Removal of Basic Dyes from Aqueous Solutions Using Starch-*Graft*-Acrylic Acid Copolymers

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ABSTRACT: Graft copolymerization of acrylic acid (AA) onto starch was carried out with ceric ammonium nitrate as initiator under nitrogen atmosphere. The grafting percentages (GP%) of starch-*graft*-AA (St-*gr*-AA) copolymers were determined. When the AA molar concentrations were 0.3 and 0.5 mol/L, GP% of St-*gr*-AA copolymers were 10.5% (St-*gr*-AA-1) and 14% (St-*gr*-AA-2), respectively. St-*gr*-AA copolymers have been used for the adsorption of basic dye (Safranine T) from aqueous solutions. Effects of various parameters such as treatment time, initial pH of the solution (pH = 2–6), initial dye concentration (50–500 mg/L), and GP% of starch graft copolymers were investigated. Basic dye removal capacities of the copolymers increase along with the augment of initial concentration of the adsorbate, GP% of the copolymers, and pH. The adsorption capacities for St-*gr*-AA-1 and St-*gr*-AA-2 reach 116.5 and 204 mg/g, respectively. Equilibrium adsorption data were obtained and fitted very well to Freundlich model. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 2422–2426, 2007

Key words: starch; acrylic acid; basic dye; Safranine T; Freundlich isotherm

INTRODUCTION

Starch is an abundant, biodegradable, natural polysaccharide, and a low-cost material. Chemical modification of starch via oxidation, hydrolysis, esterification, etherification, and grafting have been extensively studied.[1] Grafting of acrylamide,[1–4] acrylonitrile,[2,5,6] methylacrylonitrile,[7] alkyl methacrylates,[8,9] vinyl ketones,[10] 2-(dimethylamino)ethyl methylacrylate,[11] and acrylic acid (AA)[12–16] onto starch has been investigated. The chemical grafting of vinyl monomers onto polysaccharides has been the subject of extensive investigation using tetravalent cerium and other initiating systems.[5] Starch graft copolymers are becoming increasingly important because of their potential applications in industry. It has been used as hydrogels, flocculants, ion exchangers, and superabsorbents.[9]

Colored organic effluent is produced in the textile, paper, plastic, leather, food, and mineral-processing industries.[17] The main pollution source of textile effluent emerges from the dyeing process. Dyeing and finishing wastes in the textile industry have high color and organic content. Synthetic organic dyes present certain hazards and environmental problems. Effluents discharged from dyeing industries are highly colored with low biochemical

oxygen demand (BOD) and high chemical oxygen demand (COD).[18] Disposal of these effluents into water can be toxic to aquatic life.[19,20] The dyes upset the biological activities in water bodies. They cause a health problem because they may be mutagenic and carcinogenic[21,22] and can cause severe damage to human beings such as in the liver and the central nervous system.[18,23] Methods and effluent treatment for dyes may be divided into three main categories: physical, chemical, and biological. Among them, adsorption technology is generally considered to be an effective method for quickly lowering the concentration of dissolved dyes in an effluent.[24] Dyes can be effectively removed by adsorption process. Activated carbon,[18,25] natural clays,[26] modified clays,[27,28] and some industrial wastes and by-products[25] have been used as adsorbents for the removal of organic compounds from waste waters. In addition, chitin and chitosan,[29,30] starch derivatives,[31–33] carbonized wool waste,[34] agricultural residues such as banana pith,[35–37] maize cob,[37,38] coconut tree sawdust,[37] and bagasse pith,[39–41] have been investigated widely as adsorbents.

In this work, we describe the removal of Safranine T from aqueous solutions using St-*gr*-AA copolymers. Effects of various parameters such as treatment time, initial pH of the solution, initial dye concentration, and grafting percentage (GP%) of starch graft copolymers were investigated. The Freunlich equations were used to fit the equilibrium isotherms.

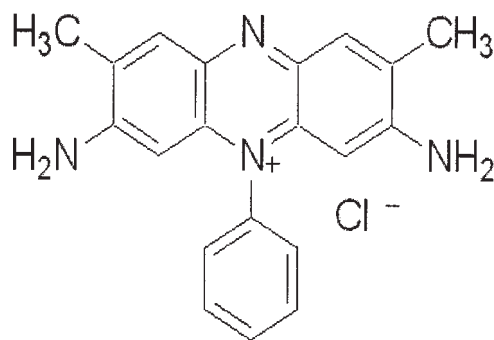*Correspondence to:* G. Güçlü (gguclu@istanbul.edu.tr).

Figure 1 Chemical structure of Safranine T.

EXPERIMENTAL

Materials

Maize starch (food grade) was dried at 110°C and then was stored in vacuum desiccator. Acrylic acid (AA; Merck, Germany) was purified by vacuum distillation and then was stored in refrigerator. CAN (Merck, Germany) was dried at 110°C and then was stored in vacuum desiccator. Basic dye (Safranine T) was obtained from Merck. The chemical structure of Safranine T is shown in Figure 1. Rest of the materials was chemically pure grade. All solutions and standards were prepared using distilled water.

Preparation of graft copolymers

The graft copolymerization of AA onto starch was carried out under nitrogen atmosphere in a 500-mL round-bottomed flask. A mixture of 4 g of dried starch and 140 mL of distilled water was stirred magnetically under nitrogen atmosphere and was then treated with CAN (0.004 mol/L) for 15 min to facilitate free radical formation on starch.[12,15] This treatment was followed by the addition of AA (0.3; 0.5 mol/L) and then the total volume of the reaction mixture was made to 200 mL with distilled water. The reactions were maintained at optimum temperature (35°C) and optimum reaction time (240 min)[12] under nitrogen atmosphere. After 240 min, the reactions were stopped by the addition of hydroquinone. The product was treated by water by changing the washing water at least three times to remove the homopolymer. The residue was separated and was dried under vacuum at 70°C.

GP% was determined by titration method.[42] The graft copolymer in 0.1N NaBr solution was titrated with 0.1N NaOH solution in the presence of phenolphthalein indicator and calculated to the following equation.

$$GP\% = \frac{M_1}{M_2} \times 100$$

where M_1 is the amount of grafted AA (g) (calculated from result of titration) and M_2 is the amount of graft copolymer (g).

Instruments

Spectrophotometric measurements were carried out using Jenway 6105 UV/vis spectrophotometer. pH measurements were carried out using Electronic Instruments Limited pH Meter 7020.

Adsorption studies

Safranine T solutions were prepared by dissolving dye in deionized water to the required concentrations. The St-*gr*-AA copolymers (0.1 g) were added into Safranine T solutions (50 mL) (initial concentrations of dye solutions were 500 mg/L). The amount of residual dye in aqueous solution was followed by UV/vis Spectrophotometer up to 24 h at different pH (2–6). In experiments of equilibrium adsorption isotherm, a fixed amount of 0.1 g adsorbents were contacted with 50 mL of aqueous solutions Safranine T with different concentrations (50–500 mg/L). The amount of residual dye in aqueous solution was determined by UV/vis Spectrophotometer after 24 h.

RESULTS AND DISCUSSION

The graft copolymerization of AA onto starch was carried out with monomer concentration of 0.3 and 0.5 mol/L. CAN was used as an initiator. The grafting reaction initiated by the CAN is characterized with first producing free radicals on the starch backbone and then adding AA molecules to the starch macroradicals formed. The GP% of St-*gr*-AA-1 and St-*gr*-AA-2 copolymers was 10 and 14%, respectively. The structures of the polymers and grafting reaction mechanism were submitted in our previous work.[15] The main purpose of this work is to investigate the removal of basic dyes from aqueous solutions by St-*gr*-AA copolymers.

Adsorption properties of St-*gr*-AA copolymers were evaluated by depending on different adsorption conditions such as different initial dye concentration, pH, GP% of St-*gr*-AA copolymers, and treatment time. The concentrations of the dyes were determined using UV/vis Spectrophotometer at wavelength 530 nm.

Effect of grafting percentage

Figures 2 and 3 show the effect of GP% of the St-*gr*-AA copolymers on the basic dye adsorption capacities. It is obvious that the adsorption capacities increased with increasing grafting yield. Whereas St-*gr*-AA copolymers have many carboxyl groups that can increase the electrostatic interaction between the cationic groups of basic dyes and carboxyl groups of St-*gr*-AA copolymers, and so dye adsorption is better[43,44] (Fig. 4).
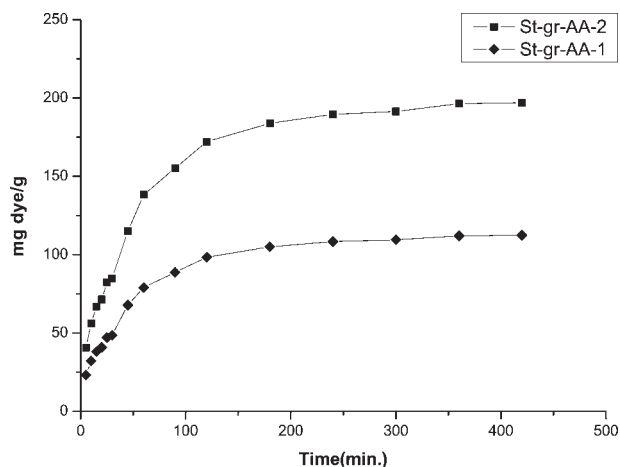
Figure 2 The effect of the treatment time on the adsorption of basic dye from aqueous solutions by St-*gr*-AA copolymers.

Effect of pH

Copolymer sample (St-*gr*-AA-2) was added to the basic dye solutions (500 mg/L) of pH = 2–6 to investigate the effect of pH. The results for basic dye adsorption at different pH are shown in Figure 3. The basic dye adsorption capacities of copolymers increased with increasing pH. The presence of ionizable group such as carboxyl group on the copolymer structure, pH will affect the adsorption capacities of this copolymer, because of the changing of ionization degree with pH.[16,45] At low pH, the carboxyl groups are present in nonionized form and no interaction can occur between the carboxyl groups and the basic dye molecules. On increasing the pH, the carboxyl groups are ionized and increased the probability of interaction between the carboxylic groups and the cationic groups of basic dyes. As a result, pH 6 is
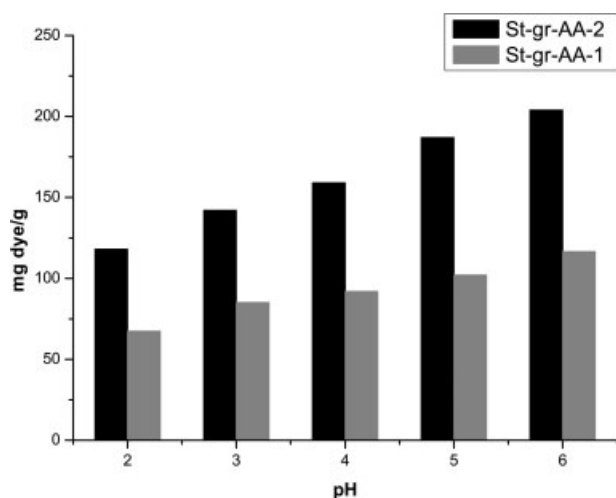

Figure 3 The effect of the pH on the adsorption of basic dye from aqueous solutions by St-*gr*-AA copolymers.
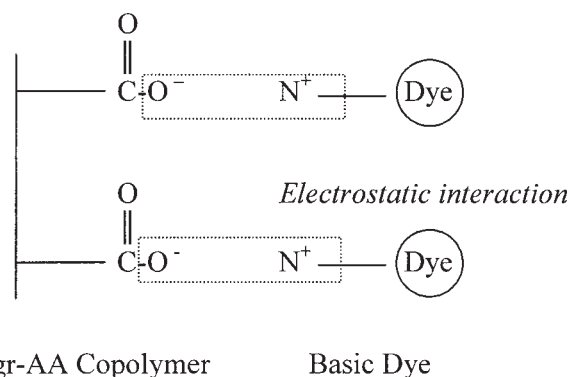
St-*gr*-AA Copolymer   Basic Dye

Figure 4 The interaction between the cationic groups of basic dye and carboxyl groups of St-*gr*-AA copolymers.

considered to be optimal pH value since the basic dyes become stable in the acidic mediums (pH < 7). Furthermore, the pH values of the basic dye effluents from the dyeing processes are below pH = 7.[46]

Effect of the treatment time

Figure 2 illustrates the effect of adsorption time on the adsorption efficiency. The adsorption capacities of copolymers for Safranine T increase with the increase in the adsorption time. The adsorption capacities of St-*gr*-AA-1 and St-*gr*-AA-2 copolymers reach about 116.5 and 204 mg/g, respectively.

Adsorption isotherms

In experiments of equilibrium adsorption isotherm, a fixed amount of 0.1 g adsorbents were contacted with 50 mL of aqueous solutions Safranine T with different concentrations (50–500 mg/L).

The equilibrium adsorption capacity, q_e (mg/g), was calculated in eq. (1).

$$q_e = \frac{(C_o - C_e)V}{W} \tag{1}$$

where C_o is the initial concentration (mg/L), C_e is the residual concentration at equilibrium (mg/L), V is the volume of solution (L), and W is the weight of the copolymer (g).

The Freundlich equations were used to fit the equilibrium isotherms. The Freundlich equation[47] is the earliest known relationship describing the adsorption equation. Freundlich isotherms were obtained by different initial dye concentrations (50–500 mg/L) and 0.1 g St-*gr*-AA copolymer dose for a constant time of 24 h. The adsorption isotherms data were correlated with the Freundlich equations and the Freundlich constants K_f (mg/g) and n (intensity

TABLE I
Freundlich Constants of Adsorption Isotherms

Copolymer samples	Freundlich constants		
	K_f	n	R^2
St-*gr*-AA-1	0.99	1.241	0.99599
St-*gr*-AA-2	1.35	1.129	0.99882

of adsorption) were calculated from the following equations:

$$q_e = K_f C_e^{1/n} \tag{2}$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{3}$$

where q_e is the amount of dye adsorbed (mg/g) onto St-*gr*-AA copolymers. The parameters of Freundlich isotherm, K_f and n as well as the correlation coefficients R^2 are given in Table I. Linear plots of log q_e vs. log C_e for the different initial dye concentrations illustrated that the adsorption follows the Freundlich isotherm (Fig. 5). Such conclusion can be drawn from data R^2 that the Freundlich adsorption law is applicable to be adsorption of Safranine T by St-*gr*-AA copolymers. The R^2 values were 0.99599 and 0.99882 for St-*gr*-AA-1 and St-*gr*-AA-2, respectively.

CONCLUSION

Adsorption properties of Safranine T (basic dye) on St-*gr*-AA copolymers were investigated. Adsorption properties of the adsorbent were evaluated depending on different adsorption conditions, such as different initial dye concentration, treatment time, pH, and GP% of starch graft copolymers. The isotherm data were fitted with Freundlich isotherm. The following conclusions can be drawn:
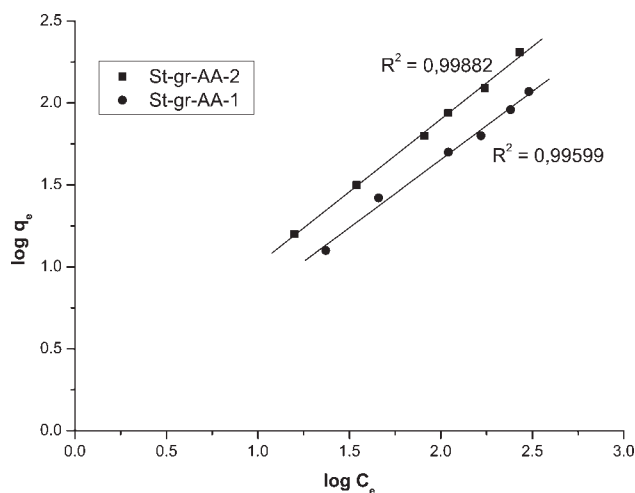
The adsorption capacities of St-*gr*-AA copolymers increase with the increase of the adsorption time.

- After 24 h, the adsorption capacities for St-*gr*-AA-1 and St-*gr*-AA-2 reach about 116.5 and 204 mg/g, respectively.
- The basic dye adsorption capacities of copolymers increased with the increasing pH. On increasing the pH, the carboxyl groups are ionized and increased the probability of interaction between the carboxylic groups and the cationic groups of basic dyes.
- Linear plots of log q_e vs. log C_e for the different initial dye concentrations illustrated that the adsorption follows the Freundlich isotherm. The R^2 values of Freundlich equations were 0.99599 and 0.99882 for St-*gr*-AA-1 and St-*gr*-AA-2, respectively.

Figure 5 Freundlich isotherm for the adsorption of basic dyes by St-*gr*-AA copolymers.

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