Asian Journal of Chemistry; Vol. 32, No. 12 (2020), 3105-3108

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2020.22917

Green Production of Potassium Sulfate by Hydrothermal Carbonization of Carrageenan

JOSE PAOLO O. BANTANG[1,2] and DREXEL H. CAMACHO[1,*]

[1]Chemistry Department, De La Salle University, 2401 Taft Avenue, 0922 Manila, Philippines
[2]Chemistry Department, Technological University of the Philippines, Ayala Blvd, Ermita, 1000 Manila, Philippines

*Corresponding author: Fax: +63 82 5360230; Tel: +63 82 5244611; E-mail: drexel.camacho@dlsu.edu.ph

Received: 28 July 2020; *Accepted*: 28 September 2020; *Published online*: 7 December 2020; AJC-20147

A novel green method of producing potassium sulfate from a sustainable source is described. Aqueous carrageenan is subjected to hydrothermal carbonization inside a pressure vessel. Separation of the liquid component from the hydrochar followed by evaporation to dryness and treatment with ethanol afforded potassium sulfate. Characterization using SEM-EDX, XRD and Raman spectroscopy confirms the identity of potassium sulfate in the form of $K_3H(SO_4)_2$. The green process allows the facile release of sulfate ester group from the carrageenan chains and combining with the residual potassium ions in the carrageenan. The new method allows for the simplification of the process of producing potassium sulfate in an environmental friendly way and using a renewable source.

Keywords: Carrageenan, Potassium sulfate, Hydrothermal carbonization, Hydrochar.

INTRODUCTION

Potassium sulfate (K_2SO_4) is an industrially important substance which is used as a major component in fertilizers, potassium alum, potassium carbonate, glass, chemical agents, veterinary compositions and other products. Conventional methods of producing potassium sulfate include extraction and separation of potassium sulfate from salt lake brines, fractional crystallization of natural sulfate ore, or the reaction of potassium chloride with langbeinite ore, schoenite, or sodium sulfate. It can also be produced by converting sulfuric acid to potassium salt through the Hargreaves process, which involves treatment of potassium chloride with sulfuric acid, or with sulfur dioxide, air and water [1]. The current world supply of K_2SO_4 is produced mainly from potassium chloride (KCl) by means of the energy-intensive Mannheim process. In this process, potassium chloride reacts with sulfuric acid to form potassium bisulfate and hydrogen chloride. The final product, potassium sulfate, is formed at high temperatures of about 600-700 °C [2]. Potassium sulfate can also be obtained by acidulation of KCl at low temperatures, under which conditions, potassium hydrosulfate is formed [3-5]. Methods of making potassium sulfate are also disclosed in a number of patent documents where potassium sulfate is manufactured *via* the treatment of a sulfate ion-containing substance such as $(NH_4)_2SO_4$ with a potassium ion-containing substance typically KCl [6,7]. Sulfates can also be obtained from cement mill dust, langbeinite, or from muriate, while potassium can be derived from potash salt produced from wood ashes or alunite [8]. Another method describes the mineral slurry mixture of kainite, potassium chloride and water to obtain a potassium sulfate *via* a solid-liquid separation [9]. The reaction of phosphogypsum and KCl at 0.1-0.2 MPa in the presence of a catalyst also afforded potassium sulfate after washing with NH_3 [10]. The treatment of Na_2SO_4 or mirabilite with KCl in the presence of NaCl-containing mother liquor also produced potassium sulfate [11]. A metathesis process described aeration of a solution containing potassium and sulfate ions with NH_3 at low-temperature to afford potassium sulfate precipitate [12]. Potassium sulfate is also manufactured by the reaction of H_2SO_4 with KCl [13], in the presence of Cu^{2+}-containing compound [14] or MgO [15]. Another process involves purification of bittern by removal of Ca^{2+} and Mg^{2+} ions to form a sodium sulfate, which upon treatment with KCl yields the potassium sulfate [16].

Potassium sulfate crystals can also be produced through recovery from sugar wastes or industrial wastewater [17]. Recovery of potassium from steel factory sintering ash followed by treatment with ammonium sulfate also produces potassium sulfate [18]. Potassium sulfate is also produced by converting particulate metal halides to corresponding sulfates using a fluidizing gas of sulfur dioxide, water vapour and air [19]. Several devices for the manufacture of potassium sulfate have been described such as the specialized reaction furnace [20] or the mixing-spraying reactor for continuous process [21]. Generally, the manufacturing of potassium sulfate is a tedious process requiring the use of specialized equipment, or the use of strong acids. Most of the processes generate much waste while some methods require the use of minerals that must be mined from the earth. A simple, robust and renewable process is highly desirable. Herein, a novel method of producing potassium sulfate is reported from the carrageenan, a renewable source.

Carrageenan is a natural polysaccharide extracted from red seaweeds. It contains sulfate groups in the polysaccharide chain. The three main commercial classes of carrageenan are κ-carrageenan (contains one sulfate group per disaccharide), ι-carrageenan (contains two sulfate groups per disaccharide) and λ-carrageenan (contains three sulfate groups per disaccharide). Of particular interest is the κ-carrageenan because of its ion specificity where potassium ions specifically bind to the helical structure of κ-carrageenan promoting helix formation and gelation. As a result, κ-carrageenan forms strong, rigid gels in the presence of potassium ions making it useful in commercial applications as thickeners, gelling agents and stabilizers in processed foods due to their excellent gelling and physical functional properties [22]. In the process of extracting κ-carrageenan, potassium ion plays a prominent role. To enhance the gelation behaviour, κ-carrageenan is extracted from *Eucheuma cottonii* by potassium hydroxide treatment, which is an important and well-known reaction of carrageenans [23,24]. Commercially, it is produced as a white refined powder where the carrageenan is first dissolved and filtered to remove cell wall debris followed by precipitation from the clear solution by potassium chloride [25]. Predominantly, commercial κ-carrageenan contains potassium 10.2%, calcium 2.7% and sodium 0.7% ions [26].

EXPERIMENTAL

In a typical hydrothermal carbonization process, κ-carrageenan (1.0 g, ACROS Organics) is dispersed in water (12 mL) and transferred in a Teflon-lined stainless-steel autoclave. The autoclave is then sealed and heated in an oven (180 °C) for 12 h to obtain a heterogeneous mixture composed of the insoluble black hydrochar and water-soluble substances. The solid hydrochar was separated from the liquid by centrifugation and filtration followed by rotary evaporation of the supernatant liquid to obtain a brown residue. The residue was washed with absolute ethanol to obtain white precipitate of potassium sulfate precipitates (10-15% yield).

RESULTS AND DISCUSSION

SEM-EDX data (Fig. 1) indicates that the precipitated salt contains 31.9% potassium, 21.8% sulfur and 39% oxygen as the major components indicating the formation of potassium salt with sulfate. XRD analysis (Fig. 2A) confirmed the formation of potassium sulfate and it exists in the form $K_3H(SO_4)_2$ in agreement with the XRD data (Fig. 2B) reported by Mientka *et al.* [27]. The result also agrees with the rough estimate in the % elemental composition using EDX data. Raman spectroscopy (Fig. 3A) further confirms the identity of the potassium salt as $K_3H(SO_4)_2$ which agrees well with the Raman spectrum of the single crystal of $K_3H(SO_4)_2$ (Fig. 3B) as reported by Barashkov *et al*. [28]. The characterization data confirms the identity of the potassium salt as $K_3H(SO_4)_2$ [28].

κ-Carrageenan forms aqueous gel in the presence of certain salts such as Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+} and Sr^{2+}. In commercial κ-carrageenan, this gelling property is attributed to the presence of potassium ions, which acts as an ionic cross-linker between the sulfate groups of the double helices allowing them to aggregate and form 3D networks of helices. Potassium ions is inherently present in the natural κ-carrageenan and the amounts further increase through alkali extraction using aqueous KOH [29] and in the refining process using KCl precipitation [25]. During hydrothermal reaction, heating the vessel results to a build-up of pressure inside the vessel. The autogenous pressure formed inside the vessel dehydrates carrageenan forming the water-insoluble, high-carbon-containing product called the hydrochar. In addition, the negatively charged sulfate moieties found in main chain of carrageenan, which is neutralized by K^+ counter ions, are released in the

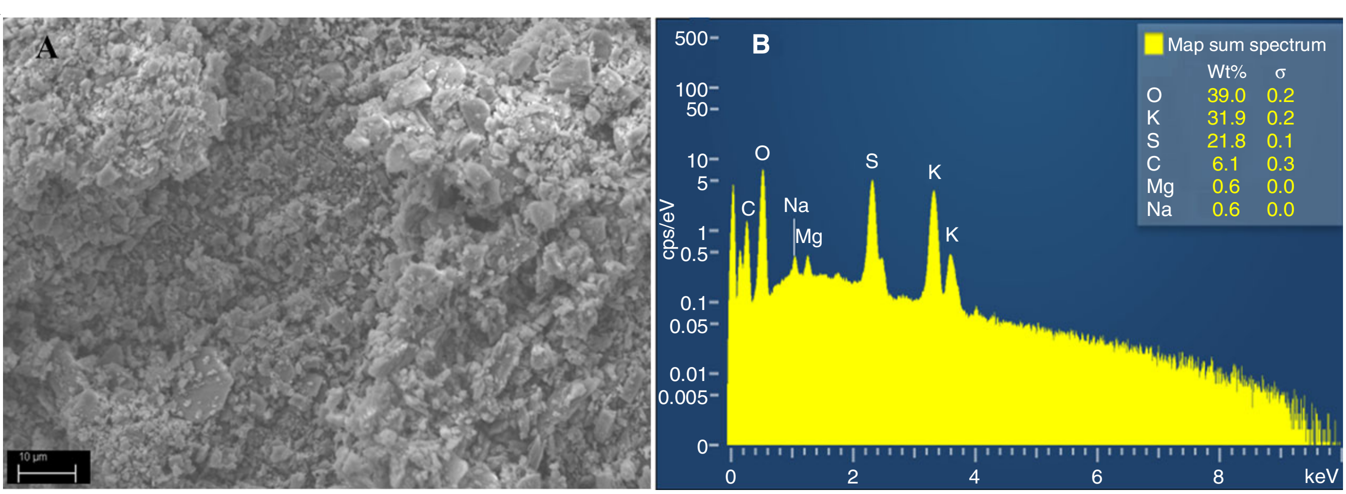

Fig. 1. SEM (A) and EDX Spectra (B) of potassium sulfate from carrageenan

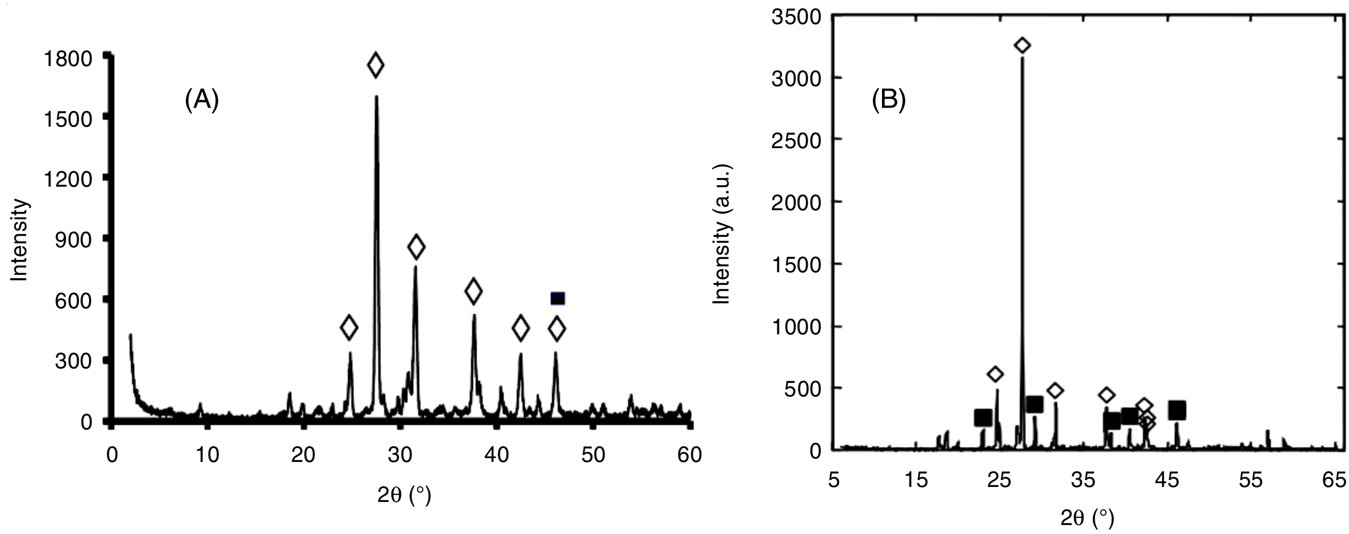

Fig. 2. XRD (A) spectra of potassium sulfate from carrageenan and X-ray diffraction (B) spectra of K_2SO_4 (■) and $K_3H(SO_4)_2$ (◇) (reprinted with permission from Mientka *et al.* [27])

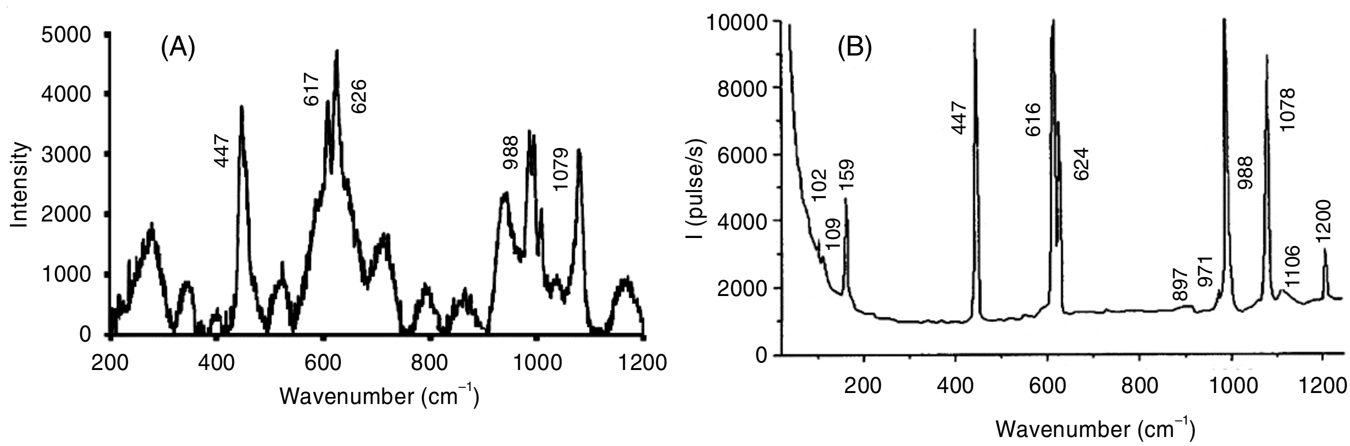

Fig. 3. Raman spectrum (A) of the $K_3H(SO_4)_2$ powder from carrageenan and Raman spectrum (B) of the $K_3H(SO_4)_2$ single crystal at T = 92 K (reprinted with permission from Barashkov *et al.* [28])

form of water-soluble potassium sulfate extracted through ethanol precipitation.

The facile production of potassium sulfate from carrageenan can explain the observed plant growth promoting effects of carrageenan. Carrageenan powder has been added as a component in the formulation of commercial fertilizers apparently as gelling agent for water retention [30]. Carrageenan is also included as one of the components in a fertilizer formulation, which is produced by fermenting the mixture. The plant-growth promoting effect was attributed to the presence of yeast or lactic acid bacteria [31]. The use of a γ-irradiated carrageenan as plant growth promoter [32] by foliar spraying has been shown to increase the production of rice to 20% more. The effect was attributed to the degradation of carrageenan into smaller molecular weight polymer that promotes easy absorption of nutrients. In another study, the same authors [33] described that carrageenan irradiated at an absorbed dose of 30 kGy afforded smaller carrageenan molecular weight of 6762 Da and fractionation of the irradiated carrageenan with 1 kDa showed better plant growth promoting activities on pechay in soil upon foliar spraying. The role of carrageenan is believed to be due to the ability of low molecular weight carrageenan to promote easy absorption of nutrients. These plant growth-promoting effects of carrageenan may after all be attributed to the facile production of potassium sulfate, which is an established fertilizer component and a known plant growth promoter along with nitrogen and potassium.

Conclusion

In conclusion, carrageenan subjected to hydrothermal carbonization afforded potassium sulfate along with the hydrochar. SEM-EDX, XRD and Raman spectroscopy confirms the identity of potassium sulfate in the form of $K_3H(SO_4)_2$. This novel method of producing potassium sulfate from carrageenan is a simple and robust technique that utilizes a renewable starting material, which could find usefulness in agriculture and industries.

ACKNOWLEDGEMENTS

One of the authors, JPOB thanks the DLSU-PhD Apprentice Fellowship Program and USAID-STRIDE research program. Another author, DHC is thankful to the De La Salle University Research Coordinating Office (DLSU-URCO).

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. G.G. Hawley, The Condensed Chemical Dictionary, Van Nostrand Reinhold Co.: New York, edn 9, p. 718 (1977).
2. H. Schultz, G. Bauer, E. Schachl, F. Hagedorn and P. Schmittinger, ed. B. Elvers, Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim (2005).
3. M.A. Giambra, *Anal. Chim. Acta*, **530**, 41 (2005); https://doi.org/10.1016/j.aca.2004.08.047
4. I. Efraim, S. Lampert and C. Holdengraber, Co-Production of Potassium Sulfate, Sodium Sulfate and Sodium Chloride, US Patent 5552126A (1996).
5. T. Zisner, C. Holdengraber and S. Lampert, Production of Potassium Sulfate using Differential Contacting, US Patent 5549876A (1996).
6. S. Xu and J. Qi, Method for Manufacturing Potassium Sulfate from Ammonium Sulfate by Two-Step Conversion Process, China Patent No. CN 1220249A, Faming Zhuanli Shenqing Gongkai Shuomingshu (1999).
7. E. Diaz-Nogueira, L. Sobrino-Portela and A.R. Abad, Process for Manufacturing Potassium Sulfate and Hydrochloric Acid, Spanish Patent No. ES 2036463A1, Spain Patent and trademark Office (1993).
8. Farm Chemicals Handbook, Willoughby, Ohio: Meister, p. B-69 (1980).
9. Y. Li *et al.*, Manufacturing of Potassium Sulfate By Using Magnesium Vanadium Potassium Salt, China Patent No. CN 105036157 A, Faming Zhuanli Shenqing (2015).
10. D. Liu, B. Zhong and Y. Zhang, Process for Manufacturing Potassium Sulfate along with Many By-products, China Patent No. CN 1283588 A, Faming Zhuanli Shenqing Gongkai Shuomingshu (2001).
11. S. Peng, Process for Manufacturing Potassium Sulfate, China Patent No. CN 1223964A, Faming Zhuanli Shenqing Gongkai Shuomingshu (1999).
12. Y. Liu, S. Hu, D. Dong, L. Luan, J. Zhong, J. Wei and H. Du, Metathesis Process For Manufacturing Potassium Sulfate in Presence of Ammonia And Water, China Patent No. CN 1227188A, Faming Zhuanli Shenqing Gongkai Shuomingshu (1999).
13. K. Song, Process for Manufacturing Potassium Sulfate, China Patent No. CN 1155515A, Faming Zhuanli Shenqing Gongkai Shuomingshu (1997).
14. C. Zhang, Z. Hu, X. Gao, R. Yao and Y. Luo, One-Step Process for Manufacturing Potassium Sulfate and Potassium Fertilizer Riched in Nitrogen and Phosphorus, China Patent No. CN 1213646A, Faming Zhuanli Shenqing Gongkai Shuomingshu (1999).
15. Z. Zhang, Y. Zhang and J. Zhang, One-Step Process in Manufacturing Potassium Sulfate for Agricultural Fertilizer, China Patent No. CN 1197039A, Faming Zhuanli Shenqing Gongkai Shuomingshu (1998).
16. T. Deng, Z. Li, Z. Niu, X. Gu, C. Su, Z. Wang, Z. Li and Z. Tian, Process for Manufacturing Potassium Sulfate Using Bittern Containing Sodium Sulfate or Calcium Sulfate or Mirabilite, China Patent No. CN 1123248A, Faming Zhuanli Shenqing Gongkai Shuomingshu (1996).
17. W. Xiang, Process for Manufacturing Potassium Sulfate Crystal Using Industrial Wastewater from 2-hydroxy-6-naphthoic Acid Production, China Patent No. CN 101798101A, Faming Zhuanli Shenqing (2010).
18. X. Liu, Y. Yang, F. Yang, Y. Shen and X. Jiang, Method for Recovering Potassium from Sintering Ash from Steel Factory and Manufacturing Potassium Sulfate, China Patent No. CN 101723410A, Faming Zhuanli Shenqing (2010).
19. W.J. Rigby, K.D. Cochran and T.G. Holt, Process for Manufacturing Potassium Sulfate Fertilizer and Other Metal Sulfates, US Patent 6365122B1 (2002).
20. Z. Yang, Mannheim Reaction Furnace for Manufacturing Potassium Sulfate, China Patent No. CN 202492375 U, Shiyong Xinxing Zhuanli Shuomingshu (2012)..
21. B. Yu, G. Zhang and Z. Song, Method and Equipment for Continuous Manufacturing Potassium Sulfate, China Patent No. CN 1147480 A, Faming Zhuanli Shenqing Gongkai Shuomingshu (1997).
22. V.L. Campo, D.F. Kawano, D.B. Silva Jr. and I. Carvalho, *Carbohydr. Polym.*, **77**, 167 (2009); https://doi.org/10.1016/j.carbpol.2009.01.020
23. R.A. Hoffmann, M.J. Gidley, D. Cooke and W.J. Frith, *Food Hydrocoll.*, **9**, 281 (1995); https://doi.org/10.1016/S0268-005X(09)80259-2
24. F. van de Velde, S.H. Knutsen, A.I. Usov, H.S. Rollema and A.S. Cerezo, *Trends Food Sci. Technol.*, **13**, 73 (2002); https://doi.org/10.1016/S0924-2244(02)00066-3
25. M.Y. Kariduraganavar, A.A. Kittur and R.R. Kamble, eds.: S.G. Kumbar, C.T. Laurencin and M. Deng, Natural and Synthetic Biomedical Polymers, Elsevier: Burlington, MA, USA, Chap. 1, p. 1 (2014).
26. S. Distantina, Rochmadi, M. Fahrurrozi, Wiratni, *World Acad. Sci. Eng. Technol.*, **78**, 738 (2001).
27. A. Mientka, B. Grzmil and M. Tomaszewska, *Chem. Pap.*, **62**, 123 (2008); https://doi.org/10.2478/s11696-007-0088-2
28. M.V. Barashkov, A.I. Komyak and S.N. Shashkov, *J. Appl. Spectrosc.*, **67**, 1110 (2000); https://doi.org/10.1023/A:1004113630634
29. H.P.S. Abdul Khalil, T.K. Lai, Y.Y. Tye, S. Rizal, E.W.N. Chong, S.W. Yap, A.A. Hamzah, M.R. Nurul Fazita and M.T. Paridah, *Express Polym. Lett.*, **12**, 296 (2018); https://doi.org/10.3144/expresspolymlett.2018.27
30. R. Ding, J. Chen, Z. Lin, W. Wang, J. Dang and D. Zhang, Forest and Fruit Base Growth Substance for Cold Regions and Arid Regions and Application Method Thereof, China Patent CN 103880557A, Faming Zhuanli Shenqing (2014).
31. E. Sakagami and I. Kono, Method for Manufacturing Plant Growth Accelerator and Plant Growth Accelerator Obtained by using the Method, Japan Patent JP 2009161358A, Jpn. Kokai Tokkyo Koho (2009).
32. L.V. Abad, G.F.O. Dean, G.L. Magsino, R.M.M. Dela Cruz, M.G. Tecson, M.E.S. Abella and M.G.S. Hizon, *Radiat. Phys. Chem.*, **143**, 53 (2018); https://doi.org/10.1016/j.radphyschem.2017.07.009
33. L.V. Abad, F.B. Aurigue, L.S. Relleve, D.R.V. Montefalcon and G.E.P. Lopez, *Radiat. Phys. Chem.*, **118**, 75 (2016); https://doi.org/10.1016/j.radphyschem.2015.03.001