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The enhanced removal of cationic dyes in binary system using novel copolymers with two kinds of acidic groups

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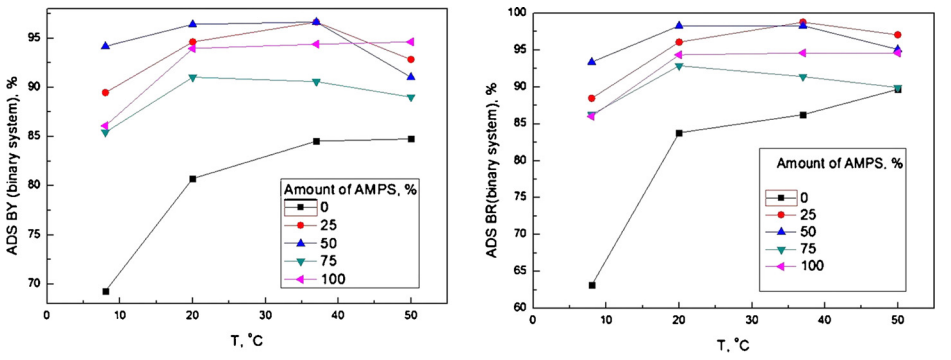
HIGHLIGHTS

- The aim was to sytnhesized novel copolymer hydrogels based on two acidic monomers.
- These hydrogels were investigated as sorbents for cationic dyes removal.
- Sorption capability is significantly improved compared to pure component hydrogels.
- Synthesized copolymer hydrogels adsorbed better dyes in binary systems.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study novel copolymer hydrogels based on methacrylic acid (MAA) and 2-acrylamido-2-methylpropane sulfonic acid (AMPS) were synthesized by free-radical aqueous copolymerization and characterized. Derived P(MAA-*co*-AMPS) hydrogels, joining well the affection of numerous anionic groups toward cations and the accessibility of active sites in the swollen network were recognized as potential sorbents for removal of cationic species. The effect of various initial parameters on sorption of two cationic dyes onto P(MAA-*co*-AMPS) hydrogels was investigated in both, single and binary, systems. Results showed that the copolymerization of MAA and AMPS significantly increased sorption capability of copolymers compared to both pure-component hydrogels—PMAA and PAMPS hydrogels. The main advantage of novel copolymer hydrogels is enhanced sorption of dyes in binary systems, reaching maximal values of 98.8% (Basic Yellow 28) and 96.4 (Basic Red 46), onto hydrogel P (MAA-*co*-AMPS) 50/50. The desorption rate of BY28 and BR46 in both, single and in binary, systems increased with the increase in AMPS content in hydrogels. This investigation showed that copolymerization of two acidic monomers, bearing different types of acid groups, could significantly improve the sorption thus decreasing the price and the amount of material needed for successful removal of pollutants.

1. Introduction

Many industries, such as textile, dyeing, paper and pulp, tannery and paint industries, are big consumers of dyes and hence the effluents of these industries tend to contain large amounts of

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dying wastewaters. The dyeing wastewaters must be treated prior to discharge into aquatic system in order to comply with the environmental protection laws for the receiving waters. Apart from the esthetic problems created when dye effluents reach the natural water currents, dyes strongly absorb sunlight, thus impeding the photosynthetic activity of aquatic plants and seriously threatening the whole ecosystem [1,2]. The poor degradability, toxicity, high pH and COD of most commercial dyes used in industry led to development of various methods for treating the dyeing wastewaters such as coagulation, flocculation, ion-exchange, membrane filtration, ozonation, sorption and biosorption [3–13]. Each method has its own limitations such as generation of secondary effluents, hazardous intermediate products, slow rates of degradation and high cost. Sorption is found to be the most appropriate method for removal of organic compounds and dyes from wastewater due to easy procedure, low cost and high efficiency.

Polymeric sorbents proved to be highly efficient in removal of dye molecules because they might contain wide variety of functional groups like hydroxyl, carboxyl or amine groups which are involved in sorption process. Hydrogels, three-dimensional polymeric structures, have ability to uptake and retain large amount of liquid and swell several hundred times of their original weight allowing free diffusion of solute molecules like dye, organic or metal species [14]. In recent years, poly(methacrylic acid) (PMAA) based hydrogels have been increasingly investigated for removal of metal ions and organic compounds from wastewater [15–20], while there are only few studies of PMAA hydrogels and their modifications employed in removal of dyes from wastewater. Poly(methacrylic acid) hydrogels have COOH functionalities and without neutralization exhibit low uptake of aqueous solutions. In order to increase their swelling ability (i.e. expansion of a network) and therefore enhance their sorption properties, PMAA can be copolymerized with other monomers. In our previous work we investigated sorption of Basic Yellow 28 on PMAA hydrogels and results have shown that at room temperature the percent of dye removal was only 76% [21]. PMAA modified biomass was used for removal of methylene blue, rhodamine B and basic magenta [22], poly(*N*-vinylpyrrolidone-*co*-methacrylic acid) hydrogels for removal of methyl violet [23] and (poly(methacrylic acid)-graft-cellulose/bentonite) for removal of methylene blue [24].

The aim of this work was to copolymerize methacrylic acid with more hydrophilic monomer such as 2-acrylamido-2-methylpropane sulfonic acid (AMPS) and to obtain new suitable hydrogel with 2 types of functional groups that can be involved in sorption process: carboxylic and sulfonic groups. AMPS was chosen as comonomer due to great hydrophilicity and proven ability to bind cationic species. Pure PAMPS hydrogels and magnetic PAMPS were investigated for removal of Cd(II), Co(II), Fe(II), Pb(II), Ni(II), Cu(II) and Cr(III) [25]. Copolymers of AMPS and other hydrophilic monomers were also used in heavy metal cations elimination, for example copolymers with *N*-vinylpyrrolidone/acrylic acid for removal of Cd(II), Cu(II) and Fe(III) [26], acrylic acid for removal Safranin T and brilliant cresyl blue [27], 2-dimethyaminoethyl methacrylate for removal of Cu(II) [28], itaconic acid for removal of Pb(II), Cu)II), Cd(II) [29] and acrylamidoxime for removal of U(VI) [30].

Although previous preliminary studies have highlighted the sorption ability of PMAA or PAMPS hydrogels for metal ions and few dyes, in depth mechanistic studies have not been performed. In this work, the attempts have been carried out to enhance the sorption of dyes in binary system by novel methacrylic acid-modified hydrogels. Methacrylic acid was copolymerized with AMPS and comporative study was carried out to check out the sorption properties of pure PMAA, PAMPS and copolymer hydrogels P(MAA-*co*-AMPS) for the removal of cationic dyes Basic Yellow 28(BY28) and Basic Red 46 (BR46) in single and binary system. To the best of our knowledge, copolymers of methacrylic acid and 2-acrylamido-2-methylpropane sulfonic acid were not synthesized and investigated previously. The sorption of cationic dyes onto P(MAA-*co*-AMPS) copolymers and corresponding pure hydrogels, was investigated as a function of copolymer composition at various operating conditions (pH, initial dye concentration, temperature). In order to elucidate sorption behavior of BY28 and BR46 onto P(MAA-*co*-AMPS) hydrogels, the sorption isotherms and kinetic models were applied to experimental sorption data.

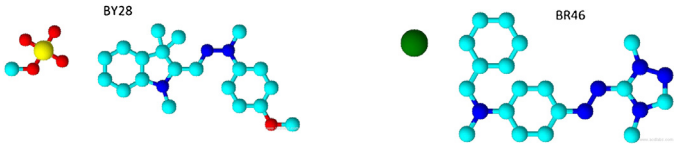

Fig. 1. Chemical structures of Basic Yellow 28 and Basic Red 46 dyes (blue—nitrogen, cyan—carbon, yellow—sulfur, red—oxygen, green—bromide). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2. Materials and methods

2.1. Reagents

Methacrylic acid (99.5%) was purchased from Merck KGaA, Darmstadt, Germany, stored in a refrigerator and melted at room temperature before use. 2-Acrylamido-2-methylpropane sulfonic acid was purchased from Acros Organics, Geel, Belgium. *N*′,*N*′-methylenebisacrylamide (MBA), potassium persulfate (KPS) (p.a.) and dimethylethanolamine (DMEA) were obtained from Aldrich Chemical Co., Milwaukee, USA. Model cationic dyes, Basic Yellow 28 (BY28) (λ_{max} = 440 nm) and Basic Red 46 (BR46) (λ_{max} = 530 nm), supplied by Bezema AG, Montlingen, Switzerland, were of a commercial quality and, as all other chemicals, were used as received. These dyes are widely used in cosmetics, for dying of acrylic fibers, in textile and leather industry. The structures of employed dyes are given in Fig. 1.

2.2. Synthesis of hydrogels

Hydrogels were synthesized via free-radical polymerization in aqueous media using the MBA, KPS and DMEA as a crosslinker, an initiator and an activator, respectively. First, adequate amounts of each monomer were dissolved in distilled water (see feed composition in Table 1). Afterward, MBA was added in amount of 1 mol% per total amount of monomers. After all of the crosslinker was dissolved, 3 mol% of initiator per total amount of monomers and DMEA as accelerator in amount of 1 mol% per amount of initiator were subsequently added into the reaction mixture. Reaction mixture was stirred for 20 min and then poured into the glass molds (plates separated by a rubber gasket 2 mm thick), and placed in an oven at 70 °C, for 5 h. The obtained hydrogels were stamped into approximately equally sized disks and immersed in excess distilled water to remove the sol fraction of polymer and unreacted monomer. Hydrogels were washed out in the next 7 days, then dried and placed in exicator until use. Molecular structure of methacrylic acid and AMPS are shown in Fig. 2 for the sake of clarity.

2.3. Characterization of hydrogels

The hydrogels were characterized by swelling studies, Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM).

In order to study the swelling behavior, hydrogels (approximately 0.02 g) were immersed in distilled water. Weights of