



## Preparation of Selective Ion Adsorbent by Gamma Radiation Induced Graft Copolymerization of n-Butyl Methacrylate & Phosphoric Acid on Jute Fiber

Md. Mobarak Hossain<sup>1</sup>, Md. Moniruzzaman<sup>2\*</sup>, Mubarak A. Khan<sup>3</sup>, Md. Shahjahan<sup>2</sup>,  
Md. Zahangir Alam<sup>1</sup>, Mohammad Shah Jamal<sup>2</sup>

<sup>1</sup>Department of Applied Chemistry & Chemical Engineering, University of Dhaka, Dhaka-1000

<sup>2</sup>Bangladesh Council of Scientific & Industrial Research (BCSIR), Dhaka-1205, Bangladesh.

<sup>3</sup>Bangladesh Atomic Energy Commission, Dhaka-1000, Bangladesh.

Received 16<sup>th</sup> February 2014; Revised 25<sup>th</sup> February 2014; Accepted 3<sup>rd</sup> March 2014

### ABSTRACT

Adsorption is one of the popular methods for the removal of pollutants from the waste water and a procedure of choice for treating industrial effluents. Jute fibers were cured with n-butyl methacrylate (n-BMA) & Phosphoric acid using  $\gamma$ -radiation. The highest polymer loading (16.9%) and Tensile strength (189.25 MPa) were found at 20% monomer concentration and 5kGy radiation dose. The optimum conc. of  $H_3PO_4$  was estimated at 9% acid conc. and the polymer loading and tensile strength were estimated 46.1% and 90.7 MPa respectively at this conc. Among virgin jute fiber, 20% n-BMA grafted jute fiber and 20% n-BMA + 9%  $H_3PO_4$  grafted jute fiber, the last one shown the lowest water uptake properties. The 20% n-BMA + 9%  $H_3PO_4$  grafted jute fiber was used for adsorbent. The quantity of Copper was measured by Atomic Absorption Spectrometer. Only 2.035 gm jute fiber adsorb 4.30ppm  $Cu^{2+}$  when the adsorbent was treated for 90 minute.

**Keywords:** Adsorption, Jute fiber, n-BMA, Gamma radiation, Polymer loading

### 1. INTRODUCTION

All over the world, environment is a great concern. Now in the world, environment is severely polluted in different ways. In case of water pollution, it is rigorously polluted by waste discharge from various ways. A different type of chemicals that are excreted from various industries pollutes water tremendously. Removal of toxic metals from waste water is important task to preserve environment [1]. There are a number of heavy metals that are candidates for removal prior to having waste solutions coming in contact with the environment. The chemical contamination of water from a wide range of toxic derivatives, in particular heavy metals, aromatic molecules and dyes are a serious environmental problem owing to their potential human toxicity. Bangladesh is an overpopulated country. Our economy depend on the agriculture but our Government emphasis their vision to industrialization. There are many chemical industries (Textile, Tannery etc) in and around Dhaka city. They are polluting the soil and surface water by discharging their effluent without treatment. This is due to the high cost in the removal of heavy metals and other polluting elements. Therefore, there is a need to develop technologies that can remove toxic pollutants found in waste waters. Among all the treatments proposed, adsorption is one of the more popular methods for the removal of pollutants from the waste water. Adsorption is a procedure of choice

for treating industrial effluents, and a useful tool for protecting the environment. In particular, adsorption on natural polymers and their derivatives are known to remove pollutants from water. The increasing number of publications on adsorption of toxic compounds by modified polysaccharides (natural polymers) shows that there is a recent increasing interest in the synthesis of new low-cost adsorbents used in waste water treatment. These chemicals contain heavy metals like copper, chromium, lead, zinc etc. These heavy metals are very harmful to human health. To serve this purpose, we use a naturally occurring fiber, jute which is a natural biodegradable renewable lignocellulosic raw material composed mainly of cellulose (58-63%), hemicelluloses (20-22%), and lignin (13-15%). In addition to those major constituents, jute also contains trace quantities of organic and inorganic pigments [2]. Jute fiber has a higher extensibility and low water absorption property. Although jute has high tensile modulus, it suffers low elongation at break compared to that of other natural cellulose fibers.

The aim of this research is to prepare an adsorbent which has a very high adsorption rate and capacity, highly selective in nature, low cost and biodegradable. To serve this purpose, we use a naturally occurring fiber, jute which is also renewable, biodegradable. Graft copolymerization is a well-establish technique to improve the desired properties of both natural and synthetic polymers.

\*Corresponding Author:

Email: monir.accedu@gmail.com

Phone: +8801717888893

Different methods of graft copolymerization have been developed in the last few decades and these are well reviewed [1].

We prepare an adsorbent by grafting the jute (unbleached) surface with n-BMA and phosphoric acids by using  $\gamma$ -radiation. In our research the highest tensile strength, polymer loading is achieved with 20% n-BMA concentration, 10 minutes soaking time and at 5kGy  $\gamma$ - radiation dose. This adsorbent has a strong affinity towards copper ion. It can selectively adsorb copper ion from different types of heavy metal contained polluted water [3]. So we can use this adsorbent to remove heavy metals from industrial waste water for the treatment of municipal waste water.

The adsorbent produced by using jute is very effective, selective, durable, low cost, non hazardous, light weight and overall environment friendly.

## 2. EXPERIMENTAL

### 2.1. Materials

The samples jute fibers were collected from the local market. n-BMA, H<sub>3</sub>PO<sub>4</sub>, Methanol and Acetone were used in this research and all were analytical grade.

### 2.2. Method

#### 2.2.1 Sample Preparation

At first the unbleached jute fibers were cut into different length (30, 25 and 20 cm) and then washed half an hour with methanol to remove the foreign particles. After washing they were dried in the oven at 105°C and stored in the desiccators for further treatment. [4].

#### 2.2.2. Formulation of monomer solution

A series of monomer solution was prepared using different proportions of n-BMA monomer (10, 20, 30, 50 and 70%) in methanol [5]. The mixtures were stirred well by a glass rod until a clear transparent solution was obtained and the beakers were covered with foil paper to resist the evaporation of both monomer and the solvent methanol.

### 2.2.3. Polymerization of jute fibers and n-BMA

#### 2.2.3.1. Optimization of the polymer loading, radiation dose and monomer concentration

The weighted and dried jute fibers were immersed in different formulated monomer solution for polymerization. Three individual weighted fibers (30, 25 and 20cm size) were taken for each polymerization. Although they were different in their length, the percentage grafting would be same in proportion that's why we got the correct polymer loading. The samples were dipped in each of the

solutions and kept immersed for 10min (soaking times). After soaking in the different formulations, they were treated by  $\gamma$ -radiation for different radiation doses (2.5kGy, 5kGy, 10kGy and 15kGy) at 1000 krad/hr dose rate.

The irradiated fibers were then left for 24 hours to completion of the polymerization reaction. After 24 hours the fibers were washed thoroughly with benzene in a soxlet to remove homopolymer and unreacted monomer on the jute fiber. Then dried in the oven at 105°C until the constant weight was found. The degree of polymerization of n-BMA in jute fiber was measured by the percentage of polymer loading. The polymer loading of n-BMA treated jute fibers were calculated by deducting the final weight from the initial weight.

$$\text{Polymer loading}(\%) = \frac{W_t - W_0}{W_t}$$

Where, W<sub>t</sub> = weight of the treated dry sample, W<sub>0</sub> = weight of the dry sample before treatment

From the polymer loading of individual fibers, the average polymer loading of each of the polymerization were calculated.

#### 2.2.3.2. Optimization of Phosphoric acid Concentration

In this step the jute fibers were again grafted by the mixture of n-BMA and phosphoric acid. The optimum radiation dose and monomer loading of the highest polymer loading of the previous treatment were kept constant for this treatment. At optimized condition, the jute fibers were again treated with mixture of n-BMA and phosphoric acid in which the concentrations of phosphoric acid were (3, 5, 7, 9, 11, and 13%) [6]. Then the polymerized jute fibers were purified by the same way of the previous treatment and calculated the polymer loading.

#### 2.2.4. Determination of tensile properties

The tensile strength of both treated and untreated virgin fibers were measured with the universal testing machine, controlled by software according to the ASTM method. The tensile properties were measured at cross head speed 10 mm/min and gage length 40 mm.

#### 2.2.5. Determination of water uptake properties

Untreated jute fiber, 20% n-BMA grafted jute fiber and (20% n-BMA+ 9% H<sub>3</sub>PO<sub>4</sub>) grafted jute fiber was soaked in water to determine the water uptake properties at 25 ± 2°C.

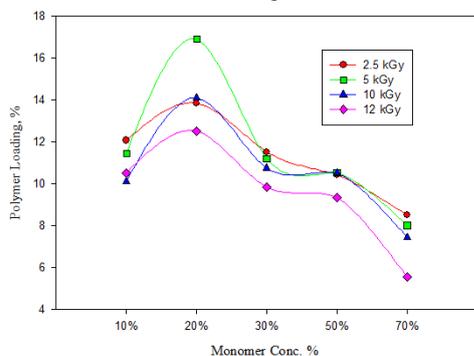
#### 2.2.6. Determination of Cu adsorption capacity

An 18.5ppm CuSO<sub>4</sub> was prepared & soaked in the solution for 30, 60, 90 min. After soaking the remaining Copper in the solution was measured by Atomic Absorption Spectrometer.

### 3. RESULTS AND DISCUSSION

#### 3.1. Optimization of monomer concentration and radiation intensities

Polymer loading values of the fibers were calculated as the weight gain (in %) after they were cured under  $\gamma$ - radiation. The Polymer loading values of the n-BMA treated fibers at different radiation intensities as a function of monomer concentration are shown figure 1.



**Figure 1:** Polymer loading values of the unbleached jute fiber against radiation intensities as a function of monomer concentration when soaking time was 10 minutes.

From the above figure 1 it is clear that the polymer loading values increases with initial radiation doses attains the maxima and then decreases as the radiation dose increases. The decrease in polymer loading values after the attainment of the maximum polymer loading values could be caused by the radiation degradation at higher  $\gamma$ -radiation doses. During the photo-grafting reaction, the n-BMA monomers promote rapid free radical propagation reaction with the aid of high energy radiation, leading to cross-linking through grafting via double bonds. When the n-BMA monomer concentration is increased, the amount of residual instauration also increases as a consequence of fast rate of formation of three dimensional network structures causing restricted mobility at the early stage.

The cross-linking rate, especially during the early stages of radiation, is proportional to n-BMA concentration. n-BMA increases the radical-radical reaction termination and hence decreases the extent of scission reaction and oxidation. The decrease in grafting at higher monomer concentration, as well as higher radiation dose is associated with the fact that the homo polymerization reaction between the monomer and monomer radicals is dominated over the monomer cellulose reaction [7].

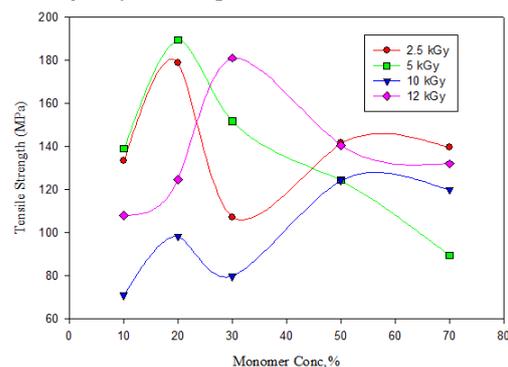
The degree of grafting increases sharply with the radiation dose. Above this limit, the grafting level tends to saturate and the increase with the further increase of radiation dose up is negligible. The saturation of grafting at high radiation doses is

however, expected in both the irradiation environments. At low radiation doses the concentration of the reactive species (peroxides or radicals) increases with radiation doses. These subsequently give rise to graft copolymerization when brought in contact with monomer units. However, at higher concentration of peroxides or radicals, these also undergo radiation induced decomposition at increasing rates in proportion to their dynamic concentration. These two competitive processes are expected to slow down and eventually level off the rate of generation peroxides or radicals needed for graft copolymer reaction [8].

In this experiment the highest polymer loading was obtained at 20% monomer concentration, 10min soaking time and 5kGy (Co-60 gamma source) radiation dose and the polymer loading was 16.9%.

#### 3.2. Tensile Properties

Tensile properties, particularly Tensile Strength and Elongation at break for both the virgin and treated jute yarn samples were determined.



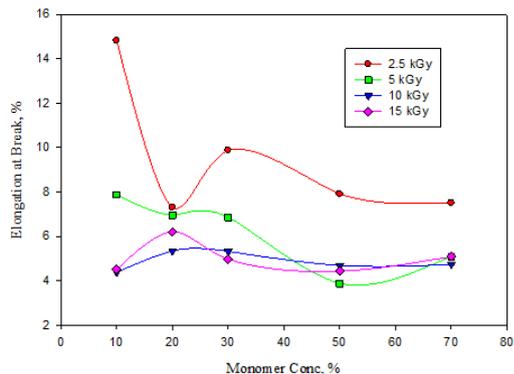
**Figure 2:** Monomer (n-BMA) concentration (%) versus Tensile Strength at different radiation dose.

The tensile strength of the raw jute fiber was 206.3MPa. The tensile strength of the treated jute fiber fell sharply after the polymer loading value of 16.9%. This is due to the fact that the gamma treated jute fibers were brittle and so their tensile strength is lower than the virgin jute fiber. Tensile Strength for the samples increases with the radiation dose after that with the increase of radiation dose tensile strength become lower [9]. Tensile strength becomes lower due to the fact that at higher energy, the bond present in the cellulose molecule may be break down. Figure 2 shows that highest tensile strength (189.25 MPa) found at 20% monomer concentration and at 5kGy radiation dose.

#### 3.3. Elongation at Break

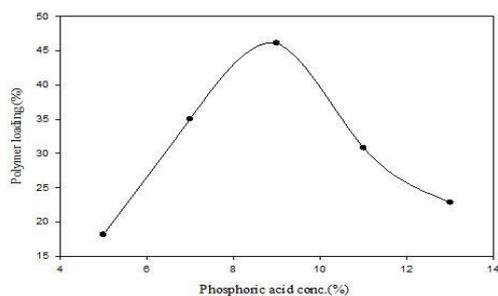
The elongation at break is the strain on a sample when it breaks. This usually is expressed as a percent. Elongation recorded at the moment of

rupture of the specimen, often expressed as a percentage of the original length. It corresponds to the breaking or maximum load.



**Figure 3:** Elongation at break of treated jute fiber with different monomer concentration at different radiation dose.

### 3.4. Optimization of Phosphoric Acid concentration

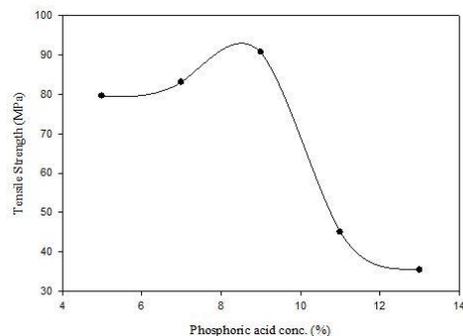


**Figure 4:** Concentration of Phosphoric Acid (%) versus Polymer Loading (%).

At the previous optimized condition the jute fibers were again treated with the mixture of n- BMA and  $H_3PO_4$  (3, 5, 7, 9, 11 and 13%). Here the highest polymer loading was obtained 46.1% at 9% phosphoric acid concentration. At 13% phosphoric acid concentration, polymer loading was very low and the fiber lost its tensile strength and it was damped. At the higher phosphoric acid concentration the polymer loading value is lower due to the fact that at this condition monomer cannot polymerize properly [3]. We used 9%  $H_3PO_4$  as the optimize concentration for the preparation of the final adsorbent.

The tensile strength of sample increases with increasing phosphoric acid up to 9% and the highest value is 90.7 MPa which is shown in the figure 5. Then at the higher concentration of phosphoric acid, tensile strength value become lower. Decrease of the tensile strength value may be due to the fact that the rate of polymerization decreases at the higher  $H_3PO_4$  concentration. Other reason is that, at the higher phosphoric acid

concentration this may change or degrade the polymeric backbone.  $H^+$  ion breaks the long chain of the jute fiber, thus it renders the tensile strength of the fiber reduced.



**Figure 5:** Tensile strength values of n-BMA and  $H_3PO_4$  grafted jute fiber as a function of  $H_3PO_4$  concentration. (Monomer concentration: 20%, Soaking time: 10 minutes, radiation dose: 5 kGy.).

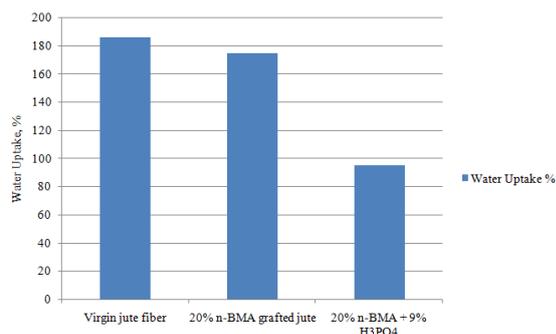
### 3.5. Water Uptake

Water uptake was measured by soaking the untreated jute fiber, 20% n-BMA grafted jute fiber and (20% n-BMA + 9%  $H_3PO_4$ ) grafted jute fiber into water contained in static bath at  $25 \pm 2^\circ C$ . It is clear from the figure that the virgin jute fiber absorbs higher amount of water when compared with the treated jute fiber. The polymerization of the treated jute fiber with the monomer produce the reaction with  $OH^-$  group of the jute fiber through graft co-polymerization reaction and hence reduces the hydrophilic nature of the jute fiber.

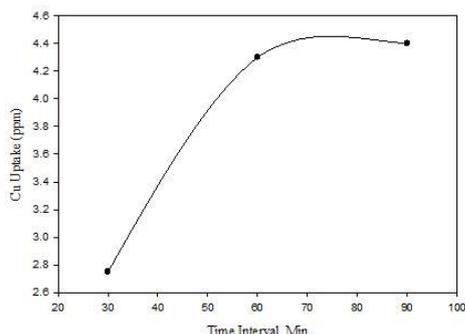
### 3.6. Cu uptake properties of the prepared adsorbent

The prepared 20% n-BMA and 9% phosphoric acid grafted jute fiber act as an adsorbent. The adsorption characteristic was measured by soaking the adsorbent in a  $CuSO_4$  solution by adsorbing the copper ion at different times (30, 60, and 90 minutes). Concentration of the solution was measured by using Atomic Absorption Spectrometer. Concentration of the prepared solution was 18.5 ppm. Figure 7 shows that copper uptake increases significantly up to 1 hour, after which Cu uptake is almost same. This happened due to the fact that after 1 hour of adsorption the adsorbent become saturated with Cu.

At 9% concentration of phosphoric acid, the grafting was highest, and that was 46.1%. Then the highest grafted jute fiber was soaked in 18.5ppm Cu solution [Copper (II) Sulfate Salt] for 30 minutes. After soaking the concentration of the solution was 15.75ppm. This measurement was done by using Atomic Absorption Spectrophotometer (AAS). Here it was observed that only 2.035g jute fiber adsorb 4.30ppm  $Cu^{+2}$



**Figure 6:** Water uptake properties of the virgin and treated jute fiber



**Figure 7:** Cu uptake properties of the prepared adsorbent.

from the solution when the adsorbent was treated for 90 minutes. After adsorption, the n-BMA and phosphoric acid grafted jute fiber was turned into different color. So it is a primary evidence of adsorption of copper ion by the grafted jute fiber.

#### 4. CONCLUSION

The basic aim of this research was to prepare a selective, effective and economic adsorbent. In this work phosphate ion was used as a functional group. PO<sub>4</sub><sup>-</sup> was grafted on the jute fiber as H<sub>3</sub>PO<sub>4</sub> and n-BMA was grafted on the fiber only as carrier of H<sub>3</sub>PO<sub>4</sub>. This research has done only for Cu. But here Cu is used only as a model ion. The same process may remove other heavy metals such as Cd, Cr, Pb, Hg etc.

**Acknowledgments** - We would like to express our grateful thanks and gratitude to the authority of Bangladesh Atomic Energy Commission &

Director, Institute of Fuel Research & Development, BCSIR, for providing us the opportunity to carry out this research work.

#### 5. REFERENCES

- [1]. N. Seko, M. Tamada, F. Yoshii (2005) Current status of adsorbent for metal ions with radiation grafting and crosslinking techniques, *Nuclear Instruments and Methods in Physics Research*, **236**, 21-29.
- [2]. A. Payen, Compt. Rend (1838) Advances in Carbohydrate Chemistry, 1052
- [3]. W. Gordon, Whaley, H. Hilton, Mollenhauer (1963) The Golgi apparatus and cell plate formation-A postulate, *Journal of Cell Biology*, **17**, 216-221.
- [4]. S. Tomoyuki, T. Masao, S. Kyouichi, S. Takanobu (2003) Recovery of cadmium from waste of scallop processing with amidoxime adsorbent synthesized by graft-polymerization, *Radiation Physics and Chemistry*, **66**, 43-47.
- [5]. K. Nalan, K. Akio, S. Takanobu (1995), Proceedings of the 29<sup>th</sup> International Meeting on Radiation Processing, Preparation of amidoxime-fiber adsorbents by radiation-induced grafting, *Radiation Physics and Chemistry*, **46**, 833-836.
- [6]. S. Hassanpour (1999) Radiation grafting of styrene and acrylonitrile to cellulose and polyethylene, *Radiation Physics and Chemistry*, **55**, 41-45.
- [7]. F. Wyssling, A. J. F. Lopeze-Saez, K. Muhlethaler (1964) Formation and development of the cell plate, *Journal of Ultrastructure Research* **10**, 422-432.
- [8]. H. F. Mark, Encyclopedia of Polymer Science and Technology (2004), *John Wiley and Sons, Inc.* **12**, 243
- [9]. K. Sukumaran, S. G. K. Pillai, P. K. Rohatgi, K. Vijayan, Structure property studies of fibres from various parts of the coconut tree (1982), *Journal of Materials Science*, **17**, 2453-2462
- [10]. W.A. Bell, Handbook of Fiber Chemistry (1969), *Bull. Br. Jute Trade R.A.*, **12**, 154

#### Bibliographical Sketch



The corresponding author **Md. Moniruzzaman** completed his B.Sc(Hons) & M.S in Applied Chemistry & Chemical Engineering from Dhaka University. Now he is working as a scientific officer at Bangladesh Council of Scientific & Industrial Research (BCSIR) which is a pioneer research organization in Bangladesh. He has published one international research paper.