Preparation of Selective Ion Adsorbent by Photo curing with Acrylic and Phosphoric Acid on Jute Yarn

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Abstract: Jute yarns were cured with acrylic acid (AA) and phosphoric acid (PA) using UV radiation in order to prepare selective ion adsorbent. A series of formulations were prepared in methanol containing varying percentages of (10-70 %) of AA and 2 % photo-initiator (PI) (Darocur-4043). jute yarns were soaked in this formulation for various soaking times (10-30 min) and cured under UV radiation of different intensities (20-50 UV passes). Concentration of AA, soaking time and intensity of UV radiation were optimized based on polymer loading (PL). The maximum PL (21 %) was observed for 50 % AA solution for 20 min soaking time at 40 UV passes. Various formulations were prepared using 5-15 % (w/w) of phosphoric acid, 50 % AA and 2 % PI in methanol. Then jute yarns were soaked in this solution for 20 min and irradiated at 40th UV pass. The concentration of PA was again optimized for maximum PL. It was found that the formulation containing 10 % PA, 50 % AA, 38 % methanol and 2 % PI showed 70.95 % of PL. To investigate the adsorbent behavior, a 10 ppm $CuSO_4$ solution was prepared and then grafted yarns were soaked in the solutions for 30-300 min at different conditions. After withdrawing the yarns, the remaining copper in the solution were measured by atomic absorption spectrophotometer (AAS). It was revealed that copper was successfully removed by using the grafted jute yarns.

Keywords: Jute yarns, Heavy metal adsorbent, Graft copolymerization, AA

Introduction

Jute is a natural biodegradable renewable lignocellulose raw material composed mainly of cellulose (58-63 %), hemicellulose (20-22 %), and lignin (13-15 %). In addition, a part of the lignin and hemicelluloses are linked chemically through ester linkage formed by the carboxyl groups of lignin. The purity and chemical structure of this cellulose affects its reactivity to chemical and radiation treatment. In addition to those major constituents, jute also contains a trace of organic and inorganic pigments. Jute has high tensile modulus; it suffers low elongation at break compared to that of other natural cellulose bers [1].

Many industries, including mining and electroplating, discharge aqueous effluents containing relatively high levels of heavy metals, e.g., copper, uranium, cadmium, and mercury. Untreated effluents from these manufacturing processes have an adverse impact on the environment [2-5]. Heavy metals released into the environment have been increasing continuously as a result of industrial activities and technological development, posing a significant threat to the environment and public health because of their toxicity, accumulation in the food chain, and persistence in nature. However, it has been proven that large amounts of many heavy metals, such as copper, lead, cadmium, or mercury seriously affect human health. The human body cannot process and dispose of the metals. As a result they are deposited in various internal organs. Large deposits may cause adverse reactions and serious damage to the body. Those toxic metals can cause the symptoms of memory loss, increased allergic reactions, high blood pressure, depression, mood swings, irritability, poor concentration, aggressive behavior, sleep disabilities, fatigue, speech disorders, high blood pressure, cholesterol, triglycerides, vascular occlusion, neuropathy, autoimmune diseases and chronic fatigue.

Traditional methods used for the removal of heavy metals from the environment are in general expensive and potentially risky due to the possibility of the generation of hazardous by-products. Physical and chemical methods have been proposed and applied to remove metal ions from effluents, but, in general, these methods are commercially impractical, either because of high operating costs or the difficulty in treating the solid wastes generated [6-8]. For example, the use of conventional technologies, such as ion exchange, chemical precipitation, reverse osmosis, and evaporative recovery, for this purpose is often inefficient and/or very expensive. Various conventional resins or adsorbents (natural and synthetic) are used. But the fact is that those resins are costly in some cases. If an effluent discharged from a chemical plant contains a large amount of Na^+, K^+, Ca^+, Mg^+, Cu^{2+}, etc. and we use a cation exchange resin to remove Cu^{2+}, then along with Cu^{2+} all those ions will be also removed. As a result the resin will be exhausted very soon and the resin cannot be used for long time and it will not be economic. It is, therefore important to develop new methods for metal exclusion and/or recuperation from dilute solutions (1 to 100 mg/*l*) and for the reduction of heavy metal ions to very low concentrations. It is well known that

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cellulosic materials can be obtained and employed as cheap adsorbents and their performance to remove heavy metal ions can be affected upon chemical treatment. In general, chemically modified cellulosic materials exhibit higher adsorption capacities than unmodified forms. Numerous chemicals have been used for modifications which include mineral and organic acids, bases, oxidizing agent, organic compounds, etc. Some of the treated adsorbents show good adsorption capacities for Cd, Cu, Pb, Zn, and Ni. Use of an ion selective adsorbent is one of the best solutions of this problem [9-19].

From the point of view of environmental preservation, fibrous adsorbents for toxic metals such as copper and lead have been extensively developed by radiation induced graft polymerization. The natural material like jute in many instances is relatively cheap and abundant in supply and has significant potential for modification and ultimately enhancement of their adsorption capabilities. Adsorbent is prepared by direct modification of cellulose with grafting of selected monomers to the cellulose backbone with subsequent functionalization. The heavy metal adsorption capacities for these modified cellulose materials were found to be significant and levels of uptake were comparable, in many instances, to both other naturally occurring adsorbent materials and commercial ion exchange type resins. Many of the modified cellulose adsorbents proved regenerable and re-usable over a number of adsorption/desorption cycles allowing recovery of the adsorbed heavy metal in a more concentrated form. A new type of adsorbent containing phosphoric acid group for the removal of heavy metals was synthesized by radiation-induced graft polymerization of acrylic acid onto jute fiber. The fibrous adsorbents could be synthesized by introducing a functional chelate group such as phosphate into the jute yarn where acrylic acid acts as a carrier of phosphate group. This fibrous adsorbent has high selectivity to heavy ions and higher rate of toxic metal adsorption than that of commercial adsorbent resin in column mode experiment. This high performance of the fibrous adsorbents is attractive for the removal of toxic metals from the streaming water [20-29].

The aim of this research is to prepare an ion selective heavy metal adsorbent. The adsorbent was made by treating jute fiber using acrylic acid (AA) and phosphoric acid (PA) through graft copolymerization technique using UV radiation. Here acrylic acid was grafted onto the surface of jute fiber which acted as a carrier for phosphate radical (functional group). The adsorbent prepared by this method adsorbed copper ion selectively from waste water successfully [30-33].

Experimental

Materials

Jute yarns were collected from Coats Bangladesh Ltd., the monomer AA, PA (H_3PO_4) and solvent methanol (MeOH) were purchased from Merck, Germany. Photoinitiator Darocur 4043 was procured from Merck, Germany and finally incorporated into the formulation to initiate free radical polymerization reaction.

Methods

The jute yarns were cut into small pieces (20-30 cm in length) and then washed with acetone to remove the foreign particles. After washing they were dried to remove acetone. A number of solutions were prepared with different proportions (10-70 wt%) of acrylic acid in methanol and 2 wt% photoinitiator (Darocur-4043). The samples were soaked in each of the solutions for different soaking time, varied from 10-30 min. After withdrawing from the solutions they were passed under UV curing lamp for different doses (20-50 passes). The samples were then kept for 20-25 h, to complete the polymerization reaction. The cured samples were washed in water for 20-25 h to remove the unreacted monomer and the homopolymers from the sample surface. Then the samples were dried at 105 °C until constant weights were achieved. From the final weight we calculated the percentage of polymer loading (PL). The percentage of AA, soaking time and radiation intensity were optimized for the highest polymer loading. A number of formulations were again prepared using optimized conc. of AA (50 %) and 5-15 % (w/w) PA (85 %) in methanol. Then the solutions were kept for 5 h. After 5 h 2 % photo initiator was again added in each of the solution. The jute yarns were again soaked in the sample for optimized soaking time 20 min and were treated with UV radiation for 40 passes (optimized). The concentration of phosphoric acid was again optimized for the maximum grafting. Tensile strength of both treated and untreated virgin yarns were measured with a tensile strength testing machine HOUNSSICLD, Model no: H50KS, Serial no: H50KS-0404, made in England. A number of solutions of $CuSO_4$ were prepared with distilled water, concentration of Cu^{2+} solutions were 10 ppm. The treated jute yarn was then used as adsorbent. The Cu solution 100 m*l* were taken in five separate beakers (1 g AA+PA) among them three were soaked for 30 min, 1 h and 5 h respectively. In the rest two beakers 1 g pure jute and 1 g AA grafted with jute yarns were soaked for 5 h. After the certain period those threads were withdrawn from the solutions and then analyzed by an atomic absorption spectrophotometer to determine the remaining Cu concentration of the solution. After adsorbing Cu^{2+} (AA+PA) grafted jute yarns were soaked in 0.04 M HCl for regeneration. They were soaked in 100 m*l* acid solution for 1 and 3 h respectively. For regeneration some Cu^{+2} containing yarns were also soaked in water for 3 h. After withdrawing the yarns the solutions were again analyzed by AAS to find out the Cu concentration of the solution.

Results and Discussion

Optimization of Monomer Concentration, Soaking Time, and the Number of UV Passes Based on Polymer Loading on Jute Yarns

Polymer loading (PL) values of the jute yarns against radiation intensities (the number of UV passes) as a function of monomer concentration for various soaking times is represented in Table 1. It was reported that PL values increased with the increase of AA concentrations up to 50 % and further increase of AA concentration, PL values was decreased. Again, the PL values increased with the increase of UV intensities attained the maximum values after the 40th UV pass then decreased as the radiation doses increased. From this investigation, this is clear that 40 UV passes showed the best performance. At 10, 30, 50, and 70 % AA concentration, the PL values were found to be 12.35, 16.00, 17.29, and 15.85 % at 10 min soaking time, respectively. So, a significant improvement of PL values was found for 50 % AA concentration at the 40th UV pass.

At low monomer concentration, the vinyl monomer promotes the rapid propagation reaction with the help of photoinitiator leading to network polymer structure through graft co-polymerization reaction of their double bonds. As the AA concentration is increased the amount of residual concentration is also increased as a consequence of faster rate of formation of three dimensional network structures causing restricted mobility. After the attainment of the maximum, the decrease in PL values at higher monomer concentration may be caused by two factors. At higher AA concentration radical-radical recombination process may be dominant, thus more homopolymers are created rather than monomer - backbone reaction. The other reason could be that the swelling of the jute backbone with MeOH was insufficient due to low methanol concentration. As a result, monomer molecules are incapable of penetrating the jute molecules in the presence of low solvent concentration. This may cause a smaller number of reacting sites at the jute backbone and thus continue to reduce the active sites. The polymer loading values decrease with increasing radiation dose because at higher radiation dose jute yarn may degrade.

In the above investigation, the soaking time was fixed at 10 min but it was found that with the increase of soaking time, a significant impact was found on the PL values. The best PL values could be obtained for 20 min soaking. Higher soaking time reduced the PL values. The highest PL value was reported 21 % at the 40th UV pass for 50 % AA concentration for 20 min soaking time. On the other hand, it was reported that the highest PL value (15.7 %) was achieved at 50 % AA solution for 30 min soaking time. From this investigation this is clear that the jute yarns soaked for 20 min in 50 % AA concentration at the 40th UV pass yielded the maximum PL values (21 %).

Optimization of PA Concentration
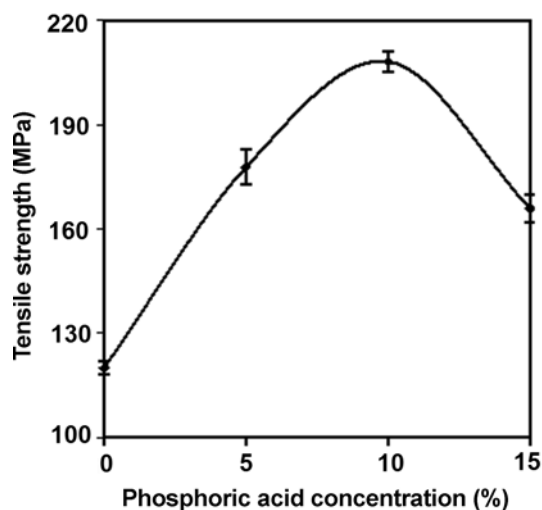#### Polymer Loading

Figure 1 shows the PL value as a function of PA concentration. The value increases with increasing PA concentration. The highest value of 70.95 % is obtained for 10 % PA. The PL value decreases with increasing phosphoric acid more than 10 % may be due to the lower rate of polymerization at the higher PA concentration. It may also be possible that the higher concentration of acid may change or degrade the main polymeric chain, and that's why the PL
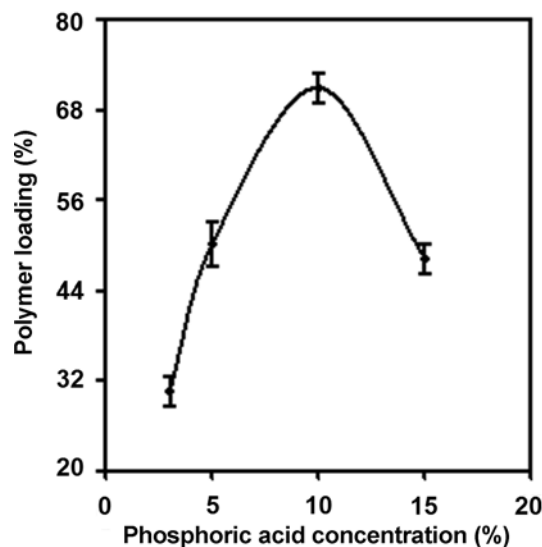
Figure 1. Polymer loading values of the jute yarn against concentration of PA. Monomer concentration: 50 %, Soaking time: 20 min, UV intensity: 40 UV passes.

Table 1. Polymer loading (%) vs. radiation intensities

Radiation intensities (Number of UV passes)		20			30			40			50	
Polymer loading		PL (%)			PL (%)			PL (%)			PL (%)		
Soaking time		10 min	20 min	30 min	10 min	20 min	30 min	10 min	20 min	30 min	10 min	20 min	30 min
Conc. (%) of AA	10	8.28	7.99	5.94	11.48	12.68	9.043	12.35	14	12.22	11.53	10.12	10.63
	30	10.31	7.27	6.6	14.28	14.94	10.5	16	17	13.36	14.8	10.3	10
	50	12.6	7.58	7.6	15.77	16.3	11.2	17.29	21	15.7	13.44	14	12
	70	10.71	8.9	6	12.57	10.9	9.3	15.85	16	13.6	13.2	12.6	8.6

Figure 2. Tensile strength values of AA+PA grafted jute yarn as a function of PA concentration. Monomer concentration: 50 %, Soaking time: 20 min, UV intensity: 40 UV passes.

Figure 3. Cu uptake of AA+H_3PO_4 incorporated jute yarn from 10 ppm solution of Cu for different time intervals.
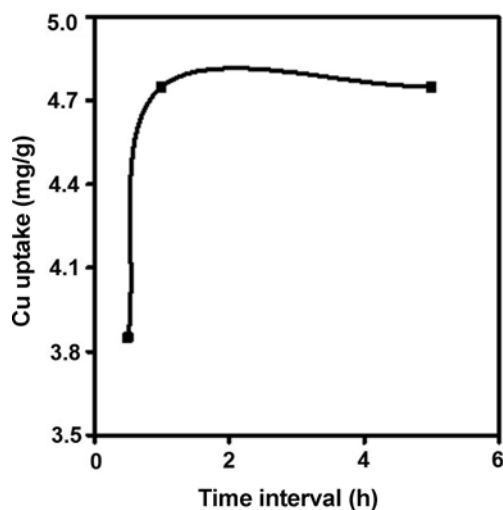
value decreases. When PA is used the polymer loading values enhance quite substantially up to 10 %. Acid helps speed up the copolymerization process through the cross linking of individually segmented units of the polymer. Acidification of solution changes the mobility of the solution at the equilibrium condition of the components during the copolymerization process at the zone of the reactivity associated with the partitioning of the various components present in the solutions. The rate of reactivity coupled with the partitioning is, thus, enhanced for the overall copolymerization process in the presence of acid.

Tensile Strength

The tensile strength of sample increases with increasing PA up to 10 % and the highest value is (208.125 MPa) which has shown in Figure 2. Decreasing of the tensile strength value may be due to the fact that the rate of polymerization decreases at high acid concentration. The other reason may be that the concentrated PA solution may change or degrade the polymeric backbone. H^+ ion breaks the long chain of the jute yarn, thus it renders the tensile strength of the yarn reduced.

Cu Uptake

Figure 3 shows that the metal uptake increases significantly up to 1 h, after which Cu uptake is almost same. This phenomenon occurs due to the fact that after 1 h the threads become almost saturated with Cu. There is no more vacant site in those threads to take more Cu from the solution. It is possible to remove more Cu within 1 h from the same solution if the amount of thread is increased so that the total vacant sites will also increase. It was found that the Cu uptake was 3.85, 4.75, and 4.75 mg per gram of thread for 30 min, 1 h, and 5 h, respectively.
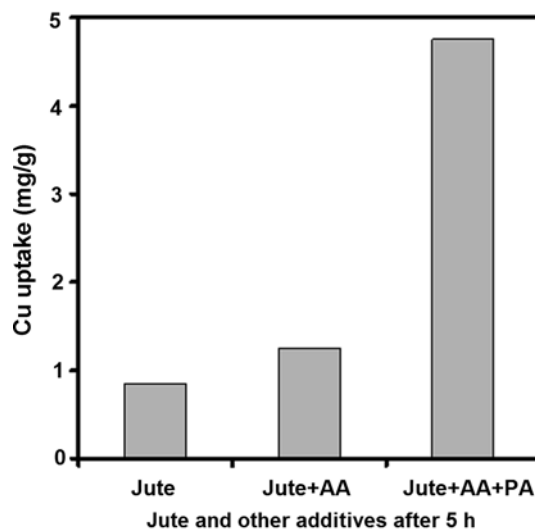

Figure 4. Comparative study of Cu uptake from 10 ppm Cu solution among pure, AA grafted, and AA+PA grafted jute yarn.
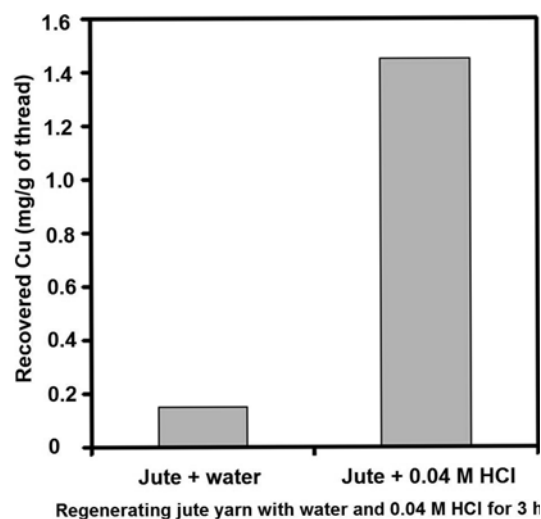
Comparative Study of Cu Uptake

The comparative study of Cu uptake between pure, AA grafted, and AA+H_3PO_4 incorporated jute is presented in Figure 4 as a function of Cu uptake. Figure 4 shows that the pure and the AA grafted threads have removed a very small amount of Cu because some molecules of Cu, which are just in touch with the surface of those threads, can be removed. Cu uptake was found 0.85, 1.25, and 4.75 mg per gram of thread for pure, AA grafted, and AA+H_3PO_4 incorporated jute yarn, respectively.

Regeneration of Adsorbent

After taking metal, the threads have to be regenerated in
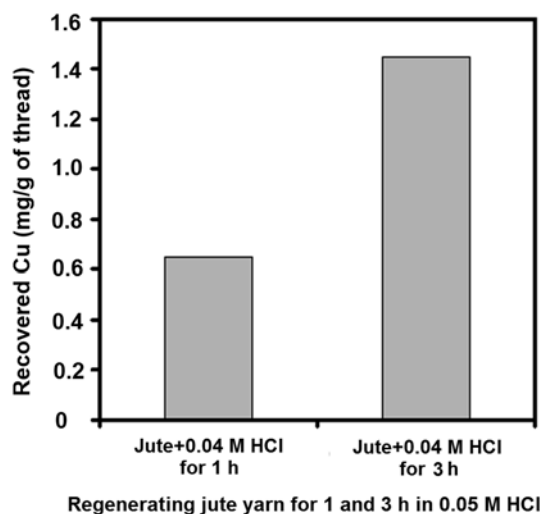
Figure 5. Recovery of Cu after regenerating jute yarn in 0.04 M HCl solution.

Figure 6. Comparative study of recovery of Cu from jute yarn after regenerating in water and acid for 3 h.

acid so that it can be used again as an adsorbent. In Figure 5, regeneration of Cu is presented as a function of time interval when threads are soaked in 0.04 M HCl. The recovered concentration of Cu in the solution is increased with increasing time. By regeneration 0.65 and 1.45 mg Cu per gram of thread was recovered for 1 and 3 h, respectively.

Comparative Study of Regeneration

Comparative study of regeneration between water and HCl acid is presented in Figure 6 as a function of recovered Cu concentration. The concentration of Cu found in water is very negligible, which indicates that the adsorption that has occurred was not simple physical adsorption, but chemisorption. If it is physical adsorption, then the Cu can be extracted from the thread by water wash only. Since it is

chemisorption, it requires external energy such as heat, stirring, or another ion exchange reaction for the adsorbed Cu to be extracted from the threads. That is why the threads must be regenerated in an aqueous HCl solution. 0.15 and 1.45 mg Cu were recovered per gram of thread in water and in acid for 3 h, respectively.

Conclusion

Jute yarns were modified by using acrylic and PA via UV treatment. Based on optimized polymer loading 70.95 % of yearns, ion selective adsorbent was prepared. The optimized formulation was found to be: 10 % PA, 50 % AA, 38 % methanol, and 2 % PI. Copper was effectively removed from the $CuSO_4$ solution and thus indicated the potentiality of the modified jute yarns as ion selective adsorbent. It was also proved that regeneration of Cu was also possible from the grafted jute yarn.

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