HPAN TEXTILE FIBER WASTES FOR REMOVAL OF DYES FROM INDUSTRIAL TEXTILE EFFLUENTS

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Abstract: *The paper presents our new results about efficiency of wastes based on hydrolyzed polyacrylonitrile textile fibers (HPAN) as sorbents in removal of some dyes from textile effluents. The effect of some experimental variables such as initial dye concentration, sorbent mass, pH, temperature, and contact time were investigated. The sorbent - dye sorption systems are described using Freundlich, Langmuir and Dubinin-Radushkevich isotherm models. The laboratory experimental results performed using the textile fibres wastes indicate the good removal of dyes from aqueous medium, suggesting that these textile solid wastes correspond to the actual tendency of using non-conventional sorbtive materials to reduce the overall cost of sorbent preparation.*

Key words: *sorption, HPAN waste, textile wastewater treatment, dyes.*

1. Introduction

By large volume and composition of wastewaters from dyeing processes, the textile industry has a great polluting impact. During the dyeing and finishing operations, 10-15% of the dye is lost in the wastewaters [7]. 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 forms, having carcinogenic and mutagenic effects. In this context, the major tendencies into the last years are the elaborations of very strict settlements concerning textile wastewaters disposal, development of new technologies and methods (ion exchange, photocatalytic decomposition, coagulation - flocculation, advanced oxidation, chemical reduction, adsorption [1], [2], [6, 7]) for textile effluent depollution and replacing of toxic synthetic organic dyes inducing toxicologic, allergen and mutagen risks with environmental-friendly dyes or materials.

Adsorption has been found to be one of the most effective techniques for color removal from wastewaters. Dye removal by sorption in batch conditions is a relatively simple method which can be carried out without sophisticated equipments. Selection of new sorbent is determined on the high efficiency of the sorption process (high affinity and dye binding capacity, sorption kinetics, regeneration properties and cost). Most sorbents presented into scientific literature are synthetic and engineered materials, such as synthetic resins, ion exchange celluloses, chemically modified fibers, activated charcoal and ashes. In order to avoid some disadvantages of conventional sorbents based on synthetic polymers (high prices, difficulties in obtaining, pollution

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produced during their synthesis), and in accordance with the tendency of replacing chemically synthesized compounds with natural wastes, unconventional materials are increasingly used for textile effluents treatment [1], [8]. These last types of wastes having a synthetic (such industrial wastes) and/or natural (such cellulosic and/or lignocellulosic agricultural wastes) structure assure large specific surface areas, high sorption rates, the possibility to be functionalized with organic ligands for increasing their sorption capacity [7].

In this context, great interest to investigate like sorbents low cost materials, from nature or by-products and/or wastes from certain industries or agriculture has been developed. These materials are characterized by high capacity for pollutants removal, employing and disposing with low cost, accessibility, high inner and outer surface, macro and micro-porous structure, rapid kinetics of the sorption process, the possibility to use some materials in different shapes (particles of different dimensions, fibres, filters, textures) [7].

This work continues our studies concerning employment of some industrial wastes as low-cost sorbents for decolorization of textile wastewater [3-5]. In this context, alkaline hydrolyzed polyacrylonitrile waste fibers (Melana, Romania) were tested as inexpensive and efficient sorbents in removal of some textile anionic and cationic dyes from aqueous solutions. The sorption experiments were performed as function of *pH*, initial dye concentration, sorbent dose, temperature and contact time. The equilibrium sorption data were fitted to different isotherm models to understand the sorption mechanism.

2. Material and Method

2.1. Materials

The experiments were carried out using Romanian poly acrylonitrile fibre Melana (PAN) wastes (composition: 90.6% acrylonitrile, 6.2% vinyl acetate and 3.2% α-methyl styrene) produced during various steps of textile technological processes. The fiber was chemically modified by thermal treatment with NaOH aqueous solutions. The synthesis of hydrolyzed sorbent (HPAN) and characterization of the developed functional groups were already published [3].

The sorbent was used in both forms, as now synthesized and, also, as reused after dye desorption from loaded sorbent (the regenerated sorbent may be reused of many times).

The selected dyes were used as commercial salts and are characterized in Table 1.

Summary data on dyes studied Table 1

Name	C.I.	Type of dye	MW [g/mol]	λ_{max} [nm]	Concentration of the stock solution [mg/L]
Reactive Orange 16 (RO)	17757	anionic reactive	617.54	495	617.5
Reactive Violet 5 (RV)	18097	anionic reactive	735.6	560	735.6
Methylene Blue (Basic Blue 9) (MB)	52015	cationic phenothiazine dye	319.85	660	320
Crystal Violet (Basic Violet 3) (CV)	42555	cationic triphenylmethane dye	407.99	590	408

2.2. Sorption experiments

Sorption experiments were carried out by contacting samples of 0.01-0.05 g of HPAN with 25 mL of solution of different initial dye concentrations into some conical flasks having a capacity of 150 mL placed in a thermostated assembly. The solution *pH* was adjusted using dilluted HCl solutions, and measured at RADELKIS OP-271 *pH*/Ion analyzer. After a specific time interval, the dye concentration in residual solution was determined spectrophotometrically, with an UV-VIS Digital Spectrophotometer, model S 104D/WPA. The sorption capacity of the sorbent was evaluated by means of the amount of sorbed dye, q (mg/g HPAN):

$$q = (C_0 - C) \cdot V \cdot 10^{-3} / G \,, \qquad (1)$$

and by percent of dye removal:

$$R\% = (C_0 - C) \cdot 100 / C_0 \,, \qquad (2)$$

where C_0 and C are the initial and equilibrium dye concentration (mg/L), G is the amount of HPAN (g) and V is the volume of solution (L).

3. Results and Discussion

3.1. Effect of some factors on the dye removal

Alkaline hydrolyzed PAN waste fibres contain both amide and carboxylic groups and imine sequences on the surface of the fibres and, thus, have amphoteric properties, removing ionic species from solutions. Interaction of the sorption sites of HPAN fibers with the functional groups of the dye is dependent on the following experimental parameters: solution *pH*, sorbent dose, initial dye concentration, contact time and temperature.

• The solution *pH*

The effect of initial solution *pH* on the sorption of studied dyes onto HPAN (Figure 1) had indicated that the anionic dyes are better retained from acidic media and cationic dyes are sorbed from slightly acidic and neutral solutions. This behavior of dyes may be correlated with the surface charge of the sorbent in function of the solution *pH*. The pH_{PZC} (*pH* of zero charge) of HPAN fibers was determined by the method described by Nouri and Haghseresht [11]; the limiting *pH* (*pH* = 3.9) was considered as value of pH_{PZC}, when the sorbent surface is neutral. At *pH* lower than pH_{PZC} sorbent surface is positive (the imine groups are protonated) and has affinity for anionic dye. At *pH* higher than pH_{PZC} the surface of HPAN sorbent is negatively charged (the carboxyl groups are dissociated) and is available for electrostatic interactions with cationic dyes.

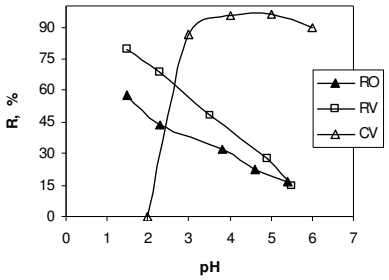

Fig. 1. *The effect of pH on dyes sorption onto PAN fibres: RO - 88.9 mg/L; RV - 88.2 mg/L; 24 h, T = 20 °C; CV - 32.64 mg/L, 2 g HPAN/L*

• Sorbent dose

The sorption of all studied dyes from solutions at the optimal value of *pH* increases with the amount of HPAN fibers, due to the higher number of available sorption sites; the sorbent dose that assures a dye removal degree higher than 80% is dependent on size of dye molecule: 2 g HPAN/L for Crystal Violet and Methylene Blue, and respectively, 10 g HPAN/L for

reactive dyes, Reactive Orange and Violet (more voluminous molecules) (Figure 2).

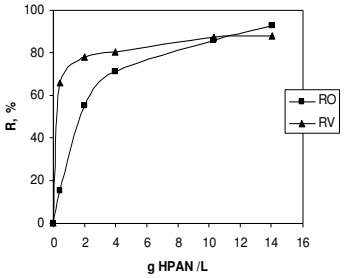

Fig. 2. *The effect of sorbent dose on dye sorption onto PAN fibres: RO - 88.9 mg/L; RV - 88.2 mg/L; pH = 1.5, 24 h, T = 20 °C*

• Initial dye concentration

The amount of retained dyes increases with the increase of initial dye concentration (Figure 3).

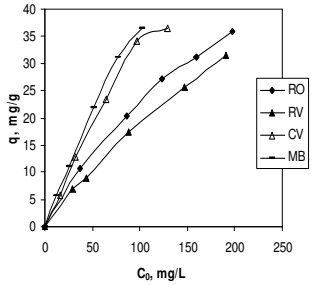

Fig. 3. *The effect of initial dye concentration on dye sorption onto HPAN; CV, MB - pH = 6; RO, RV - pH = 1.5; 2 g HPAN/L; 24 h; T = 20 °C*

• Contact time

The amount of sorbed dye increases quickly into the first 15 minutes (more rapidly into the solution with higher concentration) and then increases slowly; ca 1 hour is required for attaining of sorption equilibrium for all the dyes (Figure 4).

• Temperature

The amount of sorbed dyes from solutions at the specific solution *pH* increases with an

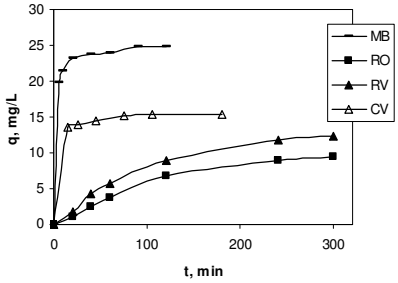

Fig. 4. *Effect of contact time on uptake of dyes on HPAN fibres: T = 20 °C; pH = 6: CV - 32.64 mg/L; MB - 51.2 mg/L; pH = 1.5: RO - 30 mg/L; RV - 50 mg/L; 2 g HPAN/L*

increasing in temperature (Table 2). This behaviour may be attributed to the fact that the sorption of dyes onto HPAN fibres is an endothermic process of chemical nature (chemosorption), controlled by the diffusion of dye ions into fibrous structure of the sorbent. This effect is more important at higher dye concentrations.

3.2. Sorption isotherm

The relationship between the amount of sorbed dye on the textile fibers and their equilibrium concentration can be described by three models [9-10]:

• the Freundlich (Eq. 3):

$$q = K_F \cdot C^{1/n}; \tag{3}$$

• the Langmuir (Eq. 4):

$$q = \frac{K_L \cdot C \cdot q_0}{1 + K_L \cdot C}; \tag{4}$$

• the Dubinin-Radushkevich (D-R) (Eq. 5):

$$\ln q = \ln q_0 - B\varepsilon^2, \tag{5}$$

where: K_F is a parameter responding of the adsorption capacity and n is a measure

Isotherm parameters for the sorption of dyes onto HPAN fibres Table 2

Dye	T [K]	Type of isotherm									
		Freundlich			Langmuir			Dubinin-Radushkevich (DR)			
		K_F [mg/g] [L/mg]$^{1/n}$	n	R^2	q_0 [mg/g]	K_L [L/g]	R^2	q_0 [mg/g]	B [mol^2/kJ]	E [kJ/mol]	R^2
	275	3.91	2.36	0.97	29.94	0.14	0.99	95.52	0.0039	11.32	0.96
	293	7.18	1.17	0.97	39.53	0.21	0.99	355.69	0.004	11.18	0.98
	313	14.18	2.73	0.96	49.51	0.35	0.99	343.08	0.0031	12.7	0.95
	275	1.787	3.09	0.95	8.64	0.07	0.99	25.902	0.0033	12.31	0.97
	293	6.34	2.15	0.98	32.15	0.20	0.95	217.24	0.0036	11.78	0.98
	313	13.37	1.00	0.94	39.53	0.52	0.99	154.39	0.0021	15.43	0.96
	275	0.26	1.07	0.98	55.25	0.0053	0.97	855.71	0.0093	7.33	0.98
	293	2.01	1.66	0.99	63.29	0.0109	0.99	520.52	0.0060	9.21	0.99
	313	1.78	1.38	0.99	90.09	0.0113	0.99	487.84	0.0042	10.91	0.87
	293	0.385	0.94	0.99	53.47	0.010	0.98	426.94	0.0057	9.366	0.98

of sorption intensity; a favorable sorption corresponds to a value of $1 < n < 10$. For $n = 1$, $K_F = K$ (linear isotherm).

The Langmuir constant, K_L, is related to sorption energy and q_0 is the maximum value of sorption capacity (corresponding to complete monolayer coverage).

B is a constant related the sorption energy and ε (Polanyi potential) = RT ln(1+1/C).

The mean sorption energy can be determined using the following equation:

$$E = \frac{1}{\sqrt{2B}}. \qquad (6)$$

For $E < 8$ kJ/mol, the sorption mechanism is dominated by physico-sorption and if E = 8-16 kJ/mol, the ion-exchange is the dominant process.

The parameters related to these three isotherms, calculated from the intercepts and slopes of the corresponding linear plots (Figures 5…7) together with their correlation coefficients (R^2) are presented in Table 2.

As can be seen from Table 2, the values of K_F, n, K_L and q_0 increases with increasing of temperature suggesting that the sorption of tested dyes is positively influenced by the high temperature.

In all cases the value of n is more than unity and indicates a positive beneficial sorption.

The values of the correlation coefficients higher than 0.99 from Table 2 suggest that the experimental data were more suitable to the Langmuir model of monolayer sorbent coverage with dye molecules.

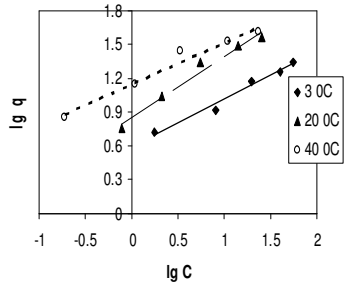

Fig. 5. *Freundlich plots for sorption of MB dye on HPAN: 2 g HPAN/L; 24 h; pH = 6*

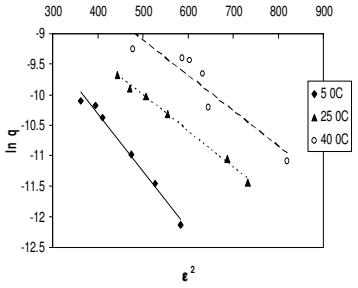

Fig. 6. *Dubinin- Radushkevich plots for the sorption of RO dye on HPAN: 2 g HPAN/L; 24 h; pH = 1.5*

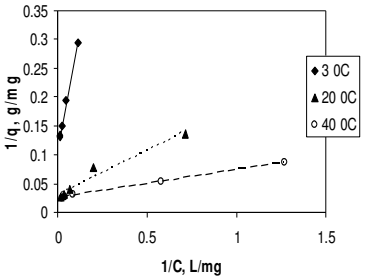

Fig. 7. *Langmuir plots for the sorption of CV on HPAN: 2 g HPAN/L; 24 h; pH = 6*

The sorption energy calculated in the DR equation (Table 2) corresponded to an ion exchange mechanism for the dye sorption on HPAN fibers (sorption energy of 8-16 kJ/mol [9]).

4. Conclusions

- The modified textile waste material may be used as non-conventional cheap and efficient sorbent for the removal of dyes, both anionic and cationic, from effluents of textile industry.
- The results performed in this study indicate that the sorption capacity of the tested waste material is dependent on the possible operational variables (temperature, sorption time, *pH*, sorbent dose, dye concentration) and, also on the dye chemical structure.
- The study of sorption equilibrium confirms a chemical mechanism for the dye removal on fibrous sorbent.
- After desorption of retained dyes, the sorbent can be reused in new cycles of dye sorption-desorption, the sorbtive capacity been kept into appreciable high limits.

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