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Adsorption of methyl violet and brilliant blue onto poly(vinyl alcohol) membranes grafted with *N*-vinyl imidazole/acrylic acid

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Abstract

Poly(vinyl alcohol) films were grafted with two monomers using gamma radiation, acrylic acid and *N*-vinyl imidazole. The ability of these membranes to adsorb the dyes, methyl violet and brilliant blue, has been investigated. The data show that untreated or alkali treated membranes adsorb methyl violet, but they did not adsorb brilliant blue. In contrast, acidic treated membranes do adsorb brilliant blue, and did not adsorb methyl violet. This indicates that these membranes could be used for the separation of both dyes. Also it was found that the dye uptake increases with the increase in the degree of grafting.

Keywords: Acrylic acid; *N*-vinyl imidazole; Poly(vinyl alcohol); Radiation grafting; Dye uptake; Methyl violet; Brilliant blue

1. Introduction

Industrial effluents are one of the major causes of environmental pollution because effluents discharged from dyeing industries are highly colored [1]. Due to their chemical structure, dyes are resistant to light, many chemicals, oxidizing agents, heat and are biologically non-degradable and therefore difficult to decolorize [2]. Disposal of this colored water into receiving waters can be toxic to aquatic life. It may be mutagenic and carcinogenic and can cause severe damage to human beings, such as disfunction of the kidneys, reproductive system, liver and brain and central nervous system [1]. Wastewaters containing dyes from the textile industry are very difficult to be treated using conventional wastewater treatment methods as coagulation, ultrafiltration, ozonation, oxidation, sedimentation, reverse osmosis, flotation, precipitation, etc., due to economic considerations. Adsorption has gained favor in recent years due to proven efficiency in the removal of pollutants from effluents to stable forms for the above conventional treatment methods [3].

Many studies have been undertaken to find suitable adsorbents in order to lower dye concentrations from aqueous solutions. They included activated carbon [4], peat [5], chitin [6] and clay [7]. For regenerative and non-regenerative systems, high capacity is essential for adsorbent selection. Since the amount of dyes adsorbed on the adsorbents is not high enough, researches are still under development to improve their adsorption performance.

Graft polymerization of vinyl monomers onto polymer substrates has attracted considerable interest because it imparts some desirable properties, such as chelation, ion exchange, biocompatibility and protein adsorption. A number of investigations have been reported in the literature to modify PVA membrane by means of radiation-induced graft copolymerization of monomers [8–10]. Investigations have been done on its use in the field separation and adsorption processes [9–13].

Poly(*N*-vinyl imidazole) hydrogels were applied to immobilize glucose oxidase [14,15], and for ion uptake [16–18]. Also hydrogels consisting of *N*-vinyl imidazole and acrylonitrile were prepared regarding chelation and separation of metals [19,20].

In our previous study, PVA-g-P(acrylic acid/imidazole) (AAc/Zol) membranes were prepared by radiation grafting

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of the AAc/Zol comonomer onto PVA films which were used for the adsorption of copper ions from wastewater [10]. In this work, the ability of PVA-g-P(AAc/Zol) membranes for extraction and separation of methyl violet and brilliant blue have been discussed.

2. Experimental

2.1. Materials

PVA (MW = 72,000, for synthesis) was supplied by Merck, Germany; *N*-vinyl imidazole (purity > 99%) and acrylic acid (purity > 99%), were purchased from Fluka, Germany. Methyl violet (MV) and brilliant blue (BB) were obtained from Sigma; the pH of the aqueous solution of MV is 6.35, and of BB is 5.9. The maximum absorptions λ_{max} of the dye solutions are 582 and 552 nm for MV and BB, as shown in Fig. 1 respectively.

2.2. Dyes adsorption measurements

Stock solutions of the dye containing approximately 20 mg/L dye in distilled water were prepared. Dried grafted membranes were immersed into a known volume of dye solution at 25 °C for different time intervals. The amounts of dye adsorbed were determined from the initial and final concentrations of the solutions, calculated from the measured absorbance. The concentrations of the dyes in the aqueous solutions were measured using a double-beam UV–vis spectrophotometer (Shimadzu, type UV-1601) after the desired treatment period.

2.3. Graft copolymerization

PVA strips were weighed and then immersed in the monomer or binary monomer solution in glass ampoules. The glass ampoules containing all the reactants were subjected to ^{60}Co gamma rays at a dose rate of about 2.8 kGy/h. The grafted films were removed and washed thoroughly with water/methanol mixture and then immersed in water to extract the residual monomer or homopolymer. The films were then dried in an oven at 50 °C, and the degree of grafting was calculated as follows:

$$\text{Degree of Grafting}\% = \frac{W_g - W_o}{W_o} \times 100,$$

where W_o and W_g are the weights of initial and grafted films, respectively.

2.4. Maximum swelling

The dried grafted films (after the washing procedure mentioned above) were soaked in water up to a constant weight (equilibrium swelling), and the maximum swelling (S_{max}%) was calculated by the following equation:

$$S_{max}\% = \frac{W_S - W_o}{W_o} \times 100,$$

where W_S is the weight of membrane at equilibrium swelling, and W_o is the weight of dried membrane.

3. Results and discussion

The preparation of the membranes was carried out using the technique of direct radiation graft copolymerization of acrylic acid (AAc) and imidazole (Zol) onto PVA. The influence of some grafting parameters on the yield and homogeneity of grafting was investigated and reported previously [10].

3.1. Swelling behavior

Fig. 2 represents the swelling% with respect to the degree of grafting. It can be seen that the water uptake decreases as the degree of grafting increases. This behavior can be

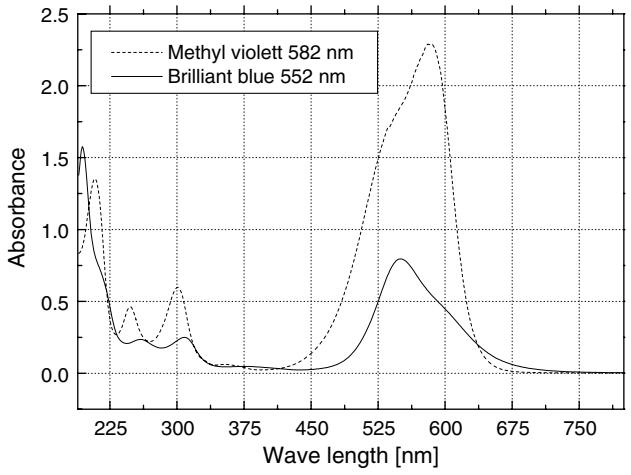

Fig. 1. Absorption spectra of the blank aqueous solutions of brilliant blue and methyl violet; initial dye concentration = 0.02 g/L.

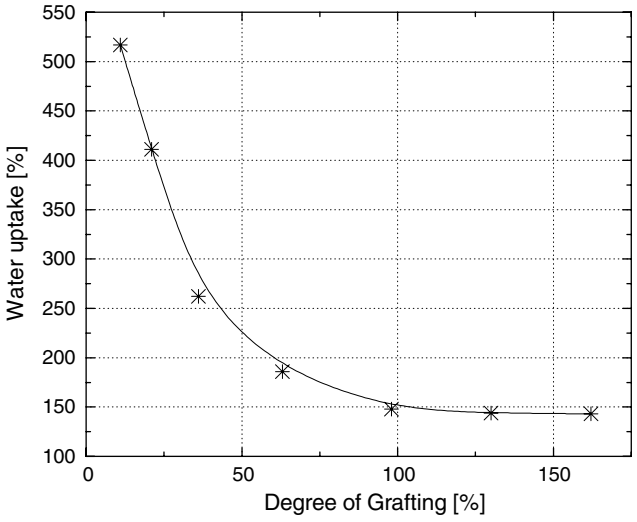

Fig. 2. Water uptake versus the grafting yield for PVA-g-AAc/Zol membranes; comonomer composition = AAc/Zol: 3/1.