

Synthesis and Characterization of Polyamide Powders for Sorption of Reactive Dyes From Aqueous Solutions

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ABSTRACT: Polyamide (PA) fine powders or granules, obtained by anionic solution/suspension polymerization of lactams, were used for the sorption of reactive dye Brilliant Red HE-3B from aqueous solutions. They provided a relatively large surface area and porosity that allowed an increased sorption rate. The visible molecular absorption spectroscopy was used to evaluate the performance of the investigated systems. Under the same conditions, the sorption capacity of polyamide particles decreases in the following manner: PA6-powders > PA12-powders > PA4-granules. The effect of pH, initial dye concentration, temperature, and sorption duration on dye removal was studied for the PA6-powder/reactive dye system. The equilibrium sorption

isotherms have been analyzed by the linear, Freundlich, and Langmuir models. The data conform to a Langmuir isotherm and a pseudosecond order kinetic model, respectively. In addition, the apparent thermodynamic parameters were calculated and the obtained values support the conclusion that the reactive dye molecules are adsorbed onto PA-powders by an entropy-driven, endothermic process. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1833–1843, 2007

Key words: wastewater treatment; reactive dye removal; polyamide powders; anionic solution polymerization; particle size; particle size distribution

INTRODUCTION

Wastewaters from many industries, such as textile, leather, food processing, cosmetics, and dye manufacturing contain various amounts of dyes, important water pollutants. They represent a relatively large group of organic chemicals, not biodegradable, with a potential toxicity for the aquatic ecosystem. When they are present even in moderate concentrations (10–200 mg/L), their presence can significantly affect photosynthesis activity and reduce light penetration, thus affecting the growth of plants and impacting on invertebrate and other forms of wildlife; dyes can cause allergy, dermatitis, skin irritation, cancer, and mutations in humans.^{1,2} Also, some dyes, such as benzidine, were identified as carcinogens that may be reformed as a result of metabolism.³ Consequently, the dyes must be removed from the industrial effluents before their discharge in the environment or in the municipal waters.

Several treatment technologies and methods exist for dye removal, such as oxidation,⁴ coagulation/flocculation,⁵ adsorption,^{2,3,5} ion exchange,^{6–8} and anaerobic biological treatments.⁹ The use of one individual technique is not enough to achieve complete discolor-

ation; therefore dye removal strategies consists of a combination of different techniques.

Sorption is a very efficient method for wastewater treatment that consists in retaining pollutants from a liquid phase onto solid sorbents. The method is based on specific physical and/or chemical interactions determined by the particularities of the systems under study. This technique use different types of sorbents,² such as activated charcoal,^{2,5,10,11} polymeric materials,^{12–15} or other various low cost adsorbents.^{1–3,16–19} The choice of the sorbent is based on requirements concerning high selectivity, large capacity of sorption, favorable kinetic features, physical-chemical stability, mechanical strength, easy regeneration, and availability. Cost becomes a major criterion for selection of a sorbent together with the possibility of its recovery, reuse, and disposal. Because of compatibleness between these criteria and their sorptive features, the macromolecular materials such as synthetic polymers (linear or crosslinked), ion exchange celluloses, and polyurethane foams constitute, in many instances, an effective alternative.

Polyamide powders, prepared by grinding of waste textile materials, have been successfully used for remove dyes from wastewater.²⁰ The authors claim that more than 90% of acid dyes were eliminated from wastewater with 1 g/L of powdered polyamide. However, neither the particles size nor the porosity or specific surface area can be controlled with accuracy by grinding technique.

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TABLE I
Some Physical Properties of PA-Powders Derived from BET and Mercury Intrusion Methods

PA-powder type	Average particle size (μm)			Total pore volume (m^2/g)		Apparent density (d_a) (g/cm^3)	BET area (m^2/g)	Porosity ^c (%)
	d_{50}	$-SD^a$	GDS ^b	BET	Mercury intrusion			
PA4	44.45	1.80	2.77	0.41	0.40	0.453	0.41	46.35
PA6	30.89	1.49	1.65	0.75	0.89	0.362	1.37	55.48
PA6 + BR	30.59	1.63	1.99	—	—	—	—	—
PA12	15.26	1.67	1.94	1.37	1.43	0.259	9.26	71.94

S_d , particles span distribution; GDS, geometrical standard deviation.

Where d_i ($i = 10, 16, 50, 84,$ and 90) stands for the diameter corresponding to $i\%$ on the cumulative volume distribution, i.e., $i\%$ of the mass is in particles smaller than d_i .

^a Evaluated by the equation $S_d = (d_{10} - d_{90})/d_{50}$.²⁷

^b Evaluated by the equation $GDS = (d_{84} - d_{16})^{1/2}$.²⁸

^c Evaluated by the equation: $P\% = (1 - d_a)/d \times 100$.

This study is focused on the testing of sorption potential of some lactam-based polyamide powders in dyes recovery. High molecular weight polyamides in the form of fine dispersions are typically obtained through anionic solution polymerization of lactams. This form facilitates polymer's purification and is very suitable for different processing procedures, such as flame spraying, electrostatic coating, paste production, dispersions, and lacquer binders. Their outstanding characteristics, such as nonirritant properties, spherical shape, very low specific weight ($<2 \text{ g}/\text{cm}^3$), sorption, and desorption properties—related to their microporous structure, and strong chemical inertia—PA-powders are widely used in cosmetics.^{21,22} Because of their extended surface, PA-powders may also be applied as an adsorbent. The bis(monochloro-s-triazine) reactive dye Brilliant Red HE-3B has been chosen as model dye to test the sorption ability of lactam-based polyamide powders. It is applicable on coloring of all types of natural as well as regenerated cellulosic materials, either alone or in blend with other fibers like wool, polyester, polyamide, etc.

EXPERIMENTAL

Polyamide powders synthesis, and characterization

For all experiments, the pre-established amount of monomer, i.e., 2-pyrrolidone (L4), ϵ -caprolactam (L6), or ω -lauro lactam (L12) was dispersed in the solvent (a mixture of aliphatic hydrocarbons with boiling point ranging from 120 to 140°C) and the mixtures were equilibrated at 50, 77, and 105°C, in accordance with the type of lactam used as monomer. Subsequently, the catalytic amount of sodium hydride (60% oil moisturized) was added to generate the corresponding lactamate anion. When the reaction was completed—as indicated by the cessation of hydrogen evolution—the temperature was rapidly brought the working temperature, i.e., 40, 90, and 100°C, for L4, L6, and L12 polymerization, respectively. The “zero” moment of poly-

merization was considered the moment of starting adding the chain initiator (stearoyl isocyanate). The whole amount of chain initiator, C.I., was added, using a syringe pump, over a certain period, typically 12, 6, and 12 h, respectively, for the three above-mentioned polymerizations, and with constant feeding rate, 60 $\mu\text{L}/\text{h}$. At the end of dosing period the mixture was maintained under stirring 2 h more. The obtained polymer particles were transferred into a large amount of methanol, separated through filtration, and then washed several times with methanol. Finally, the powders were subjected to extraction with methanol for 8 h, then vacuum-dried, weighed, and the high polymer yield calculated.

DSC measurements were carried out on DSC 821^e (Metler Toledo). The weight of extracted sample was about 5–8 mg. Measurements were performed from ambient to 350°C under nitrogen purge and a heating rate of 5°C/min. A Tian-Calvet type differential scanning transitiometer (BGR-Tech, Poland) was used to perform

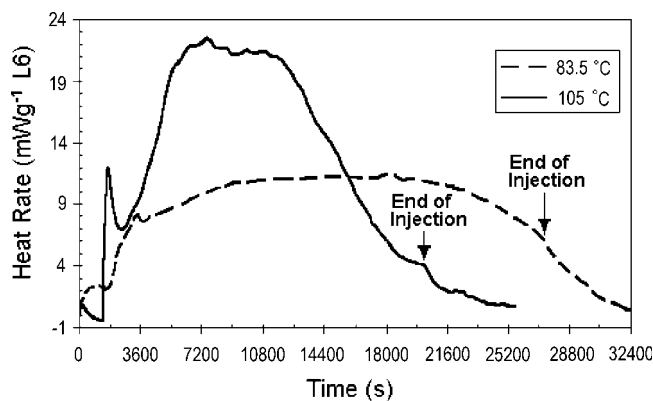


Figure 1 Concomitant effect of the feeding rate of C.I. and the temperature on the heat evolution recorded during the anionic polymerization of L6 (the same amount of C.I. was delivered for both polymerizations).²³ The feeding rates of C.I. were 40 and 30 $\mu\text{L}/\text{h}$ for the polymerizations carried out at 83.5 and 105°C, respectively.

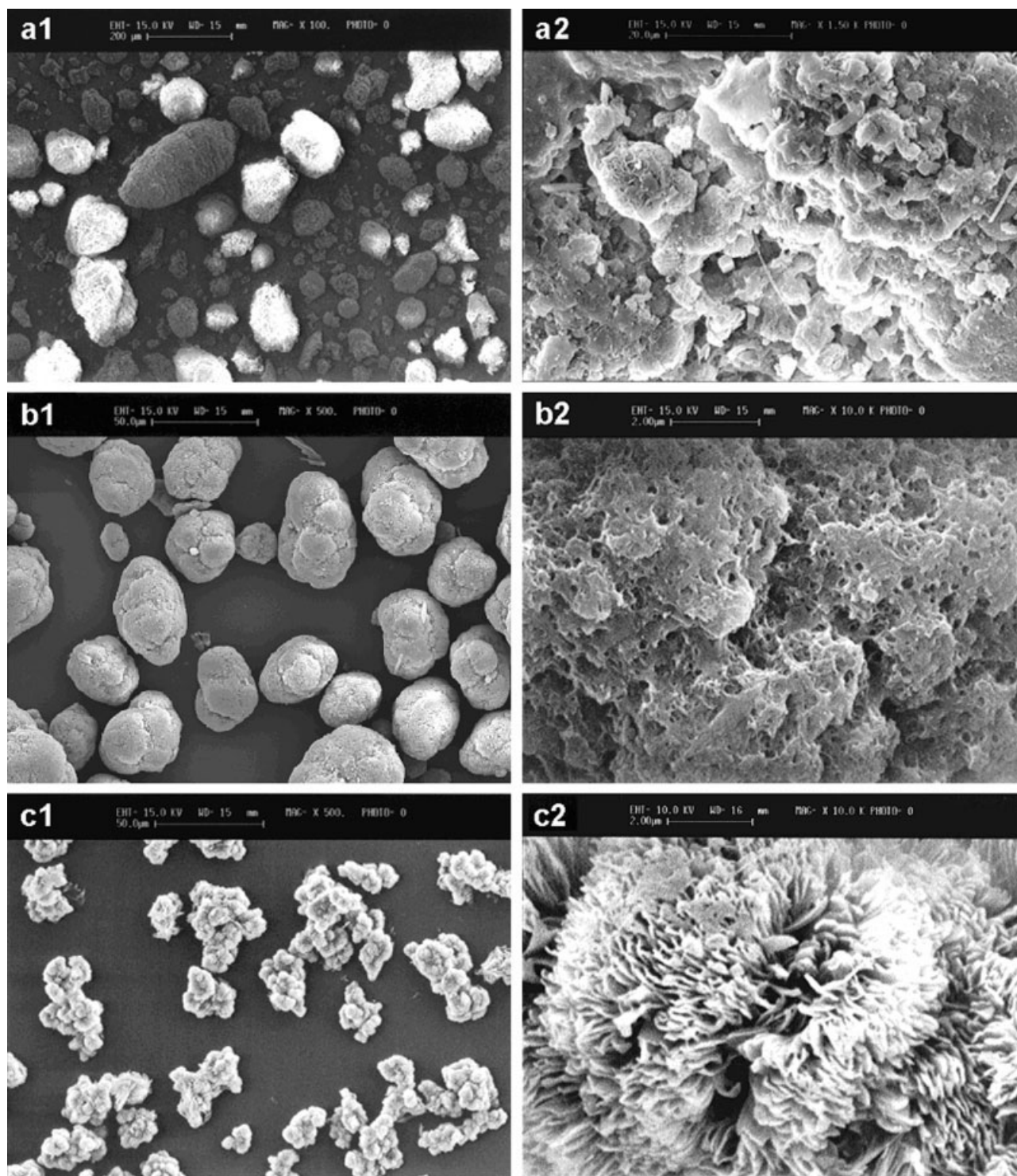


Figure 2 SEMs of the lactam-based polyamides at low (a_i) and high (b_i) magnifications (*i* = 1, 2, and 3 stands for PA4, PA6, and PA12 particles, respectively).

the reaction calorimetry (RC) measurements. A detailed scheme of the reaction calorimeter and description of its functional principle are given in Ref. 23.

Scanning electron micrograph (SEM) photos were obtained with a JEOL JSM-840 instrument; before examination, the powders were coated under vacuum with a thin layer of platinum up to a depth of about 150 Å.

Particle size distribution was determined with a Laser-Particle-Sizer "analysette 22 in. (Frisch, Germany), with a measuring range 0.1–527.62 μm. The powders were suspended in water containing 0.2% surfactant and ultrasonicated 5 min before examination.

Brunauer-Emmet-Teller (BET) surface area measurements were performed in nitrogen at 77 K using a

SORPTOMATIC-Carlo Erba instrument (Carlo Erba, Italy).

Mercury porosimetry was determined using an AG-65 model porosimeter (Fischer and Porter, Warminster, PA) able to achieve a maximum pressure of 1000 kg f/cm².

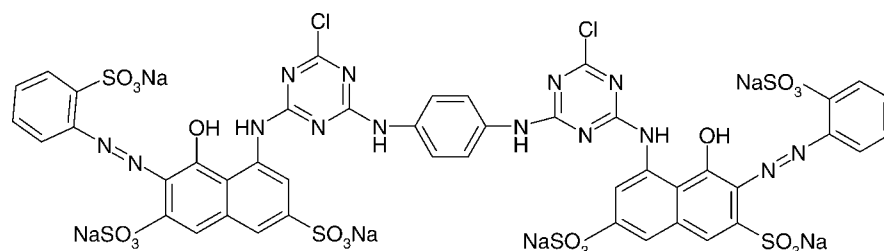
The measurement of porosity, $P\%$, was made by determining the apparent density of powders, d_a , using the mercury pycnometric method, and the specific density of polyamides, d , measured by column-gradient method with a mixture of *n*-heptane and carbon tetrachloride. The equation used for calculation of porosity is given in the footnote of Table I.

A Ubbelohde viscometer was used to determine PA6 solution viscosities and evaluate weight average molar masses. The measurements were performed on poly-

mer solutions in formic acid at 20°C for PA4 and PA6 and H₂SO₄ at 25°C for PA6 and PA12, respectively.

Preparation of dye solution

The selected reactive dye, Brilliant Red HE-3B, was dissolved in bidistilled water at a concentration of 5 g/L. The dye is rather a bulky compound, with MW = 1463, adsorption maximum $\lambda_{\max} = 530$ nm, and the molar extinction coefficient $\epsilon = 38769.5$ L/(mol cm). The pH, chemical oxygen demand (COD) and carbon content are as follows: 6.4, 651 mg/L, and 23.4% dry weight. To simulate the dyehouse effluent, 50 mL solutions of reactive dye (in the concentration range from 0.15 to 3.0 mg/mL) were prepared by appropriate dilution of the stock solution (5 g/L).



Dye sorption procedure

The experimental studies of dye retention onto the PA-powders were carried out in batch conditions. After addition of desired sorbents, typically 50 mg of PA-powders, these ones were allowed contact with 50 mL of working dye solutions of known concentration, ranging from 0.15 to 2.8 mg/mL. The sorption ability of PA-powders was investigated at three temperatures, i.e., 5, 22, and 45°C, respectively; the temperature was controlled with a thermostatic bath and maintained within $\pm 0.1^\circ\text{C}$. After a pre-established period, usually 24 h, the concentration of the dye in filtrates was determined spectrophotometrically with an UV-VIS Digital Spectrophotometer, model S-104D/WPA.

The sorption capacity of PA-powders was evaluated by amount of sorbed dye, $q = \frac{C_0 - C}{G} V \times 10^{-3}$ (mg of dye/g of sorbent), and by percent of dye removal, $R\% = \frac{C_0 - C}{C_0} \times 100$ where: C_0 and C are initial and the equilibrium concentration of dye in solution (mg/L), G is amount of sorbent (g), and V is volume of solution (mL).

Kinetic investigation

Effect of contact time was determined by the "limited bath" technique. Thus, about 1 g of PA-powder was added under stirring to 500 mL of reactive dye solution; the initial dye concentration was 100 or 200 mg/L. The temperature of solution was held constant at

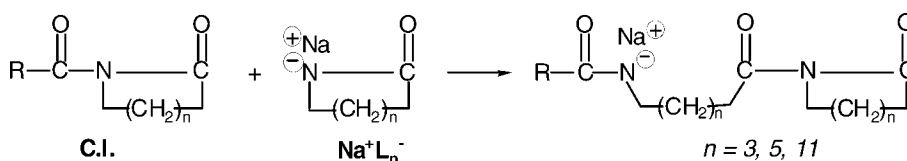
room temperature with a thermostatic bath. After different time intervals (from 30 to 120 min), volumes of 1 mL supernatant were taken for spectrophotometric measurements of dye content. The extent of sorption was expressed as the fractional attainment of equilibrium $F = q_t/q$, where q_t is the amount of sorbed dye per gram of PA-powder at time t , and q is the total amount of sorbed dye at equilibrium (usually after 24 h), respectively.

RESULTS AND DISCUSSION

Polyamide powders synthesis and characterization

Anionic polymerization of lactams in organic solvents is a complex process that takes place mainly heterogeneously and allows obtaining powdered polyamide (PA-powders).²⁴ The most important steps in polyamide formation are the following: initiation and growth of macromolecules in a homogeneous medium, nucleation, phase separation and aggregation of the growing chains, solidification, and finally, polymer crystallization.

All the above-mentioned events occur rapidly and partially overlap. The polymerization occurs by the activated monomer mechanism, which is well documented in literature.²⁵ Usually preformed *N*-acyllactams or their precursors (so-called chain initiators, C.I.) are introduced in the system to avoid the slow initiation step because of the absence of *N*-acyllactam groups at the beginning of polymerization:



There are many factors influencing powders size, size distribution, and the ultimate morphology of PA-powders, but the most important are the manner of contacting the catalytic components, the nature and the ratio of the catalytic system, the temperature, and the presence of some additives.²⁶ The best control of particles size and size distribution is achieved continuously delivering the C.I. over a pre-established period. In this way, the rapid polymerization is tempered and the high polymer yield increases gradually; a steady state is achieved whose amplitude and half-width, in terms of heat released, are proportional to the addition rate of C.I. and temperature, Figure 1. The steady state allows the obtainment of particles with well controlled particle size and narrow size distribution.

The morphologies of the three PA-powders are depicted in Figure 2. Clearly, PA6- and PA12-powders present a narrow distribution of particles size and a highly porous structure. In the case of PA6 and PA12-powders, each particle is, in fact, an agglomerate of few small particles. The polymerization of L6 and L12 occurs like a precipitation or rather like a dispersion process.²⁶ Apart from these two powders, the irregularly shaped granules, whose size ranges from several micrometers up to about 200 μm , are obtained by anionic polymerization of 2-pyrrolidone, Figures 2(a₁,b₁) and 3(a). The broad particles size distribution of the PA4-granules are related to the fact that polymerization of L4 occur like a suspension polymerization. In this case, the monomer (L4) is not soluble in the solvent and the polymerization proceeds in the droplets of L4 that are mechanically dispersed in the reaction medium. Consequently, the granules appear by collision of the small droplets containing L4 and precipitated PA4, giving rise to fused agglomerates which rapidly solidifies, because of the important undercooling (about 200°C below the melting point of the polymer). It is worth mentioning that the particle size distribution is not changed during the sorption of reactive dye, Figure 3(b); most likely the small secondary peak, located at about 400 μm and depicted in this figure, belongs to the physical agglomeration that occurred during the drying of PA-powder containing the reactive dye.

The photos taken at high magnification reveal a different morphological development of PA-particles. Thus, the external surface of PA4-grains arises from the fusion and coalescence of the initially precipitated small individual particles, with the diameter ranging from 1 to 5 μm . The external surface of PA6-powders is highly porous (the average diameter of the pores ranges from several tents of nanometers up to several

micrometers); must likely the pores were formed during phase separation of the solvent rich phase from the initially formed polymer rich phase. Finally, PA12-powder spherulitic morphology suggests a nucleation a growth mechanism, with radial leaf-like lamella. The most important physical characteristics of PA-particles are collected in Table I. As this Table illustrates, the PA-powders are highly porous entities, i.e., more than 50% of pores, with a relatively high specific surface area. Both the porosity and the specific surface area are lowest for PA4 and highest for PA12.

PA4 grains are characterized by highest molar mass (expressed as $[\eta]$) followed by PA12 and PA6-powders, Table II. Most likely, the higher intrinsic viscosity of PA4 is related to the entirely heterogeneous character of the process; only a fraction of the C.I. molecules supplied in the reaction medium succeed to diffuse inside of suspended droplets of 2-pyrrolidone and, subsequently, to initiate the chains growth. The

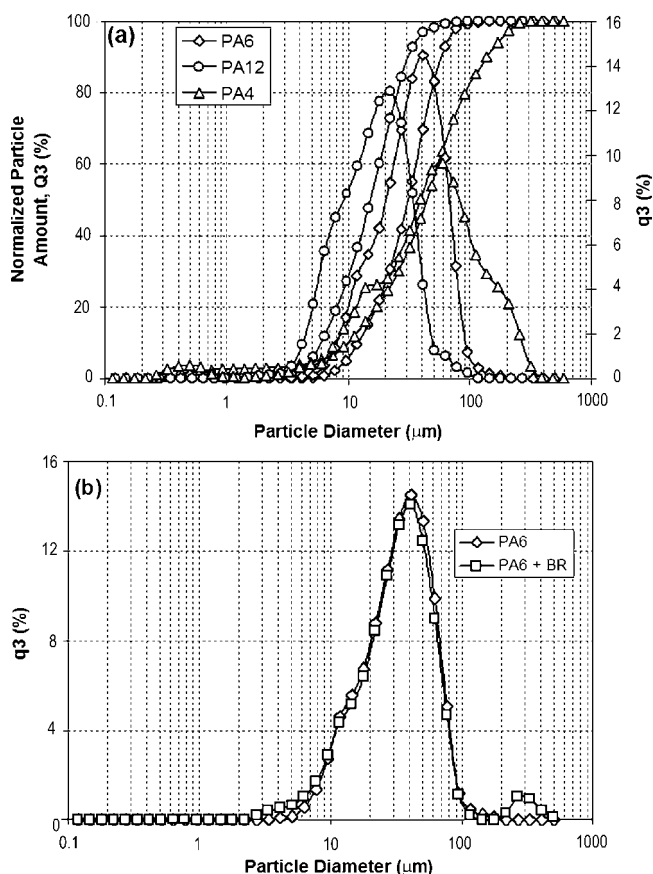


Figure 3 Particles size distribution for the PA-powders (a) and for PA6-powder, before and after sorption of reactive dye Brilliant Red HE-3B (b).

TABLE II
Thermal and Molecular Weight Characteristics of the PA-Powders Obtained by Anionic Polymerization in Organic Media

PA-powder type	T_m (peak) (°C)		ΔH_{fus} (J g ⁻¹)	α_{DSC}^a (%)	[η] (dL/g)		
	Main peak	Secondary peak			Formic acid ^b	H ₂ SO ₄ ^c	$M_w \times 10^{-4d}$
PA4	245.5	232.9	629.1	–	1.68	–	–
PA6	218.3	203.2	73.1	38.48	0.77	0.69	16 961
PA12	177.1	–	83.1	37.82	–	1.01	–

^a The degree of crystallinity determined from the enthalpy of fusion, $\Delta_{fus} H$; the values 190 J/g for PA6 and 220 J/g for PA12 100% crystalline polymers were taken from Ref. 29.

^b 0.5 g/dL, 85% formic acid, and 20°C (intensity method).

^c 0.5 g/dL, 96% H₂SO₄, and 25°C (intensity method).

^d M_w was calculated from [η] measured in sulphuric acid with the equation: $M_w = 2.81 \times 10^4 [\eta]^{1.35}$.³⁰

higher polymerization temperature and the lesser extent of the side reactions account for the observed difference between the intrinsic viscosities of PA12-powders and PA6-powders.

As is shown in Figure 4 and Table II, the PA-particles are all semicrystalline polymers whose degree of crystallinity is higher than that of the corresponding PA obtained by hydrolytic way (about 20%).

Preliminary screening of the sorption of Brilliant Red dye onto PA-powders

The optimum conditions for the maximum recovery of reactive dye Brilliant Red with different types of PA-powders were established with respect to the following experimental factors: type of polyamide, solution's pH, initial dye concentration, and temperature, respectively.

To establish the most suited type of polyamide to be used as sorbent for the selected dye, the sorption isotherms were plotted. These ones represent the func-

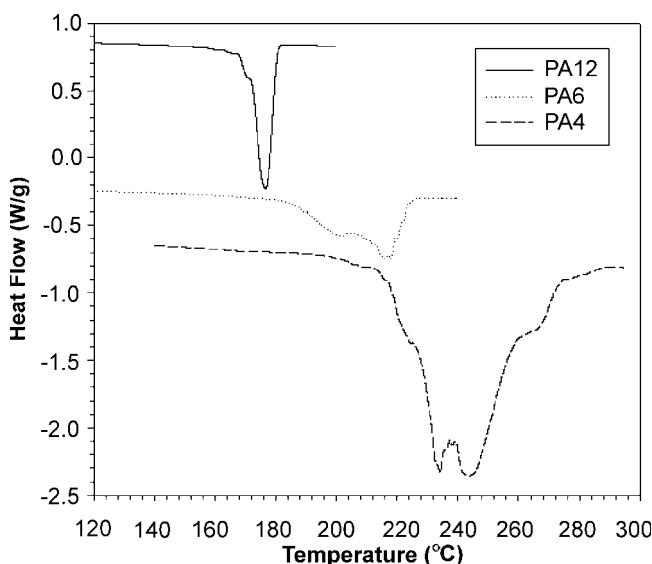


Figure 4 Thermal properties (DSC) of PA-powders prepared by anionic polymerization of the corresponding lactams in organic media.

tional dependence between the equilibrium concentration of dye in the solid sorbent and in the solution phase, $q = f(c)$, respectively. The sorption isotherms of the reactive dye, Brilliant Red HE-3B, on the three types of polyamide at 22°C (295 K) are plotted in Figure 5. It is evident that the sorption of the anionic azodye within these three of PA-powders corresponds to three types of adsorption isotherms, in the Giles's classification system for adsorption of a solute from its solution.³¹ Thus, the type L3 (Langmuir-type) for PA4-granules, the type L4 (Langmuir-type) for PA6-powders, and the type S2 for polyamide PA12-powders provide the best correlation for the sorption processes. For all investigated adsorbents the uptake of dye is relatively moderate. However, the PA6-powder has the highest adsorption capacity, followed by PA12-powder, and PA4-granules. At low initial dye concentrations, the PA4-granules adsorption capacity is higher than those corresponding to PA12-powder but always lower as compared with PA6-powders. A direct comparison between the three adsorbents is difficult to be made since they differ each to another in terms of microstructure and polarity, i.e., the number

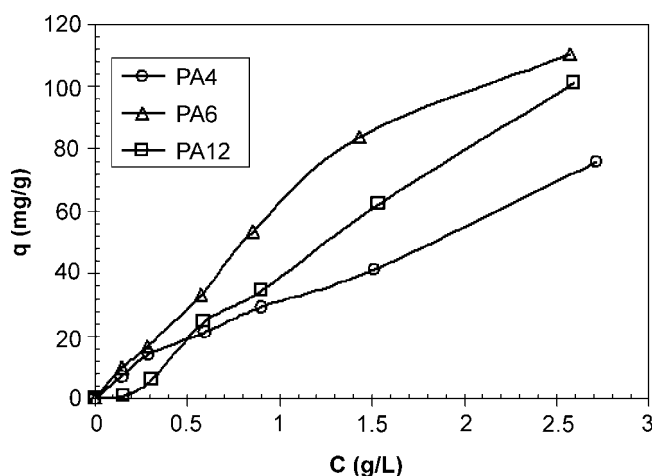


Figure 5 Sorption isotherms of reactive dye Brilliant Red HE-3B at 295 K temperature onto PA-powders.

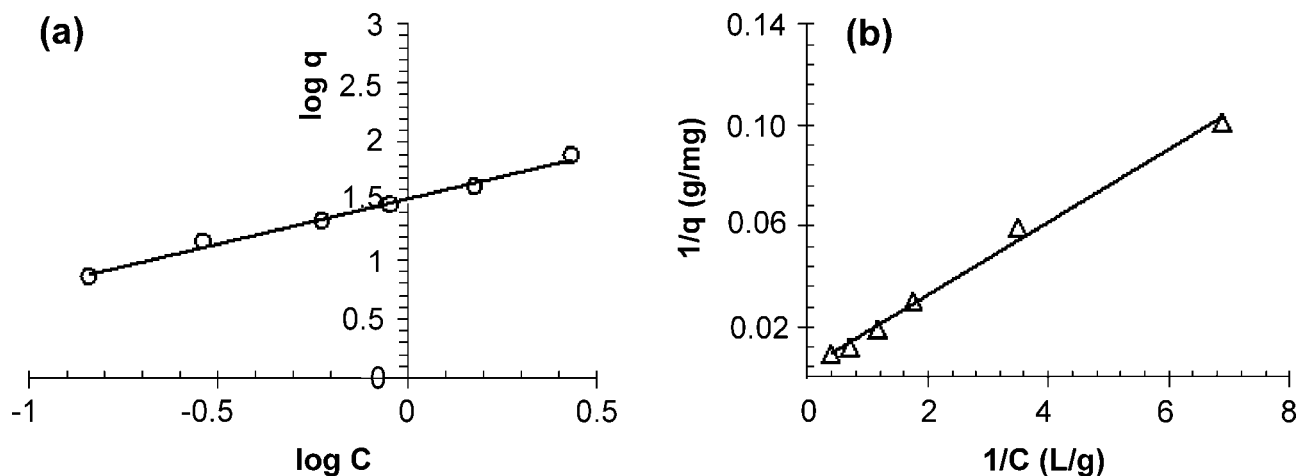


Figure 6 Freundlich and Langmuir plots for the sorption of the reactive dye Brilliant Red HE-3B on PA-powders at 295 K. (a) Freundlich isotherm on PA4-powder and (b) Langmuir isotherm on PA6-powder.

of methylene groups between two amide groups, as well as in terms of supramolecular-morphological structure. The ratio methylene/amide groups governs the hydrophilic character of the polyamide materials, which decreases from PA4 to PA12, and the number of available hydrogen bonds involved in the formation of crystalline phase. From the morphological viewpoint, the investigated adsorbents differ by particle size and size distribution, specific surface area, porosity, and pore size distribution (Table I). The amide groups from these materials are not easily protonated because the electron withdrawal by the carbonyl group makes the nitrogen from the amide group a poor source of electrons. Consequently, few electrons are available for sharing with hydrogen ions and there is less electrostatic attraction between polyamides and the dye anion. Most likely, the physical adsorption prevails for the investigated systems. In addition, the size of dye molecule is such that the adsorption is hindered and capacity reduced because of pore blockage.

The experimental equilibrium sorption data, for polyamide PA4 and PA6, which shown Langmuir behavior, were analyzed using three adsorption isotherm models, as follows: the linear,³² the Freundlich,³³ and the Langmuir³⁴ models, expressed by the eqs. (1)–(3):

$$\text{Linear isotherm: } q = KC \quad (1)$$

$$\text{Freundlich isotherm: } q = K_F C^{1/n} \quad (2)$$

$$\text{Langmuir isotherm: } q = \frac{K_L C q_0}{1 + K_L C} \quad (3)$$

where K_F parameter is related to the adsorption capacity and n is a measure of sorption energy; a favorable sorption correspond to a value of $1 < n < 10$. For $n = 1$, $K_F = K$ from eq. (1), i.e., linear isotherm. The Langmuir constant, K_L is related to intensity of the sorption process and q_0 is the maximum value of sorption capacity (corresponding to the complete monolayer coverage).

Equations (2) and (3) can be arranged in the linear form leading to eqs. (4) and (5):

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

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

Hence, a plot of $\log q$ versus $\log C$ is linear with the intercept equal to K_F and slope equal to $1/n$, while the a plot of $1/q$ versus $1/C$ gives a straight line with the intercept equal to $1/q_0$ and the slope equal to $1/K_L \times q_0$, respectively. The plots of $1/q$ versus $1/C$ and $\log q$ versus $\log C$ for reactive dye Brilliant Red HE-3B sorp-

TABLE III
The Characteristic Parameters of Sorption Process of Reactive Dye Brilliant-Red HE-3B onto Polyamides at 295 K

Type of polyamide	Linear isotherm		Freundlich isotherm			Langmuir isotherm			Millimolar dye/molar PA
	K (L/g)	R ²	K _F (mg/g) (L/mg) ^{1/n}	n	R ²	q ₀ (mg/g)	K _L (L/g)	R ²	
PA 4	26.452	0.991	32.704	1.305	0.992	90.91	0.591	0.993	7.022
PA 6	44.179	0.956	54.425	1.139	0.989	277.78	0.248	0.994	16.519
PA 12	40.610	0.994	32.534	0.609	0.937	–	–	–	–

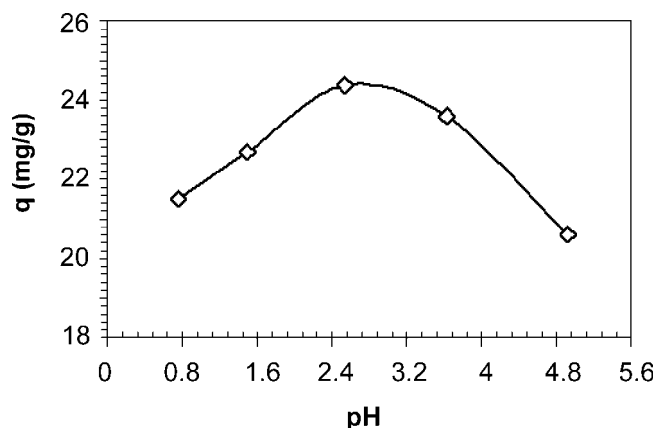


Figure 7 Influence of the solution pH on the reactive dye Brilliant Red HE-3B sorption onto PA6-powder: $C_0 = 0.1$ mg dye/mL, $T = 293$ K.

tion on three types of PA-powders at 295 K are shown in Figure 6.

The K , q_0 , K_L , K_F , and n values derived from these linear Langmuir and Freundlich plots as well as from the linear model, eq. (1), at 295 K, together with their correlation coefficients (R^2), are given in Table III. It is evident from this Table that the Freundlich data indicate an unfavorable sorption ($n < 1$) both for PA12 and PA4-powders. In addition, PA6-powder presents the best values of the quantitative sorption parameters. In which follows, we focused the attention on this polymeric material and investigated in more detail its sorption properties.

Sorption of reactive Brilliant Red HE-3B dye on PA6-powder

Effect of pH

The variation of the reactive dye recovery (R , %) with PA6-powder as a function of pH, which has been adjusted by the addition of HCl solutions with different concentrations, is presented in Figure 7. As can be seen in this figure, the sorption of reactive dye Brilliant Red onto PA6-powder is practically independent by pH in the range from 1 to 6. However, in the investigated range of pH the sorption capacity initially

TABLE IV
Influence of Solution Initial Concentration in Dye

Initial concentration in dye (mg/mL)	q (mg/g polyamide)	R (%)
0.15	18.143	16.670
0.3	41.561	13.870
0.6	63.300	11.217
1.2	118.780	9.900
1.8	128.060	7.110

$T = 318$ K.

slightly increases, passing through a maximum at pH around 2.6, to decrease at the initially level on the further increase of pH. In consequence, the following experiments were made without the adjustment of pH, i.e., the pH of the aqueous dye solutions was about 6.4.

Effect of initial dye concentration

The sorption capacity of PA6-powder for reactive dye Brilliant Red HE-3B was determined at different initial dye concentrations at the above-mentioned pH. The results collected in Table IV show that the dye amount adsorbed increases with increasing initial dye concentration in solution while the percent of dye removal, R %, decreases.

Effect of temperature

The influence of temperature on reactive dye Brilliant Red HE-3B retention by PA6-powder from its aqueous solutions is illustrated by the sorption isotherms plotted in Figure 8. The shapes of curves in Figure 8 indicate a moderate affinity of the sorbent toward the reactive dye. However, with increasing temperature the dye sorption increases, thus suggesting an endothermic sorption process. It should be assumed that the high temperature favors the diffusion of dye molecules into the internal pores of polyamide or into its amorphous zones.

Sorption isotherms

The equilibrium sorption data at three temperatures, Figure 8, were again analyzed using the linear, the Freundlich and the Langmuir isotherm models, eqs. (1)–(3). The constants of the sorption isotherms, calculated from the intercepts and slopes of the correspond-

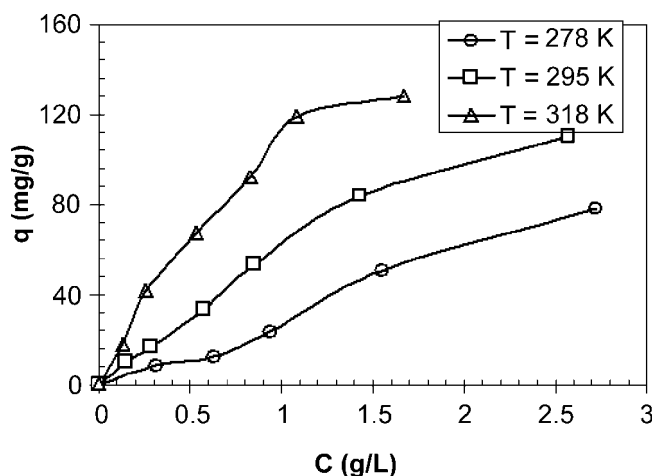


Figure 8 The sorption isotherms of the reactive dye Brilliant Red HE-3B on PA6-powder at three temperatures.

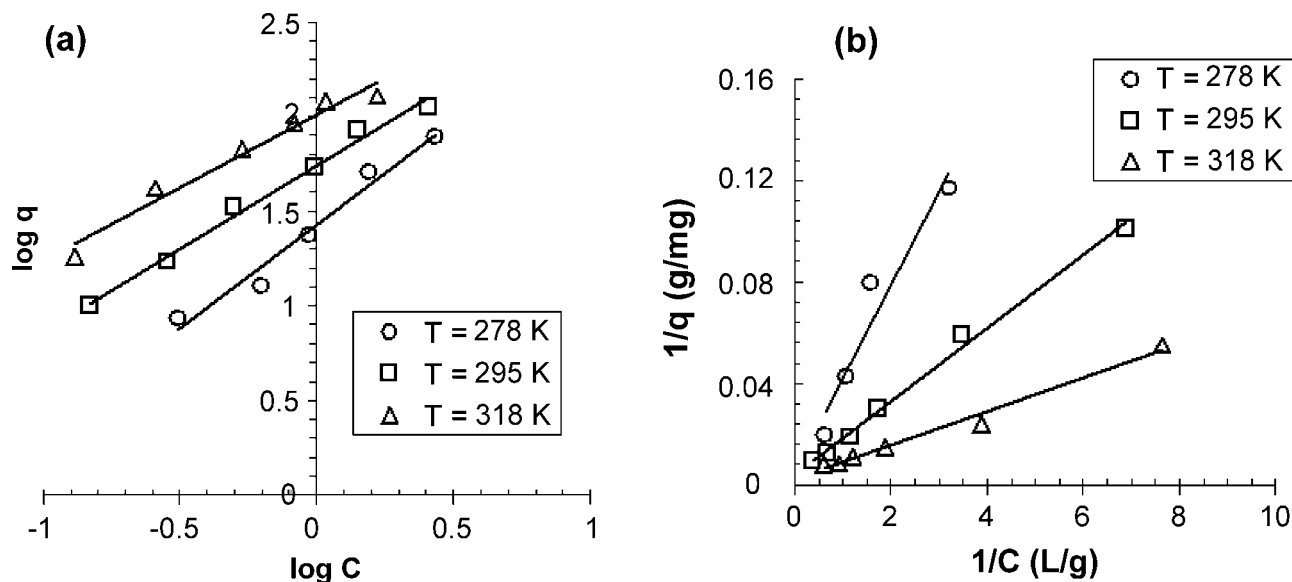


Figure 9 Freundlich and Langmuir plots for the sorption of the reactive dye Brilliant Red HE-3B on PA6-powder at three temperatures. (a) Freundlich isotherm and (b) Langmuir isotherm.

ing linear plots [Fig. 9(a,b)] for reactive dye Brilliant Red HE-3B sorption at the selected temperatures, together with their correlation coefficients (R^2), are given in Table V.

The values of maximum sorption capacity (q_0) of reactive dye on PA6-powder are relatively small and increase with increasing the temperature. This behavior might be ascribed to the fact that the large size of dye molecules impedes sorption process; if temperature increases, the sorption capacity also increases because of enhancement of dye diffusion into the complex internal porous structure of powder. The small values of Langmuir constant, K_L , may suggest a weaker binding between reactive dye and the PA surface. The increase of q_0 and K_L values with temperature, confirms the endothermic nature of sorption process.

Thermodynamics and kinetics aspects concerning dye/PA6-powder interaction

On the basis of the values of sorption constant, K_L , at different temperatures, the apparent thermodynamic parameters, ΔG^0 , ΔH^0 , and ΔS^0 , for the dye sorption process were calculated by means of the usual rela-

tions, eqs. (7)–(9), and are given in Table VI.

$$\ln K_L = -\frac{\Delta H}{RT} + \text{const.} \quad (7)$$

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

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (9)$$

where R is the gas law constant, 8.314 J/mol K, and T is the absolute temperature.

The small positive value of enthalpy change computed from the slope of linear dependence of $\ln K_L$ versus $1/T$, eq. (7), evidences the endothermic nature of physical adsorption. The negative values of ΔG confirm that the reactive dye sorption onto PA-powder occurred spontaneously. The entropy change values are almost constant over the investigated temperature range and its positive values characterize an increased disorder of the system, most likely because of the loss of the water that surrounds the dye molecules during the sorption process. It should be assumed that the driving force of the sorption process has an entropic character. This observation was confirmed by other

TABLE V
The Characteristic Parameters of Sorption Process of Reactive Dye Brilliant-Red HE-3B on Polyamides PA 6

T (K)	Linear isotherm		Freundlich isotherm			Langmuir isotherm			
	K (L/g)	R^2	K_F (mg/g) $\times (L/mg)^{1/n}$	n	R^2	q_0 (mg/g)	K_L (L/g)	K_L (L/mol)	R^2
278	29.954	0.985	26.583	0.913	0.968	196.08	0.139	203.357	0.930
295	44.179	0.956	54.425	1.139	0.989	277.78	0.248	363.277	0.994
318	79.204	0.914	102.471	1.295	0.967	454.45	0.328	480.303	0.986

TABLE VI
The Thermodynamic Parameters of Sorption Process of
Reactive Dye Brilliant-Red HE-3B onto Polyamide PA 6

T (K)	K_L (L/mol)	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (J/mol K)
278	203.357		-12.284	110.19
295	363.277	18.349	-14.458	111.21
318	480.303		-16.427	108.67

experimental results concerning organic compounds sorption mechanism on different adsorbents.³⁵

Effect of contact time on removal of Brilliant Red HE-3B reactive dye from two solutions of different initial concentrations on PA6-powder is depicted in Figure 10. As it seen in Figure 10 (a,b) the equilibrium period required for maximum removal was found to range from 45 to 60 min; however, the sorption half-time ($t_{1/2}$) was in all cases below 25 min.

The kinetic of reactive dye sorption onto PA6-powder was investigated using two different models: the

pseudofirst order^{32,34} and pseudosecond order kinetics,¹⁹ respectively. The pseudofirst order (Lagergren model), traditionally used for describing sorption kinetics, is generally expressed by the following equation:

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

where k_1 (min^{-1}) is the Lagergren rate constant of the first order sorption, evaluated from the slope of the plot $\log(q_0 - q_t)$ versus t , [Fig. 11(a)]. According to the pseudosecond order model the dye sorption kinetic is described by the eq. (11):

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

where k_2 is the rate constant of second order sorption (g/mg min) and $k_2 q_0^2 = h$ is the initial sorption rate (mg/g min). By plotting t/q_t versus t , Figure 11(b), a straight line is obtained and the values of q_0 , k_2 , and h

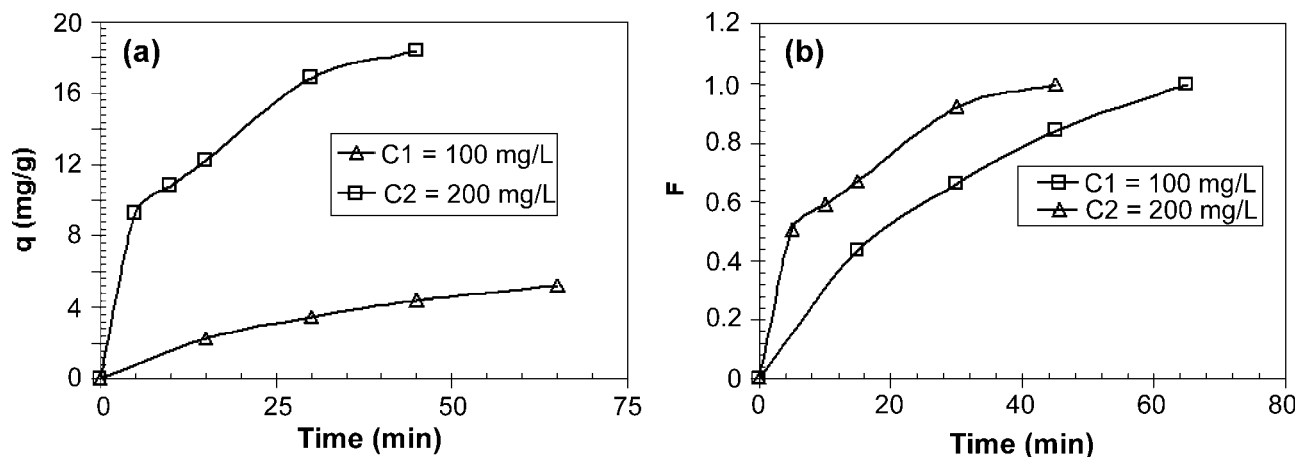


Figure 10 Effect of contact time on removal of Brilliant Red HE-3B reactive dye on PA6-powder: (a) $q = f(t)$; and (b) $F = f(t)$.

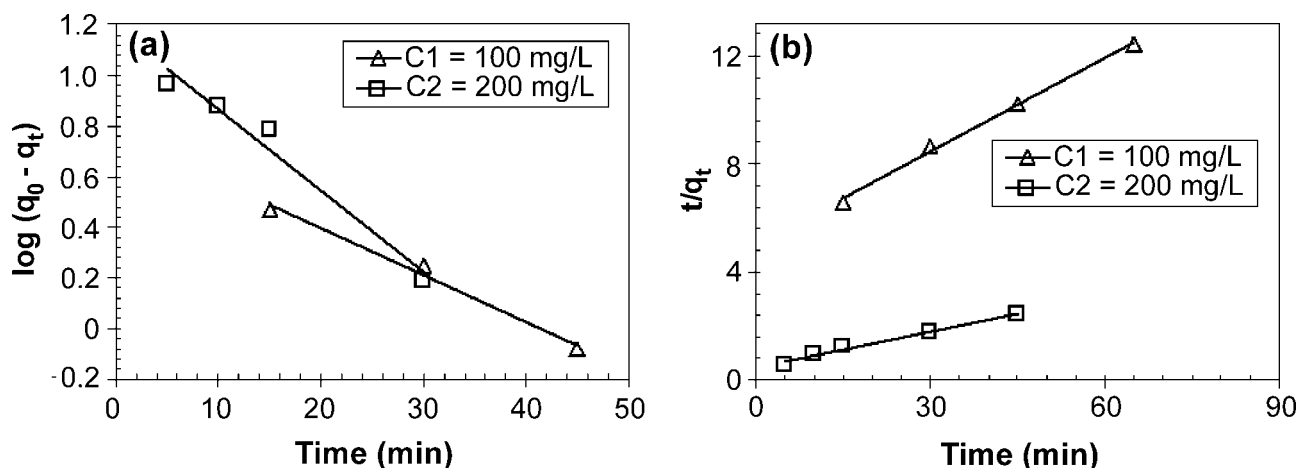


Figure 11 The applicability of the first- (a) and second-order (b) kinetic models to reactive dye Brilliant Red HE-3B sorption onto PA6-powder.

TABLE VII
The Kinetic Parameters of Sorption Process of Reactive Dye Brilliant-Red HE-3B onto Polyamide PA6

C_0 (mg/L)	$t_{1/2}$ (min)	Pseudo-first kinetic model		Pseudo-second kinetic model		
		k_1 (min^{-1})	R^2	k_2 (g/mg min)	h (mg/g min)	R^2
100	4	0.0184	0.9879	$2.66 \cdot 10^{-3}$	0.20011	0.9963
200	22	0.0322	0.9681	$4.82 \cdot 10^{-3}$	2.328	0.9868

are easily determined. The experimental kinetic data were adjusted according to the indicated models and the coefficients of correlation as well as the kinetic parameters of dye sorption are given in Table VII.

The results of Table VII indicate that the second order equation model provides the best correlation with experimental results, and the intraparticle diffusion is the rate controlling step of the sorption process.

CONCLUSIONS

To find new materials with sorptive properties for Brilliant Red HE-3B reactive dye recovery process, the sorption potential of some lactam-based polyamide powders (PA-powders) namely PA4, PA6, and PA12 was tested. To establish the most suited type of polyamide to be used as absorbent for the selected dye, the sorption isotherms were plotted. It was found the PA6- powder presents the best values from the quantitative parameters of sorption.

The sorption of Brilliant Red HE-3B reactive dye from aqueous solutions onto PA6-powders is governed by the initial dye concentration, temperature, and contact time. The apparent thermodynamic parameters of sorption suggest an entropy-driven endothermic sorption process, most likely of physical nature. From kinetic point of view, the sorption data fit well the second-order kinetic model and an intraparticle diffusion mechanism. The results of this study evidenced a limited capacity of PA-powders for Brilliant Red HE-3B reactive dye uptake and the requirement of using more dilute solutions and increased temperatures to increase the dye sorption capacity.

The system under study offers some new attractive possibilities of selective sorption of reactive dyes from aqueous effluents.

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