrophotometrically. The results are given in Table 6, which shows the suitability of TPF for water analysis (RSD ~ 1.21 %, n = 5). The results obtained are in agreement with those obtained using a visual comparison to a standard scale of neutral red and rosaniline. When these results were compared with those obtained by using direct spectrophotometric determination of dye, the data were in good agreement (Table 6).

Neutral red and rosaniline dye in different samples of untreated industrial wastewater from El-Dammam Industrial City was removed using a column technique. A 100 mL aliquots of industrial wastewater (pH values 8.5 and 5.2, respectively) were spiked with 10 and 100 mg of the tested dye. Then the solutions were passed through the TPF columns at a flow rate of 3 - 4 mL min<sup>-1</sup>. The percentage of neutral red and rosaniline removed from the water samples onto TPF columns were between 63 and 99% (Table 7). These results show that the removal percentage depends on the pH of wastewater.

Neutral red and rosaniline dyes were also removed from untreated laundry wastewater using the batch technique. A 25 mL aliquot of wastewater (pH ~ 12.9) was spiked with 100 mg of neutral red or rosaniline. The percentage of dyes removed from the water samples onto TPF were 48-50%. These results show that TPF is a suitable sorbent for use in the removal of the basic dyes from wastewater (Table 7).

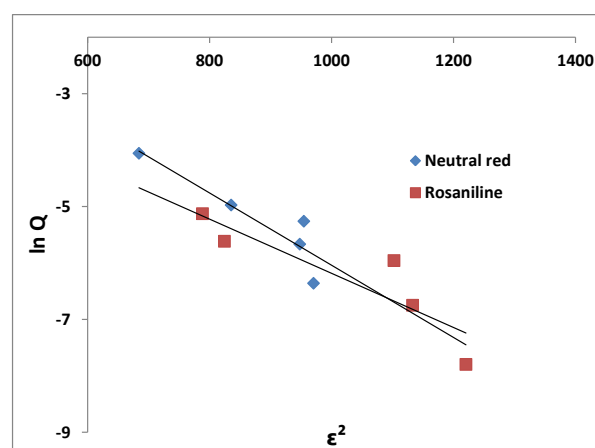


Figure 8. Dubinin Radushkevich isotherm for the sorption of neutral red and rosaniline.



Table 7. Removal of neutral red and rosaniline from industrial and laundry wastewater.

Wastewater	Dye	Technique	pH	Added, mg	Found, mg	Recovery%
Industrial-1	Neutral red	Dynamic	8.5	10	9.5	95
	Rosaniline	Dynamic	8.5	10	9.9	99
Industrial-2	Neutral red	Dynamic	5.2	100	62.8	62.8
	Rosaniline	Dynamic	5.2	100	87.3	87.3
Laundry	Neutral red	Batch	12.9	100	4.8	48
	Rosaniline	Batch	12.9	100	5.0	50

## 5. Conclusion

The present work deals with the synthesis of a new sorbent based on the coupling of tannic acid with polyurethane foam through an ester group. The tannic acid functionalized polyurethane foam has a highly acidic character, which was used for extraction and determination of neutral red and rosaniline. Experiments show that the tannic acid is not washed out from the TPF. The kinetics of sorption of the tested dyes onto TPF follows a second order rate equation. The high values of  $\epsilon$  indicate the sensitive detection of the dyes using TPF. The

negative values of  $\Delta H$  for the sorption of tested dye indicate exothermic sorption. The results show the suitability of the TPF for detection, determination and removal of basic dyes from wastewater.

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