



POLIMERIC SORBENT FOR DYE RETAINING



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INTRODUCTION

The conductive polymer has already been known for their remarkable physico-chemical and electrical properties. The polymers resulting from the polymerization of aniline, polyaniline (PANI) and 3-aminophenyl boronic acid (ABA), poly-3-aminophenylboronic acid (PABA), are highly studied conductive polymers. Their unique is give by the electrical properties reversibly controlled, by both charge transfer doping, as well as by protonation. PABA also has a relatively high surface area and porosity and aminoboronic functional groups, which it recommends for many applications. PABA-based composites add new physical and chemical properties [1,2]. The paper presents the results obtained when retaining dyes on polymethylmethacryl microspheres (PMMA), on which a layer of PABA was chemically deposited (Figure1).

Aim: The present paper is focused on the chemical oxidative polymerization of ABA on the surfaces of polymethylmetacrylate microspheres and the utilization of these PABA/PMMA as sorbents for dye retaining from residual waters.

Methods: Hollow polymethylmethacrylate (PMMA) microspheres were prepared in the laboratory in nonpolar solvents by dispersion polymerization with a macromonomeric stabilizer [3].The azo dye was also prepared in our laboratory.

Synthesis of PABA coated PMMA microspheres

8g PMMA, 3-aminophenylboronic acid monohydrate (ABA, 0.2 mmol), NaF (0.4 mmol) were dissolved in 10 mL of a 0.1 mol · L⁻¹ H₂SO₄ aqueous solution, and then 5 mL of 0.025 mol · L⁻¹ ammonium peroxydisulfate (APS) solution in one portion. The polymerization reaction was carried out for 24 h under static conditions at room temperature. The resulting green precipitates were centrifuged, washed with deionized water several times, and dried under vacuum at 60 °C for 24 h.

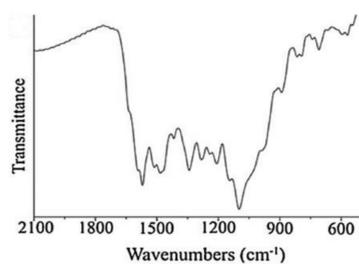
Characterization

The IR absorption spectra were recorded with a Jasco 430 spectrometer (spectral range 4000-400 cm⁻¹ range, 256 scans, and resolution 2 cm⁻¹) using KBr pellets. The density of PABA was determined according to the picnometer method, in decaline. The optical microscopic images were taken with the help of optic microscope GX Series L2020A. Optic images were recorded at 5×, 10×, 40× magnitudes. The dimensions of microspheres were analyzed with the Image J program. UV-VIS spectra were recorded in 190 ÷ 900 nm and „CECIL CE 7200” spectrophotometer was used. Removal of the azo dye by coated PABA/PMMA microspheres was carried out as follows: stock solutions of this colorant was made in distilled water (pH 6.8-7.0) and the absorption at 515 nm are investigated.

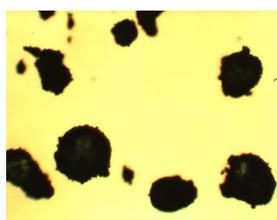
RESULTS AND DISCUSSION

The optical images of coated PABA/PMMA microspheres after the retaining of colorant RD are presented in Figure 3.

Figure 1a represents a FT-IR spectrum of the as-synthesized PABA. The peaks at 1574 and 1483 cm⁻¹ are attributed to the C=C stretching vibration of quinoid rings and benzenoid rings. The peaks at 1515 and 1285 cm⁻¹ correspond to the B-N and B-O stretching vibrations. The peaks at 1345 and 1149 cm⁻¹ are assigned to the C-N stretching vibration of secondary aromatic amine and the aromatic C-H in-plane bending vibration, respectively. The peaks at 896 and 814 cm⁻¹ are related to the F-B stretching vibrations. The UV-vis spectrum of the as-synthesized PABA in deionized water is shown in Figure 1b reveal peaks at about 400 and 800 nm attributed to polaron band → π* and the π → localized polaron band transitions, respectively. The results indicate that PABA was obtained in the form of a conducting emeraldine salt state.



a)



b)

Figure 1. a) FT-IR spectra of the as-synthesized PABA/PMMA and b) optical image of PABA/PMMA microspheres magnitudes 20×

The chemical structure of PABA and azo red dye are shown in Figure 2.

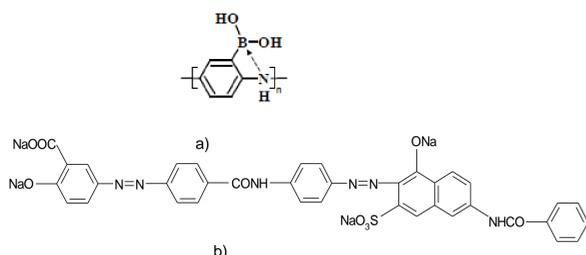


Figure 2. Chemical structures of a) PABA and b) azo red dye (RD)

References

- [1] DiCesare N., Lakowicz J.R., J. Phys. Chem. A. 105 (2001) 6834-6840.
- [2] Gumus O. Y., Ozkan S., Ural H. I., Macromol. Chem. Phys 217 (2016) 1411-1421.
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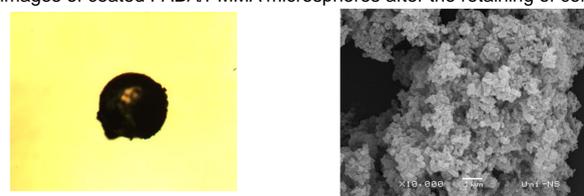
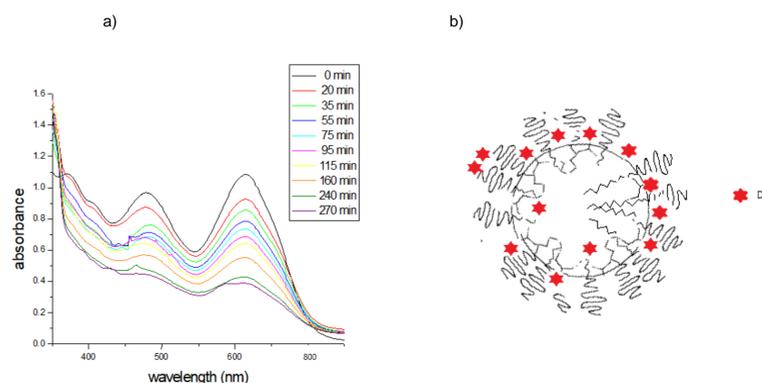


Figure 3. Optical images of PABA/PMMA microspheres/RD: a) 40× and b) SEM of PABA



a)

b)

Figure 4. a) UV-VIS spectra for PABA/PMMA and b) schematic representation of Dye adsorption on PABA/PMMA

Based on experimental data the quantity of dye retained by PABA coated microspheres are presented in Figure 5. Practically PMMA microspheres presents dye retaining properties. The absorption capacity of dye in 4.5 hours are 1.92·10⁻⁴ mmol·g⁻¹ PABA/PMMA, with a yield of 70% and 2.61·10⁻⁴ mmol·g⁻¹ PANI salt/PMMA, with a yield of 78%. This yield are promising because in this experiments the dye presents a high molar mass (818 g·mol⁻¹).The maximum rate in the first stage the adsorption in the case of PANI salt/PMMA is 0.032·10⁻⁴ (mmol·g⁻¹)·min⁻¹, and in the case of PANI base/PMMA 0.0143·10⁻⁴(mmol·g⁻¹)·min⁻¹.

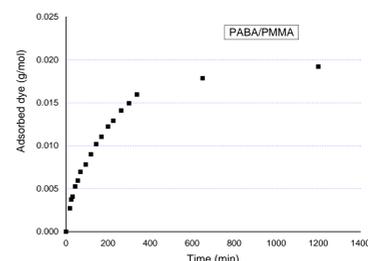


Figure 5 . Quantity of dye retained by PABA/PMMA versus time determined by absorbance at 515 nm.

The adsorption of dye in the first hour is two time higher in the case of coated PANI salt/PMMA microspheres. The driving force in the retaining process in the electrostatic interaction between polymer chain and ionic dye species. The experimental data show that in the case of PABA/PMMA microspheres and dye some repulsive interaction take place and as a results this kind of microspheres presents a low retaining capacity comparatively with the PANI salt/PMMA microspheres, closed to PANI base form.

Conclusions

- Conducting PABA/PMMA microspheres could be use as an effective adsorbent for the removal of ionic dyes from solution.
- The adsorption most likely occurs via electrostatic interaction between the polymerchain and dye ionic species.
- The absorption capacity of dye in 4,5 hours are 1.92·10⁻⁴ mmol·g⁻¹ PABA/PMMA.
- The yield of dye recovery is 70% and 78% for PANI base/PMMA and PANI salt/PMMA respectively. This results are promising due to the high molar mass of the studied dye.