International Journal of Engineering & Technology, 7 (4.42) (2018) 127-129

International Journal of Engineering & Technology

Website: www.sciencepubco.com/index.php/IJET

Research paper



Preparation and Characterization of Citric Acid Modified Cellulose in Remediation of Acid Mine Drainage

Sopiah Ambong Khalid[1], Sarifah Fauziah Syed Draman[1*], Siti Rozaimah Sheikh Abdullah[2], Nornizar Anuar[4]

[1]Faculty of Chemical Engineering, Universiti Teknologi MARA, Bukit Besi Campus, 23200 Dungun, Terengganu
[2]Department of Chemical and Process, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia
[4]Faculty of Chemical Engineering, Universiti Teknologi MARA, Shah Alam, Malaysia
**Corresponding author E-mail: sfauziah@tganu.uitm.edu.my*

Abstract

Limited application of pure cellulose has brought in modification to cellulose produce substances that are of renewable origin, biodegradable but have significant enhancement of their adsorption capabilities. In this study, cellulose was modified with citric acid and its structure was analyzed by using Fourier-Transform Infrared Spectroscopy (FTIR) spectra, Thermal Gravimetric Analysis (TGA) and Optical Microscope. FTIR results shows that there is two main important band existed in Citric Acid Modified Cellulose (CAMC) which are hydroxyl (–OH) band at 3345 cm^{-1} and carboxyl (CO) band at 1725 cm^{-1}, while TGA study shows that the mass loss attributed by the decomposition of CAMC occur at 300ºC. Crystallinity and open pore structure in the microstructure of CAMC suggesting the suitability of using this CAMC in the remediation of acid mine drainage.

Keywords: *Water_sustainability; biodegradable; adsorption; decomposition; ex-mining lake*

1. Introduction

To date, there has been an increasing awareness and interest in natural, biodegradability and environmental safety. Development of biodegradable materials based on cellulose has become a very attractive selection in the removal of heavy metal. Cellulose, one of the remarkable pure and naturally occurring organic polymer, representing about 1.5×10^{12} tons of the world's total annual biomass production, consisting solely of units of anhydroglucose held together by β-(1,4)-glycosidic linkages in a giant straight chain molecule [1]. Pure cellulose has limited application, hence modification is favoured to produce substances that have different properties from cellulose, yet they are of renewable origin and biodegradable. One of the most important properties is that most pure are not thermoplastic but cellulose esters and ethers are thermoplastic. An ester linkage or cellulose ester is produced when hydroxyl groups of cellulose is substituted by less polar ester group [2]. Several studies have revealed that citric acid is a good modifying chemical or chelating agent [3][4]. The use of citric acid modified cellulose in removal of heavy metal has been reported in several study [5][6][7] but limited study has been done on the capability of this cellulose ester in remediation of acid mine drainage. Therefore this study aim to investigate the capability of this citric acid modified cellulose for further application in remediation of acid mines drainage at Tasik Puteri, Bukit Besi.

In this study, extra pure microcrystalline cellulose has been modified using citric acid by the method adapted with modification from [8][9] with one third portion of citric acid blended with pure cellulose and sufficient water is used for the removal of unreacted citric acid. To obtain direct information on the chemical changes that occur during chemical modification with a simple method, FTIR is used [10]. Further than that, TGA is used to determine the decomposition of citric acid modified cellulose and its thermal stability with the measurement changes in the weight loss of the sample in time thermal analysis and as a function of temperature [11][12]. Meanwhile the microstructure examination is also conducted by using an HUVITZ Optical Microscope (OM) in order to analyze qualitatively microstructure of the modified cellulose.

2. Main Body

2.1. Materials and Methods

2.1.1. Chemical Modification of Cellulose

Cellulose microcrystalline, extra pure, average particle 90 µm and citric acid anhydrous were purchased from Acros Organic. Deionized water was used in all experiments.

Chemical modification of pure cellulose was conducted based on procedures adopted done by [13]. A 1g of pure cellulose was added to solution of 3g citric acid in 16 mL of water with the ratio 1:3. Using Thermostat Incubater at 320 rpm at 20°C, the solution being stirred for 30 min and then it were placed in evaporating dish and being dried using forced air oven at temperature 50°C. The thermochemical reaction between cellulose and acid was preceded after 24 h for another 12 h by raising the oven temperature to 120°C. Thus, after cooling, the CAMC formed was washed using warm distilled water until pH of filtrated water was neutral. Lastly, the modified cellulose (CAMC) was dried until constant weight at 50°C and preserved in a desiccator as adsorbent for further use. All the above was repeated three times for reproducibility.

Copyright © 2018 Authors. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

2.1.2. Characterization

Bruker, Fourier Transform Infrared system (FTIR) model Tensor 27 with OPUS 6.0 software were used to analyse infrared spectra of samples. While Attenuated Total Reflectance (ATR) were used to test samples in powder form. The scans were carried out from 400 to 4000 cm^{-1}. Thermogravimetric analysis (TGA) of all the samples was carried out using a Netzsch model STA 449F3-Jupiter. Samples of 15-16 mg were placed in alumina pans and heated from 30 to 800° C at 10 $Kmin^{-1}$, under a dynamic flow of nitrogen (50 $mLmin^{-1}$). The microstructure examination was conducted by using a Huvitz Optical Microscope (HRM300).

3. Results and Findings

The prepared sample of citric acid modified cellulose is shown in the Figure 1. Petri dish on the left show citric acid modified cellulose (CAMC) before wash with warm distilled water [1] while petri dish on the right [2] show CAMC after had been washed with warm distilled water.



Fig. 1: CAMC before [1] and after wash [2]

It can be seen that modified cellulose before been washed with warm distilled water (1) is brown in color compared to after wash (2) which is white in color. The brown in color which appear in the first petri dish (1) is indication of unreacted of citric acid after being heated [14] which is completely disappear after being washed with warm water in second petri dish (2).
The following Figure 2 shows the spectra obtained for the triplicate of prepared citric acid modified cellulose (CAMC). The FTIR spectra of the citric acid (a), pure cellulose (b) and citric acid modified cellulose (c) samples were recorded in the range 400–4,000 cm^{-1} (Fig. 2).

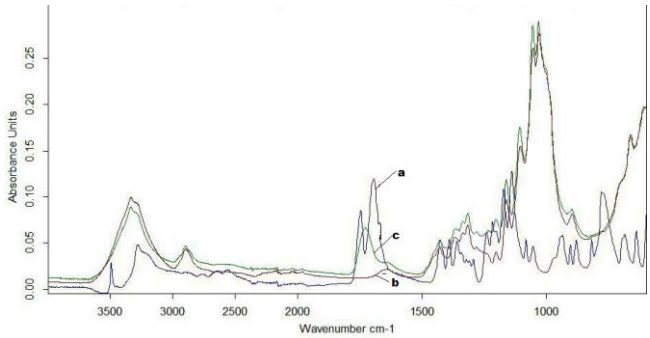


Fig.2: FTIR spectra for citric acid (a), pure cellulose (b) and citric acid modified cellulose (c)

According to Figure 2, a strong characteristic stretching vibration absorption band of carboxyl group at 1725.44 cm^{-1} in IR spectrum of citric acid modified cellulose can be seen matching with the IR spectrum of samples not citric acid modified. It reflected the result of citric acid esterification that introduced more carboxylic site [15]. In the study of cotton cellulose modified with citric acid [16], proved that the result of citric acid esterification is reflected by a strong characteristic stretching vibration absorption band of carboxyl group at 1727 cm^{-1} in IR spectrum of citric acid modified cotton straw. While in another study of modification of pineapple leaf cellulose [17], the emersion of C=O group was marked at the wavelength 1728.08 cm^{-1}. Table 1 summarizes the functional group found in FTIR spectra of citric acid, cellulose and citric acid modified cellulose.

Table 1: Summary of ftir spectra before and after modification

Functional Group	*Wavelength Range (cm^{-1})*	*Citric acid*	*Pure Celullose*	*Citric acid modified Cellulose*
Bonded –OH group	3500 - 3000	3339	3333	3336
Carboxyl Group	1740 - 1680	1743	absent	1725

So, it can be concluded that FTIR spectra obtained in this study is in line with the above studies that high amounts of free carboxyl groups is introduced when the cellulose modified with citric acid, at the same time it presents an suitable chemical and physical characteristics to adsorb metal ions. The increment of carboxyl group in the microcrystalline cellulose by the modification with citric acid has adequately prepared CAMC to be the good metal ion binding [18][19][20] in remediation of acid mine drainage at Tasik Puteri, Bukit Besi which is high in iron. It is reported in other study that via a possible symmetrical carboxylate binding, carboxyl group could chemically adsorb onto the surface of maghemite nanoparticles in aqueous solution [17].
The following Figure 3(a) dan 3(b) show thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) for cellulose, citric acid modified cellulose (CAMC) and citric acid.

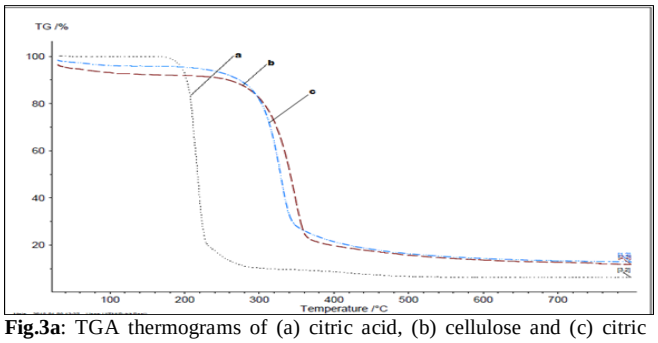


Fig.3a: TGA thermograms of (a) citric acid, (b) cellulose and (c) citric acid modified cellulose

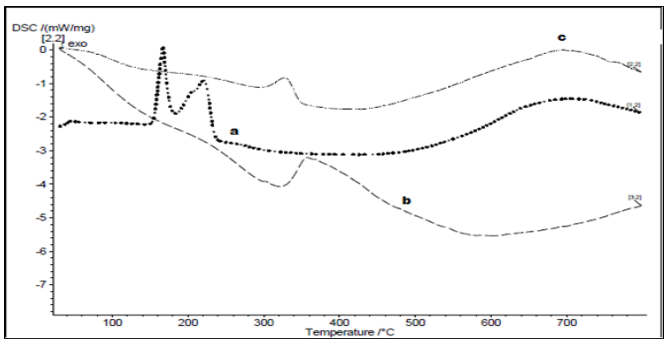


Fig.3b: DSC thermograms of citric acid (a), cellulose (b), citric acid modified cellulose (c)

Based on Figure 3 (a), the shape of the TGA curves of citric acid, cellulose and citric acid modified cellulose suggest a single step of mass loss is occur. The mass loss attributed by thermal decomposition of citric acid is around 200°C while cellulose and citric acid modified cellulose occur around 300°C.
Melting point of citric acid starts its decomposition. A broad endothermic peak with two non-symmetric inflexions showing a complex decomposition process can be seen in the DSC curve does not

reflect the single step shown in TGA thermogram. Even though the pattern is similar with the research of thermal behaviour of citric acid and isomeric aconitic acids [19] however their melting point are slightly difference. The difference might be due to difference supplier of the citric acid.

During heating especially at high temperature, changes will occur in cellulose and citric acid modified cellulose. The strength of the cellulose chain bonds will reduce, generally the cleavage of glycoside bonds, C-H, C-O and C-C bonds will occur. Finally high temperature will reduce the degree of polymerisation and crystallisation of the cellulose [7][16]. It can be seen from DSC curve, decomposition of cellulose release 89.3 J/g of heat while citric acid modified cellulose absorb 84.75 J/g of heat when calculating the area under the DSC curve suggesting that the formation bond or crosslinking etherification is also occured around 300ºC.

The following figure 4 shows the microstructure of citric acid modified cellulose, CAMC 2 by using using a Huvitz Optical Microscope (HRM300) with 200 resolution.



Fig.4: Microstructural Characteristic of Citric Acid Modified Cellulose

It can be seen that CAMC is in the form of crystalline structure with open porous structure. The possibility of the metal ions to be trapped, absorbed, penetrate into the surface and interact therein with the surface chelating groups can be at open pore structure [20].

3. Conclusion

In order to increase ion sorption property in pure cellulose, it has been modified with citric acid via etherification process. This improvement in pure cellulose property which has been confirmed through FTIR Characterization, TGA Analysis and Optical Microscope could increase its utility for contaminated water treatment, particularly in areas of acid mine drainage.

Acknowledgement

This research work is supported by the Research Management Unit, Universiti Teknologi MARA, Terengganu Branch (600-UiTMKD(PJI/RMU/ST/DANA SIG 5/2/1) Dst (10/2016)).

References

[1] Avila Ramirez, J. A., Fortunati, E., Kenny, J. M., Torre, L., & Foresti, M. L. (2017). Simple citric acid-catalyzed surface esterification of cellulose nanocrystals. Carbohydrate Polymers, 157, 1358–1364. http://doi.org/10.1016/j.carbpol.2016.11.008

[2] Bian, J., Peng, X.-P., Peng, P., Xu, F., & Sun, R. C. (2012). Cellulose From Sugarcane Bagasse : Structural. BioResources, 7(4), 4626–4639.

[3] Demirbas, A. (2008). Heavy metal adsorption onto agro-based waste materials: A review. Journal of Hazardous Materials, 157(2–3), 220–229. http://doi.org/10.1016/j.jhazmat.2008.01.024

[4] Draman, S. F. ., Daik, R., Latif, F. A., & El-sheikh, S. M. (2012). Synthesis and Characterization of Modified Cellulose and Doped-Polypyrrole Composite As Thermally Conductive Adhesive. ECCM15-15th European Conference On Composite Materials, (15TH), 24–28.

[5] El-kafrawy, A. F., El-saeed, S. M., Farag, R. K., El-saied, H. A., & Abdel-raouf, M. E. (2016). Adsorbents based on natural polymers for removal of some heavy metals from aqueous solution. Egyptian Journal of Petroleum, http://dx.doi.org/10.1016/j.ejpe.2016.02.007. http://doi.org/10.1016/j.ejpe.2016.02.007

[6] Firmansyah, D., & Rumhayati, B. (2017). Modification of Pineapple Leaf Cellulose with Citric Acid for Fe 2 + Adsorption. International Journal of ChemTech ResearchTech Research, 10(4), 674–680.

[7] Grzeskowiak, W. L., & Bartkowiak, M. (2015). Thermogravimetric Analysis of Commercial Thermally Modified Wood. Drewno, 58(194). http://doi.org/10.12841/wood.1644-3985.109.02

[8] Hokkanen, S., Bhatnagar, A., & Sillanpää, M. (2016). A review on modification methods to cellulose-based adsorbents to improve adsorption capacity. Water Research, 91(January), 156–173. http://doi.org/10.1016/j.watres.2016.01.008

[9] Kuo, C. Y., Wu, C. H., & Chen, M. J. (2015). Adsorption of lead ions from aqueous solutions by citric acid-modified celluloses. Desalination and Water Treatment, 55(5), 1264–1270. http://doi.org/10.1080/19443994.2014.926460

[10] Leyva-Ramos, R., Landin-Rodriguez, L. E., Leyva-Ramos, S., & Medellin-Castillo, N. A. (2012). Modification of corncob with citric acid to enhance its capacity for adsorbing cadmium(II) from water solution. Chemical Engineering Journal, 180, 113–120. http://doi.org/10.1016/j.cej.2011.11.021

[11] Marshall, W. E., Akin, D. E., Wartelle, L. H., & Annis, P. A. (2007). Citric acid treatment of flax, cotton and blended nonwoven mats for copper ion absorption. Industrial Crops and Products, 26(1), 8–13. http://doi.org/10.1016/j.indcrop.2006.12.011

[12] Matei, A., Cernica, I., & Schiopu, V. (2009). Preparation and characterization of TiO. Proceedings of SPIE, (May), 72970O–72970O–4. http://doi.org/10.1117/12.823634

[13] Nemeth, D., Barta, Z., Labidi, J., Gubicza, L., & Belafi-Bako, K. (2011). Study on sorption characteristics of citric acid modified rape-seed pellet considering the chemical pre-treatment processes. Hungarian Journal of Industrial Chemistry, 39(3), 407–411.

[14] O'Connell, D. W., Birkinshaw, C., & O'Dwyer, T. F. (2008). Heavy metal adsorbents prepared from the modification of cellulose: A review. Bioresource Technology, 99(15), 6709–6724. http://doi.org/10.1016/j.biortech.2008.01.036

[15] Poletto, M., Zattera, A. J., & Pistor, V. (2013). Structural Characteristics and Thermal Properties of Native Cellulose. Cellulose - Fundamental Aspects.

[16] Saravanan, R., & Ravikumar, L. (2015). The Use of New Chemically Modified Cellulose for Heavy Metal Ion Adsorption and Antimicrobial Activities. Journal of Water Resource and Protection, 7(April), 530–545. http://doi.org/10.4236/jwarp.2015.76042

[17] Tejada, C., Herrera, A., & Ruiz, E. (2016). Kinetic and isotherms of biosorption of Hg (II) using citric acid treated residual materials Cinética e isotermas de bioadsorción de Hg (II) usando materiales residuales tratados con ácido cítrico. Ingenieria Y Competividad, 18(1), 117–127.

[18] Thanh, N. D., & Nhung, H. L. (2009). Cellulose Modified With Citric Acid And Its Absorption Of Pb 2+ And Cd 2+ Ions. Journal of College of Science, Hanoi National University, 1–13.

[19] Wyrzykowski, D., Hebanowska, E., Nowak-Wiczk, G., Makowski, M., & Chmurzyński, L. (2011). Thermal behaviour of citric acid and isomeric aconitic acids. Journal of Thermal Analysis and Calorimetry, 104(2), 731–735. http://doi.org/10.1007/s10973-010-1015-2.

[20] Yu, S., & Chow, G. M. (2004). Carboxyl group (–CO 2 H) functionalized ferrimagnetic iron oxide nanoparticles for potential bio-applications. J. Mater. Chem., 14(18), 2781–2786. http://doi.org/10.1039/B404964K