Preparation of Cellulosic Membrane Containing Pyrrolidone Moiety Via Radiation Induced Grafting and its Application in Wastewater Treatment

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Abstract: Radiation induced grafting of vinyl pyrrolidone onto cellulose wood pulp was carried out in heterogeneous and homogenous media using gamma radiation. Cellulose wood pulp was used in different forms; a) in a homogenous solution by dissolving the wood pulp in N,N-dimethylacetamide/Lithium chloride (DMAc/LiCl) mixture, b) in a membrane form, by precipitating the cellulose solution in water and c) in a powder form. Factors affecting on the grafting such as radiation dose, monomer concentration, precipitator concentration and thickness of the membrane have been studied. The result showed that at the same dose, the grafting yield was higher with cellulose in soluble form than in the membrane form, whereas cellulose in powder exhibited the lowest graft yield. The grafted membrane was characterized by IR, TGA and SEM. The ability of the grafted membrane to remove dyes (acid and basic dye), heavy metals ions (Co²⁺, Ni²⁺ and Cu²⁺) and phenols from wastewater was also reported.

Key words: γ-radiation, Grafting, Cellulose Membrane, Wastewater Treatment

INTRODUCTION

All over the world, an increasing interest is focused on the quality of drinking water. Recently, attempts have been made to relate the occurrence of certain cancers and cardiovascular diseases to the presence of trace metals and organic compounds in drinking water. Therefore, information on the accumulation, release and of these toxic compounds in water and wastewater becoming highly desirable [1, 2]. Cellulose graft copolymer is the general name given to a class of cellulose derivatives containing polymeric side chains. Since 1950, different olefins have been grafted onto cellulose and starch [3] with the aim of preparing new products having certain desirable properties. As a consequence, there is a lack of knowledge about the net copolymer behavior, with particular regard to the influence of number and length of side branch on its properties [4]. The discovery of new solvents of cellulose [5] in the last decades opened the possibility of performing derivatization and / or grafting reactions in homogeneous conditions, thus assuming important advantages, such as a better contrast of the substitution degree, a more uniform distribution of substituents along the polymer chain and a higher conversion yield. By grafting of a monomer to the cellulose backbone, some of the drawbacks of cellulose can be eliminated. Radiation grafting of cellulose with vinyl monomers has been studied by several authors [6-8]. The major advantages of the radiation grafting are: a) the reaction is carried out at lower temperature than in chemical operation; b) grafting is carried out from gaseous vapor and liquid phase of the monomer; c) the modified material is free from residuals of initiator or catalyst.

The present study aims at the preparation of grafted cellulose membrane containing pyrrolidinone moiety by using radiation process. The effect of various conditions such as radiation dose, monomer concentration, duration of reaction and form of cellulose material (dissolved, powder and membrane forms) on grafting percent was investigated. The behavior of grafted membrane for some specific applications such as adsorption of dyes, heavy metals and phenol from wastewater was examined.

MATERIALS AND METHODS

Sulfide wood pulp was kindly supplied by Misr Rayon Company, Alexandria, Egypt and used as received. Dimethyl acetamide (DM Ac) was supplied by Fluka. It was dried by vacuum distillation on CaH₂ and stored on molecular sieves (Riedel- Haen type 3A). LiCl was supplied by Fluka and dried at 180°C for 24 h. Vinyl pyrrolidone (VP), was supplied by Merck. Acid R 1and Methylene Blue dyes (structure I and II, respectively) were supplied by Isma Dye Company, Egypt. All other chemical used were laboratory Grade.
Preparation of Cellulose Solution: Two grams of wood pulp was dipped in 100 mL of DMAC, heated to 120°C and stirred for 2 h. Then the cellulose was filtered and dissolved in DMAC/LiCl solution “9/1 W/W” under stirring at 90°C for 5 h. The system was then cooled to room temperature and stirred overnight for complete dissolution. The clear solution obtained was 2% by weight and used for further study.

Preparation of Cellulose Membrane: Cellulose membrane in liquid form was prepared by dissolving the powder form of cellulose (wood pulp) in definite amount of solvent (dimethyl acetamide). The solution so obtained was cast on the glass plate and left overnight. The plate was dipped in water to precipitate the cellulose in the membrane form. The membrane was washed several times with water to remove the trapped solvent and stored in water.

Preparation of Cellulose Grafted with Polyvinylpyrrolidone (Cell-g-PVP): A membrane of cellulose with definite weigh and thickness was immersed in a vinyl pyrrolidone monomer solution in a Petri dish. The grafting was carried out by using direct radiation in atmospheric air using 60Co as gamma source at different radiation doses. The grafted membrane were removed and washed thoroughly with hot water and mixture of water/methanol (1:1) and then immersed in distilled water for extraction of any residual homopolymer which may be accumulated in the grafted membrane. The membrane was then dried in an oven at 50°C. The degree of grafting was determined theoretically from nitrogen percent determination [9].

Adsorption of Phenol: The grafted membrane (0.5 g) was added to 100 mL of water solution of phenol (1 g L-1). The mixture was automatically shaken for 5 h at 25°C. The membrane was separated by filtration, and the concentration of remaining phenol in the filtrate was measured chromatographically by HP HEWLE II PACK ARD, HP 6890 Series GC System, USA.

Dye Removal: 0.2 g of cellulose membrane and 100 mL of an aqueous dye solution (100 mg L-1) were placed, without pH adjustment, in a 125 mL glass stoppered flask and automatically shaken for 5 h at 25°C. The contents of the flask were filtered and the concentration of the dye in the filtrate was measured using a Shimadzu UV/Visible Spectrophotometer. The capacity of dye removal, mg g-1 was calculated from the following equation:

\[ \text{Capacity} = \frac{(\text{Co} - \text{Cf}) \times \text{V}}{\text{Wt}} \]

Where, Co and Cf are the initial and final concentration of the dye, respectively, V is the volume of the dye solution and Wt is the weight of the membrane.

Metal Ions Removal: To a glass stoppered flask containing 0.2 g of dried membrane, 100 mL of known concentration of metal ions, without pH adjustment. The flasks were kept in a shaking water bath with 150 rpm at 30°C for 8 h. After the desired time, the content of the flask was filtered and the filtrate solution was analyzed for assessing the remaining cations using standard solution of EDTA. The capacity of metal ions removal, mg g-1 was calculated from the following equation:

\[ \text{Capacity} = \frac{(\text{Co} - \text{Cf}) \times \text{V}}{\text{Wt}} \]

Where Co and Cf are the initial and final concentration of metal ions, respectively, V is the volume of the metal ions solution and Wt is the weight of the membrane.

Infrared Spectroscopy: Analysis by infrared spectroscopy was carried out using Bruker Vector 22 Germany.

Thermal Gravimetric Analysis: Shimadzu TGA system of type TGA-50 in nitrogen atmosphere 20 mL min-1 was used in this investigation with heating rate of 10°C min-1.

Scanning Electron Microscope: JEOL ISM-5400 Scanning Microscope (JEOL, Japan) was used to determine the morphology of the membrane.

RESULTS AND DISCUSSION

Preparation of Cellulose Grafted with Polyvinyl Pyrrolidone

Effect of Radiation Dose and Monomer Concentration: Figure 1 shows the relationship between radiation dose and grafting percent at different monomer concentrations. It can be seen that, the grafting yield increases with increasing radiation dose up to 5 KGy. Further increase in radiation dose resulted in a decrease in grafting percent. A possible explanation is that, the lower radiation dose initiates mainly graft copolymerization due to lesser termination of free radicals with the polymer growing radicals and recombination of primary radicals resulting from a longer chain length of the grafted copolymer and elimination of homo polymerization [10]. In contrast at higher radiation dose the concentration of the free radical increases, and as a result, recombination of primary radicals into the inert species in the bulk medium is significant and therefore there are only a few radicals available to start copolymerization. Most
radicals undergo recombination or available for homopolymerization. Figure 1 shows also the effect of monomer concentration on the grafting percent. It can be seen that the grafting percent increases with increasing monomer concentration up to 30%, whereas further increase in monomer concentration enhances the homopolymerization process. This retards the grafting process because of restriction in its diffusivity in such viscous medium and no monomer solution can diffuse into the interior regions of the polymer to initiate new grafting sites [11].

Effect of Cellulosic Form: Figure 2 shows the effect of the form of the cellulosic material on the grafting percent. Obviously, grafting exhibits the highest values when the cellulose wood pulp was used in a dissolved (I) form. On the other hand, it displayed the lowest grafting when used in the powder form. Cellulose wood pulp in the membrane form stands in mid-way position. These results are in full agreement with the postulate assuming that grafting process in a homogenous condition assuring important advantages such as a more uniform distribution of constituents along the polymer chain and a higher conversion yield [12, 13]. On the other hand, lower grafting observed with cellulose pulp in the powder form could be attributed to the trapped radicals in the crystalline regions of wood pulp which could not contribute in grafting due to inability of the monomer to diffuse within the bulk of the matrix. It is also logical that cellulose membrane affords larger surface area for grafting than cellulose in powder form. It is as well to emphasize that cellulose pulp in the dissolved form acquires very high grafting percent. Hence, it is amenable for dissolution in water thereby enhancing the viscosity of the solution during the polymerization, meanwhile decreasing the cellulose content during precipitation of the copolymer in water. For this reason, we could not obtain the precipitated matrix in the form suitable for use to remove pollutants from wastewater.

Effect of Membrane Thickness: Figure 3 shows the effect of membrane thickness on the grafting percent. The cellulose membranes were prepared by dissolving 2% of wood pulp in DMAC/LiCl mixture and poured in Petri dish then left for 24 h. The membranes with different thickness were immersed in a vinyl pyrrolidone monomer of 30% concentration using dimethyl formamide as diluents. The reactants were subjected to γ-rays at a dose of 5 KGY. It is seen (Fig. 3) that the grafting percent increases with increasing the thickness of the membrane. Cellulose is hydrophilic in nature, consequently it can easily swell in monomer solution, and therefore vinylpyrrolidone can easily diffuse into the cellulose matrix. By increasing the thickness of the membrane the percent of cellulose content in the membrane will increase and results in the enhancement of the diffusion of vinylpyrrolidone into the polymer matrix [14]. Those more cellulosic materials will be available for grafting at higher cellulose membrane thickness.

Characterization of Grafted Membrane: Cellulose grafted with polyvinylpyrrolidone (cell-g-PVP) was characterized using IR, thermal Gravimetric analysis and scanning electron microscope. IR analysis was performed for the dried membrane before and after grafting (Fig. 4) to confirm the grafting process. The IR spectra of the grafted membrane indicate the appearance of new peaks at 1650 cm⁻¹ and at 1413 cm⁻¹ characteristics to C=O band, and C-N band, respectively. Also, new peak characteristics for N-H stretch of amide were observed at 3427 cm⁻¹.
To examine the thermal stability of cellulose membrane before and after grafting, thermogravimetric analysis (TGA) was carried out. Figure 5 shows the weight loss with a heating rate of 10°C min⁻¹ in nitrogen between 50 and 600°C. The initial thermal decomposition of cellulose membrane before heating takes place at 180°C, whereas the grafted membrane with vinyl pyrrolidone exhibit its initial thermal decomposition at 280°C. The result indicates that the grafting of monomer to cellulose backbone improve its thermal stability and heat resistance of the polymer.
Evaluation of the Grafted Membrane for Wastewater Treatment: There can be many possible mechanisms for the adsorption of phenol, dyes and heavy metal ions on the grafted membrane: a) ion – dipole interaction, b) the surface – C=O group of the PVP and –OH group of the phenol may form a hydrogen bond (diagram I), c) CH-O-R bonding may be possible (diagram II), and d) the N atom in amide can make hydrogen bonds with the –OH group of the phenol; but this mechanism is much less likely than the others.

Figure 7 shows the adsorption of Hg^{2+}, Cd^{2+} and Pb^{2+} on the cellulose membrane grafted with PVP. A high adsorption capacity is achieved with Cd^{2+} and Pb^{2+} around 362 and 323-mg g^{-1} sample, respectively. While the membrane failed to adsorb Hg^{2+} from its solution. The adsorption of metal ions on cellulose grafted with PVP is due to the presence of amide group that could act as electron donor [15]. Thus, the nitrogen electrons present in the amide groups can establish dative bonds with Pb^{2+} ions. The superior Chelating ability of
cellulose-g-PVP may be due to pyrrolidone rings in the
grafted PVP along with a significant freedom of the
grafted PVP chains.
The complexation of the metal ions to the
macromolecules is also influenced by a variety of
conformational and steric effect [16].
PVP forms complexes with a large number of inorganic
and organic ions, polyelectrolytes and other structure
[17]. PVP complexation with dyes has previously been
studied by conductance measurements, equilibrium
dialysis and difference spectroscopy [18, 19]. The
predominant contribution to the interaction is assumed
to be the hydrogen bonding between the ionized groups
of the dye and water molecules in the PVP hydrated
shell [17]. Figure 8 shows the amount of basic and acid
dyes adsorbed using 0.5 g grafted cellulose membrane.
The results reveal (Fig. 8) that the grafted membrane
has high ability to adsorb the basic dye than the acid
dye.
As already described the cellulose membrane has been
developed by introduction of polar functional group
(amide group) onto the cellulose membrane, which can
be used in the sorption of polar compounds from
environmental water. These modified membranes have
excellent hydrophilic and give high recovery of the
phenol compound from water. This can be attributed to
an increase in the surface polarity, which enables the
aqueous sample to make better contact with the
membrane surface [20]. The grafted membrane was
monitored for phenol adsorption from water solution of
phenol. The test showed that the grafted membrane
adsorbed 228 mg phenol g\(^{-1}\) sample.

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