Dye adsorbent prepared by radiation-induced graft polymerization of acrylic acid onto carboxymethyl cellulose

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Abstract. Gamma radiation was used to prepare a natural polymer-based adsorbent via radiation-induced grafting polymerization of acrylic acid (AA) onto carboxymethyl cellulose (CMC). Optimization of the grafting process was done by varying a number of parameters from radiation dose to amount of AA and CMC. Characterization by Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA) confirmed a successful grafting of AA onto CMC, with a maximum grafting efficiency (GE) of 94%. The effectiveness of the graft copolymers for the removal of two standard dyes, malachite green and methyl green, was investigated. The prepared PAA-g-CMC adsorbents resulted in more than 80% of dye removal for malachite green and methyl green, displaying its great capacity to be utilized as an alternative material for wastewater treatment.

1. Introduction

As one of the top grossing industries in Thailand, textile industry plays quite an important role for Thailand’s economy. The growth of textile industry hence has big impacts on the environments, mainly due to the release and contamination of residual dyes into the public water systems. Dyes commonly used in the textile industry are compounds containing aromatic amine groups. These compounds are generally very difficult to degrade, toxic and possibly carcinogenic. Different methods are available for the removal of dyes from wastewater, such as sorption, flocculation, oxidation and electrolysis [1]. Among them, adsorption has been proved as an effective and efficient method to transfer dyes from the effluent to a solid phase [2]. Activated carbon is one of the most common adsorbents that have been used for dye adsorption. However, there are a number of factors, especially high cost, that result in limitation of its application. Recently, natural polymers, such as starch, cellulose, chitosan and lignin, have been receiving growing attention as an alternative material for adsorbent, essentially due to the fact that they are inexpensive, biodegradable and non-toxic.

Cellulose is the most abundant natural polymer on earth. It is insoluble in water and most organic solvents. Unlike starch, cellulose is highly crystalline, making it structure compact and inactive. A number of methods, including carboxymethylization, have been utilized to chemically modify cellulose to expand its applications. One of the most important commercial cellulose derivatives is carboxymethyl cellulose (CMC). With the presence of carboxymethyl groups in its chemical structure, CMC is soluble in water and able to find its place in a large number of applications, from food to pharmaceutical industry. In recent times, further modification of CMC by grafting with vinyl monomers has been
gaining considerable attention, not only to eliminate a number of limitations but also to incorporate new functionalities [3-5].

Traditionally, grafting polymerization can be induced by thermal method, in the presence of chemical initiators. Nonetheless, nowadays, radiation has been emerging as an extremely convenient technique that can be used to induce grafting polymerization. Radiation technology offers a number of advantages over other conventional methods. For examples, using radiation, reactions can be done at room temperature without the use of chemical initiators. As a result, radiation-induced graft polymerization (RIGP) has been proved to be a powerful method with high potential for the modification of polymeric materials [6-12].

The main objective of this study is to transform CMC into a dye adsorbent for environmental application by radiation-induced grafting polymerization of AA onto CMC. Grafting polymerizations were investigated using different parameters, such as radiation dose, amount of AA and amount of CMC. The prepared dye adsorbents were characterized by FTIR and TGA. The efficiency of adsorbents, in terms of dye removal, was analyzed using two standard dyes: malachite green and methyl green.

2. Materials and Methods

2.1. Materials

Sodium carboxymethyl cellulose (NaCMC, degree of substitution = 0.90, average molecular weight = 250,000 g/mol) was purchased from Aldrich (USA). Acrylic acid was acquired from BASF Petronas Chemicals (Malaysia). Poly (acrylic acid) (MW = 750,000 g/mol) was obtained from Sigma-Aldrich (USA). Malachite green was procured from DC Fine Chemicals Ltd. (England), while methyl green was supplied by Merck (USA). All chemicals were analytical grade and used as received. Preparation of all solutions was done using deionized water.

2.2. Preparation of dye adsorbent (PAA-g-CMC) by radiation-induced grafting polymerization

3 g of CMC was dissolved in 30 mL of deionized water. The mixture was stirred until CMC was completely dissolved. 10 mL of AA was then added to the mixture. After 30 min of stirring, the mixture was neutralized to pH 7, using NaOH solution. After another 30 min of stirring, the mixture was irradiated using a Co-60 gamma irradiator (Gamma Chamber 5000, BRIT, India) at different doses (5, 10, 15, 20, 25 and 30 kGy). After irradiation, the prepared adsorbents were purified by solvent extraction method to remove poly (acrylic acid) (PAA) homopolymer from the adsorbent. The purification was done using a Soxhlet extractor, with water as a solvent, for 12 h. After the purification, the samples were dried, to a constant weight, in an air oven at 60 °C. Grafting efficiency was calculated from equation (1):

\[
\% \text{ Grafting efficiency (GE)} = \frac{\text{weight of adsorbent after solvent extraction}}{\text{weight of adsorbent before solvent extraction}} \times 100 \tag{1}
\]

For a further study for the effects of the amount of AA, experiments were done similarly, except that radiation dose was fixed at 20 kGy and different amounts of AA (5, 10, 15, 20 and 25 mL) were used. As for the effects of the amount of CMC, the radiation dose was fixed at 20 kGy and the amount of AA was fixed at 15 mL, while different amounts of CMC (1, 2, 2.5, 3 and 3.5 g) were used.

2.3. Characterization of PAA-g-CMC adsorbent

2.3.1. Fourier transform infrared spectroscopy (FTIR). Infrared spectra of samples were obtained using a Fourier transform infrared spectrometer (Tensor 27, Bruker, Germany). FTIR spectra were obtained within the range of 650 - 4000 cm\(^{-1}\) in reflection mode using an attenuated total reflection (ATR) accessory equipped with ZnSe crystal. 16 co-added scans were collected with a resolution of 4 cm\(^{-1}\).

2.3.2. Thermogravimetric analysis (TGA). Thermal decomposition of samples were analyzed using TGA. A TGA from Mettler Toledo (Thailand), TGA/DSC 2 LF/1100, was used for thermogravimetric
analysis. All experiments were performed under nitrogen purge, with a flow rate of 90 mL/min. A heating rate of 20°C/min from 36 to 80°C was used for all experiments.

2.4. Adsorption studies of PAA-g-CMC adsorbent
Effects of different factors (dye concentration, temperature and pH) on dye adsorption of the prepared adsorbents were analyzed. For the study of dye concentration effect, experiments were performed in 100 mL of dyes solution with 20 mg of dye adsorbents. The solutions were stirred at 120 rpm at room temperature for 60 min. After the equilibrium, the suspensions were centrifuged at 10,000 rpm for 5 min, after which the precipitated adsorbents were removed. The final concentration of dyes in the remaining solutions was analyzed using a UV spectrophotometer. Absorbance measurements were performed at the wavelength of 617 and 633 nm for malachite green and methyl green, respectively. For the studies of temperature and pH effects, experiments were done the same way, except that the dye concentration was fixed, while the temperature and pH were varied, accordingly. The dye removal (R) and adsorption capacity (q) of PAA-g-CMC dye adsorbents were calculated by the following equations:

\[
R = \left(1 - \frac{C_t}{C_0}\right) \times 100\%
\]

\[
q_t = \left(\frac{C_0 - C_t}{M}\right) \times V
\]

Where \(C_0\) and \(C_t\) are the initial and residual concentration of dyes in the suspension (mg/L), respectively. \(V\) is the volume of the solution (L) and \(M\) is the amount of the dye adsorbent (g).

2.5. Measurements of zeta potential and point of zero charge (PZC) of PAA-g-CMC adsorbents
0.25 g of dye adsorbents were added to 100 mL of deionized water. The solutions were stirred at 120 rpm, using a shaking water bath equipped with temperature controller. After 24 h, the adsorbents were removed. The remaining solutions were adjusted to different pH, using 0.1 M of either HCl or NaOH. The zeta potential was measured using a Zetasizer Nano ZS (Malvern Instruments Ltd., UK).

3. Results and discussion
3.1. Effects of different parameters on grafting efficiency
Figure 1 show the effects of radiation dose, amount of AA and amount of CMC on GE of PAA-g-CMC adsorbents. From Figure 1, it is obvious that GE initially increased with increasing radiation dose. This stems from the fact that increasing dose leads to a growing number of free radicals, i.e. active grafting sites, on CMC. With more free radicals available on CMC, AA free radicals thus have a much higher chance to undergo grafting reaction, hence resulting in better GE. GE reached maximum value of 94.81% at 20 kGy of gamma irradiation. However, at the radiation dose higher than 20 kGy, GE seems to drop, possibly due to the breakage at glycosidic linkages of CMC structure by ionizing radiation [13, 14].

As for the effects of amount of AA on GE, Figure 1 also clearly displays that GE initially increased as AA went up. This is mainly due to a higher number of AA free radicals generated at larger amount of AA, which results in higher possibility for grafting polymerization. A high value of GE at 94.80% was obtained at 15 mL of AA, after which GE tends to level off. This is potentially due to the limited number of active sites on CMC backbone. As for the effects of the amount of CMC on GE, it can be seen from Figure 1 that the amount of CMC had very little effects on GE. At different amount of CMC, GE remained basically constant at 95%.
3.2. Characterization of PAA-g-CMC adsorbents

3.2.1. Fourier transform infrared spectroscopy (FTIR). Figure 2 shows the FTIR spectra of CMC, PAA and PAA-g-CMC adsorbent. The peaks at 1593,1269 and 1045 cm\(^{-1}\) in the FTIR spectrum of the original CMC indicate the presence of COO\(^-\) (unsymmetrical stretching), C-O-C (unsymmetrical stretching) and C-O (stretching), respectively, while peaks at 1409 and 1326 cm\(^{-1}\) imply the presence of COO\(^-\) (symmetrical stretching). For PAA, major peaks at 2949, 1695, 1446 and 1417 cm\(^{-1}\) are assigned to \(-\text{CH}_2\) (stretching and bending), \(-\text{COO} (\text{stretching in } \text{-COOH})\) and C-O (stretching in \text{-COOH}), respectively. For PAA-g-CMC adsorbent, peaks at 1699,1566, 1460 and 1411 cm\(^{-1}\) are assigned to the following functional groups, C=O (symmetrical stretching) of carboxylic acid, \(-\text{COO} (\text{unsymmetrical stretching})\), C-H bending and \(-\text{COO} (\text{symmetrical stretching}), \text{in that order. The presence of } \text{-COOH} \text{ in the FTIR spectrum of PAA-g-CMC adsorbent confirmed a successful grafting of AA onto CMC.}

3.2.2. Thermogravimetric analysis (TGA). Figure 3 shows TGA and first derivative (dTGA) thermograms of CMC, PAA and PAA-g-CMC adsorbent. From both TGA and dTGA thermograms, CMC showed a three-stage weight loss process, with the major decomposition profile (2\(^{nd}\) process) centered at about 305 °C. PAA also displayed a three-stage weight loss process. However, the profile is different from that of CMC. For PAA, the highest rate of weight loss took place at roughly 430 °C. TGA and dTGA thermograms of PAA-g-CMC adsorbent illustrated a multiple-stage weight loss process, with the first major degradation process (290 °C) corresponding to the one seen in CMC and the second major decomposition step (470 °C) matching that of PAA. At 800 °C, the char yield of CMC, PAA and PAA-g-CMC adsorbent was approximately 30, 9 and 45%, respectively. These results displayed different thermal decomposition profile of the three samples, while simultaneously verified the presence of PAA.
in the structure of PAA-g-CMC adsorbent, which in turn confirmed the successful grafting of PAA onto CMC.

![Figure 3. TGA (a) and dTGA (b) thermograms of CMC, PAA and PAA-g-CMC.](image)

### 3.3. Adsorption studies of PAA-g-CMC adsorbent

Figure 4 shows the effects of initial dye concentration on dye removal (%) and adsorption capacity (mg/g) of the adsorbents, for malachite green and methyl green, respectively.

![Figure 4. Effects of initial dye concentration on dye removal (column) and adsorption capacity (line) of PAA-g-CMC adsorbent on malachite green (a) and methyl green (b).](image)

It can be seen that, initially, both dye removal and adsorption capacity increased with increasing dye concentration. This can be explained from the fact that at low concentration of dyes, the amount of adsorbent surfaces available for adsorption is still high, making it easier for dyes to be adsorbed, hence resulting in high dye removal and adsorption capacity. The maximum value for dye removal of malachite green and methyl green was 76% and 92%, at dye concentration of 30 and 120 mg/L, respectively. At higher dye concentration, both dye removal and adsorption capacity tended to be decreasing, most likely due to the saturation of the adsorbent surfaces.

The effects of temperature and pH on dye removal of the adsorbent on both types of dye are shown in Figure 5. Dye removal seems to increase with rising temperature. With increasing temperatures, adsorbents swell more, hence resulting in a better permeation of dyes. Also, higher temperatures enhance the mobility of dye ions [1, 15]. The changes in the pH of dyes solution affect the surface charges by protonation and/or deprotonation of the adsorbents [16]. The experiments were done by adjusting pH from 4 to 10. Figure 5 displays the effects of pH on dye removal at the dye concentration of 30 and 120 mg/L and temperature of 30 and 40 °C, for malachite green and methyl green, respectively. Figure 6 shows the physical appearances of absorbents before and after immersion in both types of dye solutions, the maximum dye removal for malachite green and methyl green was at roughly 83 and 88% at pH 7 and 5, in that order.
Figure 5. Effects of temperature (a) and pH (b) on dye removal of PAA-g-CMC adsorbent on malachite green and methyl green.

Figure 6. Physical appearances of PAA-g-CMC adsorbent before and after immersion in malachite green (a) and methyl green (b).

Figure 7. Effect of pH on zeta potential and PZC of PAA-g-CMC adsorbent.

The zeta potential as a function of pH is shown in Figure 6. The point of zero charge (PZC) of the adsorbents was found using a linear fit. It can be seen that, in the neutral aqueous solution (pH 7), the zeta potential of PAA-g-CMC adsorbent is -66.2. Figure 6 also displays that PZC for PAA-g-CMC adsorbent is 2.84. This means that at pH below 2.84, surface of the adsorbent is protonated and positively charged. The positively charged adsorbent thus has a better adsorption for anionic dyes. Conversely, at
pH above 2.84, the adsorbent will be negatively charged and hence has a better adsorption for cationic dyes. These results clearly explain why the dye removal of PAA-g-CMC adsorbent on malachite green and methyl green tends to increase with pH. This is principally due to the fact that both dyes are cationic [16, 17].

4. Conclusion
Dye adsorbents were successfully prepared by radiation-induced grafting polymerization of acrylic acid onto carboxymethyl cellulose, as confirmed by the FTIR and TGA results. The maximum grafting efficiency achieved was approximately 94%. From the adsorption studies of the prepared PAA-g-CMC adsorbent on malachite green and methyl green, both of which are cationic dyes, results have shown that the synthesized adsorbents offered the maximum dye removal at 81% (at 40 °C and pH 7) for malachite green and at 88% (at 30°C and pH 5) for methyl green. These results show that the PAA-g-CMC adsorbents have high potential to be utilized as an alternative material for wastewater treatment.

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