Study on Grafting of Acrylic Acid onto Cotton Using Gamma Radiation and its Application as Dye Adsorbent

N.C. Dafader*, N. Rahman and M.F. Alam

Nuclear and Radiation Chemistry Division, Institute of Nuclear Science & Technology, Bangladesh Atomic Energy Commission, P. O. Box 3787, Dhaka, Bangladesh

Abstract

Grafting of acrylic acid onto cotton has been performed with radiation processing technology using Co-60 gamma source. The parameters like the influence of radiation dose, acrylic acid concentration and solvent on degree of grafting has been investigated. The degree of grafting was found to depend on radiation dose, acrylic acid concentration and solvent. The maximum value of graft yield was obtained at 50 kGy radiation dose. Water was found to be a good solvent for grafting of acrylic acid onto cotton. The acrylic acid grafted cotton was applied to adsorb dye from aqueous medium. The dye adsorption was found to depend on concentration of dye in solution. The maximum value of dye adsorption capacity was calculated to be 16.86 mgg^{-1} of grafted cotton. The dye adsorption study shows that the experimental data fitted the Langmuir isotherm model and pseudo-second-order kinetic model.

Keywords: Acrylic acid, cotton, degree of grafting, dye, radiation

1. Introduction

Graft copolymerization is an effective method to modify the chemical and physical properties of polymeric materials. Grafting of polymer can provide some desirable properties such as ion-exchange [1], biocompatibility [2], thermosensitivity [3] etc. Graft copolymerization can be performed by some methods such as ionizing radiation, ultraviolet light, chemical initiator etc. Among these methods radiation grafting is a promizing method because of its penetration in the polymer matrix, resulting in rapid and uniform formation of active sites for initiating grafting throughout the matrix and it can effectively and conveniently carried out at room temperature. Ionizing radiation has provided a clean method of activating a polymer substrate. Radiation graft polymerization has also many advantages over other conventional methods, such as, chemical and photochemical grafting. For instance, the method is relatively simple and no catalyst is required to initiate the reaction.

The cotton fibre grows on the seed of a variety of plants of the genus *Gossypium*. Cotton is almost pure cellulose with softness and breath ability that have made it the world's most popular natural fibre. Cotton is mainly used as yarn or threads for preparation of cloth. Acrylic acid is a colourless liquid with the formula $CH_2{=}CHCO_2H$. It is the simplest unsaturated carboxylic acid, consisting of a vinyl group connected directly to a carboxylic acid terminus. It is miscible with water, alcohols, ethers, and chloroform. It is a monomer and easily polymerize to poly(acrylic acid). Acrylic acid has been grafted onto cotton fabric for improvement of dyeing and found that the color strength of acrylic acid grafted cotton fabric increases with increased graft yield [4]. The colour strength of grafted fabrics increases rapidly with increased dyeing time and level off within few minutes, depending on dye concentration and temperature of dye bath. The antibiotic drug gentamicin sulfate loaded acrylic acid grafted cotton fibers showed fair antibacterial action against *Escherichia coli* [5]. Swelling percentage of 2-hydroxy ethyl methacrylate (HEMA) grafted cotton shows nearly 3 times higher than that of ungrafted cotton fiber. The HEMA grafted cotton fibers also show higher wet rubbing fastness and washing fastness than that of ungrafted cotton fibers [6].

Dyes are complex organic compound used as color in textiles, leather, paper, plastic and other materials. Dye mixed wastewater from different industries pollutes the natural environment. They are firm and difficult to biodegrade; therefore dye in water as a major environmental problem. The common techniques for removal of dyes from industrial effluents include adsorption, coagulation, flocculation, oxidation, precipitation, ozonation, filtration and electrochemical processes etc. Polymeric hydrogels like Poly (vinylpyrrolidone)/ acrylic acid [7], Poly (vinyl alcohol)/ kappa-carrageenan [8] and polysaccharide based materials [9] have reported to absorb dye from aqueous medium.

In this experiment, the grafting of acrylic acid onto cotton thread was performed by irradiation method. The effect of radiation dose, acrylic acid concentration and solvent on the grafting yield was determined. The adsorption of dye from aqueous medium was studied and Langmuir isotherm model was used to interpret the adsorption data. The pseudo-first-order and pseudo-second-order models were used to analyze adsorption kinetic.

2. Material and Method

2.1 Raw materials

Cotton thread was collected from local market. Sodium hydroxide, acetone and Mohr Salt obtained from BDH England was purchased. Acrylic acid and methanol obtained from Merck India were used as received. The Methylene blue (MB), C.I number 52015, was obtained from Merck, Germany. Chemical formula of MB is $C_{16}H_{18}CN_3S$; molecular weight and λ_{max} are 319.9 and 665 nm respectively.

*Corresponding author: nirmaldafader@yahoo.com

2.2 Grafting procedure

Cotton thread was treated with ethanol in the soxhlet apparatus for 5 h and then immersed in 1% NaOH solution and boiled for 3h [10]. Treated cotton was washed in distilled water until it becomes neutral. Then it was dried in air and finally it was dried in an oven to constant weight. The cotton was taken in several glass test tubes containing 3, 5, 7 and 10% (v/v) acrylic acid in water with 0.0125M Morh's salt. The test tubes were sealed in polyethylene bag and irradiated from Co-60 gamma source at total radiation dose of 20, 30, 40, 50 and 60 kGy with dose rate 3.5 kGy/h. After irradiation grafted cotton was treated in methanol for 24 h at 50ºC temperature in water bath. Then it was washed in distilled water, dried in air and in an oven to constant weight. The degree of grafting was calculated as follows

$$\text{Degree of grafting [\%]} = [(W_g – W_0)/W_0] \times 100$$

Where, W_0 and W_g are the dry weights of cotton samples before and after grafting, respectively.

2.3 Determination of dye adsorption

The dry acrylic acid grafted cotton (AAc-g-cotton) sample was immersed in aqueous solution of dye at room temperature (27°C) and periodically the residual concentration of dye in the feed solution was determined spectrophotometrically (UV-2401PC, Shimadzu, Japan). The amount of dye adsorption per unit mass of AAc-g-cotton was evaluated by using the following equation (1)

$$Q_e = [(C_0 – C_e) \times V]/W \quad (1)$$

Where, Q_e is the amount of dye adsorbed per unit dry mass of AAc-g-cotton (mg/g), C_0 and C_e are the concentration of dye in the initial solution and aqueous phase after treatment with AAc-g-cotton sample of certain period respectively (mg/L), V is the volume of aqueous phase in liter (L) and W is the weight of dry grafted cotton (g).

3. Results and Discission

Fig. 1 shows the effect of radiation dose as well as acrylic acid (AAc) concentration on degree of grafting of AAc onto cotton. The degree of grafting increases with increased radiation dose and attained a maximum value at the radiation dose of 50 kGy. This result may be the cause of action of radiation, free radical of cotton and monomer are obtained and interaction between cotton cellulose free radicals and monomer free radicals the graft copolymer is obtained. Increase in radiation dose more free radicals on cotton and AAc are obtained and increases degree of grafting. The value of degree of grafting also increases with increased acrylic acid concentration. The value of degree of grafting is ~68%, 87%, 122% and 126% at 50 kGy radiation dose for 3%, 5%, 7% and 10% concentration of AAc respectively. This result can be explained as increase in monomer concentration more free radical of monomer are obtained and can easily interact with cotton cellulose.

Solvent plays a significant role on reaction rates and order of chemical reaction [11]. In this investigation, water, 50% ethanol and 95% ethanol were used as solvents and concentration of AAc was kept 10%. Fig. 2 shows the effect of solvent on grafting of AAc onto cotton at different radiation dose (20, 30, 40, 50 and 60 kGy). It is found that

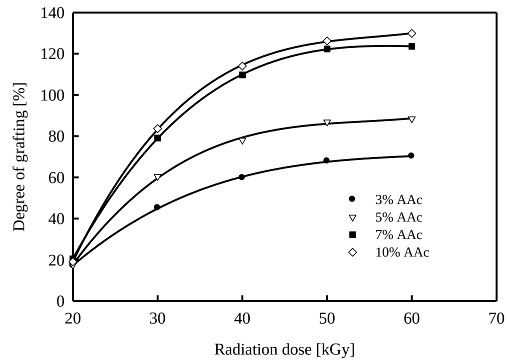

Fig. 1. Effect of radiation dose and concentration of AAc on grafting yield of cotton [Morh's salt = 0.0125M].

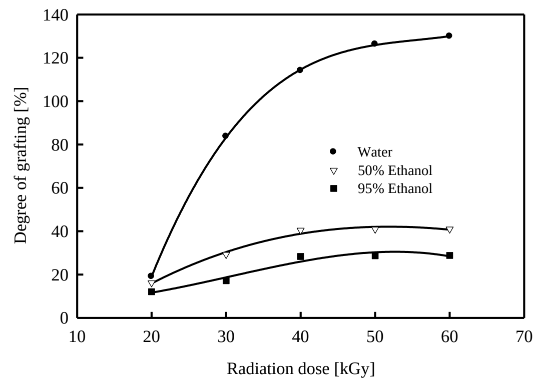

Fig. 2. Effect of solvent on degree of grafting of AAc onto cotton at various radiation dose [Morh's salt = 0.0125 M].

the highest value of graft yield is obtained from aqueous solution of AAc and lowest value of graft yield is obtained from ethanolic solution of AAc. The degree of grafting is obtained ~126%, ~48% and ~29% at 50 kGy radiation dose from water, 50% ethanol and 95% ethanol respectively. It can be explained as in water, cotton cellulose may be more swelled in aqueous medium as a result monomer can easily penetrate into cotton than that of 50% ethanol and 95% ethanol.

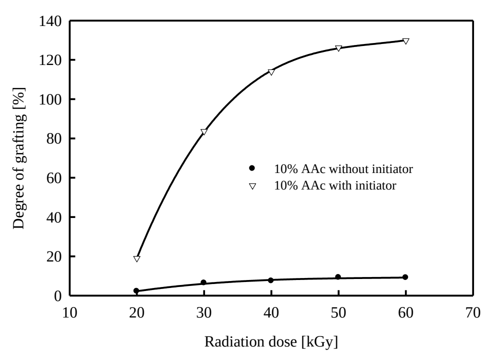

Fig. 3. Effect of additive on degree of grafting of AAc onto cotton [Mohr's salt = 0.0125 M].

Additive has a significant effect on grafting of monomer onto polymer. Additive can accelerate the rate of reaction e.g., in grafting, it increases grafting yield and reduces homopolymerization [12-13]. The addition of metallic salts as additive to the reaction mixture can suppress the formation of homopolymer, thus monomer free radical can take part in grafting reaction and facilitating the isolation of the resulting copolymer [14]. In this investigation, 10% aqueous solution of AAc was used as monomer without and with Mohr salt (0.0125 M) as additive shown in Fig. 3. It is observed that the degree of grafting is obtained ~9% without additive and with additive degree of grafting is obtained ~126% at 50 kGy radiation dose.

Fig. 4 shows the effect of standing time of AAc-g-cotton in dye solution on adsorption of dye. Adsorption of dye increases with increased standing period of AAc-g-cotton in dye solution and attained maximum values at 6 h. An ion-ion interaction may be formed between the cationic group of cationic dye and the anionic group (COOH) of AAc-g-cotton. It is also found that dye adsorption increases with increased concentration of dye in aqueous solution. The maximum value of dye (~16 mg/g of AAc-g-cotton) is adsorbed from 50 mg/L dye solution. This result can be explained as with the increased concentration of dye in solution more dye molecules may be interacted with free ionic group of AAc-g-cotton.

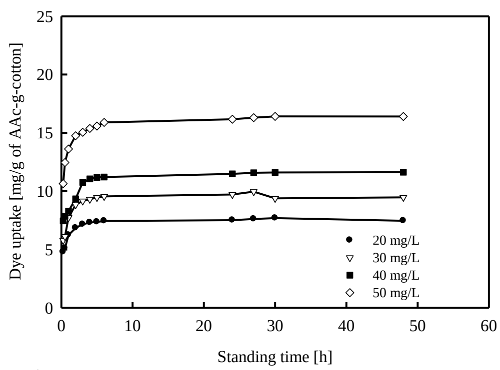

Fig. 4. Effect of standing time and concentration of dye on adsorbtion of dye by AAc-g-cotton. [Radiation dose = 50 kGy]

Adsorption kinetics of AAc-g-cotton can be analyzed by pseudo-first order model and the pseudo-second order model which are expressed by following equations (2 & 3)

$$\ln (q_e - q_t) = \ln q_e - k_1 t \text{ -----------------------------(2)}$$

$$t/q_t = 1/(k_2 q_e^2) + t/q_e \text{ ------------------------------(3)}$$

Where q_e and q_t (mg/g) are the amount of adsorbed dye at equilibrium and time of t (min.) respectively; k_1 (min^{-1}) is the pseudo-first-order rate constant and k_2 is the (g/mg min) pseudo-second-order rate constant.

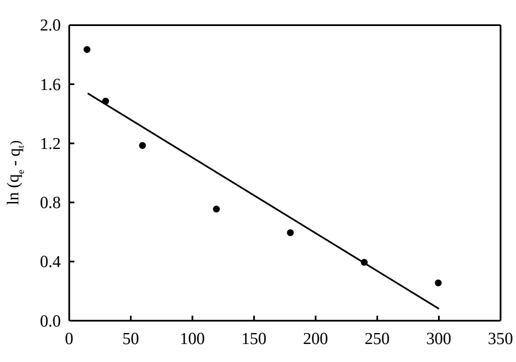

Fig. 5. Pseudo-First order plot for dye (MB) adsorption.

The pseudo-first-order and the pseudo-second-order plots are shown in Figs. 5 and 6, respectively. The values of correlation coefficients (R^2) are 0.9015 and 0.9998 for pseudo-first-order model and pseudo-second-order model respectively. The correlation coefficient value of the pseudo-second-order kinetics model is higher than that of the pseudo-first-order kinetics model and indicates that data are well fitted to the pseudo-second-order kinetics model and the adsorption is controlled by chemical process. In chemical adsorption, it is assumed that the adsorption capacity is proportional to the number of active sites of the adsorbent [15].

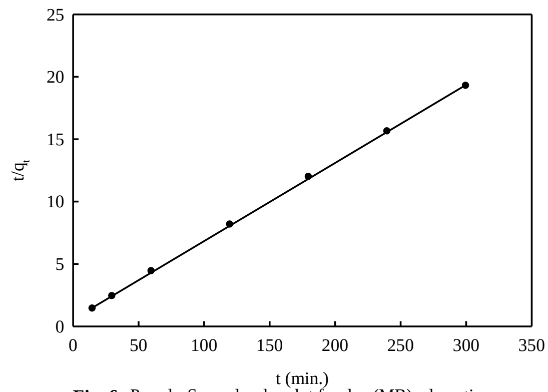

Fig. 6. Pseudo-Second order plot for dye (MB) adsorption.

Adsorption isotherm can be used to investigate the interaction of dye with AAc-g-cotton. It is characterized by certain constants. The Langmuir isotherm models can be used to study the relationship between dye uptake and equilibrium concentration and is effective for homogeneous and monolayer adsorption onto a surface with a finite number of identical sites. It is defined as following equation (4)

$$C_e/q_e = C_e/q_m + 1/K_L q_m \text{ -----------------------------(4)}$$

Where C_e (mg L^{-1}) is the equilibrium concentration of dye in solution, q_m (mg g^{-1}) is the theoretical maximum adsorption capacity, q_e (mg g^{-1}) is the amount of dye adsorbed by per gram AAc-g-cotton, K_L is Langmuir constant related to the affinity of binding sites, which is a measure of the energy of adsorption. q_m and K_L were calculated from slope and intercept of the linear plot of C_e/q_e versus C_e respectively.

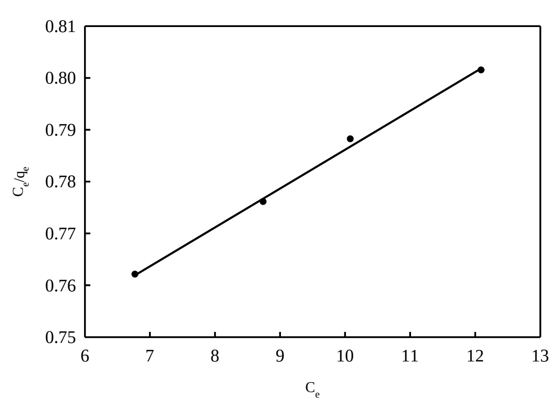

Fig. 7. Linear form of Langmuir isotherm for dye (MB) removal.

The Langmuir plot of dye adsorption onto AAc-g-cotton is shown in Fig. 7. The linear correlation coefficient (r) is 0.995, which reveals that the adsorption data is well fitted the Langmuir model. The isotherm constants q_m and K_L are calculated as 16.86 mg g^{-1} and 0.711 respectively. The experimental dye uptake is slight lower than the theoretical maximum adsorption capacity. It may be attributed to the incomplete contact of dye and the AAc-g-cotton.

4. Conclusion

Grafting of acrylic acid onto cotton can be performed by irradiation from cobalt-60 gamma source at room temperature (27°C). In respect to degree of grafting, 50 kGy radiation dose can be considered as a suitable radiation dose for the preparation of acrylic acid grafted cotton (AAc-g-cotton). For grafting of acrylic acid on to cotton, water can be considered as good solvent. The dye adsorption capacity of AAc-g-cotton is reached ca. 16.89 mg/g at room temperature (27°C). The Langmuir isotherm model and adsorption kinetic (pseudo-first-order model and pseudo-second-order model) were investigated. The experimental data fitted Langmuir isotherm model and pseudo-second-order model. Primarily the result indicates that AAc-g-cotton can be used to adsorb dye from aqueous medium.

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