Sorption of Charged Organic Dyes from Anionic Hydrogels

Georgios Linardatos, Miltiadis Zamparas, Vlasoula Bekiari, Georgios Bokias, Georgios Hotos

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. 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.

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 sorption 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.
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 N₂ 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°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 10⁻⁶M to 10⁻³M) 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.

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

\[ R = \frac{C_0 - C_e}{C_0} \times 100 \]  

where; C₀ and Cₑ (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.

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:

\[
q_e = \frac{(C_0 - C_e) V}{m}
\]

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).

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:

\[
\frac{C_e}{q_e} = \frac{1}{K_L} \left( \frac{q_{max}}{K_L} \right) C_e
\]

As we can see the experimental data fits well the Langmuir model with the correlation coefficient 0.99. \( q_{max} = 0.9 \) mmol/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) hydrogels, has been explored in the present work. It is shown that these hydrogels can be employed as efficient sorbents for retaining organic dye 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

This research has been co-financed by the European Union (European Social Fund – ESF) and Greek national funds through the Operational Program "Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF) - Research Funding Program: Archimedes III. Investing in knowledge society through the European Social Fund; research project Archimedes III: “Synthesis and characterization of novel nanostructured materials and study of their use as water purification systems”.

REFERENCES


Georgios Linardatos received his diploma in Chemical Engineering from the University of Patras, Greece in 2006 and his M.Sc in Polymers Science and Technology in 2008 from same university. Georgios Linardatos has published his research in peer reviewed scientific journals and international conferences. Her field of research focuses on polymer synthesis and characterization, materials science and hydrogels as sorbent materials. He is also a member of the Technical Chamber of Greece.

Dr. Miltiadis Zamparas is an Environmental engineer from the University of Aegean, Greece since 2008. He received his M.Sc and Ph.D. in environmental sciences in 2011 and 2015 respectively, from University of Patras, Department of Environmental and natural Resources Management. Miltiadis Zamparas has published his research in peer reviewed scientific journals and international conferences. His field of research includes environmental study and characterization as well as novel sorbent materials for water treatment.

Dr Vlasoula Bekiari is Assistant Professor of Environmental Chemistry at the Technological Educational Institute of western Greece. Her research activities focus on environmental analytical chemistry, materials science as well as novel functional materials for water treatment. She has more than 60 publications in peer review journals which are recognized more than 1000 citations (h-factor=20).

Dr. Georgios Bokias is Associate Professor of Polymer Sciences at the Department of Chemistry of the University of Patras. His research activities focus on stimuli-responsive and functional polymers, hydrogels, functional organic nanoparticles, as well as functional hybrid organic/inorganic nanoparticles. He has more than 60 publications in peer review journals which are recognized more than 1000 citations (h-factor=21).

Dr. Georgios Hotos is currently professor at the Department of Fisheries and Aquaculture Technology at the Technological Educational Institute of Western Greece. His research interests include environmental monitoring as well as aquaculture engineering He has more than 40 publications in peer review journals and international conferences.