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Grafted wood pulp containing quaternary ammonium group and its Application in The removal of different anions from aqueous solution

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Abstract

Network wood pulp based on acrylonitrile has been chemically modified through different reactions to obtain group capable of anion exchange. Graft copolymerization of acrylonitrile onto wood pulp was carried out by using γ-radiation ^{60}Co. Factors affecting on the grafting process e.g radiation dose and monomer concentration was investigated.The chemical modification of cyano groups were carried out by reaction with ethanolamine producing oxazoline group followed by quaternization of tertiary amine by reaction with benzyl chloride producing quaternary ammonium salt. The grafted and modified wood pulp were characterized by FTIR, SEM and TGA.Qualitative adsorption experiments were conducted to evaluate the ability of modified wood pulp to fix sulfate, phosphate,nitrate and dichromate from aqueous solution using batch extractions. Based on the results obtained, it may be concluded that it is possible to modify chemically wood pulp containing cyano groups by different routes to use it as anion exchanger for different anions.

Key words : radiation-grafting- quaternization-anion exchanger

Introduction

Water is of fundamental importance for life on earth.Wastewater discharges carrying nitrate,ammonium or sulfate ions create serious and often unanticipated problem to water management experts(1). About 2.66% of the total global water resources (ground water, lakes , ……etc) are fresh water, but only a small fraction (~ 0.6 %) is available as drinking water (2,3). Therefore, it is necessary that water reserves treated carefully and waste water treatment be done efficiently.

Cellulose and cellulose derivatives are cheap, renewable and the most abundant organic raw material in the world. It is modified by graft copolymerization with vinyl monomers and the graft properties,depending on the chemical structure of the monomer grafted onto cellulose (4). Graft copolymers gained new properties such as hydrophilic or hydrophobic character, absorption of dyes (5) and ion exchange capability (6,7). During recent years, removal of metal ions, both from wastewater and natural waters, has gained importance to solve and minimize both the industrial and ecological waste problems. Cellulose graft copolymers having ion-exchange property find applications for removal of metal ions from aqueous solutions (8-12).

The quaternization of tertiary amine with benzyl chloride is a bimolecular nucleophilic substitution reaction (13). Orlando et al (14,15) reacted several by- products including sugar cane , bagasse and rice hulls by cross- linking with epichlorohydrin and reacting with dimethylamine in dimethylformamide using pyridine as accelerant to form an effective anion exchanger for nitrate ion removal. The objectives of this study were to creat anion exchange wood pulp by chemical modification of grafted wood pulp based on acrylonitrile copolymer followed by quaternization and applying the resulting anion exchange material for the removal of various anions of environmental concern e.g (sulfate,phosphate,nitrate and dichromate).

Experimental

1- Materials

Wood pulp: sulfate wood pulp (viscose grade pulp) was kindly supplied by Misr rayon Company,Kafr EL-Dawar, Egypt and used as received .Acrylonitrile(AN) was supplied by Merck (Germany), benzyl chloride and ethanolamine were supplied by BDH chemical Ltd Poole (England).Cadmium acetate , dihydrogen sodium phosphate, lead nitrate and cadmium sulfate were supplied by Merck (Germany), whereas potassium dichromate by El-Nasr Company , Cairo,Egypt.All other chemical used were laboratory reagents.

Experimental techniques:-

2.1 :Radiation induced polymerization

Radiation induced grafting was carried out in a Pyrex tube containing the monomer in DMF solvent and definite weight of cellulosic wood pulp and 5% styrene of total monomer weight as inhibitor under air atmosphere using gamma rays of ^{60}Co source at different radiation doses. The grafted wood pulp was removed from the pyrex tube, washed with DMF and then water several times to remove the homopolymer occluded in the grafted wood pulp and then dried and weighed. The degree of grafting was determined by the percentage increase in weight :

$$G\% = W_g - W_0 / W_0 \cdot 100$$

Where W_0 and W_g represented the weight of original and grafted wood pulp respectively.

2.2 Chemical modification of the grafted wood pulp:

2.2.1 A volume of 6.3 ml of ethanolamine was added to a reactor equipped with magnetic stirrer and reflux condenser containing 35 ml of chlorobenzene; 5g of grafted wood pulp and 0.5 g of cadmium acetate (used as a catalyst). The reaction was conducted at 120 ^{0}C for 24 h under stirring. The modified wood pulp was washed thoroughly with ethanol and dried at 60^{0}C.

2.2.2 Quaternization of modified wood pulp

Chemically modified wood pulp and benzyl chloride were heated in a thermostat at a temperature 80 ^{0}C for 20h in a suitable reactor. the quaternized wood pulp was then withdrawn, washed with ethanol and dried at 60^{0}C .

2.2.3 Adsorption study:

0.2 g of modified wood pulp (quaternized form) was added to 100 ml of anion in the form of cadmium sulfate, dihydrogen sodium phosphate, lead nitrate and potassium dichromate(100 ppm). The mixture was automatically shaken for 5h at 25 ^{0}C. The wood pulp was separated by filtration, and the concentration of the anion in the filtrate was measured according to American Society for testing and materials (ASTM, 2000) (16).

3.Characterization :-

3.1. Fourier Transform Infrared (FTIR)

The functional groups of original , grafted and modified wood pulp were studied using Mattson 1000 FTIR spectrophotometer (Unicam Ltd., England.).

3.2. Scanning Electron Microscopy (SEM)

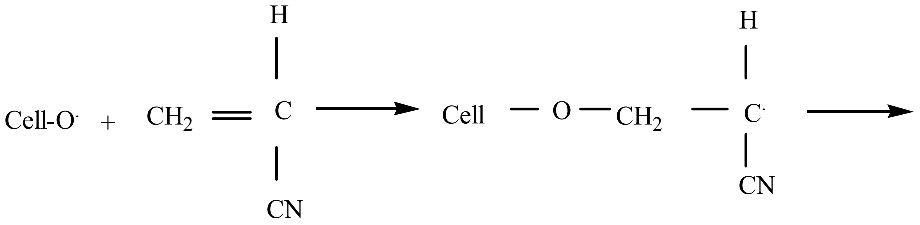
The surface topography of the original, grafted and modified wood pulp was studied using JEOL SEM-25 (Japan).

3.3 Thermogravimetric analysis (TGA)

Shimadzu TGA system of type TGA-50 in nitrogen atmosphere 20ml/min was used in this investigation with heating rate of 10 ^{0}C /min.

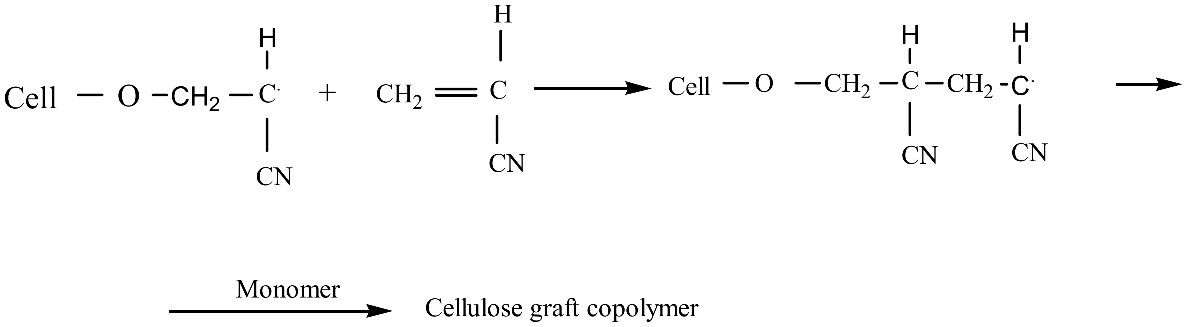
Results and Discussion

The mutual irradiation technique involves irradiation of wood pulp in the monomer solution with γ-radiation that results in radical formation on the cellulosic chain, the sites of the radical formation become the point of initation for the side chains.



$$\text{Cell-O}^{\cdot} + CH_2 = \underset{\displaystyle CN}{\overset{\displaystyle H}{C}} \longrightarrow \text{Cell} - O - CH_2 - \underset{\displaystyle CN}{\overset{\displaystyle H}{C^{\cdot}}} \longrightarrow$$

(1)



$$\text{Cell} - O - CH_2 - \underset{\displaystyle CN}{\overset{\displaystyle H}{C^{\cdot}}} + CH_2 = \underset{\displaystyle CN}{\overset{\displaystyle H}{C}} \longrightarrow \text{Cell} - O - CH_2 - \underset{\displaystyle CN}{\overset{\displaystyle H}{C}} - CH_2 - \underset{\displaystyle CN}{\overset{\displaystyle H}{C^{\cdot}}} \longrightarrow$$

(2)

$$\xrightarrow{\text{Monomer}} \text{Cellulose graft copolymer}$$

In the presence of vinyl monomer, the cellulose macroradical is added to the double bond of AN, resulting in covalent bond formation between the monomer and the cellulose. With the creation of free radical on the monomer, a chain is initiated.Subsequent addition of the monomer molecule to the initiated chain propagates grafting onto cellulose (17).

Fig (1) shows the grafting % of AN of concentration (30,40 and 50 %) vs radiation dose. The rate of grafting is linear at the initial stage of reaction and then tends to level off at high monomer concentration. An increase in the monomer concentration. An increase in the monomer concentration above the maximum value would not be expected to result an increase in the extent of graft copolymer formation. The variation of the level of incorporation of polyacrylonitrile on the wood pulp may therefore be explained in term of the non-radical mechanism of grafting. However, in such a heterogeneous polymerization system, the monomer would be distributed between the continuous aqueous aqueous phase and the cellulose interface; the relative extent would depend on the polarity of the monomer. It would be expected that a relatively high proportion of a polar monomer , such as acrylonitrile, would be in aqueous phase, resulting in reduced effective concentration at the cellulose interface (grafting site) and hence low graft levels (18).

Effect of radiation dose.

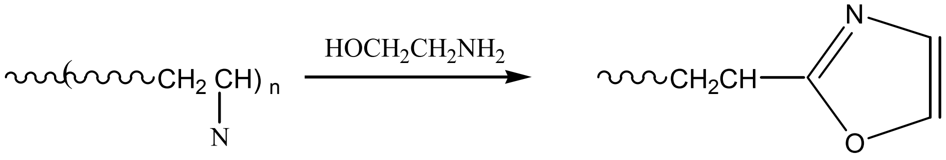
The variation of grafting with radiation dose in graft polymerization of acrylonitrile onto wood pulp at monomer concentration (10,20 %) in DMF is also shown in fig (1). Grafting increase with radiation dose up to 15 KGy at first and then tends to level off at 20 KGy. The amount of radicals formed by radiation at first increases linearly with radiation dose and then reaches certain limiting value at a higher dose due to recombination of the formed radicals (19). Therefore at higher irradiation dose, the grafting tends to level off due to the recombination of some of the free radicals without initiating graft polymerization (20). Huang and Rapson (21) suggested that the leveling off grafting could be traced back to the fact that at higher level of grafting, the reaction becomes diffusion controlled process.

An alternate method using the styrene comonomer procedure (22) show that if styrene is one of the monomers used in the mixture, copolymerization of the second reactive monomer can be achieved by mutual irradiation with a minimum homopolymer formation. The technique leads to a reduction in Kp of the acrylonitrile in the presence of styrene, ie the presence of styrene 0.05 % (w/v) in monomer feed reduces homopolymerization reaction and consequently decreases its competition process with graft polymerization (monomer-cellulose reaction).

Characterization of the wood pulp

The IR spectra of original (a), grafted (b) modified grafted with ethanolamine (c) and finally quaternized wood pulp with benzyl chloride (d) were carried out to certify that the modification reaction has produced the desire pendant groups on the wood pulp surface. Fig (2) show the IR analysis of unmodified and modified wood pulp. The presence of a sharp peak at 2244 cm^{-1} related to the CN group clarify that the wood pulp has been grafted fig (2b). Modification of the grafted wood pulp with ethanolamine shows that the bond associated with the nitrile group at 2244 cm^{-1} disappears and is replaced by the band at 1651cm^{-1} Characterize the oxazoline ring and 1251-1120 cm^{-1} of the C-O-C ether bond fig (2c). Modification with benzyl chloride exhibit band at 1250 cm^{-1} characterisze the CH_2Cl group , two bands at 1490 and 1615 cm^{-1} characterize CH vibration of benzene ring.

Thus the reactions on the wood pulp based on acrylonitrile can be represented as follows:-



(3)

$$R_3N + phCH_2Cl \longrightarrow phCH_2R_3NCl \qquad (4)$$

Fig (3) shows the SEM of the unmodified and modified wood pulp (a), grafted wood pulp (b), modified grafted wood pulp with ethanolamine (c) and the quaternized form of the modified wood pulp (d). Fig (3a) shows the fibrous structure which contains randomly-layred smooth fibers with greater porosity. The grafted wood pulp with polyacrylonitrile of 260 % grafting is totally different from the untreated wood pulp fig (3b). The fibers became thicker and covered with rough layers of polymer-deposits caused by the hydrophobic nature of polyacrylonitrile. The entire fiber also appeared to be coated with polymer- deposits as a result of monomer penetration, diffusion and consequently grafting through the fibers. Polymer bridges were formed in some areas leading to bond individual fibers together. Modification of the grafted wood pulp with ethanolamine results in the change of both polymer-deposits and pore- size. The polymer –deposits of the modified wood pulp appeared to be soft and concentrated only on the fibers as shown in fig (3c). The modified wood pulp possesses more porosity as compared with the grafted wood pulp. The fibrous structure and the fibers are not damaged after modification with ethanolamine as a result of the protection by graft polyacrylonitrile. Furthur modification with benzyl chloride shows that the porous of the fibers are almost enclosed due to the formation of quaternary ammonium salt along all the fibers as shown in fig (3d). To examine the thermal stability of unmodified and modified wood pulp, thermogravimetric anlysis (TGA) was carried out. Fig (4) shows the weight loss with heating rate 10 ^{0}C min $^{-1}$ in nitrogen between 50 and 600 ^{0}C. The original wood pulp fig (4a) is thermally stable up to 375 ^{0}C, whereas grafted wood pulp fig (4b) is thermally stable up to 320 ^{0}C. The decomposition curve of grafted then modified wood pulp with ethanolamine fig (4c) starts from 200 ^{0}C and distributed over a broad temperature range and the maximum rate of weight loss is lower than that of grafted wood pulp. TGA of the chemically modified wood pulp after treatment with benzyl chloride shows four steps of weight loss. The first step, 50-100 0C, is due to the weight loss of adsorbed water molecules. The first step of the weight loss indicates the degree of hydrophilicity ,which increases with furthur modification of wood pulp with benzyl chloride. Fig (4) shows that the ratio of water content increase from 2% fig (5a) to 12% fig (4d) after modification of wood pulp with benzyl chloride.The second step indicate 10% weight loss, which arises from the evolution of the quaternary salt, the third step arises from the decomposition of the back bone graft chain and the last step of cellulose chain at higher temperature.

Anion adsorption by quaternized wood pulp:-

The adsorption of four anions (sulfate, phosphate, nitrate and dichromate) as individual species by quaternized wood pulp was carried out ,whereas the standard anion solutions used in the experiment were prepared from cadimium sulfate, dihydrogen sodium phosphate, lead nitrate and potassium dichromate.The sorption studies have been carried out at anion concentrations (20,40,60 and 100 ppm) and at different pH values (4.5,6 and 9). Fig (5) show the % removal of anions by modified wood pulp at initial concentration at 100 ppm and at pH 4.5. The results showed that dichromate showed high percent removal, followed by phosphate, nitrate, whereas sulfate showed the lowest percen removal t. Because a standard anion is chloride ion, sulfate and nitrate ions are less hydrated while phosphate and dichromate are strongly hydrated compared with chloride ions. Moreover sulfate and nitrate ions are larger than chloride ions. On the other hand, sulfate ions are more hydrophilic and has high hydration energy than nitrate ions. Although the sulfate ions has higher hydrophilicity and hydration energy than nitrate, its removal % is lower than nitrate. This can be attributed to the bulky of sulfate ions (23).

Effect of initial anion concentration

The effect of sorbate concentration on the removal of the anions from aqueous solutions was shown in fig (6). Sorbate concentrations were varied from 20 to 60 ppm. The results showed that (sulfate, phosphate and dichromate) removal efficiency decreased with increasing the sorbate concentration (24,25) , whereas the removal efficiency of nitrate increased with increasing the concentration of the sorbate. In general, ion exchange membrane shrink with increasing concentration of the salt solution , which causes the decrease in water content of the membranes. Thus the hydrophilicity of the ion exchange membranes decreases with increasing concentration of the salt solution and the affinity of the less hydrated anions, nitrate ions , to the membrane increases, which increase their permeation.In fact the ion exchange equilibrium constant of nitrate ions to chloride ions of commercial anion-exchange membrane was reported to be increased with increasing concentration of mixed salt solution (26).

Effect of pH on adsorption process

The effect of pH on the removal of different anions were investigated by testing three values of pH = 4.5, 6 and 9 for concentration of anions 100 ppm. The contact time has been fixed to 24h for all the experiments. The experimental results are represented in fig (7). It can be seen that the anion adsorption occurs at the lowest pH value (pH = 4.5). Furthermore, the adsorption efficiency increases with decreasing pH. Indeed pH has a strong effect on the removal of Cr (VI). This finding has been reported by several investigations (27-29). As mentioned by Rao (29). Favorable effect of low pH can be attributed to the neutralization of negative charges on surface of adsorpents by excess hydrogen ions, thereby facilitating the diffusion of hydrogenchromate ions ($HCrO_4^-$) and their subsequent adsorption. Analyzing the distribution diagrams of Cr (VI) forms as a function of pH , the predominate species at pH 4.5 is $HCrO_4^-$, and at pH 9.0 it is CrO_4^{2-} (30). The decrease in capacity at basic pH is attributed to the fact that to neutralize a CrO_4^{2-} species two quaternary ammonium groups are necessary, whilst only one is needed to neutralize $HCrO_4^-$ species. The acidic phosphates ($H_2PO_4^-$, HPO_4^{2-}) are the predominant aqueous species for the pH range of 5-9 (31). Polyphosphates ($H_2P_3O_{10}^{-3}$, $HP_3O_{10}^{-4}$ and $HP_2O_7^{3-}$) may also be present in the same pH range but typically at concentration less than the orthophosphates (32). In general , at the lower pH range, coulombic attraction can readily occur in conjunction with specific chemical adsorption due to an exchange reaction. In the higher pH range, the concentration of hydroxide groups is too high, competing strongly with anions for the active sites (33).

Conclusion

In this study,grafted wood pulp was modified with quaternizing agent , (benzyl chloride), via its grafting with acrylonitrile and treated the grafted wood pulp with ethanolamine followed by quaternization, to create an anion exchange resin, which is reflected in the adsorption of four anions of environmental interest. The study of different parameters which influence the exchange process showed that, the ion exchange sensitivity decrease with increasing salt solution , also for all anions, the most suitable condition for ion exchange process to proceed was carried out at lower pH (pH = 4.5).

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