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Removal of reactive dye brilliant red HE-3B from aqueous solutions by hydrolyzed polyacrylonitrile fibres: equilibrium and kinetics modelling

Research Article

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Abstract: A cheap and efficient fibrous hydrolyzed polyacrylonitrile (HPAN) sorbent was obtained by alkaline hydrolysis of Romanian polyacrylonitrile fibres. Scanning electronic microscopy and infrared spectroscopy were used to characterize the hydrolyzed product and to confirm its functionalization. The adsorptive potential of the proposed sorbent for reactive dye Brilliant Red HE-3B removal from aqueous solutions of pH=2 was examined by the batch technique as a function of dye concentration, temperature solution and contact time. The Freundlich, Langmuir and Dubinin-Radushkevich adsorption models were applied to describe equilibrium sorption data and to determine the corresponding isotherm constants. The thermodynamic parameters ΔG, ΔH and ΔS were also determined; the values obtained show that sorption of reactive dye on HPAN fibres is a spontaneous, endothermic and entropy-driven process. The kinetics of sorption of the reactive dye were analyzed using pseudo-first order and pseudo-second order kinetic models. The kinetic data fitted well to pseudo-second order kinetics, indicating the chemisorption of reactive dye onto the fibrous sorbent. The sorption mechanism of the dye onto hydrolyzed fibres was confirmed by FTIR spectroscopy. The dye-loaded HPAN sorbent can be regenerated by treatment with 0.1M NaOH and the regenerated sorbent may be reused in several adsorption-desorption cycles. The results of this study provided evidence that the HPAN fibres are effective for removing reactive dye Brilliant Red HE-3B from aqueous effluents.

Keywords: *Sorption • Aqueous solutions • Equilibrium • Kinetic study • Thermodynamic parameters*

1. Introduction

Dyes represent an important group of water pollutants which appear in the effluents discharged from textile, leather, food processing, dyeing, paper and dye manufacturing industries. During the dyeing and finishing operations in the textile industry 10-15% of the dye is lost in the wastewaters [1]. Most dyes are synthetic compounds with complex aromatic molecular structures, which make them resistant to light, heat and oxidizing agents, non-biodegradable, and toxic to life, with carcinogenic and mutagenic effects [2]. The removal of dyes from wastewaters before their final disposal is a major environmental problem, not only because of their potential toxicity but also because of their colour and the aesthetic impact on receiving waters.

The wide diversity of chemical structures of dyes, their variable content in effluents together with considerable amounts of auxiliary products make the development of a method with general applicability for decolourisation of textile wastewaters difficult. Some methods have been employed to remove colour from industrial effluents, such as chemical precipitation, membrane technologies, adsorption, flocculation, foam flotation, biological

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processes, and oxidation and photocatalytic degradation. Many of these methods have certain efficiencies but require considerable operational costs [3-5].

Adsorption has been found to be one of the most effective techniques for colour removal from wastewaters due to simple design and ease of operation, non-toxicity, superior removal of waste constituents and low cost of application. Decolourisation by adsorption is primarily determined in equal extent by the structure and properties of the dye and the surface chemistry of the sorbent. Interaction of the functional group of the dyes (one or more –OH, -COOH, -SO_3H, -N=N- groups, *etc.*) with the sorbent surface could be result from covalent, coulombic, hydrogen bonding or weak van der Waals forces [6]. Selection of a sorbent for a potential dye should be based on characteristics such as high affinity and dye binding capacity, sorption kinetics, regeneration properties and cost. A large number of materials have been used as suitable sorbents for decolourization of industrial effluents: activated carbon (the most common but expensive adsorbent), polymeric resins, and various low-cost adsorbents (agricultural products, peat, chitin, silica, bentonite clay, fly ash) [7-11].

Due to the structural features of many synthetic dyes resulting in very large molecules, nanoporous sorbents with larger specific surface areas are of great interest for colour removal. Chemically modified fibres, having high external specific surface area, high adsorption rate and good selectivity, controlled by the nature of the functional groups grafted onto the surface of the fibre, have been investigated as sorbents for heavy metal removal from aqueous media [12,13], but their applications for the removal of dyes from wastewater have not been reported. Many fibrous sorbents for selective removal and recovery of various metal ions have been prepared from polyacrylonitrile fibre, a cheap commercial synthetic product, widely used in the textile industry as well as in production of carbon fibres [14,15].

In this research, alkaline hydrolyzed polyacrylonitrile (HPAN) fibre was prepared via reaction of textile-grade Romanian polyacrylonitrile fibres with sodium hydroxide. The hydrolyzed product was characterized and investigated as a sorbent for the removal of reactive dye Brilliant Red HE-3B from aqueous solutions. The sorption experiments were performed as function of initial dye concentration, temperature and contact time. The equilibrium sorption data and kinetic data were processed using different models to understand the sorption mechanism of dye molecules on the fibrous sorbent proposed.

2. Experimental Procedures

2.1. Materials

The Romanian polyacrylonitrile fibre (PAN), Melana (commercially available and/or wastes produced during various stages of textile processes), a ternary copolymer with 90.6% acrylonitrile, 6.2% vinylacetate and 3.2% α-methylstyrene, was used for synthesis of hydrolyzed polyacrylonitrile fibrous sorbent.

The reactive dye, bifunctional monochlortriazine, Brilliant Red HE-3B from BEZEMA (MW =1463, λ_{max} = 530 nm, λ = 38769.5 L mol^{-1} cm^{-1}) was used as a commercial salt. The structure of the reactive dye is shown in Fig. 1. The stock solution (500 mg L^{-1}) was prepared in distilled water and working solutions were obtained by appropriate dilution.

Analytical reagent grade chemicals (NaOH, HCl) were used throughout.

2.2. Preparation of the sorbent (alkaline hydrolyzed fibre)

Alkaline HPAN was prepared by treating a 10 g amount of dried PAN with 200 mL of 20% (w/w) NaOH aqueous solution in a 500 mL reaction vessel. The mixture was heated while stirred on a water bath at 90-92°C for 30 min. Subsequently, the hydrolyzed product was separated from solution, washed with distilled water until the pH of the filtrate was about 7.0 and air dried.

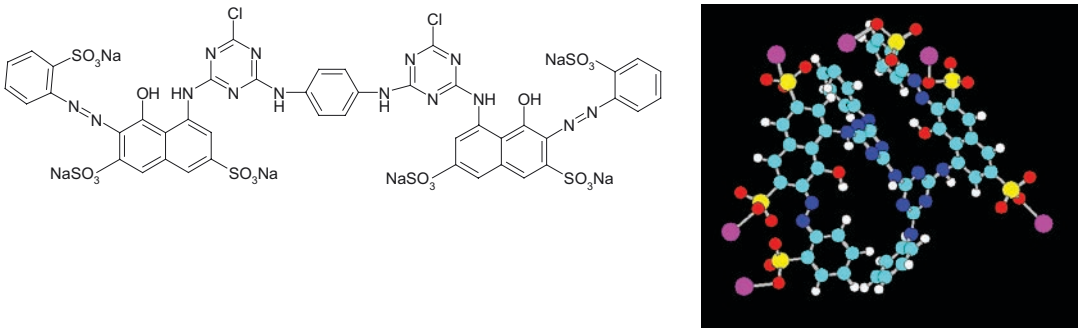
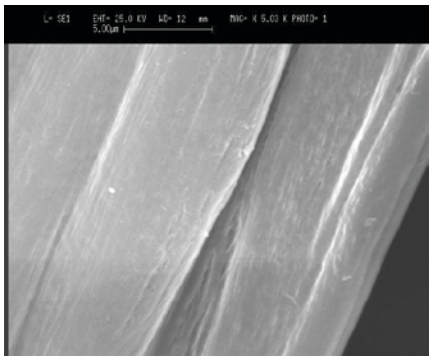


Figure 1. Structure of reactive dye Brilliant Red HE-3B.



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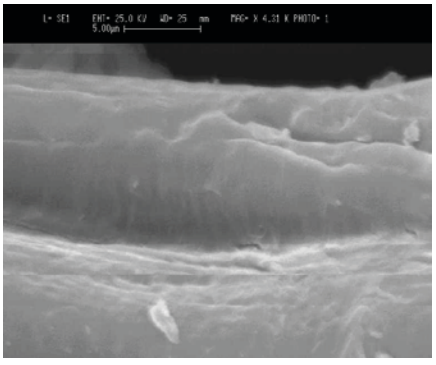


b)

Figure 2. SEM images of (a) PAN and (b) HPAN (b) fibres.

2.3. Characterization of sorbent

A scanning electron microscope (SEM), MICROSPEC WDX-2A using a 25 kV accelerating potential, was used to study the morphology of the fibrous samples before and after hydrolysis. Infrared spectra of PAN and HPAN (cut into small pieces) as KBr pellets were recorded on an FT-IR BioRad spectrometer FTS2000, with 4 cm^{-1} resolution for 32 scans.

2.4. Equilibrium studies

Batch sorption experiments were performed by shaking 0.1 g of HPAN sorbent with 50 mL aqueous solution of reactive dye with various initial concentrations in 150 mL conical flasks placed in a temperature-controlled bath (5°C, 20°C and 45°C). The pH of the solutions was adjusted to the value of 2 by adding diluted solutions of HCl; pH was measured with a RADELKIS OP-271 pH/Ion analyzer. After equilibrium (24 h), the final concentration of dye in the solution was determined spectrophotometrically with an UV-VIS Digital Spectrophotometer Model S 104D/WPA.

The amount of dye sorbed at equilibrium (q, mg g^{-1}) was calculated using following relationship:

$$q = \frac{(C_0 - C) \cdot V}{G} \quad (1)$$

where C_0 and C are the initial and equilibrium concentrations of dye in solution (mg L^{-1}), respectively, G is the amount of sorbent (g) and V is the volume of solution (L).

2.5. Kinetic studies

The effect of contact time on the sorption of reactive dye onto HPAN was determined by the limited bath technique. A sample of HPAN sorbent (1 g) was added under stirring to a 500 mL solution of dye with pH=2 and initial concentration of 80 or 120 mg L^{-1}. The temperature of the solution was maintained at 20°C with a thermostatted bath. After different times (5 - 400 min), 1 mL volumes of supernatant were collected for

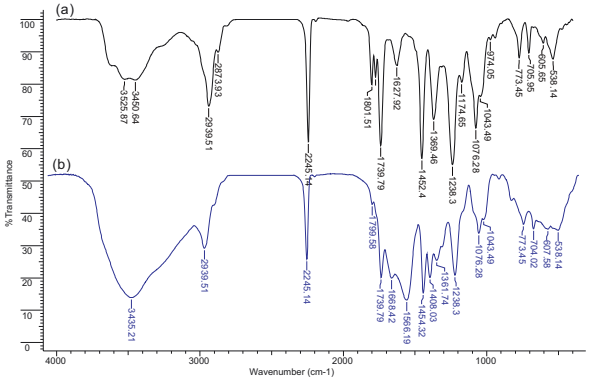


Figure 3. FTIR spectra of (a) PAN and (b) HPAN samples.

spectrophotometric measurements of dye content. The extent of sorption was expressed by the fractional attainment of equilibrium, expressed in Equation 2,

$$F = \frac{q_t}{q} \quad (2)$$

where q_t and q (mg g^{-1}) are the amounts of dye sorbed at time t and at equilibrium (24 h), respectively.

3. Results and Discussion

3.1. Preparation and characterization of alkaline HPAN fibres

Alkaline hydrolysis of PAN fibres is a well known reaction and recently was investigated as a means of obtaining superabsorbent materials [16-18]. Preliminary studies showed that the saponification degree of the nitrile groups is determined by alkali concentration, reaction temperature and the time of hydrolysis. Therefore, in order to prepare a product with considerable sorption capacity and a high mechanical and chemical stability, the following hydrolysis conditions were selected: 20% (w/w) concentration of NaOH solution, 90°C and a 30 min reaction time.

The surface morphologies of PAN and HPAN

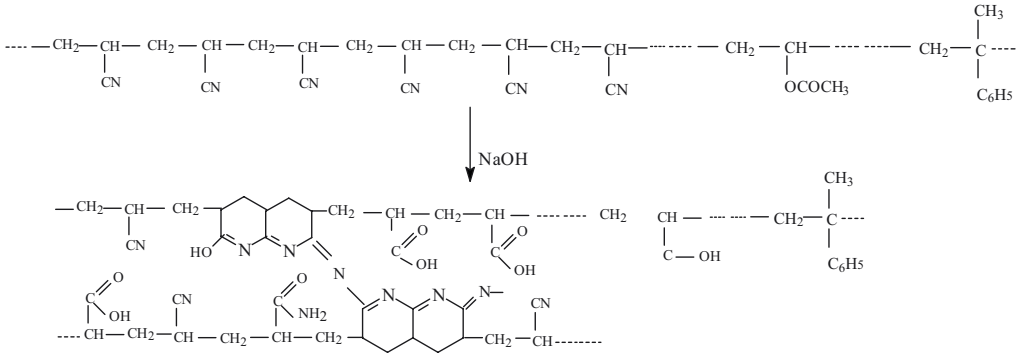


Figure 4. Schematic illustration of the PAN and HPAN structures.

Table 1. Analysis of FTIR spectra of PAN and HPAN samples.

Wavenumber, cm^{-1}		Peak assignments
PAN	HPAN	
3525.87; 3450.64	3435.21	γ OH , γ NH (in combination)
2939.51	2939.51	γ CH asymmetric in CH, CH_2 and CH_3 groups
2873.93	2873.93	γ CH symmetric in CH, CH_2 and CH_3 groups
2245.14	2245.14	γ C≡N
1739.79	1739.79	γ C=O in COOR
1627.92	1668.42	γ C=O in amide I
	1566.19	γ –C=N– imines groups in conjugated sequences δ CNH in amide II combination of C-N stretching and N-H bending
1452.4	1454.32	δ CH_3 and δ_s CH_2
	1408.03	γ C-O and δ O-H in COOH groups
1369.46	1361.74	δ CH_3 symmetric in CCH_3
1076.28	1076.28	γ C-O in acetate ester
538.14	538.14	δ_t C= O

γ – stretching vibration, δ – bending vibration, δ_s – scissor vibration, δ_t – twisting vibration

samples were evaluated by SEM (Fig. 2a and b).

As illustrated, the surface of PAN is relatively smooth, with a number of longitudinal cracks created during fibre formation [19,20]. However, after treatment with NaOH the fibre surface became rougher and more eroded, indicating that the hydrolysis reaction occurs on the surface of fibres.

FTIR spectra were examined to indicate the chemical modification of PAN fibres via hydrolysis. Fig. 3a and b show FTIR spectra of fibrous samples before and after alkaline hydrolysis. Characteristic bands of PAN and HPAN fibres are listed in Table 1.

The FTIR spectrum of hydrolyzed product HPAN exhibited many significant changes. The broad absorption band from 3650-3450 cm^{-1} for PAN was replaced by a strong broad band with a peak at 3435.2 cm^{-1}, suggesting formation of many -OH and -NH groups on the fibre surface. The -OH groups may be

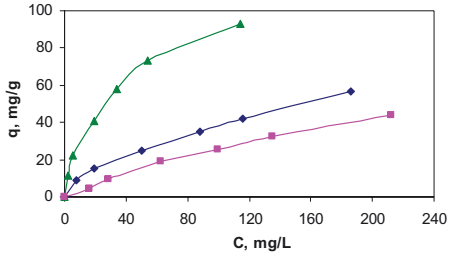


Figure 5. Sorption isotherms of the reactive dye Brilliant Red HE-3B on HPANat ▲ 45°C, ■ 20°C and ■ 5°C.

produced by the hydrolysis of an ester group (vinyl acetate) [21]; this supposition is confirmed by the significant decreases of the peaks at 2939.51 cm^{-1} (γ CH), 1739.79 cm^{-1} (γ C=O) and 538.14 cm^{-1} (δ_t C=O). Conversely, the -OH groups and –NH groups may result during hydrolysis of some nitrile groups to a mixture of hydrophilic carboxamide (-$CONH_2$) (1668.42 cm^{-1}, γ C=O in amide I); and carboxylic groups (-COOH) (1408.03 cm^{-1}, γ C-O and δ O-H in COOH groups); the intensity of the peak at 2245.14 cm^{-1} for the C≡N groups decreased significantly, indicating that the nitrile groups are involved in hydrolysis reaction. The new peak at 1566.19 cm^{-1} is attributed to imine (-C=N-) conjugate sequences in the hydrolyzed fiber [21], in agreement with formation of partly hydrogenated naphthyridine type structures, initiated by the nucleophilic attack of $-OH^-$ on the carbon atom of the nitrile group [22].

The presence of these functional groups on the HPAN surface, proved by FTIR analysis, demonstrates that the alkaline hydrolysis of PAN is a complex process, initiated through cyclization of nitrile groups, followed by hydrolysis to amide functional groups, and finally, carboxylic groups of the $–(C=N)_n–$ segments are formed [23,24]. However, in different stages of the hydrolysis, it is possible for the resulting product to have ampholytic characteristics caused by both weakly basic groups (-C=N–) and weakly acidic groups (-COOH), bound to the same fibrous matrix. The change of the chemical structure of PAN during alkaline hydrolysis to HPAN is illustrated in Fig. 4.

3.2. Sorption equilibrium

In previous work in this laboratory [25], batch sorption experiments were performed to establish the optimum retention conditions of reactive dye Brilliant Red HE-3B from aqueous solutions onto HPAN fibres. The experimental results showed that the anionic dye is adsorbed on HPAN only from acidic solutions (pH = 1-3, lower than 3.9, which is the pHPZC of HPAH fibres [25]), when the sorbent surface is positively charged.

In evaluation of the sorption process as the unit operation, the equilibrium of sorption and kinetics are two important physicochemical aspects. Sorption equilibrium is established when the concentration of sorbate in the bulk solution is in dynamic balance with that of the interface sorbent-solution.

The equilibrium sorption of reactive dye Brilliant Red HE-3B on HPAN fibres from aqueous solutions of pH=2 was measured at 5, 20 and 45°C using different initial concentrations varying from 25 to 300 mg L^{-1}. The sorption isotherms are presented in Fig. 5.

The relationship between the amount of dye adsorbed and its equilibrium concentration was described by the Freundlich, Langmuir and Dubinin-Radushkevich [26-28] adsorption isotherm equations. The Freundlich isotherm, one of the most frequently applied, assumes surface heterogeneity and the exponential distribution of active sites of the sorbent according to Equation 3:

$$q = K_F \cdot C^{1/n} \quad (3)$$

where K_F is a parameter related to the degree of adsorption and n is a measure of sorption intensity. The constants K_F and n are calculated from the linearized equation:

$$\log q = \log K_F + \frac{1}{n}\log C \quad (4)$$

According to the Langmuir isotherm, a monolayer of sorbate exists on the homogeneous surface of the sorbent which has equally available sites of the same energies according to Equation 5:

$$q = \frac{K_L \cdot C \cdot q_0}{1 + K_L \cdot C} \quad (5)$$

where the constant K_L is related to the energy of sorption and q_0 is the maximum sorption capacity. The Langmuir constants, K_L and q_0, are calculated from the linearized equation:

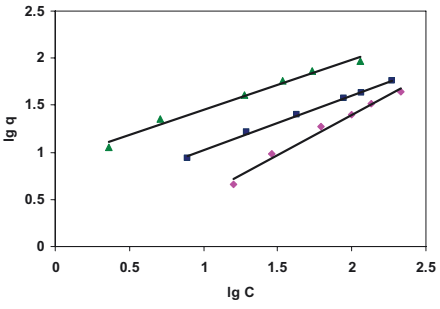
$$\frac{1}{q} = \frac{1}{q_0} + \frac{1}{K_L \cdot q_0} \cdot \frac{1}{C} \quad (6)$$

The Dubinin-Radushkevich (DR) equation has the form:

$$\ln q = \ln q_0 - B\varepsilon^2 \quad (7)$$

where q_0 is the maximum sorption capacity, B is the activity coefficient related to the mean sorption energy and ε is the Polanyi potential, equal to:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C}\right) \quad (8)$$



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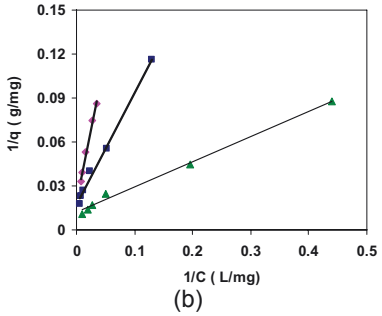

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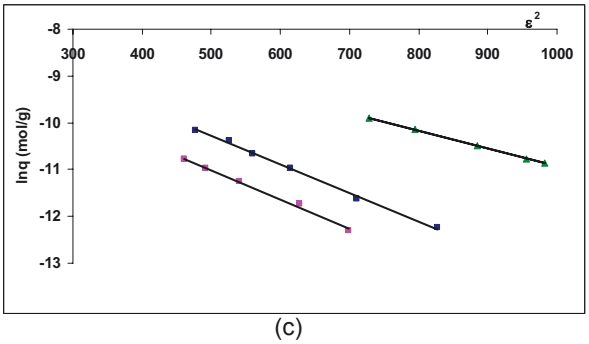


(c)

Figure 6. Fitted (a) Freundlich, (b) Langmuir and (c) DR plots of sorption of the reactive dye Brilliant Red HE-3B on HPAN fibres at ■ 5°C, ■ 20°C and ▲ 45°C.

The sorption energy can be determined using the following equation:

$$E = \frac{1}{\sqrt{2B}} \quad (9)$$

The parameters related to each isotherm, calculated from the intercepts and slopes of the corresponding linear plots (Fig. 6a, b and c), together with their correlation coefficients (R^2), are presented in Table 2.

As presented in Table 2, the values of K_F and n increased as the temperature increased demonstrating that the sorption of reactive dye is favourable at high temperature. In all cases, the value of n is greater than unity indicating beneficial adsorption.

The values of the correlation coefficients in Table 2 indicate that the experimental data were more suitable to the Langmuir model representing monolayer coverage of the fibrous sorbent with reactive dye molecules. This observation agrees with the shape of the sorption

Table 2. Isotherm parameters for the sorption of reactive dye Brilliant-Red HE-3B on HPAN fibres.

Type of isotherm	T (K)		
	278	293	318
	Freundlich		
K_F (mg g^{-1})(L mg^{-1})$^{1/n}$	0.497	2.736	8.329
n	1.174	1.715	1.878
R^2	0.986	0.990	0.984
	Langmuir		
q_0 (mg g^{-1})	49.5	58.48	84.03
K_L (L g^{-1})	10.40	22.20	68.80
R^2	0.994	0.994	0.993
	Dubinin-Radushkevich (DR)		
q_0 (mg g^{-1})	567.08	1053.21	1236.45
B (mol^2 kJ^{-1})	0.0063	0.0061	0.0039
E (kJ mol^{-1})	8.91	9.05	11.32
R^2	0.9950	0.9975	0.9993

Table 3. The apparent thermodynamic constants of the sorption process of reactive dye Brilliant-Red HE-3B onto HPAN fibres.

T(K)	ΔG(kJ mol^{-1})	ΔH(kJ mol^{-1})	ΔS(J mol^{-1}K^{-1})
278	-22.257	34.784	205.1
293	-25.310		
318	-30.457		

isotherms which correspond to type L2 (Langmuir type) in the Giles classification [29]. The values of q_0, which reflect the accessibility of sorption sites, and of the Langmuir constant, K_L, which reflect the binding energy between reactive dye molecules and HPAN fibres, increased as the temperature increased indicating that the sorption is an endothermic process; the high K_L values suggest the chemical nature of sorption.

The sorption energy determined in the DR equation (Table 2) revealed an ion-exchange mechanism for the sorption of the reactive dye on HPAN (sorption energy of 8-16 kJ/mol [30]). The sorption capacity in the DR equation, which may represent the total specific meso- and macropore volume of the sorbent [30], was determined to be 1053.21 mg g^{-1} (25°C).

The adsorption of dyes from solution onto sorbents occurs primarily through physical adsorption due to van der Waals, hydrogen and dipole – dipole bonds or by chemical adsorption (chemisorption) due to covalent and ionic bonds [3,31]. The reactive dye Brilliant Red HE-3B is a charged organic molecule consisting of polar and non-polar regions. These molecular properties suggest a combined sorption process. The results of this research indicates a dominant sorption mechanism involving electrostatic interaction of the anionic groups of dye molecules with protonated imine groups of the

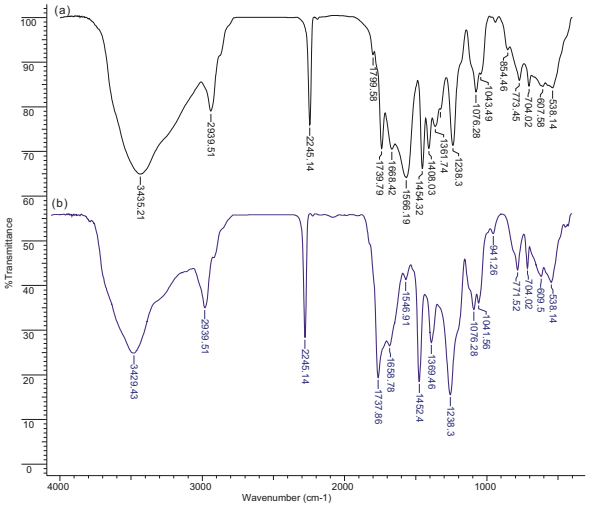


Figure 7. FTIR spectra of (a) HPAN and (b) red HPAN samples.

modified fibrous sorbent surface. Similar results have been reported for the adsorption of some reactive dyes at pH 3-4 onto cross-linked chitosan beads [32] and biomass [33]. Simultaneously, weak interactions between the sorbent matrix and numerous benzene rings in the dye molecule, as well as hydrogen bonding, could play an important role.

3.3. Thermodynamic parameters

To evaluate the effect of temperature on sorption of the dye Brilliant Red HE-3B on HPAN fibres and to understand the nature of sorption, apparent thermodynamic parameters were determined (Table 3), using the values of the Langmuir binding constant, K_L (L mol^{-1}), and following equations [27]:

$$\Delta G = -RT\ln K_L \quad (10)$$

$$\ln K_L = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (11)$$

where ΔG is the free energy, ΔH is the enthalpy, ΔS is the entropy change of sorption, R is the universal gas constant and T is the absolute temperature.

The negative values of the apparent free energy change indicate that sorption of the reactive dye on HPAN fibres is spontaneous. The positive value of the apparent enthalpy change computed from the slope of linear dependence, $\ln K_L$ *vs.* 1/T (R^2 = 0.9999), demonstrate the endothermic nature of dye sorption. The values of ΔH are greater than 20 kJ mol^{-1}, suggesting chemisorption of the reactive dye on HPAN. The positive value of the entropy change characterizes the increased randomness at the solid-solution interface during the sorption of the dye and some structural changes in the adsorbate and the sorbent [26]. The positive entropy value reflects the release of water molecules due to the sorption of large hydrated anions onto the hydrophilic fibrous sorbent

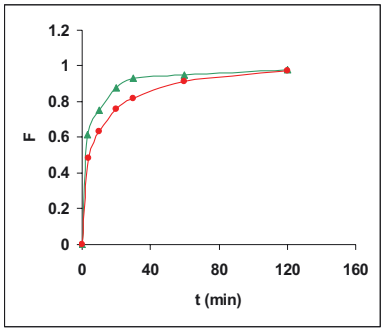


Figure 8. The fractional attainment of equilibrium (F) versus time for the sorption of the reactive dye Brilliant Red HE-3B on HPAN fibres; ● - 80 mg L^{-1} , ▲ - 120 mg L^{-1}.

and the electrostatic interactions between oppositely charged groups. The driving force of sorption is an entropy effect--the entropic contribution is greater than the free energy of sorption.

3.4. Infrared study of Brilliant Red HE-3B dye binding on HPAN fibres

Infrared analysis also provides information regarding the mechanism of dye binding onto the hydrolyzed fibrous sorbent. FTIR spectra of HPAN fibres before and after the sorption of the reactive dye Brilliant Red HE-3B from aqueous solutions of pH = 2 (red HPAN) are presented in Fig. 7.

Comparing these spectra indicated that the intensity of the absorption band at 1566.19 cm^{-1} decreased and the peak shifted to lower frequency (1546.91 cm^{-1}). These changes can be attributed to electrostatic interactions between protonated imine groups (positively charged at pH=2) in the HPAN structure and the sulphonyl group of the dye molecule (negatively charged) [31]. Additionally, the absorption peak at 1668.42 cm^{-1} shifted to 1658.7 cm^{-1}, suggesting that the amidic groups in the HPAN fibre were involved in sorption of the anionic dye.

3.5. Sorption kinetics study

The effect of contact time on the removal of Brilliant Red HE-3B reactive dye by sorption onto HPAN fibres from two solutions of pH=2 with different initial concentrations, is shown in Fig. 8.

The time period required for maximum removal of reactive dye was determined to be 1 hour; however, the sorption half-times ($t_{1/2}$) were 10 min.

In order to investigate the mechanism of sorption and potential rate controlling step, reaction-based kinetic models were used to test experimental data concerning reactive dye sorption onto HPAN [2,28]. The pseudo-first order Lagergren model, traditionally used for describing sorption kinetics, is expressed by equation 10:

$$\log(q_0 - q_t) = \log q_0 - k_1 t \qquad (10)$$

where k_1 (min^{-1}) is the rate constant of the pseudo-first order sorption, evaluated from the slope of the plot $\log(q_0-q_t)$ *vs.* t (Fig. 9a).

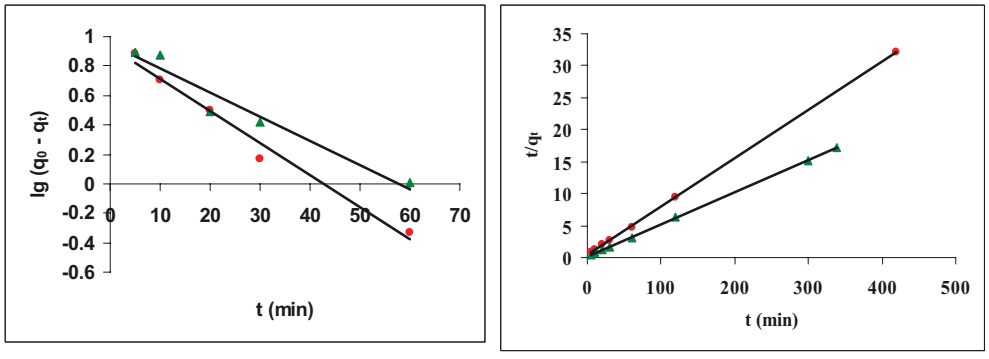
According to the pseudo-second order model the dye sorption kinetic is described by the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_0^2} + \frac{t}{q_0} \qquad (11)$$

where k_2 is the rate constant of pseudo-second order sorption (g $mg^{-1} min^{-1}$) and $h = k_2 . q_0^2$ is the initial sorption rate (mg $g^{-1} min^{-1}$). By plotting t / q_t versus t (Fig. 9b), a straight line should be obtained and q_0, k_2 and h can be calculated.

The experimental kinetic data were adjusted according to each model (Fig. 9) and the kinetic parameters of Brilliant Red HE-3B sorption on HPAN as well as the correlation coefficients are given in Table 4.

Using the data presented in Table 4, it can be concluded that the pseudo-second order reaction model provided the best correlation with experimental results. This observation demonstrated that the sorption of reactive dye follows a pseudo-second order rate equation and suggested that chemical sorption instead of mass transfer is the rate-limiting step for the sorption



(a) (b)

Figure 9. The applicability of the (a) pseudo-first order and (b) pseudo-second order kinetic models to the sorption of reactive dye Brilliant Red HE-3B on HPAN; ● - 80 mg L^{-1}, ▲ - 120 mg L^{-1}.

Table 4. The kinetics parameters of reactive dye Brilliant-Red HE-3B sorption onto HPAN fibres.

C_o(mg L^{-1})	pseudo-first order kinetic model		pseudo-second order kinetic model			
	k_1 (min^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	h (mg g^{-1} min^{-1})	q_0 (mg g^{-1})	R^2
80	0.0163	0.947	0.0144	2.529	13.24	0.999
120	0.0219	0.981	0.0276	5.123	20.04	0.999

process. Increasing the initial dye concentration has a favourable effect on the rate of sorption by increasing the concentration gradient between the solution and the fibrous sorbent. Values of calculated q_0 show good agreement with experimental q_0 values.

3.6. Desorption and regeneration studies

The reactive dye retained onto PAN fibres can be desorbed by treating the loaded fibrous sorbent with 0.1 N NaOH solution. After desorption and washing with deionized water, the HPAN sorbent can be reused in repeated cycles of sorption-desorption. This behaviour is a new confirmation of the fact that the sorption of anionic reactive dye on the surface of HPAN fibrous sorbent involves chemical bonding by ion-exchange.

4. Conclusions

Romanian PAN fibres--commercially available or as wastes of the textile industry--were modified by alkaline hydrolysis in order to obtain a new, inexpensive and efficient sorbent for removal of dyes from aqueous solutions. SEM and FTIR spectra revealed that the hydrolyzed product (HPAN) contained conjugated imine sequences, and amide and carboxylic groups on the surface of the fibres. The HPAN fibrous material is an effective adsorbent for the removal of Brilliant Red HE-3B reactive dye from aqueous solutions of pH = 2; sorption is dependent on the dye concentration, solution temperature and contact time of the phases. The experimental data were analyzed with Freundlich, Langmuir and Dubinin-Radushkevich models. The Langmuir isotherm best represented the equilibrium sorption data; a monolayer sorption capacity of 84 mg g^{-1} was obtained at 45°C. The values of apparent thermodynamic parameters confirm the feasibility of the sorption and suggest an entropy-driven, endothermic sorption process. The results indicated an ion-exchange mechanism of reactive dye sorption on HPAN fibres; this mechanism is confirmed by infrared spectral data. The kinetics of sorption of the reactive dye on fibrous HPAN was determined to follow a pseudo-second order rate equation. Quantitative desorption of the dye from HPAN fibres was performed with 0.1 M NaOH; the regenerated sorbent can be reused many times. The results of this study provided evidence that HPAN fibres can be used as an effective sorbent for the removal of reactive dye Brilliant Red HE-3B from aqueous effluents of pH 1-3.

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