IONIC HYDROGELS AS POTENTIAL SORBENT MATERIALS FOR CHARGED ORGANIC DYES

BEKIARI V.[1], ZAMPARAS M.[1], LINARDATOS G.[1] and BOKIAS G.[2]

[1]Technological Educational Institute of Western Greece, Department of Fisheries and Aquaculture Technology, 30200, Messolonghi, Greece
[2]University of Patras, Department of Chemistry, GR26504, Patras, Greece
E-mail: mpekiari@teimes.gr

ABSTRACT

Hydrogels are three-dimensional, hydrophilic, polymeric networks capable to adsorb large amounts of water. The networks are composed of homopolymers or copolymers and are insoluble due to the presence of chemical or physical cross-links. When hydrogels come in contact with aqueous solutions, they can effectively adsorb 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. In this study, anionic hydrogels bearing negatively charged groups and cationic hydrogels bearing positively charged groups were prepared. PANa hydrogels are based on the anionic monomer sodium acrylate (ANa) and the nonionic one N,N-dimethylacrylamide (DMAM). In addition, PAPTAC hydrogels are based on the cationic monomer APTAC (3-acrylamidopropyl trimethyl ammonium chloride) and the nonionic one DMAM. A series of copolymeric hydrogels [P(DMAM-co-ANa_x) and P(DMAM-co-$APTAC_x$)] were synthesized. The molar content x of ANa or APTAC units (expressing the molar charged content of the hydrogel) varies from 0 up to 1 (fully charged hydrogel). The main objective of the present work was to examine the effectiveness of using these hydrogels as potential sorbents for Toluidine Blue, Basic Blue and Orange II from aqueous solutions.

Keywords: oragnic hydrogels, sorbent materials, organic dyes

1. Introduction

Hydrogels are three-dimensional, hydrophilic, polymeric networks capable to adsorb large amounts of water. The networks are composed of homopolymers or copolymers and are insoluble 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 (Chauhan *et al*., 2006, Cong *et al.*, 2015, Ray *et al.*, 2007, Thivaios and Bokias, 2010). 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 (Caemen and Suteu, 2012). 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 (Vaiano *et al.*, 2015). In the recent years several works have been appeared in the scientific literature reporting adsorption of several dyes by both natural and synthetic sorbents (Bekiari and Lianos, 2006, Umpuch and Jutarat B, 2013).

In the present work, firstly P(DMAM-co-ANa_x) hydrogels containing sodium acrylate units (ANa) and nonionic N,N-dimethylacrylamide units (DMAM) have been prepared. Moreover, cationic hydrogels P(DMAM-co-$APTAC_x$) containing cationic 3-acrylamidopropyl trimethyl ammonium chloride units (APTAC) and nonionic DMAM units were also synthesized. The molar content x of

the anionic ANa units or the cationic APTAC units varies from 0 (nonionic hydrogel) up to 1 (fully charged hydrogel, either anionic or cationic). The chemical structures of the synthesized hydrogels are depicted in Figure 1. UV-vis absorption spectrophotometry is applied to investigate the sorption of selected organic by these hydrogels. In fact, the sorption of the cationic dyes Toluidine Blue (TB, Fig. 1) and Basic Blue (BB, Fig. 1) was investigated in the case of the anionic P(DMAM-co-ANax) hdrogels, whereas the sorption of anionic dye Orange II (OR, Fig. 1) was investigated in the case of the cationic P(DMAM-co-APTAC$_x$).

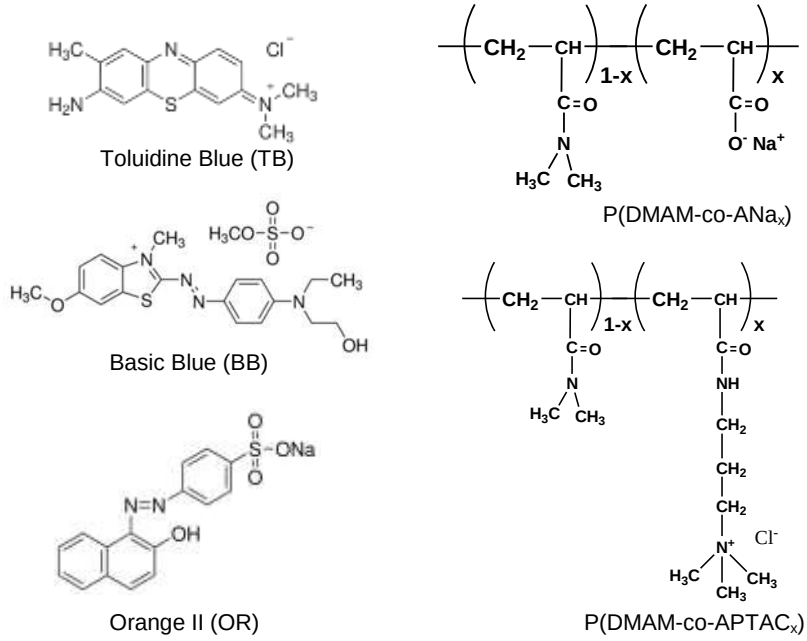

Figure 1: Chemical structure of the dyes and the hydrogels used in the present work. The structural units in the case of the hydrogels are cross-linked with BIS (not shown).

2. Experimental methods

Materials

Acrylic acid (AA), 3-acrylamidopropyl trimethylammonium chloride (APTAC), *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. Toluidine Blue, Basic Blue and Orange II for dyes stock solutions were obtained from Aldrich. Water was purified by means of a TKA smart2Pure apparatus.

Synthesis of the hydrogels

The P(DMAM-co-ANa$_x$) and P(DMAM-co-APTAC$_x$) hydrogels were synthesized according to the following procedure: x mol AA (APTAC in the case of positively charged hydrogels) 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 (negatively charged ANa units or positively charged APTAC units) were synthesized according to the experimental procedure outlined previously.

Sorption of charged 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 20 mL of aqueous solution of the dyes of varied initial 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.

3. Results

The results for TB and BB (10^{-3}M) sorption by the five different negatively charged P(DMAM-co-ANa$_x$) hydrogels are presented in Figure 2a. The respective results for OR (10^{-3} M) sorption by the five different positively charged P(DMAM-co-APTAC$_x$) hydrogels are presented in Figure 2b. The dye solution, in all cases, is very strongly coloured before equilibration, while after equilibration with the hydrogel, the absorption was remarkably weaker, in agreement with the discoloration of the aqueous solution, which can be even visually detected. In contrast, the hydrogels are now strongly coloured, showing that almost the whole dye was adsorbed under the present experimental conditions.

Fig. 3 shows the Langmuir isotherm for OR, 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 the following equation:

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

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 Figure 4 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 the following equation:

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

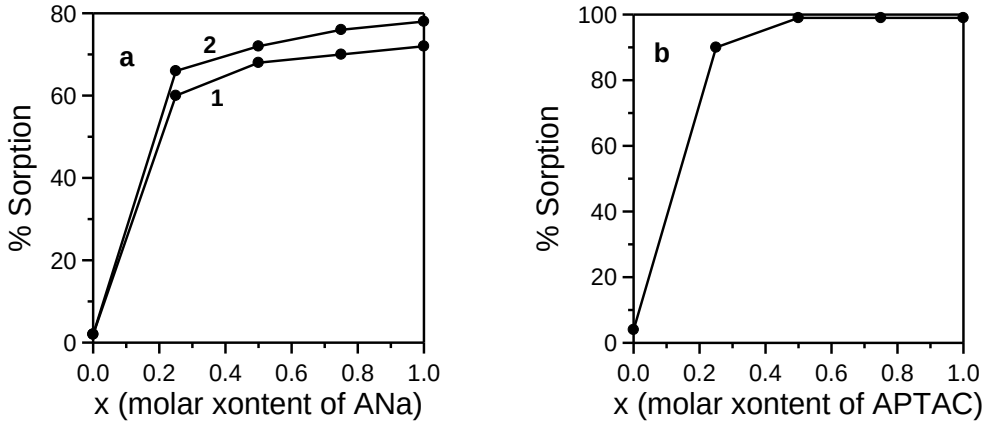

Figure 2: (a): % Sorption vs. charge content of the P(DMAM-co-ANa$_x$) hydrogels for TB (1) and BB (2) dyes; (b): % Sorption vs. charge content of the P(DMAM-co-APTAC$_x$) hydrogels for OR dye. Initial concentration of dyes solution: 10^{-3}M.

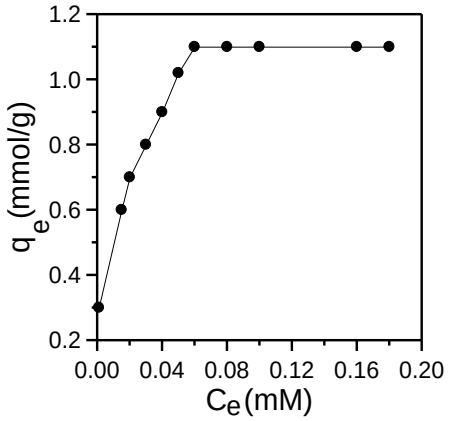

Figure 3: Plot of the quantity q_e of the sorbed OR dye as a function of the concentration C_e of the dye remaining in solution.

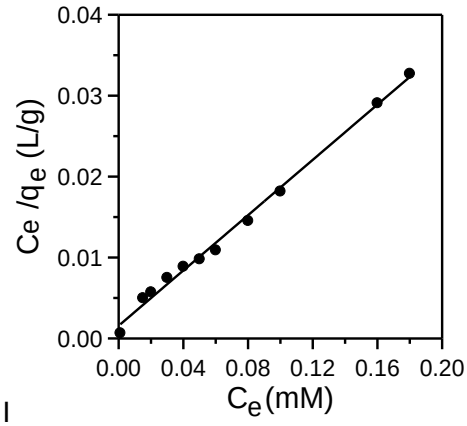

Figure 4: Plot of the quantity C_e/q_e of the adsorbed OR dye as a function of the concentration C_e of the dye remaining in solution.

As we can see the experimental data fits well the Langmuir model with the correlation coefficient 0.99. $q_{e,max}$=1.1 mmol/g in the case of OR dye. Similar values were obtained for TB and BB dyes (0.86 mmol/g and 0.78 mmol/g respectively) in the case of the anionic hydrogels, indicating that these materials are very effective for the sorption of organic dyes from aqueous solutions.

4. Conclusions

The sorption of charged organic dyes, by two series of oppositely charged hydrogels, namely the anionic P(DMAM-co-ANa$_x$) and the cationic P(DMAM-co-APTAC$_x$) 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.

ACKNOWLEDGEMENTS

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

1. Bekiari V. and Lianos P., (2006), Ureasil Gels as Highly Efficient Adsorbent for Water Purification, Chem. Mater., 18, 4142-4146.
2. Caemen Z. and Suteu D., (2012), Textile Organic Dyes –Characteristics, Polluting Effects and Separation/Elimination Procedures from Industrial Effluents – A Critical Overview, book: 'Organic Pollutants Ten Years After Stockholm Convention-Environmental and Analytical Update' , www.intechopen.com, chapter 3.
3. Chauhan G.S., Singh B., Sharma R.K., Verma M., Jaswal S.C. and Sharma R. (2006), Use of biopolymers and acrylamide-based hydrogels for sorption of Cu^{2+}, Fe^{2+} and Cr^{6+} ions from their aqueous solutions, Desalination, 197, 75-81.
4. Cong H.-P., Qiu J.-H. and Yu S.-H., (2015) Thermoresposive poly(N-isopropylacrylamide)/Graphene/Au nanocomposite hydrogel for water treatment by a laser-assisted approach, Small, 11, 1165-1170
5. Ray S., Das A.K. and Banerjee A., (2007), pH-responsive, bolaamphiphile-based smart metallo-hydrogels as potential dye-adsorbing agents, water purifier, and vitamin B_{12} carrier, Chem. Mater., 19, 1633-1639.
6. Thivaios I. and Bokias G., (2010), Adsorption of Nile Red by poly(N-isopropylacrylamide) gels in binary water/tetrahydrofuran mixtures, J. Appl. Polym. Sci., 116, 1509-1514.
7. Umpuch C. and Jutarat B., (2013), Adsorption of Organic Dyes from Aqueous Solution by Surfactant Modified Corn Straw, International Journal of Chemical Engineering and Applications, 4, 134-139
8. Vaiano V., Sacco O., Sannino D. And Ciambelli P., (2015), Nanostructured N-doped TiO_2 coated on glass spheres for the photocatalytic removal of organic dyes under UV or visible light irradiation, Appl. Catal., B, 170-171, 153-161.