VALORISATION OF BLACK LIQUOR FROM PULP AND PAPER INDUSTRY INTO ACTIVATED CARBON

SASI KUMAR N

DEPARTMENT OF CIVIL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY DELHI

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by

SASI KUMAR N

Department of Civil Engineering

Submitted

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Certificate

This is to certify that the thesis entitled "**Valorisation of black liquor from pulp and paper industry into activated carbon**", being submitted by **Mr. Sasi Kumar N**, to the **Indian Institute of Technology Delhi** for the award of the degree of '**Doctor of Philosophy**' in Department of Civil Engineering is a record of the bonafide research work carried out by him under our supervision and guidance. He has fulfilled the requirements for the submission of this thesis, which to the best of our knowledge, has reached the requisite standard.

The material contained in the thesis has not been submitted in part or full to any other University or Institute for the award of any other degree or diploma.

Prof. Babu J. Alappat
Department of Civil Engineering
Indian Institute of Technology Delhi

Prof. Pascaline PRÉ
Department of Energy Systems and Environment
IMT Atlantique, Nantes, France

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(Sasi Kumar N)

Abstract

Black liquor (BL), a by-product of the pulp and paper industry, has always been challenging for small-scale industries. Traditionally, BL is concentrated in multiple-effect evaporators (MEE) and combusted in boilers for energy recovery. However, the process is capital-intensive, requires frequent maintenance, and is inefficient for energy and chemical recovery. Among other valorisation options, activated carbon (AC) preparation is very efficient since the inorganics in black liquor can act as chemical activators. This study deals with the valorisation of highly pollution-causing black liquor into the porous carbon material. This study uses raw black liquor without any pre-purification as a precursor. ACs are prepared under conventional heating and microwave heating, and the energy consumption is calculated. AC samples are prepared under different experimental conditions, i.e., with a set of different temperatures, single-step self-activation without carbonization, pre-carbonization followed by different times of activation, and activation with the porogen potassium hydroxide. The prepared AC samples were characterized with iodine number, nitrogen physisorption analysis, X-ray Diffraction (XRD), Fourier-transformed infrared (FTIR), Raman spectroscopy, Thermogravimetric analysis (TGA), CHNSO analysis and SEM imaging. The iodine number obtained in one of the samples was 1022, more than equal to the commercially available activated carbons. The oxygen content in the AC indicates the presence of functional surface oxygen groups, which aids in the adsorption applications along with the textural characteristics. A single-step self-activation of black liquor under conventional heating fetched AC with 1000 m^2/g specific surface area (SSA), and micropore volume (MPV) of 0.5 cm^3/g. The maximum SSA and micropore volume among the prepared activated carbons is 2046 m^2/g and 0.86 cm^3/g, respectively. Microwave activation supports the precursor with high moisture content for the rapid preparation of activated carbon in 30 minutes. At the lab-scale, it was estimated that microwave activation consumes less than half of the energy required for conventional

activation. AC prepared under microwave heating with CO_2 activation fetched AC with 980 m^2/g specific surface area and micropore volume of 0.53 cm^3/g. Relying on the existing experimental data set from literature, this study proposes regression models that describe the variation of the textural properties of lignin-derived AC as a function of operation conditions, such as temperature, activation time and impregnation ratio for different activators (KOH, NaOH). The statistical significance of model parameters was verified by relying on the t-test results. Using the proposed models, it was found that the activation temperature and impregnation ratio parameters are the principal factors controlling the activation process, while activation time has a less significant effect on the development of porous structure. The optimum temperature range, to yield carbons with higher SSA and MPV, for single step lignin-KOH/NaOH activation was shown to be 700-800 ºC. Similarly, CMMR of 0.5-1 was observed to be optimum for both single-step and lignin-char activation. Carbons produced by lignin activation in the presence of KOH exhibit higher SSA and MPV than NaOH-activated carbons and require shorter activation time to reach the highest porosity. KOH activation of lignin-derived char requires a lower activation temperature than direct KOH activation of lignin.

Keywords: Black liquor, valorisation, activated carbon, conventional heating, microwave heating, carbon metal molar ratio, regression model

सारांश

लुगदी और कागज उद्योग का उप-उत्पाद काली शराब हमेशा छोटे पैमाने के उद्योगों के लिए चुनौतीपूर्ण रही है। परंपरागत रूप से, इसे बहु-प्रभाव बाष्पीकरणकर्ताओं में केंद्रित किया जाता है और ऊर्जा पुनर्प्राप्ति के लिए बॉयलर में दहन किया जाता है। हालाँकि, यह प्रक्रिया पूंजी-गहन है, इसके लिए लगातार रखरखाव की आवश्यकता होती है, और यह ऊर्जा और रासायनिक पुनर्प्राप्ति के लिए अक्षम है। अन्य मूल्यवर्धन विकल्पों में, सक्रिय कार्बन की तैयारी बहुत सक्षम है क्योंकि काली शराब में अकार्बनिक पदार्थ रासायनिक उत्प्रेरक के रूप में कार्य कर सकते हैं। यह अध्ययन अत्यधिक प्रदूषण पैदा करने वाली काली शराब के छिद्रपूर्ण कार्बन सामग्री में मूल्य निर्धारण से संबंधित है। यह अध्ययन अग्रदूत के रूप में बिना किसी पूर्व-शोधन के कच्ची काली शराब का उपयोग करता है। सक्रिय कार्बन को पारंपरिक हीटिंग और माइक्रोवेव हीटिंग के तहत तैयार किया जाता है और ऊर्जा खपत की गणना की जाती है। इसके नमूने अलग-अलग प्रायोगिक स्थितियों के तहत तैयार किए जाते हैं, यानी, अलग-अलग तापमान के सेट के साथ, कार्बोनाइजेशन के बिना एकल-चरण स्व-सक्रियण, पूर्व-कार्बोनाइजेशन के बाद सक्रियण के विभिन्न समय और पोरोजेन पोटेशियम हाइड्रॉक्साइड के साथ सक्रियण। तैयार नमूनों को आयोडीन संख्या, नाइट्रोजन फिसिसोरेशन विश्लेषण, एक्स-रे विवर्तन (एक्सआरडी), फूरियर-ट्रांसफॉर्मेड इंफ्रारेड (एफटीआईआर), रमन स्पेक्ट्रोस्कोपी, थर्मोग्रैविमेट्रिक विश्लेषण (टीजीए), सीएचएनएसओ विश्लेषण और एसईएम इमेजिंग के साथ चित्रित किया गया था। एक नमूने में प्राप्त आयोडीन संख्या 1022 थी, जो व्यावसायिक रूप से उपलब्ध सक्रिय कार्बन के बराबर से अधिक थी। सक्रिय कार्बन में ऑक्सीजन सामग्री कार्यात्मक सतह ऑक्सीजन समूहों की उपस्थिति को इंगित करती है, जो बनावट संबंधी विशेषताओं के साथ-साथ सोखने के अनुप्रयोगों में सहायता करती है। पारंपरिक हीटिंग के तहत काली शराब के एकल-चरण स्व-सक्रियण से 1000 मीटर^2/ग्राम विशिष्ट सतह क्षेत्र , और 0.5 सेन्टीमीटर^3/ग्राम के माइक्रोपोर वॉल्यूम के साथ सक्रिय कार्बन प्राप्त हुआ। तैयार सक्रिय कार्बन के बीच अधिकतम एसएसए और माइक्रोपोर की मात्रा क्रमशः 2046 मीटर^2/ग्राम और 0.86 सेन्टीमीटर^3/ग्राम है। माइक्रोवेव सक्रियण 30

मिनट में सक्रिय कार्बन की तीव्र तैयारी के लिए उच्च नमी सामग्री वाले अग्रदूत का समर्थन करता है। प्रयोगशाला-स्तर पर, यह अनुमान लगाया गया था कि माइक्रोवेव सक्रियण पारंपरिक सक्रियण के लिए आवश्यक ऊर्जा के आधे से भी कम की खपत करता है। कार्बन डाइऑक्साइड सक्रियण के साथ माइक्रोवेव हीटिंग के तहत तैयार सक्रिय कार्बन को 980 मीटर^2/ग्राम विशिष्ट सतह क्षेत्र और 0.53 सेन्टीमीटर^3/ग्राम के माइक्रोपोर वॉल्यूम के साथ एसी प्राप्त हुआ। साहित्य से मौजूदा प्रयोगात्मक डेटा सेट पर भरोसा करते हुए, यह अध्ययन प्रतिगमन मॉडल का प्रस्ताव करता है जो ऑपरेशन स्थितियों के एक फ़ंक्शन के रूप में लिग्निन-व्युत्पन्न एसी के बनावट गुणों की भिन्नता का वर्णन करता है, जैसे तापमान, सक्रियण समय और विभिन्न सक्रियकर्ताओं के लिए संसेचन अनुपात (पोटेशियम हाइड्रॉक्साइड, सोडियम हाइड्रॉक्साइड). मॉडल मापदंडों के सांख्यिकीय महत्व को टी-परीक्षण परिणामों पर भरोसा करके सत्यापित किया गया था। प्रस्तावित मॉडलों का उपयोग करते हुए, यह पाया गया कि सक्रियण तापमान और संसेचन अनुपात पैरामीटर सक्रियण प्रक्रिया को नियंत्रित करने वाले प्रमुख कारक हैं, जबकि सक्रियण समय का छिद्रपूर्ण संरचना के विकास पर कम महत्वपूर्ण प्रभाव पड़ता है। एकल चरण लिग्निन-पोटेशियम हाइड्रॉक्साइड / सोडियम हाइड्रॉक्साइड सक्रियण के लिए उच्च विशिष्ट सतह क्षेत्र और माइक्रोपोर वॉल्यूम के साथ कार्बन उत्पन्न करने के लिए इष्टतम तापमान सीमा 700-800 डिग्री सेल्सियस दिखाई गई थी। इसी तरह, 0.5-1 का सीएमएमआर सिंगल-स्टेप और लिग्निन-चार सक्रियण दोनों के लिए इष्टतम माना गया। पोटेशियम हाइड्रॉक्साइड की उपस्थिति में लिग्निन सक्रियण द्वारा उत्पादित कार्बन सोडियम हाइड्रॉक्साइड -सक्रिय कार्बन की तुलना में उच्च विशिष्ट सतह क्षेत्र और माइक्रोपोर वॉल्यूम प्रदर्शित करते हैं और उच्चतम सरंध्रता तक पहुंचने के लिए कम सक्रियण समय की आवश्यकता होती है। लिग्निन-व्युत्पन्न चार के पोटेशियम हाइड्रॉक्साइड सक्रियण के लिए लिग्निन के प्रत्यक्ष केओएच सक्रियण की तुलना में कम सक्रियण तापमान की आवश्यकता होती है।

कीवर्ड: ब्लैक लिकर, वैलोराइजेशन, सक्रिय कार्बन, पारंपरिक हीटिंग, माइक्रोवेव हीटिंग, कार्बन मेटल मोलर अनुपात, रिग्रेशन मॉडल

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List of abbreviations and acronyms

€	Euro
°C	Degree Celsius
AC	Activated carbon
ASTM	American society for testing and materials
BET	Brunauer, Emmett and Teller
BL	Black liquor
BO	Burn-off
C	Carbon
cm	Centimetre
cm^3/g	Cubic centimetre per gram
CKMR	Carbon-potassium molar ratio
CMMR	Carbon-metal molar ratio
CNMR	Carbon-sodium molar ratio
CO_2 `	Carbon dioxide
DBL	Dried black liquor
EDX	X-ray spectroscopy
$F\ g^{-1}$	Farad per gram
FTIR	Fourier-transformed infrared
g	Gram
GHz	Gigahertz
GJ	Giga Joule
h	Hours
H_2	Hydrogen
HCl	Hydrochloric acid
H_2S	Hydrogen sulphide
H_3PO_4	Phosphoric acid
ICP-MS	Inductively coupled plasma mass spectrometry
IUPAC	International union of pure and applied chemistry
IN	Iodine nu
KOH	Potassium hydroxide
m	Metre
$mAh\ g^{-1}$	Milli ampere-hour per gram

MEE	Multiple effect evaporators
min	Minute
m^2/g	Square metre per gram
MHz	Megahertz
mm	Millimetre
MPV	Micropore volume
MT	Million tons
N_2	Nitrogen
NaOH	Sodium hydroxide
nm	Nanometre
NLDFT	Non-local density functional theory
NO_2	Nitrogen dioxide
PSD	Pore size distribution
RSM	Response surface methodology
S	Sulphur
SEM	Scanning electron microscope
SSA	Specific surface area
T	Temperature
TGA	Thermogravimetric analysis
TPV	Total pore volume
USD	United States Dollar
XRD	X-ray Diffraction
$ZnCl_2$	Zinc chloride