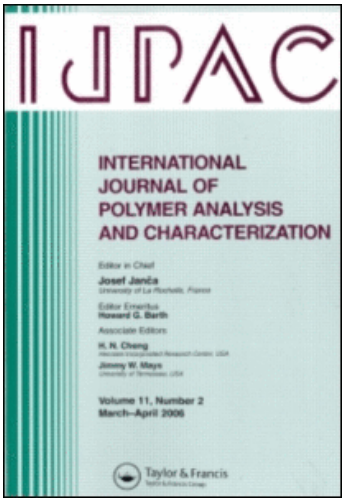

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Characterization of Acrylic Polymers by Dye Adsorption

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Adsorption uptake of methylene blue and alizarin yellow by polyacrylonitrile (PAN), poly(acrylic acid) (PAC), polyacrylamide (PA) and poly(methylenebisacrylamide) (PMBA) from aqueous solutions was measured as a function of time. The adsorption of methylene blue was higher for PAN and lower for PAC; however, the adsorption of alizarin yellow was higher for PAC, PA, and PMBA, and lower for PAN. The acrylic polymers can be classified according to their adsorption characteristics using both dyes. The theoretical treatment of the experimental results was performed in terms of kinetics of dye adsorption, which is directly related to diffusion. A similar equation for diffusion-limited adsorption on textile materials and other diffusion-limited systems has been used. The equation was applied for short reaction times and the parameters were determined graphically from log–log plots: the specific rate constant k from the intercept A and the parameter n ($0 < n < 1$) from the slope. The diffusion coefficient D was calculated from Fick's equation. A comparison of the experimental data with theoretical results showed that increased adsorption is promoted by an increase of the intercept A, or decrease of the slope n, and an increase of the diffusion coefficient D.

KEY WORDS Acrylic polymers, adsorption of dyes, kinetics of adsorption.

INTRODUCTION

An important application of acrylic polymers is in the field of ion exchangers, adsorbents, and flocculants [1, 2]. In ion exchange resins, ions that can be exchanged must diffuse through the gel structure to the exchange sites. The intermolecular distances, which limit the size of ion that can migrate through the gel, is often referred to as the apparent porosity. Adsorption resins often contain hydrophilic groups in order to increase their wetting ability and facilitate the entrance of water into their macroporous skeleton. Usually, macroreticular resins have an average pore diameter of 1300 Å. High-molecular-weight ions can be removed from solution and eluted from the resin during regeneration, because of the large discrete pores of resin. Acrylic polymers are also chosen as soluble polymeric flocculants, which are used for the removal of suspended solids from liquids. The usage of polymeric reagents in the form of linear or cross-linked polymer, depends on the application field. Linear polymers have the advantage that diffusion restrictions are small and all functional groups are accessible compared to cross-linked polymers.[3]

The aim of this work was to study the interaction between different groups of acrylic polymers and some dyes. Such a model can facilitate the design of acrylic polymers in the above mentioned applications.

EXPERIMENTAL

Acrylonitrile was washed successively with solutions of H_2SO_4 (5%), Na_2CO_3 (5%), and then with water in order to remove the inhibitor. Then it was dried with anhydrous $CaCl_2$ and distilled under vacuum. The polymerization was performed in solution using a redox system (5% aq. solution of $Na_2S_2O_5$, 5% aq. solution of $K_2S_2O_8$, 0.01 g $FeSO_47H_2O$ in 100 mL H_2O and 2 mL conc. H_2SO_4) at 20°C under N_2. The polymer was precipitated with methanol containing 0.5% hydroquinone, followed by filtration, washing with distilled water, and drying at 50°C. The yield of polyacrylonitrile (PAN) after 4 h of polymerization, was approximately 97%. Poly(acrylic acid) (PAC), polyacrylamide (PA), and poly(methylenebisacrylamide) (PMBA) were prepared by similar methods. The molecular weights of the polymers were determined by viscometry: 45,000 for PAN, 200,000 for PAC, and 60,000 for PA. PMBA was insoluble because of its cross-linked structure.

The adsorption abilities of the homopolymers were examined from aqueous solutions of two dyes, methylene blue (MB) and alizarin yellow (AY), at initial concentrations 0.0320 g/L. The adsorbent concentration, that is, the amount of adsorbent per liter of solution A_0 was 20 g/L. The adsorbed amount of the dye was determined after various time intervals.

THEORETICAL

The theoretical treatment of the experimental results was performed in terms of kinetics of dye adsorption, which is directly related to diffusion. A similar equation for diffusion-limited adsorption on textile materials and other diffusion-limited systems has been used [4, 5]:

$$a = A_e(1 - \exp(-kA_0t))^n \tag{1}$$

where

a = the adsorption in time t
A_e = the equilibrium adsorption (at $t \to \infty$)
A_0 = the concentration of an adsorbent
k = the specific rate constant
n = the heterogeneous structural diffusion resistance constant ($0 < n < 1$)

Rearrangement of Equation (1) yields:

$$-kA_0t = \ln\left(1 - (a/A_e)^{1/n}\right) \tag{2}$$

For low values of the parameter t, the ratio of a/A_e becomes also low, so that

expanding the right hand side of Equation (2) into a Taylor series and neglecting higher order terms, the following equation is obtained:

$$kA_0t = \text{approx.}\ (a/A_e)^{1/n} \tag{3}$$

Substituting $t = 1$ min and $A = a$ $(t = 1)$,

$$k' = kA_0 = \text{approx.}\ (A/A_e)^{1/n} \tag{4}$$

where

k' = the rate constant
A = the intercept (at $t = 1$ min)
n = the slope (on diagramm $\log a - \log t$)

For short reaction times, Fick's equation applied for a cylinder can be approximated:

$$D = (\pi r^2/16t)(a/A_e)^2 \tag{5}$$

where

D = the diffusion coefficient
r = the radius of the cylinder.

Comparing Equation (5) with (4) (for $t = 1$ min), the following is obtained:

$$D = (kA_0)^{2n}(\pi r^2/16) \tag{6}$$

$$D = (k')^{2n}(\pi r^2/16) \tag{7}$$

This model was applied for short reaction times and the parameters were determined graphically from the log–log plots of adsorbed dye versus time (t): the parameter A (mol) from the intercept at $t = 1$ and the parameter n from the slope. The rate constant k' is determined from Equations (4). The diffusion coefficient$D$ was calculated from Equation (7) assuming a radius of $r = 0.0010$ cm, which is also determined for the adsorption of dyes on cotton[4] and other polymers.[5]

RESULTS AND DISCUSSION

Methylene blue is more adsorbed on PAN than alizarin yellow (Fig. 1). The adsorption of methylene blue is higher for PAN and lower for PAC (Fig. 2); however, the adsorption of alizarin yellow is higher for PAC, PA, and PMBA, and

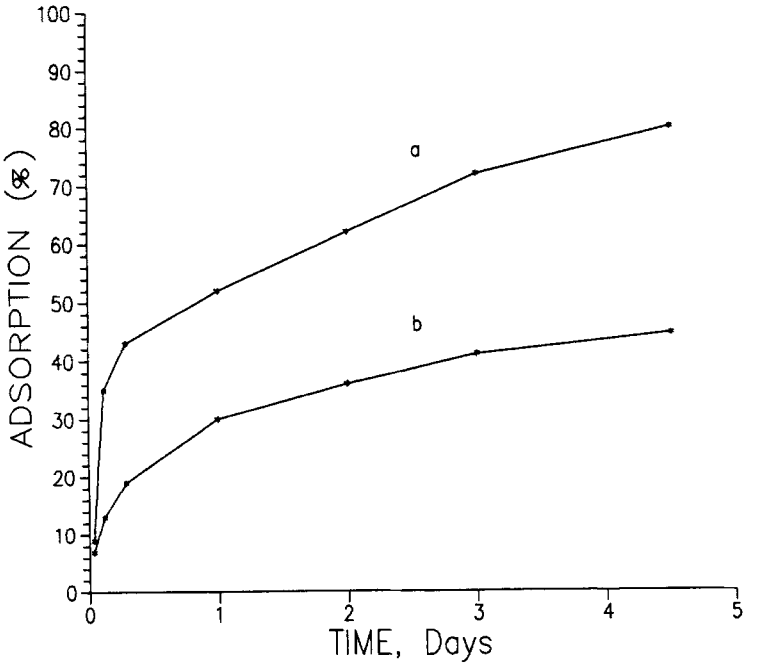

FIGURE 1 Adsorption of dyes on PAN with time. a: methylene blue; b: alizarin yellow.

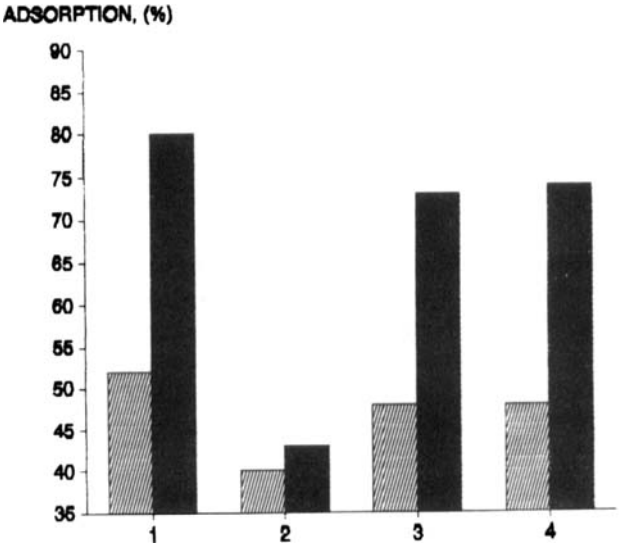

FIGURE 2 Adsorption of methylene blue on acrylic polymers. Slashes: 1 day; horizontal hatches: 4.5 days. 1. PAN; 2. PAC; 3. PA; 4. PMBA.

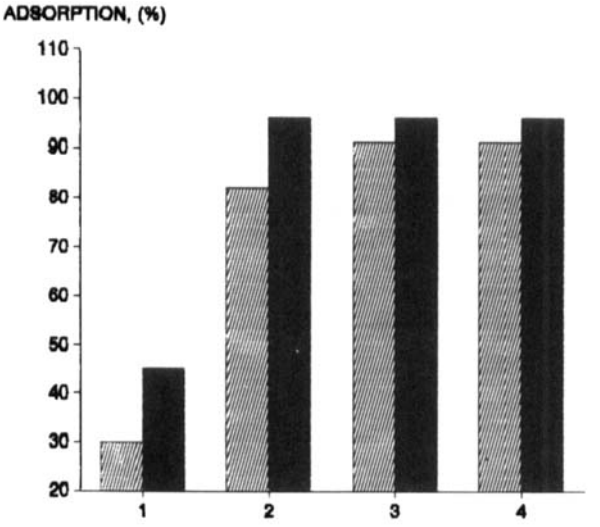

FIGURE 3 Adsorption of methylene blue on acrylic polymers. Slashes: 1 day; horizontal hatches: 4.5 days. 1. PAN; 2. PAC; 3. PA; 4. PMBA.

lower for PAN (Fig. 3). For all cases adsorption increases with time. The polymers can be classified according to the following increasing rate of adsorption:

$$\text{for MB: PAC} < \text{PA or PMBA} < \text{PAN}$$

$$\text{for AY: PAN} < \text{PAC or PA or PMBA}$$

Table I shows the kinetic constants of acrylic polymers for both dyes. There are deviations from the Fickian behavior $n = 1/2$ for most cases. This can be expected because n depends mainly on structural changes of the adsorbent and not on other factors.[4] The adsorption of the dyes on the acrylic polymers is influenced by the electron acceptor–donor interactions of the different groups of the polymers and dyes. Comparing the increased rates of adsorption for both dyes with the results of Table I, we can conclude that increased adsorption is promoted by an increase of

TABLE I

Kinetic constants of adsorption of dyes on acrylic polymers (obtained from data taken at times less than 180 min)

Acrylic Polymer	Dye*	n	A (mol) $\times 10^{-8}$	k' (min^{-1}) $\times 10^{-2}$	D ($cm^2 \cdot s^{-1}$) $\times 10^{-10}$
PAN	MB	0.18	8.3	0.02	22.1
PAC	MB	0.50	1.9	0.78	0.2
PA	MB	0.19	7.2	0.02	16.1
PMBA	MB	0.18	8.2	0.02	22.1
PAN	AY	0.47	1.3	0.18	0.1
PAC	AY	0.34	10.8	0.91	4.9
PA	AY	0.33	5.6	0.11	1.4
PMBA	AY	0.34	10.3	0.79	4.5

*MB: methylene blue; AY: alizarin yellow.

the intercept A, a decrease of the slope n, and an increase of the diffusion coefficient D.

References

1. M. Biswas, *Adv. Polym. Sci.*, **70**, 71 (1985).
2. B. A. Bolto, *Prog. Polym. Sci.*, **9**, 89 (1983).
3. W. Heitz, *Adv. Polym. Sci.*, **23**, 1 (1977).
4. J. Chrastil, *Text. Res. J.*, 413 (July) (1990).
5. Simitzis, *Polymer*, **36** (1995) (in press).