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Sorption of Charged Organic Dyes from Anionic Hydrogels

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***Abstract*—**Hydrogels are three-dimensional, hydrophilic, polymeric networks composed of homopolymers or copolymers and are insoluble in water due to the presence of chemical or physical cross-links. When hydrogels come in contact with aqueous solutions, they can effectively sorb and retain the dissolved substances, depending on the nature of the monomeric units comprising the hydrogel. For this reason, hydrogels have been proposed in several studies as water purification agents. At the present work anionic hydrogels bearing negatively charged $–COO^-$ groups were prepared and investigated. These gels are based on sodium acrylate (ANa), either homopolymerized (poly(sodiumacrylate), PANa) or copolymerized (P(DMAM-co-ANa)) with N,N Dimethylacrylamide (DMAM). The hydrogels were used to extract some model organic dyes from water. It is found that cationic dyes are strongly sorbed and retained by the hydrogels, while sorption of anionic dyes was negligible. In all cases it was found that both maximum sorption capacity and equilibrium binding constant varied from one dye to the other depending on the chemical structure of the dye, the presence of functional chemical groups and the hydrophobic-hydrophilic balance. Finally, the nonionic hydrogel of the homopolymer poly(N,N-dimethylacrylamide), PDMAM, was also used for reasons of comparison.

***Keywords*—**Anionic organic hydrogels, sorption, organic dyes, water purification agents.

I. Introduction

THE development of various adsorbents for the removal of organic or inorganic pollutants from wastewaters is a very interesting and promising research area for novel wastewaters treatment techniques [1]-[4]. So, in this research field different types of materials have been synthesized such as zeolites [5], organically modified silicas [6], nanocomposite materials [7] and organic hydrogels [8].

The residual dyes from textile wastewater are considered as a very crucial source of organic pollutants into the natural water resources or wastewater treatment systems [9]. More than 10% of synthetic textile dyes are lost during the dyeing process and enter into the environment through the derived effluents. This high discharge into the water environments creates a very important environmental problem on the ecological system not only because of the colour but also since most of the dyes and their degradation products are toxic and carcinogenic [10]. In the recent years several works have been appeared in the scientific literature reporting adsorption of several dyes by both natural and synthetic sorbents [11], [12].

In this work, P(DMAM-co-ANa_x) hydrogels containing sodium acrylate units (ANa) and nonionic N,N-dimethylacrylamide units (DMAM) have been prepared. The molar content x of the anionic ANa units varies from 0 (nonionic hydrogel) up to 1 (fully charged hydrogel). UV-Vis absorption spectrophotometry was applied to investigate the sorption of selected model organic dyes by these hydrogels. The main objective of the present work was to study the effectiveness of using these hydrogels as potential sorbents for Methylene Blue, Toluidine Blue, Crystal Violet and Acid Orange-7. The chemical structures of the hydrogels and the dyes used in the present work are presented in Fig. 1.

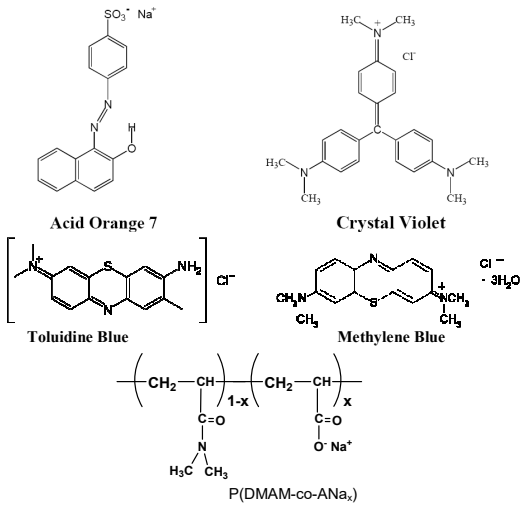

Fig. 1 Chemical structure of the organic dyes and the P(DMAM-co-ANa_x) hydrogels used in the present work. The structural units of the hydrogels are cross-linked with BIS (not shown)

II. Materials and Methodology

A. Materials

Acrylic acid (AA), *N,N*-dimethylacrylamide (DMAM), *N,N,N,N*-tetramethylethylenediamine (TEMED), methylene bisacrylamide (BIS) and ammonium persulfate (APS) were purchased from Aldrich. All reagents were used as received. Methylene Blue (MB), Toluidine Blue (TB), Crystal Violet (CV) and Acid Orange-7 (OR) for dyes stock solutions were

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obtained from Aldrich. Water was purified by means of a TKA smart2Pure apparatus.

B. Synthesis of the Hydrogels

The P(DMAM-co-ANa$_x$) hydrogels were synthesized according to the following procedure: x mol AA and y mol DMAM (x+y=1), 0.005 mol BIS (crosslinker, 5 mol% over the total monomer concentration) were dissolved in 20 mL ultrapure water under stirring at room temperature. After deoxygenation of the solution by N_2 bubbling for 30 min, 0.1 g APS (dissolved in 2 mL ultrapure water) and 3 drops of TEMED were added. The formation of the gel was almost immediate. The reaction was left to proceed for 24 h and, then, the gels were immersed in ultrapure water. Water was decanted and renewed daily for 1 week. Finally, the purified swollen gel was cut into-2mL pieces and water was removed by heating up to 100^{o}C. In the case of P(DMAM-co-ANa$_x$) hydrogels, the pH of the solution was adjusted around 7 by addition of an adequate volume of a NaOH 1M solution after the dissolution of the monomers, while the formed gels were fully neutralized by adding an excess of the NaOH 1M solution before purification. A series of hydrogels with five different (0, 0.25, 0.50, 0.75, 1) molar charged contents were synthesized according to the experimental procedure outlined previously.

C. Sorption of Organic Dyes from Aqueous Solutions

The sorption of charged organic dyes was studied by the following procedure: ~0.05 g of dry hydrogel samples was introduced in 50 mL of aqueous solution of the dyes of varied initial removed concentrations (ranging from 10^{-6}M to 10^{-3}M) and was left to sorb for 24h. Then the gels were removed from the solution and the remaining concentrations (C_e) of the studied dyes in solution were monitored by UV-Vis absorption spectrophotometry by using a Shimadzu UV-1800 spectrophotometer.

III. Results and Discussion

The results for MB sorption by the five different negatively charged P(DMAM-co-ANa$_x$) hydrogels are presented in Fig. 2.

The aqueous MB solution (10^{-3} M) is very strongly blue colored before equilibration. For this initial concentration of the dye it was not possible to monitor the UV-Vis absorption spectrum because of the very high extinction coefficient. So the solution was diluted 4 times for the spectrum monitoring, as it appears in Fig. 2 with the characteristic absorption band of the dye centered at ~660 nm. After treatment with P(DMAM-co-ANa$_x$) hydrogels, absorbance of all the solutions decreases remarkably in agreement with the discoloration of the solutions, which can be visually detected. In contrast, the hydrogel was now strongly colored, indicating that almost the whole amount of the dye was sorbed under the specific experimental conditions.

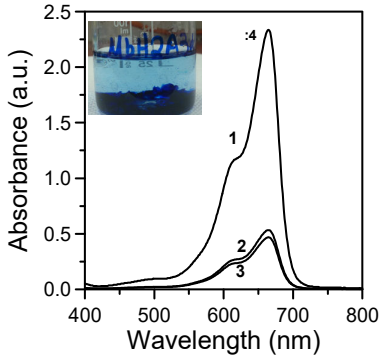

Fig. 2 Absorption spectra of aqueous 10^{-3} M MB before (1) and after (1, 2, 3) equilibration with the hydrogels (1: x=0; 2: x=0.25; 3: x=0.5, 0.75, 1). The appearance of the P(DMAM-co-ANa$_{0.5}$) hydrogel at the end of the sorption experiment is shown in the inset.

The removal efficiency (R, %) was calculated by:

$$R = \frac{C_0 - C_e}{C_0} 100 \quad (1)$$

where; C_0 and C_e (moL/L) are the initial and equilibrium concentrations of organic dye solutions, respectively; V (L) is the volume of the organic dye solution and m (g) is the weight of the hydrogel used for the sorption experiment.

The results for the removal efficiency for all studied dyes (10^{-3} M) by the five different negatively charged P(DMAM-co-ANa$_x$) hydrogels are presented in Fig. 3.

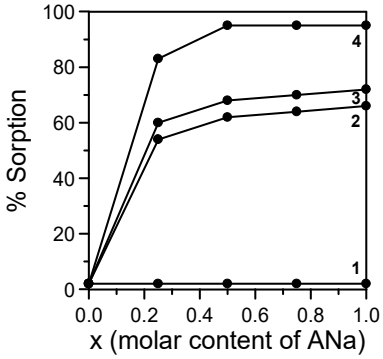

Fig. 3 % Sorption vs. charge content of the P(DMAM-co-ANa$_x$) hydrogels for OR (1), CV (2), TB (3) and MB (4) dyes: Initial concentration of dyes solution 10^{-3} M

The remarkable result is that in all cases the removal efficiency is too high for the positive charged dyes even at negative low charge content of the hydrogels (x=0.25). These results indicate that the driving force for the sorption of the dyes is not just the electrostatic attractions with the oppositely charged hydrogels. Hydrophobic interactions between the polymer segments and the organic part of the dyes, as well as aggregation of the sorbed dyes should also be taken into account. Previous works have clarified that ionic dyes tend to aggregate at the adsorbed state [13], [14].

Fig. 4 shows the Langmuir isotherms for the three positively charged dyes, that is, the variation of the quantity q_e of the sorbed dye per gram of the sorbent versus the concentration C_e of dye remaining in solution. q_e was calculated by:

$$q_e = (C_0 - C_e)\frac{V}{m} \quad (2)$$

where; C_0 is the initial dye concentration (in mmol/L), V the volume of the solution (in L) and m is the mass of the sorbent (in g).

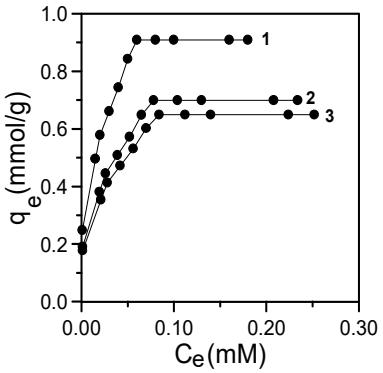

Fig. 4 Plot of the quantity q_e for MB (1), TB (2) and CV (3) sorbed dyes as a function of the concentration C_e of the dye remaining in solution.

In Fig. 5 we show the variation of the ratio C_e/q_e versus C_e. It represents an analysis of the Langmuir isotherm, and it produces the binding constant K_L by:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \left(\frac{\alpha_L}{K_L}\right)C_e \quad (3)$$

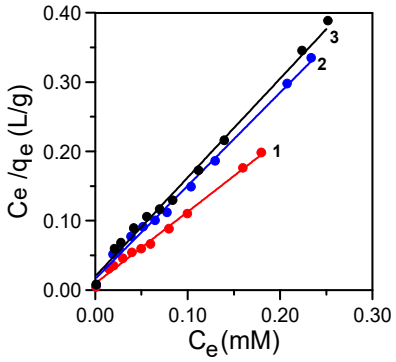

Fig. 5 Plot of the quantity C_e/q_e for MB (1), TB (2) and CV (3) sorbed dyes as a function of the concentration C_e of the dye remaining in solution

As we can see the experimental data fits well the Langmuir model with the correlation coefficient 0.99. $q_{e,max}$=0.9mmol/g in the case of MB dye. Similar values were obtained for TB and CV dyes (0.7 mmol/g and 0.6 mmol/g respectively) in the case of the anionic hydrogels. As seen these values are comparable or even higher with related literature data concerning other sorbent materials with high sorption capacity [15], [16]. The above results indicate that these materials are very effective for the sorption of positively charged organic dyes from aqueous solutions.

IV. Conclusions

The sorption of charged organic dyes, by the anionic P(DMAM-co-ANa$_x$) hydrogels, has been explored in the present work. It is shown that these hydrogels can be employed as efficient sorbents for retaining organic dyer from aqueous solutions. Strongly colored water solutions become almost crystal clear when they are brought in contact with these materials. The sorption of organic dyes is much more pronounced, even when the charge content of the hydrogels is limited, suggesting that, apart electrostatic interactions, other phenomena such as hydrophobic interactions as well as aggregation of the dyes play a decisive role for the sorption process.

Acknowledgments

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