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Chemical and physical characteristics of optimal synthesised activated carbons from grass-derived sulfonated lignin versus commercial activated carbons

Nasir M.A. Al-Lagtah [a, b, *], Ala'a H. Al-Muhtaseb [c], Mohammad N.M. Ahmad [d, e], Yousef Salameh [e]

[a] School of Chemical Engineering and Advanced Materials, Newcastle University, Singapore 599493, Singapore
[b] School of Chemical Engineering and Advanced Materials, Newcastle University, Newcastle upon Tyne NE1 7RU, United Kingdom
[c] Department of Petroleum and Chemical Engineering, Faculty of Engineering, Sultan Qaboos University, Muscat, Oman
[d] School of Chemistry and Chemical Engineering, Queen's University of Belfast, Belfast, United Kingdom
[e] Chemical Engineering Program, Faculty of Engineering and Architecture, American University of Beirut, Beirut, Lebanon

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ABSTRACT

This study aims to evaluate the surface characteristics and chemistry of optimal activated carbons (ACs) synthesised from water-soluble grass-derived sulfonated lignin (SL) using three dehydrating salts ($ZnCl_2$, KCl and $Fe_2(SO_4)_3 \cdot xH_2O$). The optimal AC synthesised by each dehydrating salt was chosen as the carbon that achieved the highest removal efficiency of Cd^{2+}, Cu^{2+} and Zn^{2+} ions from aqueous solutions. These optimal sulfonated lignin-based activated carbons (SLACs) showed the highest surface areas, total pore and micropore volumes among all the synthesised ACs. These SLACs were named SLAC-ZC (optimal grass-derived SLAC activated by zinc chloride); SLAC-PC (optimal grass-derived SLAC activated by potassium chloride) and SLAC-FS (optimal grass-derived SLAC activated by ferric sulphate). The surface characteristics of two commercial activated carbons (CAC1 and CAC2) were also appraised for comparison purposes. The optimal SLACs showed similar, or even better, properties to the two CACs. The N_2 adsorption/desorption isotherms showed that the micropore fraction of SLAC-ZC was greater and its mesopores were narrower than SLAC-PC. For SLAC-FS, the amount of adsorbed N_2 was markedly lower than all other ACs and hence its values of BET surface area (A_{BET}) and total pore volume (V_{total}) were the lowest. The iodine volume capacities of SLAC-ZC and SLAC-PC were higher than CAC1, suggesting that they could operate better in continuous adsorption processes. FTIR and SEM analysis illustrated that chemical activation had changed the surface chemistry of SL. Overall; synthesis of ACs from this novel precursor will add value to sulfonated lignin, which is considered as an industrial waste.

1. Introduction

Activated carbon (AC) adsorption is a well-known and very effective method for gas separation and water decontamination applications. It has been found to be an outstanding process in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. Also, it does not normally result in the formation of harmful substances [1]. Commercial activated carbon (CAC) is usually prepared from coal, coconut shells or wood, using the physical activation process. Because of its great adsorption capacity, CAC is practically the most effective adsorbent. This capacity is mainly due to the structural characteristics and porous structure that gives CAC a large surface area [2]. However, the main disadvantage of CAC is its cost; the higher the quality, the greater the cost. The high cost of CAC is mainly due to the reactivation cost and associated losses requiring partial replacement, typically 5–10%. Also, CAC is non-selective and requires complexion agents to improve its removal performance [3]. This has resulted in attempts by various researchers to find more economically viable starting materials (i.e. precursors) to produce activated carbons. These precursors must be, by definition,

* Corresponding author. School of Chemical Engineering and Advanced Materials, Newcastle University International Singapore, 537 Clementi Road, #06-01, Singapore 599493. Tel.: +65 6469 7053; fax: +65 6467 3473.
E-mail address: nasir.al-lagtah@ncl.ac.uk (N.M.A. Al-Lagtah).

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Abbreviations and nomenclature

AC	activated carbon
A_{BET}	Brunauer–Emmett–Teller (BET) surface area (m^2 g^{-1})
A_{ext}	external surface area (m^2 g^{-1})
A_{micro}	micropore surface area (m^2 g^{-1})
C_o	liquid phase initial concentration (mg L^{-1})
C_e	liquid phase equilibrium concentration (mg L^{-1})
CAC	commercial activated carbon
FTIR	Fourier transform infrared spectroscopy
GAC	granular activated carbon
pH_{ZPC}	zero point of charge
pH_{sol}	pH of solution
SEM	scanning electron microscopy
SL	sulfonated lignin
SLAC	sulfonated lignin-based activated carbon
SLAC-ZC	optimal grass-derived SLAC activated by zinc chloride
SLAC-PC	optimal grass-derived SLAC activated by potassium chloride
SLAC-FS	optimal grass-derived SLAC activated by ferric sulphate
V_{me+ma}	the sum of mesopore and macropore volume (cm^3 g^{-1})
V_{micro}	micropore volume (cm^3 g^{-1})
V_{total}	total pore volume (cm^3 g^{-1})
ρ_B	bulk density (g cm^{-3})
ρ_R	real density (g cm^{-3})

cheap, readily available, contain high carbon content and require little processing for activation [4].

Lignin is a major component of plant's tissue, which enhances its mechanical strength and structural integrity. Lignin consists 20–30% of hardwood and softwood weight. However, lignin content in agro wastes extremely varies from 3 to 35% [5]. Lignin is a waste stream of biorefineries, paper and pulping industries. The content and structure of lignin depend predominantly on its source and pretreatment recovering process. Two major types of lignin are kraft lignin and sulfonated lignin. Kraft lignin is water insoluble and constitutes about 85% of total world lignin production. Sulfonated lignin (SL) is water-soluble anionic polymer with a considerable number of charged groups. SL is produced in sulfite cooking process. SL is manufactured in fairly sizeable capacities (around 1 million tons annually as dry solids) [6].

Most of the lignin is consumed as a low-grade fuel for pulping boilers. However, this use of lignin has many disadvantages. For example, lignin has to be extracted and dried before burning and has to be burnt immediately. Additionally, the emission of combustion gases and ash will cause environmental problems [7]. Therefore, finding various applications and value-added products from lignin has drawn the attention of substantial number of researchers. The variation of functional groups and other structural characteristics of sulfonated lignin offer exceptional colloidal properties. These properties allow using SL as a stabiliser in colloidal suspensions; a dispersing agent; a binder; a detergent; a glue; a surfactant; an adhesive or cement additives. But until now, no major large-scale application of lignin utilisation has been commercially proven. Only 1–2% of the various types of lignin are utilised in non-fuel value-added applications [6].

Lignin is a carbon-rich renewable source, with carbon content of 60–65%, which could represent a remarkable substitute for the synthesis of AC [6]. The synthesis of AC from lignin is carried out through two processes; carbonisation of lignin into a char and consequent activation to develop a microporous structure with high surface area. These processes can be accomplished simultaneously using chemical activation process, where lignin is premixed with chemicals such as $ZnCl_2$, KOH, K_2CO_3 and H_3PO_4, and charred at temperatures of 450–900 °C. These charring temperatures are moderately lower than those of physical activation process [8]. Most of the published work investigated the synthesis of activated carbons from water-insoluble kraft lignin [6]. In contrast, the publications on the synthesis of activated carbons from sulfonated lignin are very limited [6,9,10]. Therefore, this research addresses this gap by exploring the feasibility of activated carbon synthesis from a new material (water-soluble grass-derived sulfonated lignin) using three dehydrating salts ($ZnCl_2$, KCl and $Fe_2(SO_4)_3 \cdot xH_2O$). Up to the authors' knowledge, the last two activating agents have not been used before to produce ACs from SL. The first part of this research [11] included the study of different variables that may affect the quality of synthesised sulfonated lignin-based activated carbons (SLACs). These variables included: the concentration of the dehydrating salt solution, the charring temperature and time. The produced SLACs were subsequently used for the removal of three heavy metal ions (Cd^{2+}, Cu^{2+} and Zn^{2+}) from aqueous solutions. Depending on their removal efficiencies of these three heavy metal ions, the optimal SLAC for each dehydrating salt was selected. The second part of this research, which is presented in this paper, appraises the chemical and physical characteristics of the three optimal SLACs and weighs against the characteristics of their precursor (grass-derived SL) and two commercial activated carbons.

2. Materials and methods

2.1. Precursor characteristics

The pre-treatment step of grass hydrolysis process produces a liquor that contains considerable amount of lignin and small quantities of sugars, inorganic and organic salts. Water-soluble sulfonated lignin was extracted from the liquor by firstly removing the major portion of sugars, inorganic and organic salts by acidification to a *pH* of approximately 3–4 with a 30% aqueous solution of sulphuric acid. This acidification step precipitated lignin that was separated, filtered and washed to decrease its residual sulphuric acid content. The lignin slurry was finally sulfonated by adding sodium sulphite enough to increase its *pH* from 4 to 9. This reaction was carried out in an autoclave, where the contents were heated and kept at 140 °C for about 4 h under constant rotation. After cooking, the product was removed from the autoclave, filtered to eliminate insoluble by-products and treated in order to reduce its sulfonate content and then dried [11].

2.2. Synthesis of activated carbons

Water-soluble grass-derived SL was mixed with prepared stocks of three dehydrating salts ($ZnCl_2$, KCl and $Fe_2(SO_4)_3 \cdot xH_2O$) at concentrations of 10, 20 and 30% w/w to form a paste. Charring of the samples took place in a muffle furnace at two charring temperature of (600 or 700 °C). When the charring temperature was achieved, the samples were then held at this temperature for 1 or 2 h. At the end of charring time, the furnace was then switched off and allowed to cool till it reached room temperature [11].

The optimal SLAC produced by each dehydrating salt was selected based on the maximum removal efficiency of three heavy metals (Cd^{2+}, Cu^{2+} and Zn^{2+}) from aqueous solutions prepared in a