



GRAFT COPOLYMERIZATION OF ACRYLAMIDE MONOMER ONTO RECYCLED CELLULOSE BACKBONE AND ITS EFFICACIES FOR REMOVAL OF SOME HEAVY METAL IONS IN WASTE WATER

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ABSTRACT

Acrylamide was grafted onto cellulose backbone of old newspaper by CAN initiator in aqueous medium. Grafting parameter such as percentage grafting (GP%) and Grafting yield (GY%) was evaluated at different reaction conditions such as temperature, time, monomer and initiator concentration. Hence it was after 150 minutes (at Temperature of 50 °C, 2.5 g of CAN, 4 g of AAM) had highest GP% of 97% and GY% of 160% for CE-g-PAAM respectively. The products were characterized by FTIR and TGA analyses. Removal of heavy metals from wastewater was evaluated using the grafted copolymer. The results revealed promising potential of the grafted cellulose as adsorbent for remediation of waste water.

Keywords: Acrylamide, Grafting parameter, FTIR characterization, remediation of waste water

INTRODUCTION

Significant advances in cellulosic modifications and the resultant production of derivatives with unique chemical and physical properties have dramatically increase interest in cellulose research over the past decade. Polymers comprise of both natural and synthetic materials with a wide range of properties which makes them very much essential in daily's life. Some of the naturally occurring polymers are proteins, starches, cellulose and latex. Cellulose is a polymer (macromolecule) which consists of repeating units of structure that are typically interconnected via covalent bonds. Cellulose comprises of large numbers of hydroxyl groups which are chained together linearly (Badawyet *et al.* 2005). The availability of cellulose constitutes are most abundant worldwide and it's one of the renewable polymer resources as well. Although, annually 1011×10^{12} ton of cellulose is being generated by photosynthesis in its pure form yet, commonly, cellulose merges with lignin and other hemicelluloses of woody plant's cell wall (Malaque *et al.*, 2007) Copolymerization increases the physical components and the efficacy of a polymer for many applications. Copolymerization changes the structure of the polymer chain and modulates all intramolecular and intermolecular forces, Characteristics like crystallinity, temperature, glass transition, chemical reactivity, permeability and elasticity can be change within wide range (Chhatbar *et al.*, 2009). Graft copolymer, are branch molecules where the key chain is made completely of one repeated unit, while the branch-chain are made of different another repeated unit (Crini *et al.* 2004). Hence, it is essential to modify the properties of polymers in order to align them to designed tailor-made specification for target applications. Grafting is a simple technique used to incorporate desired active functional groups on the backbone of a polymer for different purposes. Grafting copolymerization onto cellulose induces physical changes, since the introduction of side chains leads to different structural characteristics in raw materials. Grafting of cellulose shows new

properties such as hydrophobic or hydrophilic character and resistance to chemical and biological agents (Nada, 2010).

EXPERIMENTAL

MATERIALS

All the glass wares used throughout the experiment were rinsed using fresh solution of HNO₃/HCl (3:1, v/v) washed with distilled water and dried before used. Measuring cylinder, test tube, stainless sieve, conical flask, Ceric ammonium nitrate, Acrylamide, Sodium hydroxide and sodium hypochlorite were purchased from sigma Aldrich chemicals pvt. Ltd, sulfuric acid paraffin oil and Nitrogen gas were obtained from Umaru Musa Yar'adua University laboratory.

GRAFT COPOLYMERIZATION

250 ml three-neck flasks equipped with a stirrer and condenser was used by immersing it into paraffin oil. N₂ was purge into the flask to remove oxygen during the reaction. 5 g of cellulose was prepared was added into 100 ml distilled water and was preheated at 80°C for 30 min with stirring. The contents of the flask were cooled down to 50°C and then 2 ml of H₂SO₄:H₂O (1:1) was added to the reaction mixture. The required amount of 0.1M CAN solution was added after 5 min., and the reaction mixture was stirred uniformly. The required amount of AAM monomer (1, 2, 3 and 4 g) after 10 min was added and stirred for 60 minutes throughout the process. At the end of the reaction, the product was cooled and poured into 200 ml of methanol/acetone to create precipitation. The grafted sample was washed several times with methanol/ H₂O at the ratio of 4:1, and then dried in oven at 50°C to constant weight (Kaur *et al.*, 2013)

Grafting parameters such as monomer concentration, Initiator concentration, time, temperature were optimized using the procedure described above. The Grafting percentage (%GP) was calculated according to Fernandez *et al.*, (1990).

$$GP(\%) = \frac{\text{weight of polymer grafted}}{\text{initial weight of backbone}} \times 100 \quad \text{3-1}$$

$$GP\% = \frac{W_i - W_0}{W_i} \times 100 \quad \text{3-2}$$

$$\text{Grafting yield percentage} = \frac{W_i - W_0}{W_2} \times 100 \quad \text{3-3}$$

W_i= final weight of grafted Cellulose, W₀= initial weight of cellulose before grafting and

W₂= is the weight of monomer

CHARACTERIZATION METHODS

The non-grafted cellulose and the grafted cellulose were characterized by Fourier transform infrared spectroscopy (FT-IR) and Thermogravimetric analysis (TGA). FTIR analysis was carried out using an 8400S Shimadzu Japan spectrometer, and TGA of the samples were analyzed for its thermal stability with Perkin Elmer

BATCH ADSORPTION EXPERIMENT (GENERAL PROCEDURE)

Adsorption experiments on CE-g-PAAM were carried out by batch adsorption method. Various Parameters such as contact

time, adsorbent dosage and Temperature were studied at constant agitation rate of 200rpm. The adsorption measurements were conducted in 250cm³ Elemental flask, containing 50 cm³ wastewater samples. The solutions were agitated using an orbital shaker, to reach equilibrium which later, the sample was removed and the supernatant solutions was removed from the adsorbent by filtration using Whatman No. 41 Filter paper. The filtrates were analyzed using AAS. Thereby, the percentage adsorption was evaluated using equation 3-4

$$\%adsorbed = \frac{C_0 - C_e}{C_0} \times 100 \quad \text{3-4}$$

Where C₀ (mg/L) is early metal conc., C_e(mg/L) is the equilibrium conc., V stand for the volume of metal solution used and W(g) stand for the gram of the adsorbent used (Nada,2010)

RESULTS AND DISCUSSION

GRAFT COPOLYMERIZATION

Cellulose obtained from old newspaper was grafted with polyacrylamide using CAN as an initiator. Various grades of graft copolymers were synthesized by optimizing various parameters such as the initiator (CAN) concentration, Monomer concentration, time and temperature. The results were presented in Table 1.

Table 1: Effect of Reaction Conditions on Grafting Parameters on CE-g-PAAM

A. Effect of optimization of CAN on CE-g-PAAM		B. Effect of optimization of monomer Conc. on CE-g-PAAM				C. Effect of optimization of Time on CE-g-PAAM				D. Effect of optimization of Temperature on CE-g-PAAM					
CAN (g)	Wi	GP %	GY%	Monomer (g)	Wi	GP %	GY%	Time (min)	Wi	GP %	GY%	TEMP. (°C)	Wi	GP %	GY%
1.0	7.68	53.6	67.00	1	6.7	34	170	60	9.65	93	155.00	50	9.65	93.0	116.25
1.5	8.15	63.0	78.75	2	7.3	46	115	90	9.72	94	157.33	55	9.77	95.4	119.25
2.0	7.49	49.8	62.25	3	7.6	52	87	120	9.79	96	159.66	60	9.19	93.8	104.75
2.5	7.03	40.6	50.75	4	6.4	28	35	150	9.86	97	160.00	65	8.82	76.4	95.50

- A. Reaction conditions: Conc. AAM = 4 g, Time = 60 (min), Temp. = 50°C, and W₀ = 5 g
- B. Reaction conditions: Conc. CAN = 1.5 g, Time = 60 (min), Temp. = 50°C, and W₀ = 5 g
- C. Reaction conditions: Conc. CAN = 1.5 g, Conc. Monomer = 3 g, Temp. = 50°C & W₀=5 g
- D. Reaction conditions: Conc. CAN = 1.5 g, Conc. Monomer = 4 g, Time = 150min, and W₀=5 g

The graft copolymerization was carried out at various reactions conditions. The highest percentage grafting GP% and percentage yield GY% were 97% and 160% respectively at 150mins (time), 50°C (temp.), 1.5g (CAN) and 3g (AAM) (Table 1). The results also showed that as the monomer concentration increased there was an increased in %GP, reaching a maximum value of 52% at 3 g for PAAM. Thereafter, there was decrease in % GP with increase in PAAM concentration (Sharma *et al.*, 2003, Gupta, 2002). The increase in GP% with the initial increase in PAAM concentration was resulted by the positive change in the rate of diffusion of the monomer into the cellulose backbone which provided more chances for graft copolymerization to occur and thereby the GP% increased. The enhancement in % GP by increasing monomer concentration to higher value could be due to the greater availability of monomer to grafting site (Salisu *et al.*, 2015). Hence, the decreasing tendency of % GP and beyond higher monomer concentration could be as a result of the

competition between homopolymerization and graft copolymerization, where the homopolymerization prevails over the graft copolymerization at higher PAAM concentration (Sharma *et al.*, 2003) similar trends have been reported by other researchers. (Yong *et al.*, 2005; Sadeghi *et al.*, 2011).

CHARACTERIZATION

THERMOGRAVIMETRIC ANALYSIS

TGA of CE and CE-g-PAAM was presented in Figure 1. It was observed that the TGA of CE and CE-g-PAAM shows a two-step weight decrease. The first weight decrease of almost 25.97 % (70 w %) at 300-400 °C was due to vaporization of moisture (Shah *et al.*, 1994) and the second weight loss of about 70.37 % (30w %) in the range 400–500 °C, this was resulted from the intricacy of the process, which led to the dilapidation of the sample, which leads to formation of H₂O, Methane and release of Carbondioxide and N₂ for CE-g-PAAM (Bagheri *et al.*, 2009). the initial step of the weight decrease of almost 32.29 % (70 w %), started from 300 to 400°C, was due to the release of CH₄ and H₂O while the corresponding step of weight decrease of 91.57 % (10 w %) started at 500–600 °C for CE. This might be as a result of breaking of cellulose chains and finally to change formation of the inorganic components. Hence these indicate that the graft copolymer has increased thermal stability as related to CE. A drastic weight loss was observed for ungrafted cellulose (CE) this may be due to decomposition of ungrafted cellulose in structural form. Another thermal stability

analysis was performed by Bagheri *et al.*, 2009 on acrylic monomer grafted fibers. The thermal stability of the fibers increases as the grafting yield increases.

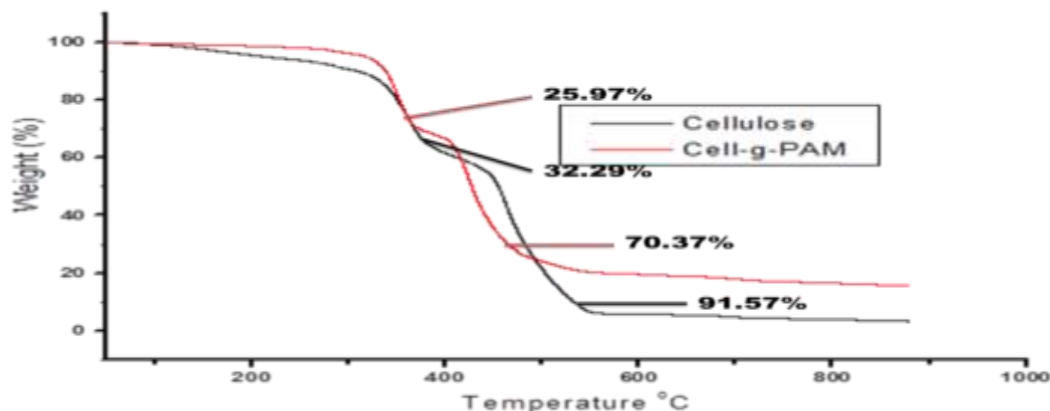


Figure 1: TGA Thermogram of CE and CE-g-PAAM

FTIR ANALYSIS

FTIR Spectra of CE and CE-g-PAAM

FTIR spectra of CE and CE-g-PAAM were shown in Figure 2. Had wave number starting from 650 to 4000 cm^{-1} . The absorption peak of 3400 cm^{-1} could be as a result of the presence of hydroxyl group stretching in the CE (El-hady and Ibrahim 2004). The peaks at 1026 cm^{-1} and 2983 cm^{-1} may be due to C-C and C-H stretching vibrations (Ibrahim *et al.*, 2002) and the

peaks at 896 cm^{-1} may be due to stretch C1-O-C4 (Dhiman *et al.*,2008). In case of the CE-g-PAAM, additional absorption bands appeared at 3164 cm^{-1} and 1670 cm^{-1} . This could be attributed to Amide group stretching of the grafted chains and carbonyl group stretching (primary amide) and scissor vibrations in polyacrylamide, respectively (El-hady and Ibrahim 2004). The appearance of these bands successfully confirmed the grafting of old newspaper with acrylamide.

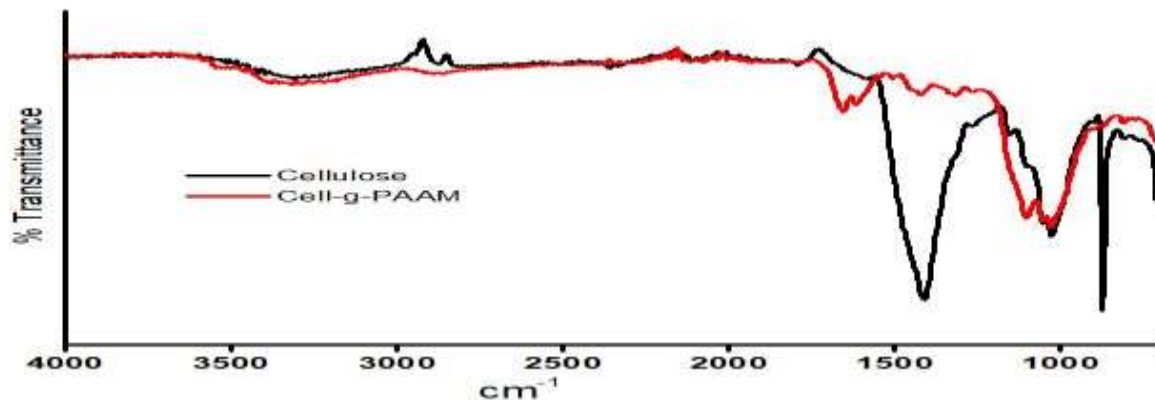


Figure 2: FTIR spectra of CE and CE-g-PAAM

ADSORPTION STUDY

Adsorption studies of CE-g-PAAM

Optimum Values For Heavy Metals Removal By CE-g-PAAM

The efficacy of CE-g-PAAM as adsorbent for the removal of metals ions (Fe^{2+} , Pb^{2+} and Cu^{2+}) from waste water was also determined using batch adsorption system. The initial concentration of Fe^{2+} , Cu^{2+} and Pb^{2+} ions in waste water were 43.44ppm, 69.02ppm and 11.22ppm respectively. The optimum percentage removal was indicated in Table 2.

Table 2: Optimum percentage removal of Heavy Metal ions by CE-g-PAAM

PARAMETERS	Fe(%R)	Cu (%R)	Pb (%R)
Time ^a	99.99	99.99	99.84
Temp. ^b	99.99	100	99.68
Dosage ^c	99.43	100	99.84

Key:

a: dosage=0.2g,Temp=25°C and Time =15 mins for both Fe and Cu while 5 mins for Pb

b: dosage=0.2g,Time=60 mins and Temp. = 40°C

c: dosage=1g,Time=60 mins and Temp. = 25°C

CONCLUSION

Poly Acrylamide was successfully grafted onto cellulose backbone obtained from old newspaper (CE) which improved its stability and it has been confirmed by FTIR and TGA analysis. FTIR results showed additional peaks on the entire grafted samples which was not observed on the ungrafted cellulose. Appearance of these band confirmed chemical modification of the cellulose. The TGA also indicate that the grafted cellulose (CE-g-PAAM) was thermally stable than the ungrafted cellulose (CE). It was also observed that CE-g-PAAM copolymer has an excellent adsorption capacity and can be used as an efficient and stable adsorbent material for the removal of heavy metal ions.

References

- Badawy, S.M., Sokker, H.H., Othman, S., Hashem, A., (2005). Cloth filter for recovery of uranium from radioactive waste. *Rad.Phys and Chem* 73 (2), 125-130.
- Bagheri, A.R., Abdouss, M. and Shoushtari, A.M.(2009) Characterization and modification of commercial acrylic fibers grafted acrylic acid. *Materialwissenschaft und Werkstofftechnik..* 40(11), 842-847.
- Chhatbar, M., Meena, R., Prasad, K.,Siddhanta, A., (2009).Studies on grafting of cellulosic materials. *Ind j. chem* .48A. 1085 – 1090 .
- Crini, G.(2004). Characterization of cellulose graft copolymers *prog polymer sci*, 30,38-78
- Dawood, S. and Sen, T.K.(2012) .Removal of anionic dye congo red from aqueous solution by raw pine and acid treated pine cone powder as adsorbent; equilibrium, thermodynamics, kinetics, mechanism and process design, *water Res*,46(6),1933-1946
- Dhiman, P.K., Kaur, I., Mahajan, R.K. (2008). Synthesis of a cellulose-grafted polymeric support and its application in the reductions of some carbonyl compounds. *J ApplPolymSci* 108:99–111
- El-said,G.F.;Draz,S.E.O.(2010). Physiochemical and geochemical characteristics of raw marine sediment in fluoral removal.*J.Env.Sci.Eng*.45,1601-1615
- Fernandez, M. J., Casinos, I., Guzman, G. M. (1990).Effect of the way of Addition of the Reactants in the Graft Copolymerization of a Vinyl Methyl Acrylate mixture onto Cellulose. *J. Polym Sci. A*, 28, 2275-2292.
- Gupta,V.K., Gupta, B., Rastogi, S., Agarwal, U., and Nayak, A.(2011) A comprehensive investigation on adsorption performance of mesoporous activated carbon,113,*J.Hazard.Matter.*,186(1),891-901
- Heikal, S. O., El-Kalyubi, S. F.: Graft copolymerization of acrylonitrile onto bagasse and wood pulp. *J. App Poly Sci*, **27**, 3027–3041 (1982).
- Ibrahim, M.M., Flefel, E.M., and El-zawawy, W.K (2002). Cellulose membrane grafted with vinyl monomers in a homogenous system, *polymadv tech* 13:548-557
- Kaur I., Sharma N. and Kumara V. (2013).Modification of fiber properties through grafting of acrylonitrile to rayon by chemical and radiation method *J.adv res Cairo Uni* 4, 547-557.
- Liu S, and Sun, G. (2008) Radical graft functional modification of cellulose with allyl monomers: chemistry and structure characterization. *CarbohydrPolym* 71:614–625
- Malaque, M.A., Belal, F.Y., Sapuan, S.M. Mechanical properties study of pseudo-stem banana fiber reinforced epoxy composite. *Arab J.Sci and Eng.* 2007. 32(2B), 359-364.
- Malik R., Ramteke, D.S., and Wate, S. R. (2007). Adsorption of malachite green on groundnut shell waste based powdered activated carbon. *J.Waste management*,(27) pp 1129-1138.
- Nada, A. M. A., El-Gendy, A. A., and Mohamed, S. H. (2010). Banana leaves as adsorbents for removal of metal ions from waste water. *CarbohydratePolymers*. 82: 1025-1030
- Sadaf.S. and Bhatti.H.N, (2013)Evaluation of peanut husk as a novel, lowcost biosorbent from removal of indosolorange,*Clean technol. Policy*,16(3),527-544.
- Sadeghi, M., Ghasemi, N., Soleimani, F. (2011). Optimization of synthetic conditions of a novel graft copolymer based on alginate. *Eur J Sci Res* 4:587–597
- Salisu A, Sanagi M.M, Naim A.A, Abd Karim K.J, Ibrahim W.A.W and Abdulganiyu U. (2016), Alginate graft polyacrylonitrile beads for the removal of lead from aqueous solutions. *Polymer Bulletin (73) 2, Springer*.
- Shah, S.B., Pate, I C.P, Trivedi H.C. (1994).Fenton's reagent-initiated graft copolymerization of acrylonitrile onto sodium alginate. *J ApplPolymSci* 51:1421–1426
- Sharma, BR., Kumar, V., Soni, P.L. (2003). Graft copolymerization of acrylonitrile onto Cassia tora gum with ceric ammonium nitrate–nitric acid as a redox initiator. *J ApplPolymSci* 90:129–136

