

**PERFORMANCE EVALUATION OF SILVER IMPREGNATED
BIOCHAR DERIVED FROM PADDY STRAW TO MAKE
WATER POTABLE ALONG THE INDO-GANGETIC PLAIN**

ANIL KUMAR SAKHIYA



**CENTRE FOR RURAL DEVELOPMENT & TECHNOLOGY
INDIAN INSTITUTE OF TECHNOLOGY DELHI
OCTOBER 2024**

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by

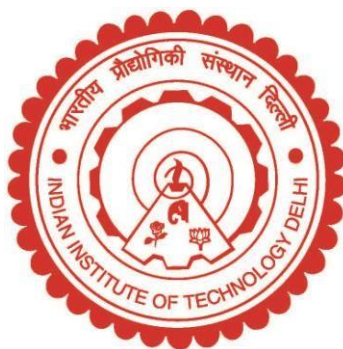
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CERTIFICATE

This is to certify that the thesis entitled " **Performance Evaluation of Silver impregnated Biochar derived from Paddy straw to make Water Potable along the Indo-Gangetic Plain**" being submitted by **Mr. Anilkumar Vallabhbhai Sakhiya** to the Indian Institute of Technology Delhi for the award of "**Doctor of Philosophy**" is a record of bona fide research work carried out by him. He has worked under our guidance and supervision and has fulfilled the requirements for the submission of this thesis.

To the best of our knowledge, the results contained in this thesis have not been submitted in part or full to any other university or institute for the award of any degree or diploma.

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Almighty and the divine nature.

New Delhi

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Anil Kumar Sakhiya

ABSTRACT

Most heavy metal contamination is found in Asian and African nations, and late water filtration methods rely heavily on electricity. Also, a large population living in rural Asian and African countries consumes heavy metal-contaminated water due to the lack of electricity. Additionally, heavy metal pollution in groundwater is a significant concern for human health in the Indo-Gangetic Plain of India. Moreover, due to a lack of economically and sustainable rice straw waste management options for rice straw utilization, around 84 Mt of rice straw is burned on the field in India. We aim to transform rice straw waste into biochar and utilize it to remove heavy metals from groundwater. Therefore, this study produced biochar from rice straw at different temperatures (300-600 °C) through pyrolysis. The result indicated an increase in process temperature led to the decreased biochar yield (57.87 – 35.63%), while the yield of bio-oil (30.22-39.6%) and syngas (11.91-26.16%) increased. Moreover, pH (8.28-11.4), fixed carbon (43.91-57.63%), pore-volume (0.0087-0.059 cm³ g⁻¹), surface area (12.78-83.06 m² g⁻¹), and HHV (17.63-20.13 MJ kg⁻¹) of biochar increased. The energy (76.7-82.39%) and exergy efficiency (63.97-81.57%) of the pyrolysis system increased with process temperature, and the thermodynamic optimization was achieved at 600 °C.

The single-step physical activation (CO₂ and H₂O) of rice straw was planned and optimized the activation process parameters to get better biochar yield and surface area. The biochar activation parameters were optimized using the central composite design method. The CO₂ activated biochar has an optimum surface area and product yield of 399.99 m² g⁻¹ and 26.79 %, whereas H₂O activated biochar has an optimum product yield and surface area of 31.53 % and 300 m² g⁻¹. The SEM analysis shows that CO₂ activated biochar has a more uniform porous structure compared to H₂O activated

biochar. Cost analysis revealed that CO₂ and H₂O activated biochar had a manufacturing cost of 1.287 and 1.672 U.S. \$ kg⁻¹, respectively.

Biochar derived at 600 °C had a higher surface area (78.17 m² g⁻¹) and adsorption capacity for As (4.51 mg g⁻¹) and Mn (3.61 mg g⁻¹) in a binary metal system. The PSO kinetics (R^2 : 0.97) and Langmuir isotherms (R^2 : 0.94) model better explained the adsorption of As and Mn. The adsorption was takes place by electrostatic attraction between metalloids and oxygenated (-COOH and -O.H.) surface functional groups. Health risk assessment indicated that field water (50 ml) treated with 0.1 g biochar had the highest As and Mn removal efficiency (>85 %) and hence lowered the cancer risk in the community. The cost of biochar produced at 600 °C (0.913 U.S. \$) is comparable with other adsorbents. Furthermore, CO₂-activated biochar was used to study the comparative analysis of As and Mn adsorption in a single and binary metal approach. Findings showed that the maximal sorption capacity of As and Mn in single metal systems was 18.26 and 12.18 mg g⁻¹ and 8.51 and 5.42 mg g⁻¹ in binary metal systems. The highest removal efficiency of As (99.53 %) and Mn (96.23 %) was achieved in naturally contaminated water (Sahibganj, district of Jharkhand, India). Health risk assessment indicates chances of cancer (CR> 1× 10⁻⁴ and HQ>1) in humans due to the high concentration of As (192 µg L⁻¹). Water treated with 0.1 g activated biochar had lower CR and HQ values, and metal concentration was below the WHO safe drinking water standard.

Apart from this, silver and copper impregnated CO₂ activated biochar was produced and studied its efficacy in removing heavy metals as well as microbial contaminants from groundwater. Results indicated that silver-impregnated activated (As: 87.29% and Mn: 99%) biochar had higher metal removal efficiency than copper-impregnated activated biochar (As: 84.38% and Mn: 99%). The antibacterial rate of silver-impregnated activated (92.74%) biochar was higher than copper-impregnated activated biochar

(76.70%). The concentration of As and Mn ions in the field water after adsorption by silver and copper-impregnated activated biochar was found in the range of the BIS safe drinking water guidelines.

अधिकांश भारी धातु संदूषण एशियाई और अफ्रीकी देशों में पाए जाते हैं, और देर से पानी छानने के तरीके बिजली पर बहुत अधिक निर्भर करते हैं। साथ ही, ग्रामीण एशियाई और अफ्रीकी देशों में रहने वाली एक अच्छी आबादी बिजली की कमी के कारण भारी धातु दूषित पानी का सेवन करती है। इसके अतिरिक्त, भारत के गंगा के मैदान में भूजल में भारी धातु प्रदूषण मानव स्वास्थ्य के लिए एक महत्वपूर्ण चिंता का विषय है। इसके अलावा, चावल के भूसे के उपयोग के लिए आर्थिक रूप से और टिकाऊ चावल के भूसे अपशिष्ट प्रबंधन विकल्पों की कमी के कारण, भारत में लगभग 84 मीट्रिक टन चावल के भूसे को जला दिया गया था। हमारा लक्ष्य चावल के भूसे के कचरे को बायोचार में बदलना है और इसका उपयोग भूजल से भारी धातुओं को निकालना है। इसलिए इस अध्ययन में पायरोलिसिस के जरिए चावल के भूसे से अलग-अलग तापमान (300-600 °C) पर बायोचार का उत्पादन किया गया। परिणाम ने संकेत दिया कि प्रक्रिया तापमान में वृद्धि के कारण बायोचार उपज (57.87 - 35.63%) में कमी आई, जबकि जैव-तेल (30.22-39.6%) और सिनगैस (11.91-26.16%) की उपज में वृद्धि हुई। इसके अलावा, पीएच (8.28-11.4), फिक्स्ड कार्बन (43.91-57.63%), पोर-वॉल्यूम (0.0087-0.059 cm³ g⁻¹), सतह क्षेत्र (12.78-83.06 m² g⁻¹), और एचएचवी (17.63-20.13 MJ kg⁻¹) बायोचार में वृद्धि हुई। पायरोलिसिस प्रणाली की ऊर्जा (76.7-82.39%) और ऊर्जा दक्षता (63.97-81.57%) प्रक्रिया तापमान के साथ बढ़ी, और थर्मोडायनामिक अनुकूलन 600 °C पर हासिल किया गया था। चावल के भूसे के एकल-चरण भौतिक सक्रियण (CO₂ और H₂O) की योजना बनाई गई थी और बेहतर बायोचार उपज और सतह क्षेत्र प्राप्त करने के लिए सक्रियण प्रक्रिया मापदंडों को अनुकूलित किया गया था। केंद्रीय समग्र डिजाइन पद्धति का उपयोग करके बायोचार सक्रियण मापदंडों को अनुकूलित किया गया था। CO₂ सक्रिय बायोचार का एक इष्टतम सतह क्षेत्र और उत्पाद उपज 399.99 m² g⁻¹ और 26.79% है, जबकि H₂O सक्रिय बायोचार में एक इष्टतम उत्पाद उपज और सतह क्षेत्र 31.53% और 300 m² g⁻¹ है। SEM विश्लेषण से पता चलता है कि H₂O सक्रिय बायोचार की तुलना में CO₂ सक्रिय बायोचार में अधिक समान छिद्रपूर्ण संरचना होती है। लागत

विश्लेषण से पता चला है कि CO₂ और H₂O सक्रिय बायोचार की निर्माण लागत क्रमशः 1.287 और 1.672 अमेरिकी डॉलर किलो-1 थी। 600 °C पर प्राप्त बायोचार में एक उच्च सतह क्षेत्र (78.17 एम² जी-1) और एक द्विआधारी धातु प्रणाली में आर्सेनिक (4.51 mg g⁻¹) और मैंगनीज (3.61mg g⁻¹) के लिए सोखने की क्षमता थी। छद्म-द्वितीय क्रम कैनेटीक्स (R²> 0.97) और लैंगमुइर इज़ोटेर्म्स (R²> 0.94) मॉडल बैटर ने As और Mn के सोखने की व्याख्या की। अधिशोषण को मेटलॉइड्स और ऑक्सीजन युक्त (-COOH और -O.H.) सतह कार्यात्मक समूहों के बीच इलेक्ट्रोस्टैटिक आकर्षण द्वारा सुगम बनाया गया था। स्वास्थ्य जोखिम मूल्यांकन ने संकेत दिया कि 0.1 ग्राम बायोचार के साथ उपचारित क्षेत्र के पानी (50 ml) में उच्चतम आर्सेनिक और मैंगनीज हटाने की क्षमता (> 85%) थी और इसलिए समुदाय में कैंसर के जोखिम को कम किया। 600 °C (0.913 यूएस डॉलर) पर उत्पादित बायोचार की लागत अन्य पी लेनेवाला पदार्थ के साथ तुलनीय है। इसके अलावा, CO₂-सक्रिय बायोचार का उपयोग एकल और द्विआधारी धातु दृष्टिकोण में आर्सेनिक और मैंगनीज सोखना के तुलनात्मक विश्लेषण का अध्ययन करने के लिए किया गया था। निष्कर्षों से पता चला है कि एकल धातु प्रणालियों में आर्सेनिक और मैंगनीज की अधिकतम सोखने की क्षमता 18.26 और 12.18 mg g⁻¹ और 8.51 और 5.42 mg g⁻¹ बाइनरी मेटल सिस्टम में थी। PSO गतिज मॉडल (R²> 0.99) और लैंगमुइर इज़ोटेर्म्स मॉडल (R²> 0.95) प्रयोगात्मक डेटा के साथ अच्छा समझौता दिखाते हैं। प्राकृतिक रूप से दूषित पानी (रांची, भारत) में आर्सेनिक (99.53%) और मैंगनीज (96.23%) की उच्चतम निष्कासन क्षमता हासिल की गई थी। स्वास्थ्य जोखिम मूल्यांकन आर्सेनिक (192 µg L⁻¹) की उच्च सांद्रता के कारण मनुष्यों में कैंसर (सीआर> 1 × 10⁻⁴ और मुख्यालय> 1) की संभावना को इंगित करता है। 0.1 ग्राम सक्रिय बायोचार से उपचारित पानी में सीआर और मुख्यालय के मान कम थे, और धातु की सांद्रता डब्ल्यूएचओ के सुरक्षित पेयजल मानक से नीचे थी।

इसके अलावा, सिल्वर और कॉपर इंप्रेग्रेटेड CO₂ एक्टिवेटेड बायोचार का उत्पादन किया गया और भूजल से भारी धातुओं के साथ-साथ माइक्रोबियल संदूषकों को हटाने में इसकी प्रभावकारिता का अध्ययन किया गया। परिणामों ने संकेत दिया कि सिल्वर-इंप्रेग्रेटेड एक्टिवेटेड (As: 87.29% और

Mn: 99%) बायोचार में कॉपर-इम्प्रेग्रेटेड एक्टिवेटेड बायोचार (As: 84.38% और Mn: 99%) की तुलना में मेटल रिमूवल दक्षता अधिक थी। सिल्वर-इम्प्रेग्रेटेड एक्टिवेटेड (92.74%) बायोचार की जीवाणुरोधी दर कॉपर-इम्प्रेग्रेटेड एक्टिवेटेड बायोचार (76.70%) की तुलना में अधिक थी। चांदी और तांबे-गर्भवती सक्रिय बायोचार द्वारा सोखने के बाद क्षेत्र के पानी में As और Mn आयनों की सांद्रता बीआईएस सुरक्षित पेयजल दिशानिर्देशों की सीमा में पाई गई

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ABBREVIATIONS AND NOMENCLATURES

ADD	Average Daily Dosage
Ag-CO ₂	Silver impregnated CO ₂ activated biochar
AgNO ₃	Silver nitrate
NaAsO ₂ .7H ₂ O	Sodium arsenate
ANOVA	Analysis of variance
ASTM	American Society for Testing and Materials
AT	Average lifetime
BET	Brunauer–Emmett–Teller
BIS	Bureau of Indian Standard
BJH	Barrett-Joyner-Halenda
BW	Body weight
CCD	Central Composite Design
CFU	Colony Forming Unit
CH ₄	Methane
CH ₄ %	Mass fraction of methane
CO	Carbon monoxide
CO%	Mass fraction of carbon monoxide
CO ₂ %	Mass fraction of carbon dioxide
CRDT	Centre for Rural Development and Technology
CRF	Centre Research Facility
Cu-CO ₂	Silver impregnated CO ₂ activated biochar
CuCl ₂	Copper chloride
DTG	Derivative Thermo-gravimetric Analysis

CR	Cancer Risk
CRF	Cancer Risk Factor
EBC	Energy Balance Closure
ED	Exposure Duration
EF	Exposure frequency
EDX	Energy dispersive X-ray
FC	Fixed Carbon
FCC	Face Cubic Center
FTIR	Fourier transforms infrared spectroscopy
H ₂	Hydrogen
H ₂ SO ₄	Sulfuric acid
H ₂ %	Mass fraction of hydrogen
HCl	Hydrochloric acid
HGE	Hot gas efficiency (%)
HHV	Higher Heating Value (MJ kg ⁻¹)
HQ	Hazard Quotient
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
LHV	Lower Heating Value (MJ kg ⁻¹)
MnSO ₄ .H ₂ O	Manganese (II) sulfate
MALDI	matrix-assisted laser desorption/ionization
MBC	Mass Balance Closure
Mt	Million tons
NaOH	Sodium hydroxide
RSB300	Rice straw biochar produced at 300 °C
RSB400	Rice straw biochar produced at 400 °C

RSB500	Rice straw biochar produced at 500 °C
RSB600	Rice straw biochar produced at 600 °C
R _f D	Reference Dose
R-CO ₂	Rice straw derived CO ₂ activated biochar
R-H ₂ O	Rice straw derived H ₂ O activated biochar
SEM	Scanning Electron Microscope
TGA	Thermogravimetric analysis
USD	U.S. Dollar
VM	Volatile Matter
WHO	World Health Organization
XRD	X-ray diffraction
wt%	Weight percent
ΔH°	Enthalpy
ΔG°	Standard Gibbs function of formation
B	Correlation factor
η	Energy efficiency
Ψ	Exergy efficiency