

## Synthesis of Acrylate-Modified Cellulose via Raft Polymerization and Its Application as Efficient Metal Ions Adsorbent

Yasser Assem<sup>1\*</sup>, Ragab E. Abou-Zeid<sup>2</sup>, Korany A. Ali<sup>3,4</sup>, Samir Kamel<sup>2</sup>

<sup>1</sup>Department of Polymers and Pigments, National Research Centre, 12622 Dokki, Giza, Egypt.

<sup>2</sup>Cellulose and Paper Department, National Research Centre, 12622 Dokki, Giza, Egypt.

<sup>3</sup>Center of Excellence, Advanced Material & Nanotechnology Group, National Research Centre, 12622 Dokki, Giza, Egypt.

<sup>4</sup>Applied Organic Chemistry Department, National Research Centre, 12622 Dokki, Giza, Egypt.

**P**OLY acrylic acid-co-methyl methacrylate was grafted *via* reversible addition fragmentation chain transfer polymerization to cellulose. The graft copolymer was characterized by FTIR spectrum, thermo gravimetric analyzer, and scanning electron microscope. The adsorption behavior of the grafted cellulose for Ca<sup>2+</sup>, Cu<sup>2+</sup> and Pb<sup>2+</sup> ions was investigated. The adsorption capacity was improved as the molar ratio of acrylic acid increased. The grafted cellulose showed good adsorption performance for Ca<sup>2+</sup> ion with 97 % rather than Cu<sup>2+</sup> and Pb<sup>2+</sup>. That revealed the adsorption process increased due to the increase of the COOH group of acrylic acid, which improves the chelation activity of the grafted polymer.

**Keywords:** Cellulose, Graft copolymer, Reversible Addition Fragmentation Chain Transfer (RAFT), Adsorption, Heavy metals.

### Introduction

Water has a wide impact on all aspects of human life like health, food, energy and economics. In the last decades, many methods have been studied for treatment of underground water like; ion exchange, chemical precipitation, nano-filtration, reverse osmosis and adsorption. In particular, adsorption method has attracted scientific focus due to high availability of different adsorbents, low cost, and easy handling [1]. In recent decade, scientists have focused to prepare adsorbent from new, sustainable, environment-friendly, and inexpensive natural polymer due to variation in raw material prices, international difficulties in raw material supplies, and increasing public consciousness on environmental issues.

Cellulose is the most widespread polymeric raw material in nature and it is obtained from different plants and bacterial sources [2]. In the last few decades, cellulose graft copolymers have gained a substantial interest, due to their unique properties. These properties make them suitable for using in a wide range of applications such as medical, water treatment [3,4], pharmaceutical [5], textiles, filtration, etc. To modify cellulose and control this modification, understanding

its structure is a pre-requisite. The molecular structure of cellulose is composed of linear chains of glucose unit with three OH groups. These groups are capable of forming inter and intra hydrogen bonds, yielding a straight and crystalline chain nature [6,7]. Cellulose has high dense hydrogen bonded network, so it is insoluble in water and most organic solvents. Thus, most cellulose reactions, including polymer grafting, are heterogeneous reactions which carried out at the solid or swollen state. To enhance metal-binding ability of cellulose, the introduction of new functional groups via graft copolymerization is one of the activations of cellulose. Various functional groups can be grafted to cellulose such as acrylonitrile [8], acrylic acid [9] and acrylamide [10].

In the last decades, attempts to minimize the chain transfer and to control the molecular weight polydispersity on the grafted cellulose, a controlled/ "living" radical polymerization methods have been investigated [11]. Among them atom transfer radical polymerization (ATRP) and reversible addition fragmentation transfer polymerization (RAFT) are the two suitable methods to prepare grafted cellulose.

\*Corresponding author e-mail: ya.assem@nrc.sci.eg

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In heterogeneous process, polystyrene graft cellulose by a RAFT process was reported by Perrier, et al. [12] and Carlmark et al prepared a poly(2-hydroxyethyl methacrylate) graft cellulose using an ATRP process [13]. Huang, et al. prepared cellulose graft copolymers with different monomers using a homogeneous ATRP process [14,15].

RAFT polymerization is a powerful and useful living polymerization method for synthesizing well-defined, advanced graft polymer features and controlling the polymerization of numerous vinyl monomers over moderate conditions. RAFT can be used to graft various monomers onto solid supports such as silica [16], silicon [17], carbon nanotubes [18], polypropylene, gold, and core-shell microspheres. Also, it has been reported to graft vinyl monomers on cellulosic materials. But there is a very limited study on modification of cellulose via RAFT-mediated graft polymerization. The first modification of cellulose by RAFT polymerization in heterogeneous media was done by Roy & Perrier [19,20].

In this study, the grafting of polyacrylic acid and polymethylmethacrylate from bagasse cellulose was reported. Preparation and characterization of cellulose-based macro chain transfer agent and its use to mediate the reversible addition-fragmentation chain transfer polymerization of acrylic acid and methyl methacrylate are reported. The adsorption of the grafted cellulose for Ca<sup>2+</sup>, Cu<sup>2+</sup> and Pb<sup>2+</sup> ions were also investigated.

## **Experimental**

### *Materials*

Cellulose was extracted from bagasse pulp which delivered from Quena Paper Industry Company, Egypt. Acrylic acid, dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP) as a catalyst, 3-mercaptopropionic acid, carbon disulfide, benzyl bromide, chloroform, hydrochloric acid, sodium chloride solution, sodium sulfate, n-hexane and ethyl acetate, potassium hydroxide dichloromethane are from ACROS and used as received.

### *Preparation of cellulose-RAFT*

Cellulose (2 g) was immersed into 50 mL round flask containing RAFT agent (5g) dissolved in 15 mL of dichloromethane (DCM). Dicyclohexylcarbodiimide (DCC) (0.8 g, 4 mmol) was dissolved in 10 mL DCM and added to

the cellulose containing reaction flask at room temperature. 4-Dimethylaminopyridine (DMAP) (0.44 g, 3.6 mmol) was dissolved in DCM (15 mL) and slowly added to the reaction mixture. The reaction mixture was left to stir, at room temperature, on magnetic stirrer for 72h. At the end of the reaction, the samples were thoroughly washed with different solvents in the following sequence; DCM, THF, THF: water (1:1), water, and methanol. Finally, the product was placed in a drying oven at 50 °C to dry overnight.

### *Polymerization*

Cellulose-RAFT (1 g) was stirred in 10 mL deionized water for AA homopolymerization and H<sub>2</sub>O/DMF 70/30 respectively for the AA and MMA copolymerization in 50 mL Schlenk flask and purged with Argon for 30 min. A degassed stock solution of the monomers acrylic acid and methylmethacrylate (AA, MMA) and 10 mL solution of 2,2'-Azobis(2-methylpropionamide) dihydrochloride (V50) initiator (0.01 g/mL H<sub>2</sub>O) were prepared. After that the stock solution of the macro-RAFT was placed in an oil bath at 70 °C. Then, the required amounts of monomers (at various AA/MMA weight ratios) and initiator were fed into the reactor with dosing rate 1 mL/min and 0.1 mL/min for both monomers and initiator, respectively (Table 1).

The required amount of monomers and initiator were fed with dosing rate 1 mL/min and 0.1 mL/min for both monomer and initiator respectively, the AA and MMA monomers were fed into the reaction mixture at different AA/MMA weight ratios (Table 1). After last addition the polymerization reaction was left to run for 8h followed by addition of few drops of methanol at the end of polymerization process. The final obtained product was a mixture of grafted cellulose and free homo/copolymers. The grafted cellulose was collected by filtration in a Buchner funnel and subjected to Soxhlet extraction using de-ionized water followed by extraction by THF for 6h. The grafted cellulose samples were dried in a drying oven at 40 °C [21].

### *Cleaving of polymer chains from cellulose backbone*

Two transesterification methods (i.e. acid-base catalyzed) were studied to hydrolyze the PAA and PAA-co-PMMA chains from the cellulose backbone. In a base catalyzed hydrolysis experiment, 1 g of cellulose-g-PAA and cellulose-g-PAA-co-PMMA samples was immersed into a

bottom flask containing 200 mL of KOH (2.0 M solution in H<sub>2</sub>O). The reaction mixture was refluxed for 48 h. After the completion of the reaction, 10 mL of H<sub>2</sub>O/THF 9/1 was added to the flask and the solid cellulose substrate was removed from the mixture, subsequently the solvents were evaporated. The solid was washed with methanol to remove the excess of KOH; the remaining product (cleaved polymer grafts) was separated by filtration. In case of acid hydrolysis, 0.1 g cellulose-g-PAA and cellulose-g-PAA-co-PMMA samples were immersed into a round-bottomed flask containing 150 mL of 2.0 M HCl aqueous solution. The mixture was stirred at 90 °C for 48 h. The reaction mixture was filtered to separate the solid cellulose particles. Then 200 ml of THF was added and the reaction mixture was stirred for 20 minutes. The organic layer was separated by separating funnel. Upon evaporation of THF, the solid polymer was obtained and was left to dry at 50 °C in a drying oven for 48 h. [22].

#### *Instrumentation and characterization*

##### *Gel permeation chromatography (GPC)*

The molecular weights of all polymers were measured by Chloroform GPC at 25°C. Sample concentration was 1 g/L. The apparatus consists of a Gynkotek HPLC pump, an Agilent Autosampler 1200, linear columns (PSS, polystyrene) consisting of a pre-column 10 μ, 8 x 50 mm, a column 10 Å, 8 x 300 mm and two columns 3000 Å, 8 x 300 mm. As detector, RI detector of Knauer Company was used. For calibration, linear PMMA with a narrow mass distribution and molecular weight between 500 and 1,000,000 was used. Toluene was used as an internal standard. The elugram was evaluated with PSS- WinGPC Unity program.

##### *Nuclear magnetic resonance spectroscopy (NMR)*

<sup>1</sup>H (400.13 MHz) NMR spectra were recorded on a Bruker DRX-300 spectrometer located at Faculty of Pharmacy Ain Shams University, Egypt. Tetramethylsilane (TMS) was used as an internal standard.

##### *Infrared spectroscopy (FTIR)*

The IR spectra were measured on a FT-IR spectrometer of type Bruker with an attached IR microscope of the type UMA 600 from Digilab. Infrared spectroscopy (IR) was performed by means of Digilab (Excalibur series) instrument with ATR crystal ZnSe at the Textile Research Division NRC, Egypt.

##### *Thermo gravimetric analysis (TGA)*

The thermal stability of cellulose samples before and after grafting was tested by thermo gravimetric analysis (TGA, Shimadzu DTG-60, Japan) at a heating rate of 10 °C/min from 25 to 800 °C under a nitrogen atmosphere.

##### *Scanning electron microscopy*

Scanning electron microscopy (SEM) photomicrographs of the cellulose before and after modification were observed by a Quanta 200 environmental scanning electron microscope (Philips-FEI Co., Holland) operated at an accelerating voltage of 5 kV, and the dried samples were coated with a gold layer using a diode sputter coating unit. Electron micrographs of each sample were recorded at a magnification of 500.

##### *Adsorption of Ca<sup>2+</sup>, Cu<sup>2+</sup> and Pb<sup>2+</sup>*

The adsorption experiments were performed on a platform shaker at 200 r/min and 25±2 °C for 2 h using 100 mL shaker flask. Cations concentrations were analyzed using atomic absorption spectroscopy (PerkinElmer 3110, USA). The adsorption capacity  $q_e$  (mg/g) was calculated as described by the following equation:

$$q_e = (C_o - C_e) V / m \quad \text{Eq. 1}$$

Where,  $C_o$  (mg/L) is the initial metal ion concentration,  $C_e$  is the metal ion equilibrium concentration,  $V$  (L) is the volume of the metal ion solution and  $m$  (g) is the mass of adsorbent.

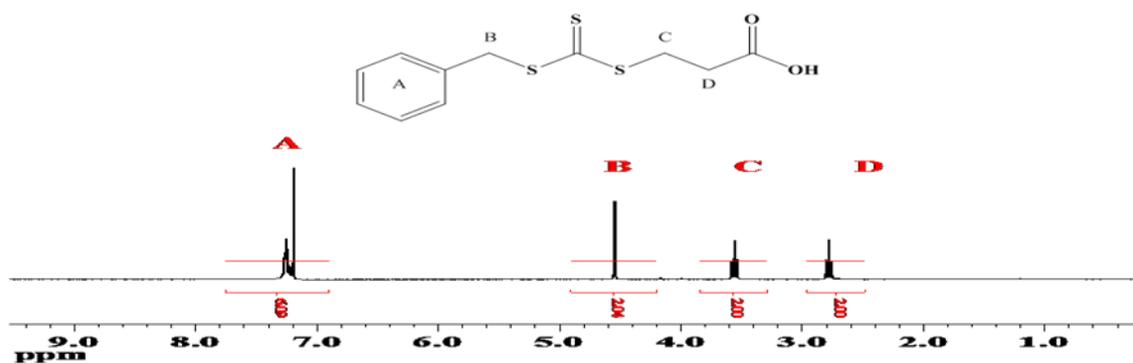
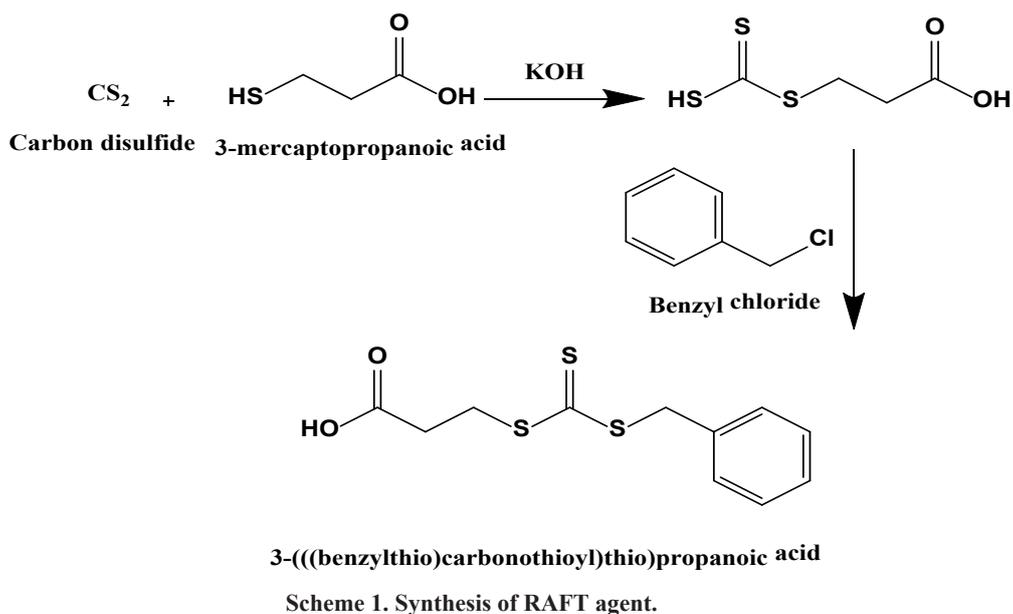
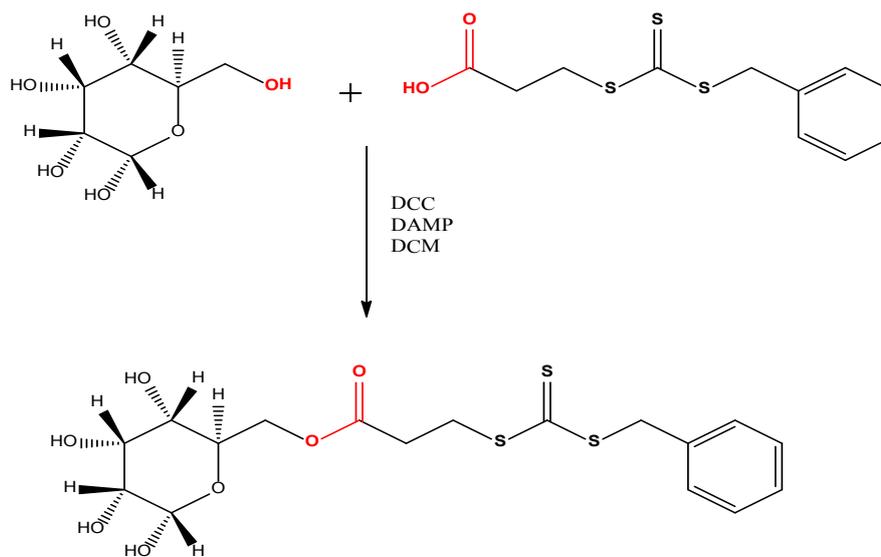
## **Results and Discussion**

### *Synthesis of RAFT and Macro-RAFT agents*

Cellulose was grafted with acrylic acid and methyl methacrylate in order to increase the chelating carboxylic groups on its surface. At first, a suitable RAFT agent namely; Benzylsulfanylthiocarbonylsulfanyl-propionic acid was synthesized according to Scheme 1.

As shown in Fig. 1, the <sup>1</sup>H NMR of the prepared RAFT agent revealed 3CH<sub>2</sub> groups which correspond to 2 triplets bands at 1.85, 2.5 and singlet band at and 4.5 ppm [23].

After that a macro RFAT agent was prepared by introducing the RAFT agent (1) onto the surface of cellulose via Steglich esterification mechanism, in presence of dicyclohexylcarbodiimide (DCC) as a coupling reagent and 4-dimethylaminopyridine (DAMP) as a catalyst. This reaction generally takes place at room temperature using dichloromethane as a solvent, as illustrated in Scheme 2.

Fig.1.  $^1\text{H}$  NMR of RAFT agent in  $\text{CDCl}_3$ .

Scheme 2. Functionalization of cellulose by RFAT agent via Steglich esterification mechanism to produce Macro-RAFT agent.

### FT-IR of cellulose and its graft Copolymers

The FTIR spectra of cellulose, cellulose-RAFT and its graft copolymers are shown in figures 2 and 3. In the spectrum of cellulose and cellulose-RAFT (Fig. 2), a characteristic stretching vibration band of carbonyl group (C=O) at around 1750  $\text{cm}^{-1}$  appeared that is related to the RAFT agent.

After that, the RAFT polymerization of acrylic acid (AA) and methyl methacrylate (MMA) took place in THF using AIBN as azo initiator at 70  $^{\circ}\text{C}$ . At first a homo-polymer of acrylic acid was

grafted onto the cellulose surface. The grafting reaction was followed by FTIR (Fig. 3). The characteristic absorption peaks of grafted cellulose with AA and MMA appeared at about 1800  $\text{cm}^{-1}$  due to the aliphatic C-H stretching vibration of the monomeric repeating units and a carbonyl (C=O) stretching vibration at around 1750  $\text{cm}^{-1}$  were present, respectively [24, 25].

A portion of acrylic acid (AA) was replaced by methyl methacrylate (MMA) in order to insert MMA segments between AA polymer chains.

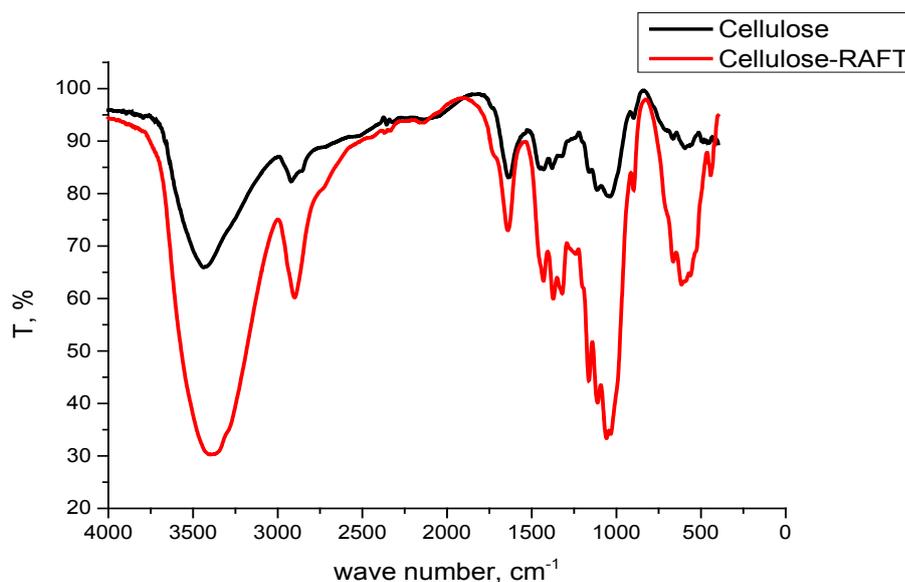


Fig. 2. FT-IR of neat cellulose and Cellulose-RAFT.

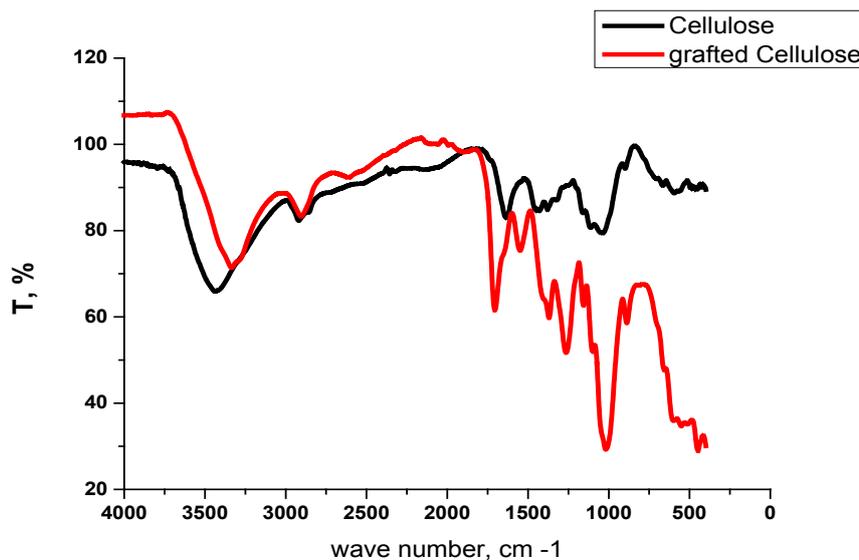


Fig. 3. FT-IR of Cellulose and grafted Cellulose.

This step aims to increase the spaces between the pendant carboxylic groups in AA moieties on the cellulose surface. The AA/MMA ratios were shown in Table 1.

*Cleaving of polymer chains from cellulose backbone*

Two transesterification methods were studied to hydrolyze the PAA and PAA-co-PMMA chains from cellulose. The hydrolyzed products were subjected to GPC and  $^1\text{H}$  NMR analyses. In Fig. 4 and 5, the  $^1\text{H}$ NMR spectra of hydrolyzed PAA and PAA-co-PMMA are represented. The peaks assignments were done easily.

The molecular weights of the hydrolyzed samples were represented in Table 1 and the GPC elugrams are plotted in Fig. 6. The  $M_n$  values of the hydrolyzed polymers are slightly decreased as the amount of the PMMA increased in the matrix. The PDIs values are within the normal range of the common values obtained by RAFT polymerization. A slight elevation was observed in the PDI values in case polymers containing higher amount of PMMA as also indicated by the shoulder in the GPC elugram (Table 1 sample 5).

*Scanning Electron Microscopy*

SEM micrographs of cellulose and grafted

TABLE 1. GPC analysis of PAA-co-PMMA at different AA/MMA ratios.

Code	AA/MMA molar ratio, %	GPC analysis of hydrolyzed samples	
		$M_n$	PDI
1	100/0	12000	1.10
2	95/05	11500	1.30
3	90/10	10200	1.20
4	85/15	9500	1.20
5	75/25	9100	1.30

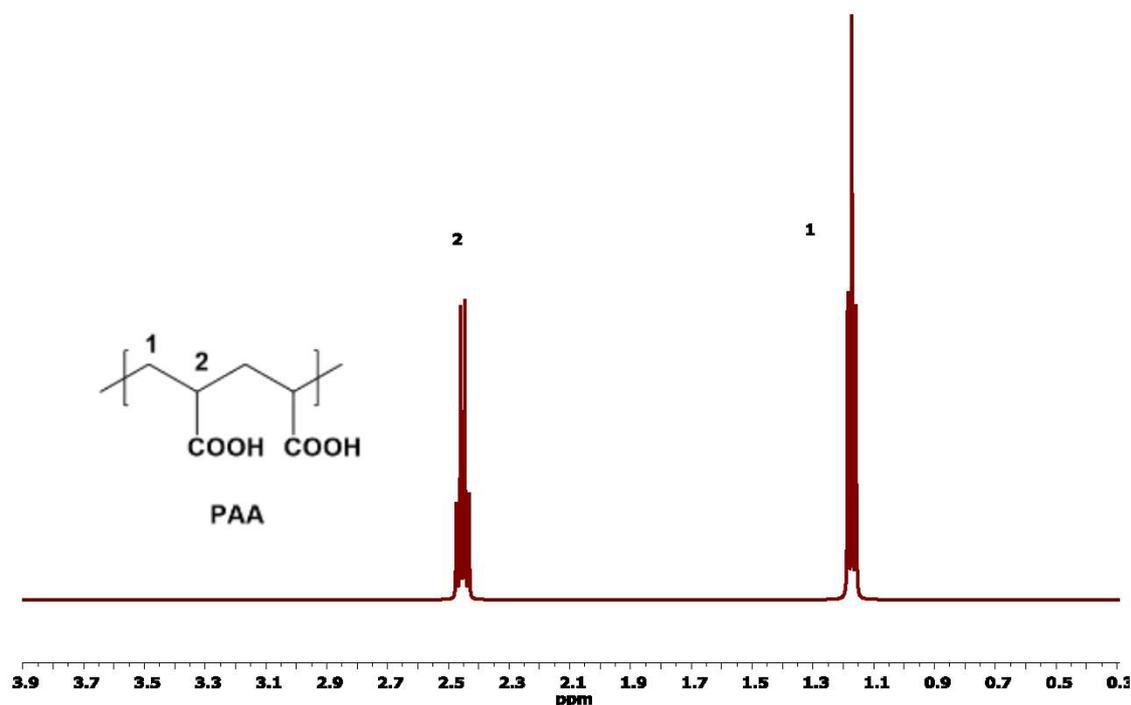


Fig. 4.  $^1\text{H}$ NMR of hydrolyzed PAA.

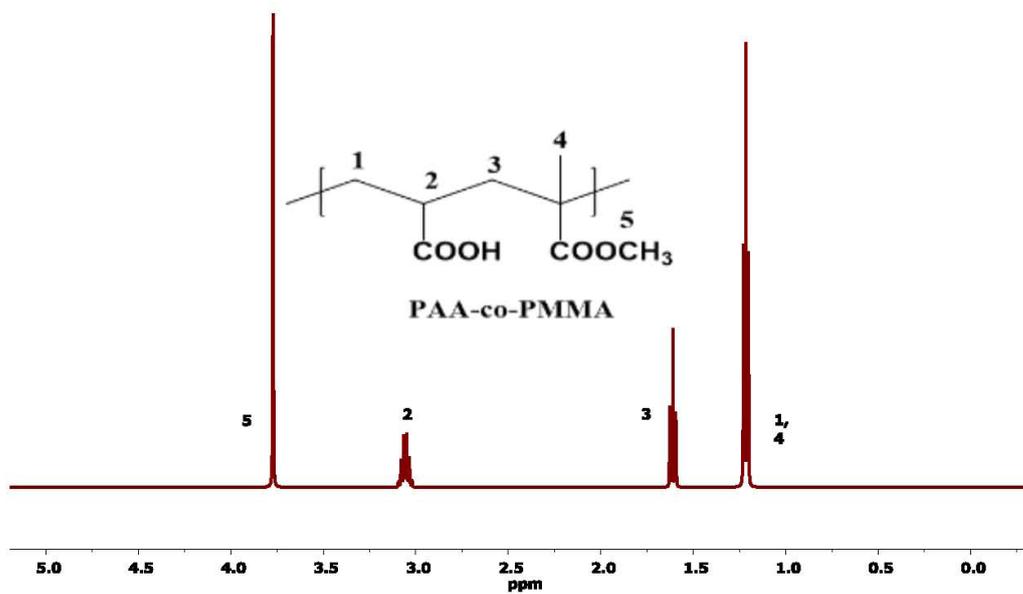


Fig.5. <sup>1</sup>H NMR of hydrolyzed PAA-co-PMMA.

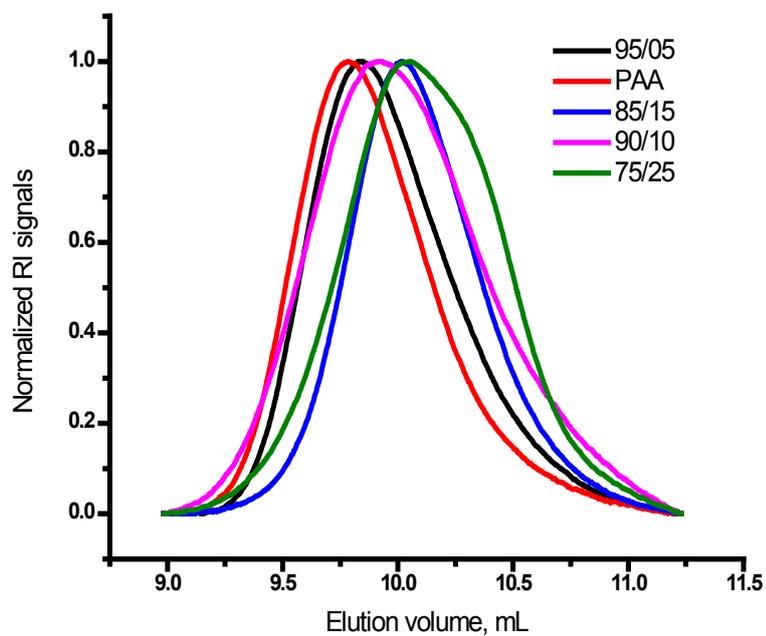


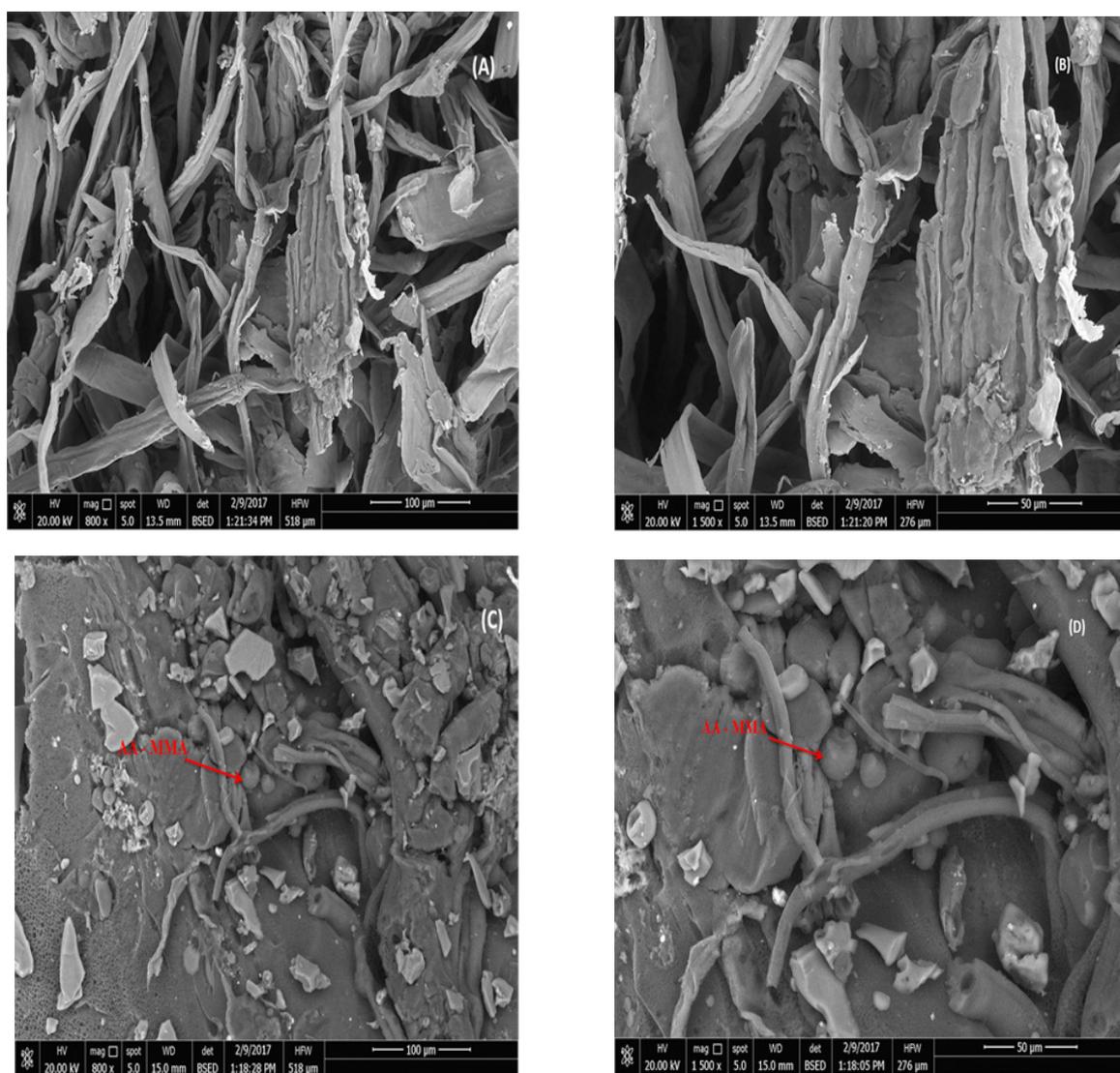
Fig. 6. GPC Elugrams of the hydrolyzed polymers.

cellulose PAA-co-PMMA with AA/MMA 75/25 molar ratio% copolymers are shown in Fig. 7. From Fig. 7, it is evident that the grafted and ungrafted cellulose have different structural features. The surface of the modified cellulose is smoother, less fractured, that is due to the entanglement of the polymeric chains.

#### *Thermo gravimetric analysis*

Figure 8 displays the thermal gravimetric analysis of unmodified cellulose fiber and cellulose-g- PAA-co-PMMA (AA/MMA 75/25 molar ratio). It demonstrates that the thermal stability of the grafted cellulose is higher than that of cellulose itself in the temperature range of 25–600°C. As cellulose-g- PAA-co-PMMA

is hygroscopic, nearly 10 wt % weight losses have occurred at 100°C, due to the evaporation of residual water compared to only 8 wt% weight loss for the cellulose. In case of cellulose-g-PAA-co-PMMA, In case of cellulose-g-PAA-co-PMMA, a considerable enhancement in thermal stability has been noticed as compared with the ungrafted cellulose; however, a considerable enhancement in thermal stability has been seen. As the temperature increases, the main mass loss of the grafted cellulose starts at about 420°C corresponding to cellulose degradation at 420°C. Finally, weight loss for cellulose is much more than that of grafted cellulose. So, the grafting of cellulose can enhance the thermal stability of cellulose.



**Fig.7.** SEM photomicrographs of (A & B) unmodified cellulose fiber and (C & D) cellulose-g- PAA-co-PMMA (AA/MMA 75/25 molar ratio).

*Egypt.J.Chem.* 62, No.1 (2019)

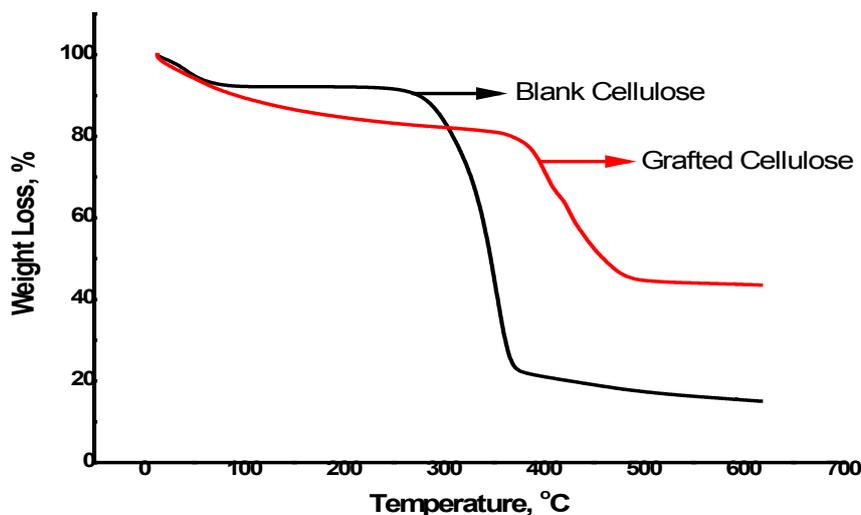


Fig. 8. TGA of cellulose fiber and cellulose-g- PAA-co-PMMA (AA/MMA 75/25 molar ratio).

#### Metal ion adsorption

We have screened the grafted cellulose samples on  $\text{Ca}^{++}$  (250 mg/L),  $\text{Cu}^{++}$  (30 mg/L) and  $\text{Pb}^{++}$  (30 mg/L) solutions to test their adsorption activity in removing  $\text{Ca}^{++}$ ,  $\text{Cu}^{++}$  and  $\text{Pb}^{++}$  cations. Cations concentrations were analyzed using atomic absorption spectroscopy. The adsorption capacity  $q_e$  (mg/g) was calculated as described in equation 1.

The data presented in Fig. 9 and 10 revealed the improvements in the adsorption process with

using grafted cellulose on the three tested cations. The grafted cellulose showed good adsorption performance for  $\text{Ca}^{2+}$  ion with 97% rather than  $\text{Cu}^{++}$  and  $\text{Pb}^{++}$ . The adsorption studies demonstrated that the adsorption process of metal ions decreased with increasing MMA ratio in the cellulose-g-PAA-co-PMMA. In other words, the adsorption capability of cellulose-g-PAA-co-PMMA could be enhanced by increasing the COOH groups of acrylic acid that improve the chelation activity of the grafted cellulose.

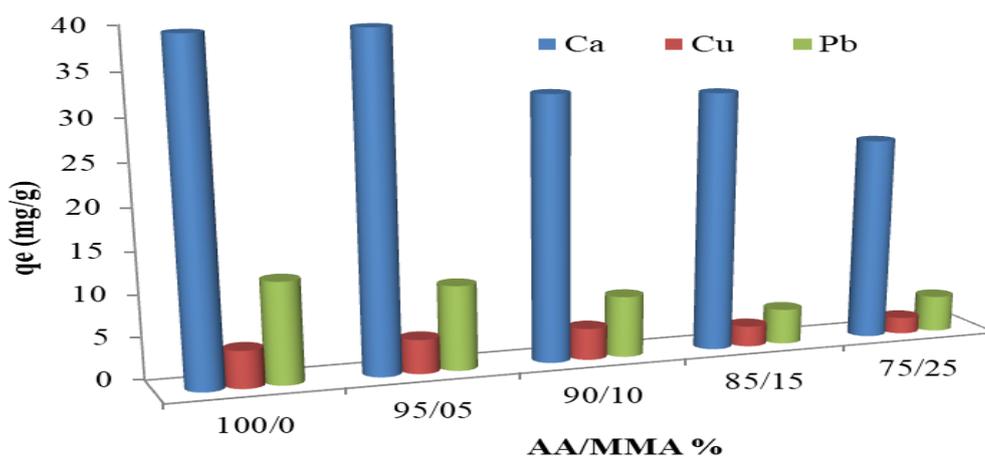


Fig. 9. Effect of AA/MMA ratios on adsorption capacity of grafted cellulose.

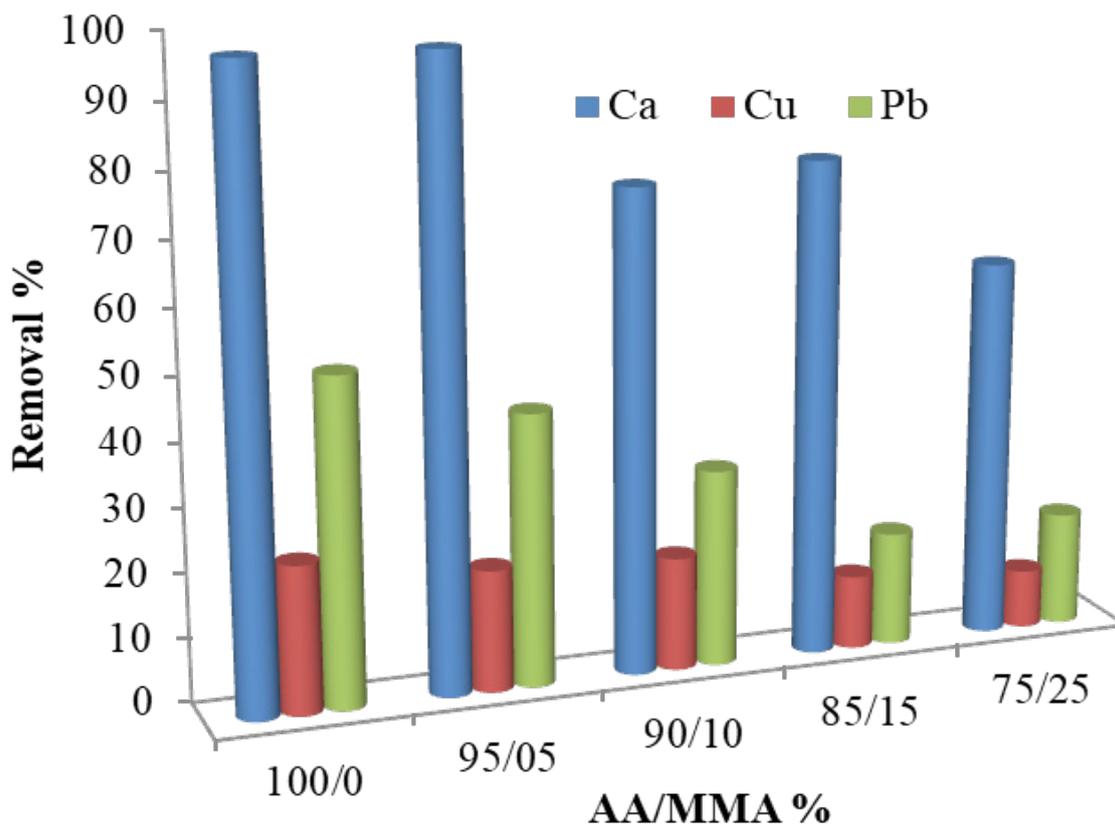


Fig. 10. Effect of AA/MMA ratios on Removal % of grafted cellulose.

### Conclusion

The graft copolymerization of acrylic acid and methylmethacrylate onto cellulose was successfully carried out by RAFT Polymerization, which considered as one of the most versatile method that gives a well-defriend polymeric chains with narrow disperse polymers. The grafting process was confirmed by the characterization of FTIR, TGA, and SEM. The grafted cellulose showed good adsorption performance for  $\text{Ca}^{2+}$  and  $\text{Pb}^{2+}$  ions than  $\text{Cu}^{2+}$  ion. The studies of adsorption demonstrated that the grafting of cellulose with acrylate copolymers is promising in removing  $\text{Ca}^{2+}$  ions from aqueous solutions.

### Conflict of Interests

The authors declare that they have no conflict to interests.

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## تخليق سبيلوز مطعم بالاكريلات عن طريق البلمرة الجذرية RAFT وتطبيقه كمادة مازة للأيونات الفلزية

ياسر عاصم<sup>١</sup>، رجب أبو زيد<sup>٢</sup>، قرنى على<sup>٣</sup>، سمير كامل<sup>٤</sup>  
<sup>١</sup>قسم البلمرات و المخضبات - المركز القومي للبحوث - الجيزة - مصر.  
<sup>٢</sup>قسم السبيلوز و الورق - المركز القومي للبحوث - الجيزة - مصر.  
<sup>٣</sup>مركز التميز العلمي- مجموعة المواد المتقدمة و النانوتكنولوجي- الجيزة - مصر.  
<sup>٤</sup>قسم الكيمياء العضوية التطبيقية - المركز القومي للبحوث - الجيزة - مصر.

في هذا البحث تم تطعيم السبيلوز ببوليمرات حمض الاكريك و ميثيل ميثاكريلات وذلك بطريقة بلمرة انتقال السلسلة المضافة و المتكسرة عكسيا وهي نوع من أنواع البلمرة الجذرية المحكمة. تم توصيف السبيلوز المطعم بواسطة مطياف الأشعة تحت الحمراء، و التحليل الحراري الوزني و الميكروسكوب الإلكتروني الماسح. و تم تقييم السبيلوز المطعم كمادة مازة لبعض الكاتيونات مثل الكالسيوم و النحاس و الرصاص. و وجد ان سعة الامتزاز تحسنت كلما زادت نسبة حمض الاكريك في السبيلوز المطعم. حيث وجد ان كفاءة السبيلوز المطعم في امتزاز كاتيون الكالسيوم تصل الى ٩٧٪ مقارنة بكاتيون النحاس و الرصاص. ويرجع زيادة كفاءة السعة الامتزازية للسبيلوز المطعم لزيادة مجموعات الكربوكسيل المتواجدة في حمض الاكريك. و هذا بدوره يؤدي الى تعزيز القدرة الخاطفية للسبيلوز المطعم.