Synthesis and Characterization of Radiation Grafted Copolymer for Removal of Nonionic Organic Contaminants

H. H. Sokker,[1] A. M. Abdel Ghaffar,[1] A. M. A. Nada[2]

[1]*National Center for Radiation Research and Technology, Nasr City, Cairo, Egypt 11731*
[2]*Cellulose and Paper Department, National Research Center, Dokki, Cairo, Egypt*

ABSTRACT: Nonionic organic contaminants such as phenol, benzene, and toluene from contaminated wastewater on laboratory scale can be effectively sorbed by cellulosic wood pulp sheet incorporated with three polar functional groups. The synthesis was carried out by graft copolymerization reaction of *N,N*-dimethylaminoethylmethacrylate with methacrylic acid onto wood pulp. The preparation conditions at which the grafting process proceeds homogeneously are determined. Characterization and some selected properties of the original and grafted wood pulp were evaluated using FTIR and scanning electron microscope, also, the removal of phenol, benzene, and toluene on laboratory scale was investigated by using gas chromatography. It was found that phenol shows the highest removal percent than that of benzene and toluene. The efficiency of removal of the nonionic contaminants is found to be 97%, which shows a great promise for its applicability in the removal of organic contaminates from wastewater. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 3589–3595, 2006

Key words: radiation; copolymerization; nonionic organic contaminants; adsorption

INTRODUCTION

Removal of organic pollutants from contaminated wastewater and ground water is critical to ensuring the safety of water supplies worldwide. Because these contaminants are often flammable, toxic, and/or carcinogenic, their presence in drinking water sources is of major environmental concern. Benzene is known to be carcinogenic with long-term exposure resulting in nonlymphocytic leukemia.[1] Phenol rank among undesirable pollutants and therefore serious attention has been devoted to their removal from water and other media.[2] Environmental protection Agency (EPA), USA, has defined significant pollutant parameters for the petroleum refining industry,[3] such as oil and grease, phenolic compounds, sulfides, etc. EPA considered 65 compounds as potentially toxic compounds.

The major water contaminants from oil in the order of importance are sulfide, dissolved phenols, and nitrogen compounds.[4] This study is focused on developing effective and modified adsorbent available for the removal of nonionic organic contaminants (NOCs) such as phenol, benzene, and toluene, which are the major components of the wastewater from petroleum refiners.[5]

Copolymers of dimethylaminoethylmethacrylate (DMAEMA) with methacrylic acid (MAAc) received much attention.[6–9] The graft copolymer containing polyelectrolyte blocks is easily produced by copolymerization of DMAEMA and MAAc. Gamma radiation as initiator serves not only for the polymerization of MAAc that has one polar functional group[10] but also for the polymerization of DMAEMA that has two polar functional groups.[11]

In this study, radiation and characterization of DMAEMA/MAAc grafted onto wood pulp were investigated. The grafted wood pulp was prepared by irradiation of binary monomer mixture, using gamma rays at ambient temperature. Water is used as a solvent to provide the homogenous polymerization. The influence of radiation dose and comonomer composition were investigated, and the application of the grafted wood pulp for the removal of NOCs from contaminated wastewater is also evaluated.

EXPERIMENTAL

Materials

Reagent grade dimethylaminoethylmethacrylate (DMAEMA) of purity 99.9% was supplied by Fluka (Germany); methacrylic acid (MAAc) of purity 98.9% was supplied by Merck (Germany). Other chemicals,

such as phenols, benzene, and toluene, were reagent grade. Paper grade wood pulp (bleached sulfate pulp) was supplied by Cellulose and Paper Department, National Research Center (Egypt), with composition of α-cellulose (87%), hemicellulose (12%), and ash (0.5%).

Grafting method

The direct radiation grafting method was used as a technique in which the polymer and monomers solution was subjected to radiation. Wood pulp with definite weight was immersed in glass ampoule containing the comonomer solution, then sealed and subjected to ^{60}Co-γ-rays at different radiation doses 5,10,and 15 kGy. The grafted wood pulp was washed thoroughly with hot distilled water and soaked overnight in bidistilled water to extract the residual monomer and the homopolymer. The grafted wood pulp was then dried in a vacuum oven at 50°C for 24 h and weighed. The degree of grafting was determined by the percentage increase in weight as follows:

$$\text{Degree of grafting (\%)} = \frac{W_g - W_0}{W_0} \times 100$$

where W_g and W_o represent the weight of grafted and wood pulp, respectively.

Scanning electron microscopy

The surface topography of the original and grafted wood pulp was studied using JEOL SEM-25 (Japan). Before the examination, the cellulosic materials were dried and coated with gold under sputter.

Fourier transform infrared

The molecular structure of grafting and grafted wood pulp was studied using Mattson 1000 FTIR spectrophotometer, product of Unicam (England).

Gas chromatography analysis

Hewlett Packard 5890 gas chromatograph with an HP, 30-m capillary column, injector, 200°C oven, 60°C isotherm, FID 200°C, and nitrogen as carrier gas flowing at a rate of 20 mL min^{-1}, was used for analysis of the sample. The investigated samples were introduced in microquantity (1.2×10^{-3} cm^3) by the aid of microsyringe in the form of pulse into the instrument. The reaction was transferred directly by inert gas (nitrogen) to the gas chromatograph.

Swelling measurement

The water uptake of the known weight of original and grafted wood pulp was measured by immersing the samples in distilled water for 24 h. After whipping with filter paper, the samples were weighed as quickly as possible. The water uptake percent was calculated from the following equation:

$$\text{Water uptake (\%)} = \frac{W_s - W_g}{W_g} \times 100$$

where W_g and W_s are the weights of dry and wet original and grafted wood pulp, respectively.

Adsorption of phenol, benzene, and toluene

The ability of original and grafted wood pulp to adsorb phenol, benzene, and toluene was investigated in batch wise condition. The adsorbent (0.1 g) was added to 100-mL ethanol solution containing 500-ppm phenol, benzene, and toluene. The suspension was left at 25°C for 24 h. Samples are taken from the solution after 24 h and the residual concentration of phenol, benzene, and toluene in the solution were determined by gas chromatography.

The amount of phenol, benzene, and toluene captured by the absorbent was calculated from the difference between the initial and final concentration of the nonionic organic contaminants (NOCs) in feed solution as follows:

$$\text{NOCs uptake (\%)} = \frac{C_i - C_f}{C_i} \times 100$$

where C_i and C_f represent the initial and final concentration of the NOCs, respectively.

RESULTS AND DISCUSSION

Functionalized polymers based on cellulosic materials have several advantages over the usual synthetic polymer materials because of high hydrophilicity, sorption capacity, and fibrous structure of cellulosic materials, as compared to synthetic polymer.[12] It is not easy to introduce directly the functional group into stable cellulosic wood pulp without a change in the favorable properties of cellulose, because the hydroxyl groups in cellulose are not reactive enough as a result of hydrogen bonding. The grafting approach presents a means for modifying the cellulose through the creation of branches, which impart to cellulose certain desirable properties in addition to its favorable properties. The properties of the grafted wood pulp will be determined by the nature of both cellulose and monomer or polymer, which is grafted onto the cellulose backbone.
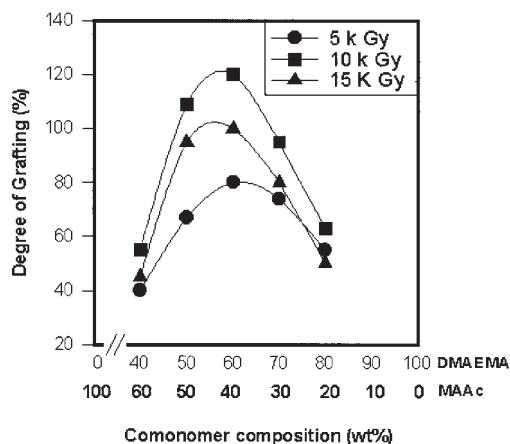
Figure 1 Effect of irradiation dose on the degree of grafting (%) at ambient temperature.

Grafting by irradiation is one of the most successful grafting methods and has been applied to a large number of polymer–monomer systems. The mutual irradiation grafting is the most efficient method of grafting, since, the radicals can react as fast as they are produced.[13] The mutual irradiation technique involves irradiation the wood pulp in the monomer solution with gamma radiation. This results in radical formation on the cellulose chain; the sites of radial formation become the points of initiation for the side chains. At the same time, radiation-induced graft polymerization and homopolymer were obtained. The graft wood pulp was then extensively washed to remove the homopolymer and the unreacted monomer.

Many factors affect the radiation grafting process of binary monomer mixture. Among them, investigated here are comonomer composition and total exposure dose. The effects of these factors are considered and determined from the viewpoint of obtaining reasonable grafting yields with homogenous distribution in the graft copolymer. Meanwhile, the inhibition of homopolymer formation during radiation grafting process is also taken into consideration.

Effect of comonomer composition

The grafting of DMAEMA/MAAc binary monomer mixtures of various relative composition onto wood pulp is investigated at comonomer concentration of 40 wt % in water as a diluent. Figure 1 shows the effect of comonomer composition on the degree of grafting of DMAEMA/MAAc binary mixture onto wood pulp in the presence of distilled water as a diluent for this mixture. It is obvious that, for DMAEMA/MAAc binary mixture, the grafting yield increases with increasing the content of MAAc in comonomer feed solution to reach maximum value at 60/40 wt % of DMAEMA/MAAc comonomer composition. Therefore, at high

contents of MAAc, the degree of grafting falls down to reach a lower value at 20/80 wt % of DMAEMA/MAAc comonomer composition, where a dense-gelled homopolymer is formed, which restrict the diffusion of the comonomer into the interior part of the polymer to initiate new grafting site[14] and thus, retard the grafting process.

The experimental results show that the reactivity ratio of DMAEMA and MAAc was 0.9 and 0.98, respectively. According to these results, it is very clear that:

a. The present poly(DMAEMA-co-MAAc) can be depicted as a random copolymer.
b. The present poly(DMAEMA-co-MAAc) can be depicted as diblock copolymer, which probably composed of PMAAc mixed with some DMAEMA units, or of DMAEMA sequence formed after consumption of MAAc.[15]

Effect of irradiation dose

As this graft copolymerization is initiated by the ^{60}Co gamma irradiation in which the process is mainly a free radical mechanism. Therefore, the grafting is governed by the concentration of free radicals formed in both the polymer substrate and comonomer solution. The influence of dose on the grafting yield of DMAEMA/MAAc onto wood pulp was investigated and shown in Figure 1.

It is obvious that the grafting yield increases with increasing dose for the binary mixture DMAEMA/MAAc up to 10 kGy, then, at high radiation dose, a curvature relationship is observed. It can be assumed that the increase in the irradiation dose resulted in increasing concentration of free radicals formed in trunk polymer as well as in comonomer binary system. At higher dose, no more active sites are formed and the constant concentration of free radicals also give curvature relationship for grafting yield with dose. This is due to recombination of some radicals without initiating new grafting sites.[16,17] The copolymerization of DMAEMA/MAAc can be represented by Scheme 1.

The mutual irradiation technique involves irradiation of wood pulp in the monomer solution with gamma radiation, which results in radical formation on the cellulose chain and the sites of radical formation become the point of initiation for the side chains.

In the presence of vinyl monomer, the cellulose macroradical is added to the double bond of the comonomer, resulting in covalent bond formation between the monomer and the cellulose with the creation of free radical on the monomer, thus, a chain is initiated. Subsequent presence of monomer molecules to the initiated chain propagates grafting onto cellulose.[18]
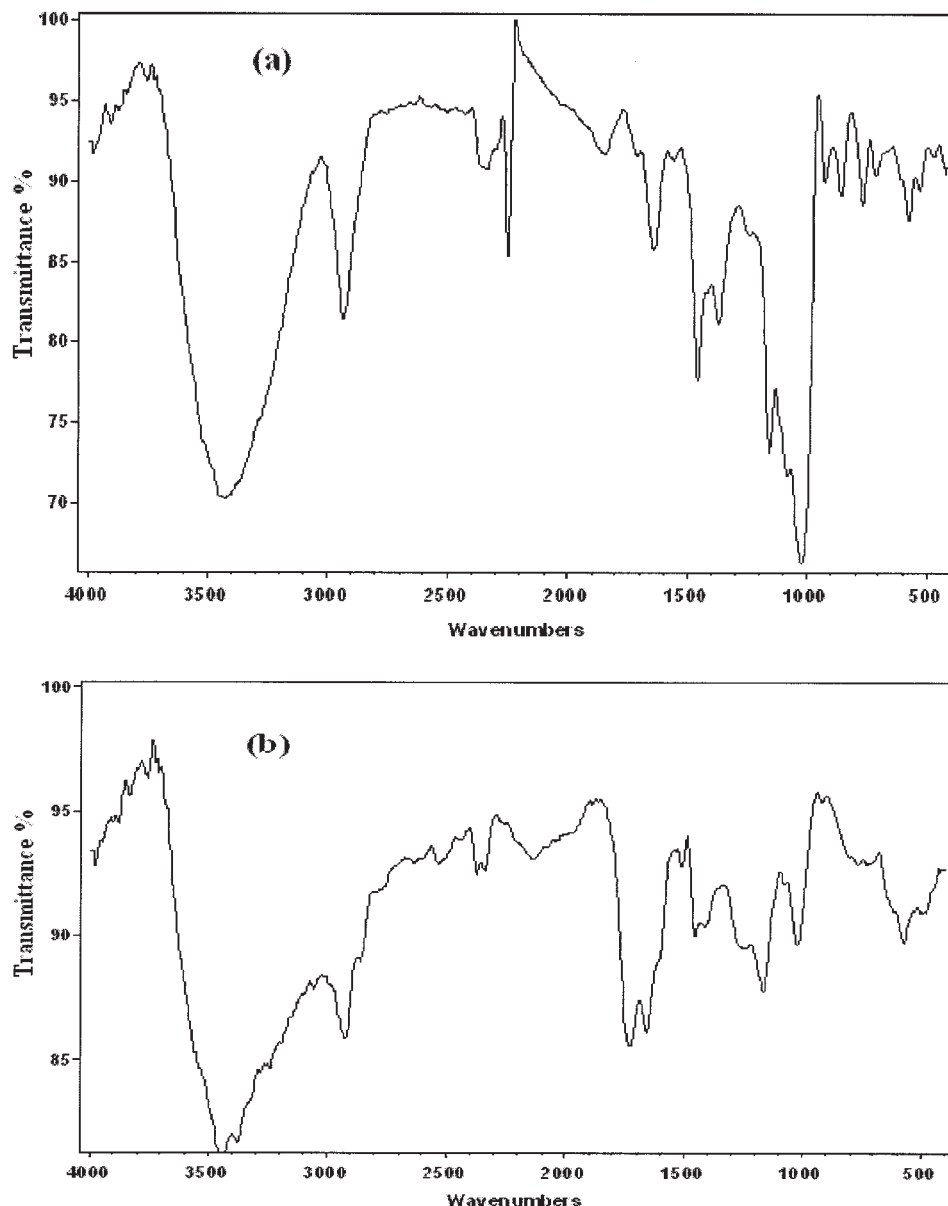
Wood pulp-(DMAEMA / MAAc) graft copolymer

Scheme 1 Reaction of wood pulp with comonomer DMAEMA/MAAc.

Characterization of the graft copolymer

Swelling behavior

The swelling behavior of different graft wood pulp copolymers (with composition of DMAEMA/MAAc: 40/60, 50/50, 60/40, 70/30, 80/20 wt % and degree of grafting G% = 55, 109, 120, 95, 63%, respectively) is shown in Figure 2.

It is found that, the graft wood pulp copolymer of composition DMAEMA/MAAc (60/40) wt % having G% = 120 has the maximum water uptake percent. This can be attributed to higher degree of grafting, thus, it is reasonable to conclude that the swelling behavior of the graft wood pulp copolymer is dependent mainly on the degree of grafting, i.e., on the amount of hydrophilic groups introduced in the graft copolymer.

The increase of DMAEMA content above 60 wt % leads to decrease of swelling behavior of the graft copolymer. It is quite well known that, increase of weak acid or base concentration in the system decreases percentage of ionizable groups in the copolymer.[19] Also the variation of hydrophilicity/hydrophobicity ratio with variation of composition may be an-

other reason for this behavior, although, decrease of ionizable groups with decreasing DMAEMA content increases hydrophilicity or swelling.

The reduction of water uptake (%) with the increase of MAAc above 40 wt % is due to hydrogen bond

Figure 2 Influence of comonomer composition on the swelling behavior of DMAEMA/MAAc grafted wood pulp at different comonomer composition.

Figure 3   FTIR spectra of (a) Wood pulp, (b) 34% grafted wood pulp.

formation in the graft copolymer that contains free COOH groups resulting in a crosslinking network structure.[20]

### Infrared spectroscopic analysis (FTIR)

The infrared spectroscopic analysis of ungrafted and grafted wood pulp was recorded in the region from 400–4000 cm^{-1}. From the Figure 3, it is clear that a new band appeared at 1715 cm^{-1}, which was characteristic to C=O vibration of carbonyl group. This band appeared due to the grafting of wood pulp with MAAc. This can be confirmed by the higher ratio of band intensity at 2920 cm^{-1} (which was characteristic to CH vibration of CH$_2$ group) to the band intensity at

3350 cm^{-1} (which was characteristic to OH group), it was 0.7 and 0.62 for grafted and ungrafted wood pulp. This means that there is increase of CH$_2$ group in the grafted wood pulp as represented in Scheme 1. On the other hand, a new band appeared at 3300 cm^{-1}, which is characteristic to N—H of amino group in the grafted wood pulp. The presence of these characteristic bands confirms that DMAEMA and MAAc molecules are grafted into cellulosic wood pulp.

Surface morphology

The surface characteristics of original and different levels of grafted wood pulp are investigated by scanning electron microscopy and are represented in Fig-
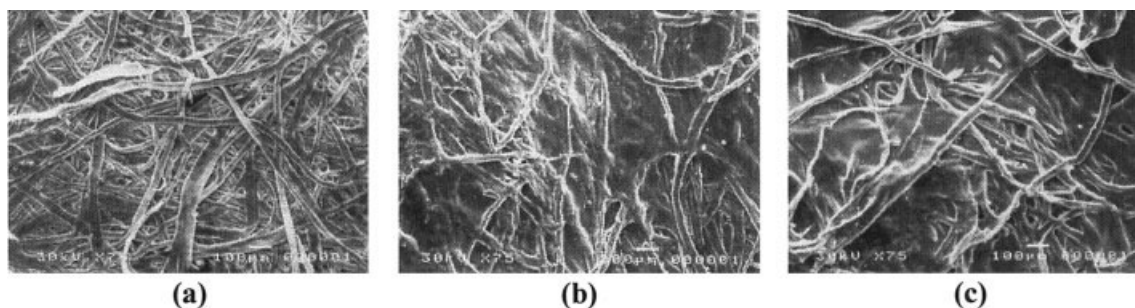
Figure 4 SEM for (a) Wood Pulp; (b) 60/40 wt % DMAEMA/MAAc grafted wood pulp; and (c) 50/50 wt % DMAEMA/MAAc grafted Wood pulp.

ure 4, in order to elucidate the topological changes occurring under grafting reactions. The results show that, for the untreated wood pulp (Fig. 4(a)), the fibrous structure contains randomly-layered smooth fibers.

The grafted wood pulp with comonomer DMAEMA and MAAc of composition 60/40 wt % (G% = 120) is different from the untreated wood pulp as shown in Figure 4(b). The fiber becomes thicker and covered with smooth layer of polymer deposits caused by the hydrophilic nature of the comonomer. The entire fiber also appeared to be coated with polymer deposits as a result of monomer penetration, diffusion, and consequently, grafting through the fiber. Polymer bridges were formed in some areas, leading to bond individual fibers together.

The grafted wood pulp with comonomer DMAEMA and MAAc of composition 50/50 wt % (G% = 109) [Fig. 4(c)] shows that the layer formed along the fibers is not smooth enough as that in Figure 4(b). Also, the polymer bridge is not completely formed due to lower degree of grafting than 60/40 wt % thus, the cellulose fiber seems to apart from each.
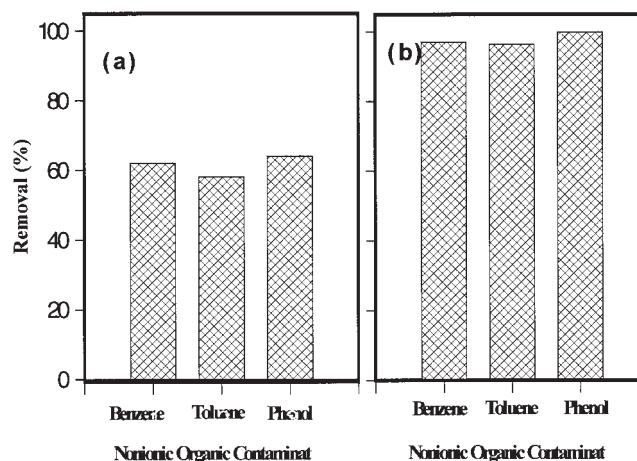
Adsorption of NOCs onto wood pulp

Adsorption of copolymers is a complete process. Solution from which the adsorption proceeds may contain only individual macromolecules or individual and aggregated species of different shapes and properties. Each of these entities possesses its own affinity for the surface, defined not only by its intrinsic properties but also by the chemical and physical properties of the surface.[21–23]

Figure 5(a,b) show the removal (%) of phenol, benzene, and toluene prepared at initial concentration of 500 ppm, after adsorption by using original and grafted wood pulp. It can be seen that the removal (%) of benzene and toluene by the grafted wood pulp is 97%, 96% respectively, whereas, the removal (%) of phenol is about 99%. For the ungrafted wood pulp (original), the removal (%) of phenol, benzene, and

toluene is 62 (%), 58 (%), and 64 (%), respectively. Because the different polar functional groups of DMAEMA and MAAc have been introduced onto wood pulp, this modified wood pulp has excellent hydrophilicity and they also give higher recovery than their unmodified analogues.[24–27]

This has been attributed to an increase in the surface polarities that enables the aqueous samples to make better contact with the grafted surface. This sorbent has a higher degree of crosslinking, and so have an open structure (high porous material), which increases its specific surface area and allows greater π—π interaction between analytes and sorbent.[28] The removal percent will therefore be higher than that those obtained, when less crosslinked sorbent are used.[29]

The high tendency of wood pulp for adsorption of phenol than benzene and toluene may be attributed to the electrostatic interaction (hydrophobic interaction and hydrogen bond).[30,31] Hydrophobic effects are specifically aqueous solutions interactions, which in the present case will involve the aromatic rings and ethyl,

Figure 5 Removal (%) of nonionic organic contaminant by 0.1 g adsorbent (a) wood pulp and (b) DMAEMA/MAAc 60/40 wt % grafted wood pulp, initial concentration of NOCs 500 ppm, volume 10 mL at pH 6.

methyl, and methine groups on the NOC molecules and the ethyl, methyl, and methine group on the co-polymer.

Hydrogen bond will be expected to occur between hydrogen, hydroxyl, and methyl groups on the NOC molecules and the carbonyl groups, hydroxyl groups on the comonomer unit of the crosslinked wood pulp copolymer. Thus, the electrostatic interactions between the NOC molecules and wood pulp graft copolymer is very dominant due to hydrophobic and hydrogen bonds.

CONCLUSIONS

It can be concluded that, the most important parameter affecting the swelling behavior and characteristic of the prepared copolymer is the type of conversion due to radiation and chemical treatment occurred. It was found that the graft wood pulp possessed good hydrophilic character suitable for practical application. The capacity of the obtained copolymer towards different NOC pollutants is mainly dependent on the amount of active group present in the copolymer. It could be concluded that, the grafted wood pulp with composition of DMAEMA/MAAc, 60/40 wt %, can be used as adsorbent of NOCs in aquatic fields involving environmental treatment, pharmaceutical, agricultural, and biomedical applications.

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