

2021

# Proceedings of the 1st NSE Minna Branch Engineering Conference



The Nigerian Society of Engineers  
**Minna Branch**

1<sup>st</sup> NSE Minna Branch Engineering Conference

Conference theme

**Role of Engineering in  
Sustainable Development Goals**

Nigerian  
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Minna Branch



Conference theme

## **Role of Engineering in Sustainable Development Goals**

**Conference Date: Wednesday 9th to Thursday 10th June 2021**

### **Conference Overview**

Primarily, Engineering innovations are concerned with improving human living standards, protecting and restoring the environment. To this end, sustainable Engineering strives to design or operate systems for efficient usage of resources. As a major stakeholder in sustainable development, the NSE Minna Branch, in partnership with COREN, NITDA, NASENI and SEDI-Minna, is organizing the 1st National Conference. The theme focuses on the roles of Engineering in attaining the 17 sustainable development goals within and outside Nigeria.

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## Role of Engineering in Sustainable Development Goals

Conference Date: Wednesday 9th to Thursday 10th June 2021

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**The Nigerian Society of Engineers**  
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**Role of Engineering in Sustainable  
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**Conference Date: Wednesday 9th to Thursday 10th June 2021**

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Conference theme

## Role of Engineering in Sustainable Development Goals

Conference Date: Wednesday 9th to Thursday 10th June 2021

### TABLE OF CONTENT

Paper ID	Paper Title and Authors	Page No
Lead Paper	<i>University Research and Innovation for Regional Economic Development: Panacea for Eradication of Extreme Poverty in Nigeria.</i> OKOPI ALEX MOMOH	01-12
1	<i>A Topsis-based Methodology for Prioritizing Maintenance Activities Suitable for A Municipal Water Works. Case Study: Chanchaga Water Works, Minna.</i> Musa Kotsu, U. G Okoro and I. A. Shehu	13-22
2	<i>The Effectiveness of Flood Early Warning by Nigerian Meteorological Agency for Sustainable Development in Nigeria.</i> Abdullahi Hussaini and Mansur Bako Matazu	23-29
3	<i>Evaluation of Hydraulic Model for Water Allocation in a Large Rice Irrigation Scheme, Malaysia</i> Habibu Ismail, Md Rowshon Kamal, N.J. Shanono and S.A. Amin	30-35
4	<i>Ultrasonic Motion Detector, A Panacea for Theft Related Security Challenges in the 21st Century.</i> Adebisi J.A. and Abdulsalam K. A.	36-44
5	<i>A Brief Review of Proposed Models for Jamming Detection in Wireless Sensor Network</i> Grace Audu, Michael David and Abraham U. Usman	45-49
6	<i>Design and Implementation of a Fire/Gas Safety System with SMS and Call Notification</i> M. A. Kolade, K.A. Abu-bilal, U.F. Abdu-Aguye, Z.Z Muhammad, and Kassim A. Y	50-59
7	<i>Non-linear Scaling in Global Optimisation. Part I: Implementation and Validation</i> Abubakar, H. A., Misener, R. and Adjiman, C. S.	60-68
8	<i>An Automatic Bus Route Monitoring System for the Federal University of Technology, Minna</i> Hamza Farouk, Michael David, Nathaniel Salawu, Ebune Emmanuel Opaluwa, Mamud Michael Oluwasegun, and Akabuike Kingsley Ikenna	69-75
9	<i>Reformation of Engineering Education for Health, Wealth and Sustainable Development in Nigeria.</i> Oluwadare Joshua Oyebode	76-83



## Role of Engineering in Sustainable Development Goals

Conference Date: Wednesday 9th to Thursday 10th June 2021

- 10 *A Review of the Different Biomass Materials Used to Produce Activated Carbon for Water Treatment.* Korie C.I, Afolabi E.A, Kovo A.S., Muktar A. 84-94
- 11 *Risk Analysis of Power Transmission Infrastructure for Sustainable Development: A Case Study of the Nigerian 330 kV- 41 Bus Network.* Jethro Shola, Emmanuel Sunday Akoji, UmbugalaKigbu F., Yusuf Isah, & A. A. Sadiq 95-103
- 12 *Non-linear Scaling in Global Optimisation. Part II: Performance Evaluation.* Abubakar, H. A., Misener, R. and Adjiman, C. S. 104-112
- 13 *A Review of Different Proposed Image Detection Techniques for Road Anomalies Detection.* A. M. Oyinbo, A. S. Mohammad, S. Zubair, and E. Michael 113-119
- 14 *A Review on Leach: An Energy Efficient Protocol in Wireless Sensor Networks* P. O. Odeh, S. Zubair, A. U. Usman, and S. Bala 120-127
- 15 *Finite Element Modelling and Analysis of a 4-Span T-Beam Bridge* Nyam, J. P. & Sadiku, S. A. 128-138
- 16 *Automatic Radio Selection for Data Transfer in Device to Device* C. E. Igbokwe, S. Bala, M. David, and E. Michael 139-149
- 17 *Sustainable Development in Construction Industry Using Palm Kernel Shell Ash as Partial Replacement for Cement.* S.O. Atuluku and T.E. Adejumo 150-157
- 18 *Effect of Strengthening Vertical Circular Openings with Various Materials on the Behaviour of Reinforced Concrete Beams* Paul Peter Maiyamba and S.M. Auta 158-166
- 19 *Opportunities for Engineers in the Solar Energy Value Chain* Mahmud, J. O., Mustapha, S. A. 167-174
- 20 *Development of an Electric Tricycle with Adjustable Wheel Camber* Jamilu Shehu Musawa and ikechukwu C. Ugwuoke 175-183
- 21 *Development and Characterisation of Briquettes from Biomass Wastes: A Review* Medashe, Michael Oluwasey and Abolarin, Mathew Sunda 184-193



Conference theme

**Role of Engineering in Sustainable Development Goals**

**Conference Date: Wednesday 9th to Thursday 10th June 2021**

- 22 ***Treatment of Industrial Waste Water to Remove Heavy Metal (Zinc) Using Palm Flower Activated Carbon as Adsorbent.*** Samson Adeiza Okeji, Patience Oshuare Sedemogun 194-201
- 23 ***Irrigation with Unsafe Industrial Wastewater and Associated Health Risks: An Emerging Technology for Heavy Metals Removal.*** A. S. Mohammeda, c, E. Danso-Boatengb, G. Sandac, A.D. Wheatleyc, M.I. Animashaund, I.A. Kutic, H.I. Mustaphad, M.Y. Otache, J.J. Musad. 202-214
- 24 ***Formulation of Cutting Oil Using Green Base Extract (Soya-Bean and Groundnut)*** Oketa A.J and Okoro U. G 215-223
- 25 ***Friction Stir Welding of Some Selected High Strength Aluminium Alloys- A Review*** B. I. Attah, S. A Lawal, E.T Akinlabi, K. C Bala, O. Adedikpe1 O. M Ikumapayi 224-229
- 26 ***The Failure Analysis in Steel Reinforced Beams with different Reinforcement Ratio*** Ayandokun W. A1, Balogun B. T, and Abdulrahman A. S 230-237
- 27 ***Oxidative Stability and Cold Flow Properties of Non-Edible Vegetable Oil for Industrial Biolubricant Applications*** Timothy Yakubu Woma, Sunday Albert Lawal, Asipita Salawu Abdulrahman, M.A. Olutoye, and A.A. Abdullahi, 238-243
- 28 ***Effect of Turning Process Parameters on Surface Roughness of AISI 1045 Medium Carbon Steel Using Aluminum Coated Carbide Tool*** Salawu Morufu Ajibola and Sunday Albert Lawal 244-248
- 29 ***Thermal and Physicochemical Characterization of Locally Sourced Lignite Coal*** C. O. Emenike, P. E. Dim and J. O. Okafor 249-254
- 30 ***Thermal and Physicochemical Characterization of Biochar Produced from Waste Bamboo.*** E. Daniel, P.E. Dim and J.O. Okafor 255-258
- 31 ***Synthesis of Ni-Al<sub>2</sub>O<sub>3</sub> Nanocatalyst for Low Temperature Production of Carbon Nanotubes (CNTs)*** Yerima, M. L., Abdulkareem A. S., Abubakre, O. K, Ndaliman, M. B. Khan, R. H., and Muriana, R.A. 259-266
- 32 ***Evaluation of Strength Properties of Lateritic Soil Stabilized with Cement Kiln Dust*** T.E. Adejumo and F.A. Okeshola 267-272
- 33 ***Development of A Low-Cost Briquette Making Machine*** Abdullahi A., Abolarin. M. S., Olugboji. O. A 273-276



**The Nigerian Society of Engineers**  
**Minna Branch**  
**1st NSE Minna Branch Conference 2021**

Conference theme

# **Role of Engineering in Sustainable Development Goals**

**Conference Date: Wednesday 9th to Thursday 10th June 2021**





Conference theme

# Role of Engineering in Sustainable Development Goals

## Irrigation with Unsafe Industrial Wastewater and Associated Health Risks: An Emerging Technology for Heavy Metals Removal

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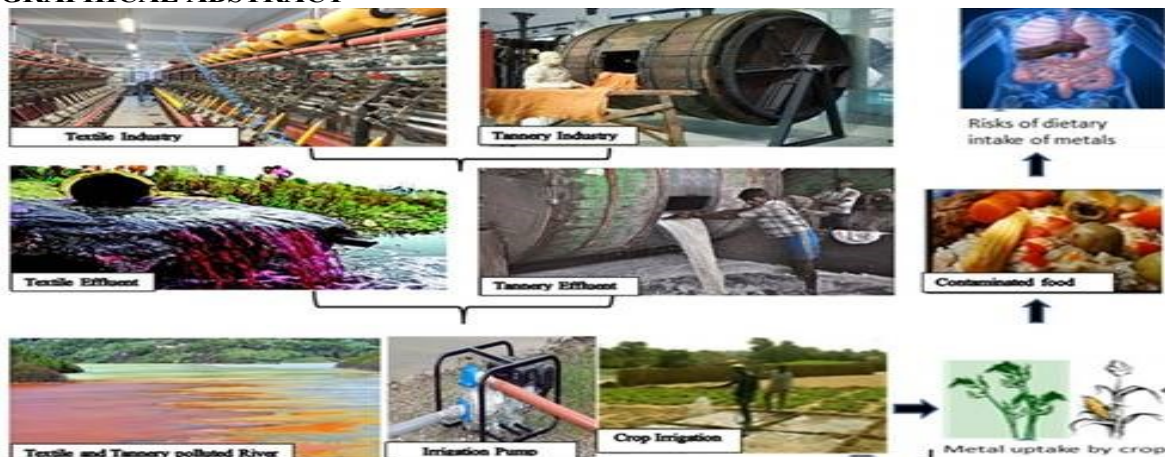
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### GRAPHICAL ABSTRACT



### ABSTRACT

The scarcity of freshwater resources, being currently experienced in water-stressed countries has prompted millions of smaller farming communities to depend on wastewater for crop irrigation, drinking, bathing and fishing. However, in this context, the treatment of wastewater from textile and tannery industries is the subject of interest, this paper aim to address. The rule of thumb suggests, wastewater to constitute beneficial nutrients recycling due to rich organic matter content. Inherently, the same kind of wastewater has been investigated and analysed by several researchers and found to contain micro-pollutants such as inorganics (heavy metals, salts) and organics (dyestuff, starch). Regrettably, the presence of these pollutants in wastewater used for irrigation is of concern particularly as it relates human health. Although, several conventional wastewater treatment technologies exist; their applications are now hamstrung by high procurement, operation and maintenance costs. Recent studies on cheap and readily available biomass wastes have confirmed their high sorption potential and can therefore, be used as adsorbents for micro-pollutants removal from industrial wastewater. In this study, chicken eggshell, coconut peat, coconut shell, rice husk and lemon peel were all used for the wastewater treatment. Hydrothermal carbonisation (HTC), was used to change the surface functional characteristics of the adsorbents for enhanced adsorption. To achieve this, batch experiments using raw biomass were carried out in triplicates at 3 different contact times and pH values. After 2 hr of contact time at pH9, the coco-peat was proven to have Cr removal efficiency of 91.6% against 73.2% using a bonechar; and 95.0% for Pb (II) against 91.2% for the bonechar. The outcome of this study suggests that coconut-peat and eggshell even without been carbonised can provide a cost-effective means for metal removal from industrial wastewaters.

**KEYWORDS:** Adsorption, biomass waste, crop irrigation, freshwater scarcity, wastewater reuse



Conference theme

# Role of Engineering in Sustainable Development Goals

## 1 INTRODUCTION

One-third of the world's population currently live in developing and water-deficit countries, with overall water need is expected to rise by 2025 (Gu, et al., 2019; Dubey and Swain 2019). As a consequence of the resource exploitation, about two-third of the global population would suffer from water shortages (Mahfooz, et al., 2020). Scarcity of freshwater resources may limit food production and supply, as about 70% of all freshwater withdrawals go to irrigated agriculture ( $\approx 2800 \text{ km}^3$  of freshwater/year). Scarcity of freshwater resources may limit food production and supply, as about 70% of all freshwater withdrawals go to irrigated agriculture ( $\approx 2800 \text{ km}^3$  of freshwater/year) (UN-Water, 2012). Water is an essential resource for the sustenance of life and plays a cardinal role in agriculture and allied industries, consequently, it also receives a variety of wastes from different sources (Merchant and Painter, 2019; Kennedy, et al., 2018). Studies have shown that there is global decline in the amount of available freshwater resources due to intensified agricultural practices such as excessive application of fertilizers, pesticides, insecticides and herbicides (Gu, et al., 2019) as well as climate change and increasing urbanization but its severity is mostly experienced in developing and water-stressed countries (Mahfooz, et al., 2020). The economic contributions of peasants farmers especially in developing and water-stressed countries are now hamstrung by freshwater scarcity, and this is observed to affect the expansion of crop yields and their quality. As a consequence of artificial scarcity of freshwater resources, wastewater stem to provide a great deal of relieve to farmers for year-round production of crops (Dubey and Swain, 2019). The use of wastewater for agriculture permits the cultivation of wide range of crops in multiple cycles, thereby promoting potentials for high yields.

Surmise to the above, reuse of wastewater for agriculture has become a norm and its practical application in developing and water-stressed countries has historical precedence which is likely to increase in the near future (Bougnom and Piddock, 2017). Although, several benefits of wastewater reuse, particularly in agriculture have been widely

reported; it's practical application is most beneficial and cost-effective in developing nations (Drechsel, et al., 2009). However, despite the huge economic benefits of wastewater reuse, it is apparent that this important resource is recording varying concentrations of heavy metals and pigments due to uncontrolled discharge of industrial effluents into waterways (Becerra-Castro et al., 2015; Mohammed et al., 2020).

Regrettably, the peasant farmers along the fringes of these waterways utilize such resource for crop irrigation, hence compromising crop quality and food safety (Dickson, et al., 2016). There are several documented articles from developing countries reporting varying concentrations of organic and inorganic chemical substances in agricultural soils and crops that have been receiving perpetual wastewater (Qu, et al., 2019). Ironically, the concentrations of these pollutants in wastewater, agricultural soils and crops usually exceeds the FAO/WHO recommended thresholds. Seemingly, prolong exposure to wastewater pollutants are impediments that hinders safe agricultural practice and farmers' productivity, which culminate to pervasive health implications on humans through food supply chain. There are several research articles establishing the epidemiological and carcinogenic links between the consumption of poorly irrigated crops with individual or societal illnesses (Qu, et al., 2019; El-Azazy et al., 2019). Other likely ailments resulting from excessive exposure to heavy metals and metalloids include mutagenicity, carcinogenicity and teratogenicity. Mutagenicity is the alteration of genetic structure, while carcinogenicity causes damage to specific regions of the genome, Carcinogenic substances can get into a biological tissue through inhalation, ingestion and contact with skin. Teratogenicity on the other hand, is a specific mutagen that cause damage to the genome which then causes abnormality in the developing foetus (Tong et al., 2000). It's worthy to know, that humans, animals and plants do not have good mechanisms for fixing or excreting heavy metals; hence bio-ccumulate and remain for life (Zhuang et al., 2009 QU, et al., 2012).

Policymaking bodies such as World Health Organisation (WHO), Food and Agriculture Organisation (FAO), International Commission on



Conference theme

# Role of Engineering in Sustainable Development Goals

Irrigation and Drainage (ICID), among others have been exploring modalities to safeguard humans and environment from excessive exposure to micro-pollutants found in wastewater used for irrigation. In a quest to define these modalities, these international bodies jointly issued some guidelines to regulate the concentrations of micro-pollutants in irrigation water worldwide. Adoption of these guidelines is highly desirable; but in reality, their implementation is hard to achieve practically, particularly in developing countries (Chang et al., 2002). The probable reasons for the unsuccessful implementation of those guidelines may be due to any or combination of the following: 1) high procurement and installation costs for modern wastewater treatment facilities; 2) non-compliance with policy guidelines governing effluent discharge into waterways and environment by industries; and 3) poor monitoring and enforcement strategy.

The essence of these guidelines is to safeguard agricultural soils, plants and humans from excessive exposure to organic and inorganic chemical substances (Dickson, et al., 2016). Although, application of these guidelines has recorded tremendous success in developed nations; regrettably, their effective implementation in developing countries is still looming and unsuccessful (Ensink and Van Der Hoek, 2009). Proffering an alternative wastewater treatment method is the purpose for which this paper is anchored.

Over the years, chemical precipitation, ion-exchange, electro-dialysis, reverse-osmosis, membrane and adsorption using activated carbon and other industrial by-products have been the most widely treatment technique for wastewater (Geetha and Belagali, 2013; Bhattacharjee et al., 2020; Ajiboye, et al., 2021). Of all the treatment methods mentioned, activated carbon is reported to be the most commonly used for the removal of ions and pigments from industrial wastewater at much lower concentrations (Phadtare and Patil, 2015; Bhattacharjee, et al., 2020). However, the major limitation with the use of activated carbon is that its procurement is quite expensive.

Furthermore, limitations of conventional wastewater treatment methods mentioned above, other than activated carbon include high initial

operating cost and generation of secondary toxic wastes which may require additional cost of treatment. The toxic wastes generated are mostly non-environmentally friendly. Against these backdrops, researchers are now exploring cheaper, sustainable and more effective method for the removal of organic and inorganic pollutants in wastewaters (Bhattacharjee, et al., 2020).

To this end, the work herein, explores the potentials of biomass wastes that comprise rice husk, coconut shell, coconut peat otherwise called coir, chicken eggshell and lemon peel. All these wastes are readily available in Nigeria. The raw biomass wastes are needed for the preliminary adsorption tests. However, for column tests, the biomass wastes were carbonised to produce hydrochar. The technology used for the conversion of biomass wastes into hydrochar is called hydrothermal carbonisation (HTC). Hydrochar is mainly composed of 40–45wt% cellulose, 25–35wt% hemicellulose, 15–30wt% lignin and up to 10wt% for other compounds (Sevilla and Fuertes, 2009).

Hydrothermal carbonisation is an exothermic process that takes place in water at temperature between 180 – 250 °C within a time period ranging from 30–500 min to produce a carbon-rich coal-like derivative commonly called hydrochar at saturated pressure of 15 – 20 bar which releases CO<sub>2</sub> and other volatiles (Titirici et al., 2007; Funke and Ziegler, 2010; Libra et al., 2011). The HTC involves dehydration and decarboxylation of biomass in order to raise the carbon content which enhances sorption characteristics and increases hydrochar energy values (Libra et al., 2011). For the purpose of his paper, only raw biomass wastes are used to investigate the effectiveness of the metal ions removal.

## 2 MATERIALS AND METHODS

### 2.1 RAW MATERIALS

All the materials used herewith were obtained locally; these include the following: the chicken eggshell were gotten from the Loughborough University kitchen; lemon from a street market in Loughborough town, Leicestershire; the coconuts bought from a supermarket also in Loughborough;



Conference theme

# Role of Engineering in Sustainable Development Goals

the coconut peat was purchased from Fertile Fibre, Withington Hereford; and rice husk from E-Coco Products, Tewkesbury, all in the UK.

## 2.2 PREPARATION OF THE ADSORBENT

Commercial activated bonechar (BS) was supplied by Jaret Limited, 4 Birch groves, Houston, Johnstone, Renfrewshire, Scotland. The bonechar was meant to serve as the reference adsorbent material to the raw biomass wastes and their corresponding hydrochars used for the adsorption. See Figure 1.

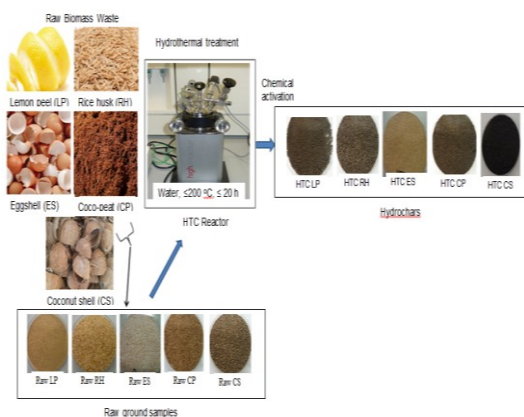


Figure 1: A graphical illustration of hydrochar production from biomass wastes using HTC

## 2.3 REAGENTS AND INITIAL CONCENTRATION OF SIMULATED WASTEWATER

All reagents used in this study were of analytical grade, supplied by Fisher Scientific Equipment Laboratories Ltd., Loughborough, United Kingdom. The standard ICP solution was prepared in nitric acid with concentration of 10,000 mg/L for  $\text{CuSO}_4$  and  $\text{Pb}(\text{NO}_3)_2$ , and 1000 mg/L for  $\text{K}_2\text{CrO}_4$  and  $\text{FeSO}_4$ . Procedure for the synthetic wastewater preparation was based on the method outlined in Standard Methods for the Examination of Water and Wastewater (APHA, 2012). To prepare the required 5 mg/L of the standard solution needed for the adsorption studies, approximately 0.5 ml of  $\text{Pb}(\text{NO}_3)_2$  and  $\text{CuSO}_4$  were withdrawn and poured into an empty 1000 ml (1 L) volumetric flask,

followed by addition of 5.0 ml of  $\text{K}_2\text{CrO}_4$  and  $\text{FeSO}_4$ . Deionise water was added to the flask to make up to 1 litre. The stock solutions of the synthetic wastewater on the other hand, was meant to contain a mixture of Cr(VI), Cu(II), Fe(II) and Pb(II) at six different concentrations (0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 mg/L); given initial concentration,  $C_1$  as 100 mg/L; initial volume,  $V_1$  (0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 ml) and final volume,  $V_2$  (100 ml). The mixture was poured into separate volumetric flasks and labelled according to the concentrations. In order, to produce a fair representation of a typical textile and tannery wastewater, 2 g/kg of corn starch, 6.13 g/kg of anhydrous sodium sulphate ( $\text{Na}_2\text{SO}_4$ ) and 0.09466 g/kg of methylene blue were added to the undiluted constituents in each volumetric flask before deionised water was added to make-up 1 litre. The dosages of corn starch, salt and methylene blue stated above were chosen and used based on the recommendations of Awomeso *et al.* (2010), Ong *et al.* (2010) and Randall *et al.* (2014).

## 2.4 Adsorbent dosage

Batch adsorption tests were conducted by starting with measuring 1.5 g of each raw biomass waste (eggshell, rice husk, coconut shell, coconut peat and lemon peel) in a conical flask before adding 50 mL of ordinary deionised water. The purpose for this is to determine a baseline concentration of each inherent analyte of interest and pH in the aqueous samples. The conical flasks were then placed on a pH meter incorporated with magnetic stirrer (pH-8+ DHS Benchtop meter, Czech Republic) and various sample pH taken. Then the conical flasks were transferred to a mechanical shaker (Gallenkamp Orbital Incubator-cooled Shaker, INR-200 INR-250, Netherlands) for thorough mixing. The incubator was pre-set at room temperature ( $25 \pm 2$  °C) and speed of 150 rpm. At each time lap (10, 20, 30, 40, 50, 60, 120, 240 and 360) mins, a corresponding flask was withdrawn from the shaker, filtered using Whatman paper No. 42 (2.5  $\mu\text{m}$ ) membrane filter to separate treated water from the solid sorbents. The filtrates were analysed for the baseline concentrations of Cr(VI), Cu(II), Fe(II) and Pb(II). The baseline concentrations served as the controls for the experiments and were deducted from the sample analysed using wastewater. Similarly, the



Conference theme

# Role of Engineering in Sustainable Development Goals

procedure was followed using the same adsorbent dosage, operating conditions and volume of wastewater.

## 2.5. Effect of contact time on adsorption.

At the preliminary stage of this study, the effect of three (3) different contact times (2, 4, and 6) h on adsorption were examined using the raw biomass wastes. The chosen contact time were for the purpose of optimisation in order to explore to shortest possible time to achieve maximum adsorption yield.

## 2.6 Effect of pH

A polygon F371220040 spin bar was dropped into each volumetric flask containing ordinary water different adsorbent and placed on magnetic stirrer to examine the effect of solution pH on adsorption. While the magnetic stirrer is switched ON, the mixture begins to stir, and the initial pH taken. and that was repeated after adjustment with 1M NaOH. Based on typical scenarios as documented in several literature, textile and tannery wastewaters are known to be alkaline in nature with pH values ranging from 9 to 11. Hence, this justifies the choice of pH9 and pH11 for alkalinity medium used in this study. Whereas, the pH of solutions that contain hydrochar in natural state ranges from 4 to 6, which is relatively acidic. However, in order to adjust the acidic pH to alkalinity, 1M of sodium hydroxide (NaOH) was gradually added to the solution until the desired pH for each mixture was attained.

## 2.7 Heavy metal removal efficiency

To determine the percentage adsorption of heavy metals by the adsorbents, the following equation as described by (Chen and Wang, 2008) was used.

$$R\% = \left[ \frac{C_i - C_f}{C_i} \right] \times 100$$

(1)

Where;

$C_i$  is initial metal concentration (mg/L) and  
 $C_f$  is the final metal concentration (mg/L).

## 2.8 CHARACTERISATION OF BIOMASS WASTE

The analytical method used in carrying surface characterisation are as follows: (i) Scanning Electron Microscopy (SEM); (ii) Energy Dispersive X-Ray Spectroscopy (EDS); (iii) Brunauer, Emmett and Teller (BET), (vi) Fourier transformed Infrared Ray (FTIR).

## 2.9 BATCH ADSORPTION TESTS

At the end of the batch adsorption tests after, the filtrates (treated water) were all collected in 50 mL labelled plastic bottles and stored at 4 oC to analyse and determine the residual concentration of each interacting heavy metals and pigment in the synthetic textile and tannery wastewater.

## 3. RESULTS AND DISCUSSION

### 3.1 CHARACTERISATION OF RAW BIOMASS AND CORRESPONDING HYDROCHAR

Details on surface characterization, including morphology, pore volume, pore size and Fourier Transform Infrared Ray (FTIR) of both raw biomass wastes and the corresponding hydrochar can be found in the author's recent publication by Danso-Boateng et al. (2021)

### 3.2 EFFECT OF CONTACT TIME ON METAL ADSORPTION BY RAW BIOMASS WASTE

The effect of contact time on adsorption of Cr(VI), Cu(II), Fe(II) and Pb(II) ions from an aqueous textile and tannery wastewater by various raw biomass wastes (ES, RH, CP and LP) was investigated. The preliminary results of the batch tests that were carried out using only raw biomass wastes are presented in Figure 8. To start with, a careful study of Figure 8 (b), (c) and (e) displayed very low uptake of Cr(VI) ions. This implies that the surface chemistry of the raw ES, RH, LP have poor sorption affinity for the Cr(VI) ion and even with progressive increased in contact time, there is no significant change on the amount of Cr(VI) ions removed. However, Figure 8 (a) and (d) indicates removal of about 80% and 90% of Cr(VI) by BC and CP respectively after the first 2 h.



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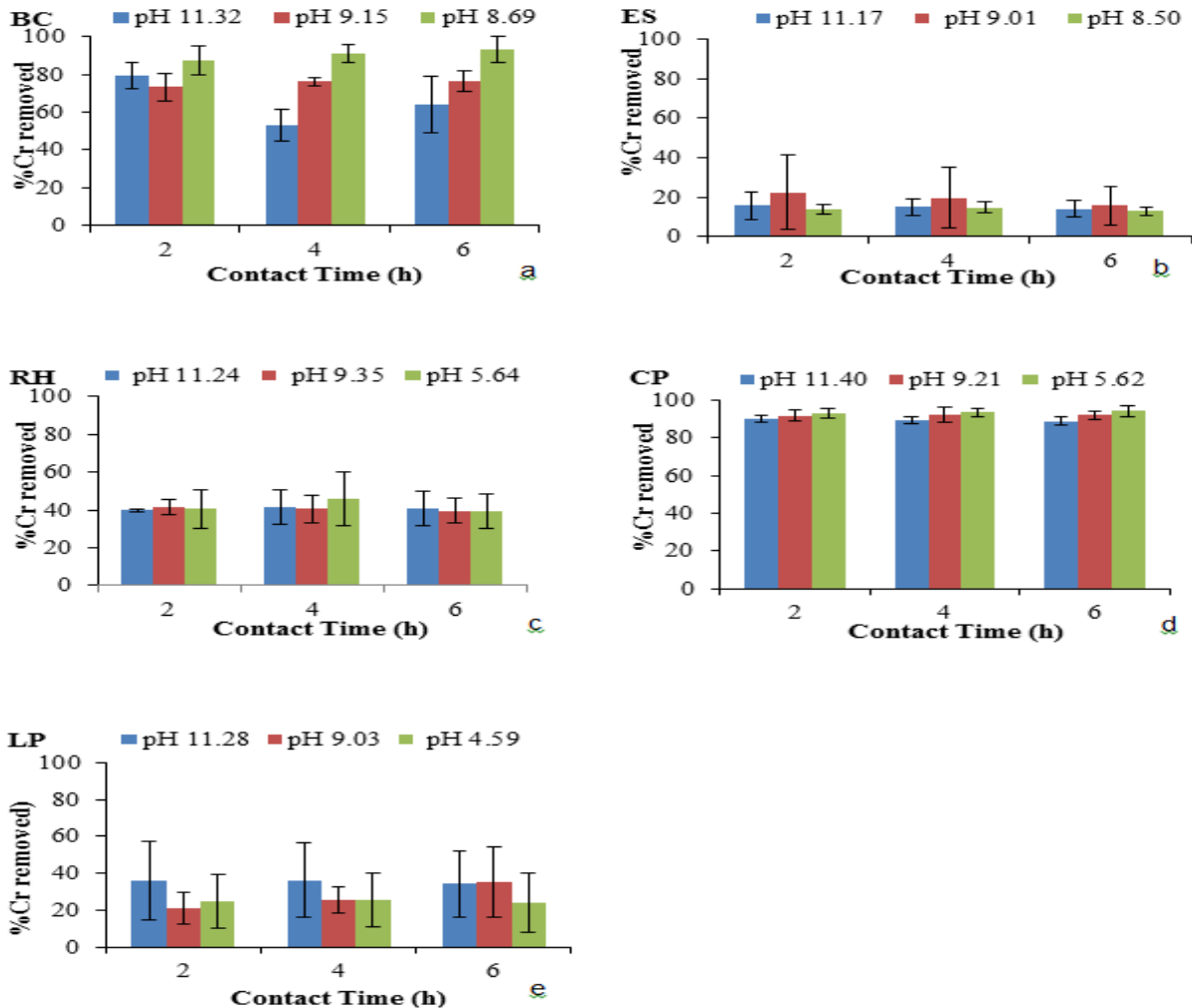


Figure 2 shows the effect of contact time on % removal of Cr(VI) by: (a) BC (b) ES (c) RH (d) CP and (e) LP

Surprisingly, Figure 3 (d) the raw CP appears to have sorption ability almost equal the reference adsorbent, though the BC has been a derivative of a pyrolytic process and characterised with larger surface area than the CP. In Figure 9 over 95% Cu(II) was removed by ES and CP as shown in Figure 3(b) and (d) respectively within the first 2 h

and the adsorption rate remain constant. This shows that increase in contact time did not affect the amount of Cu ions adsorbed. About 50% of Cu ions was removed by RH and LP as shown in Figure 3 (c) and (e) after 2 h of contact; thereafter the percent adsorption decreased.



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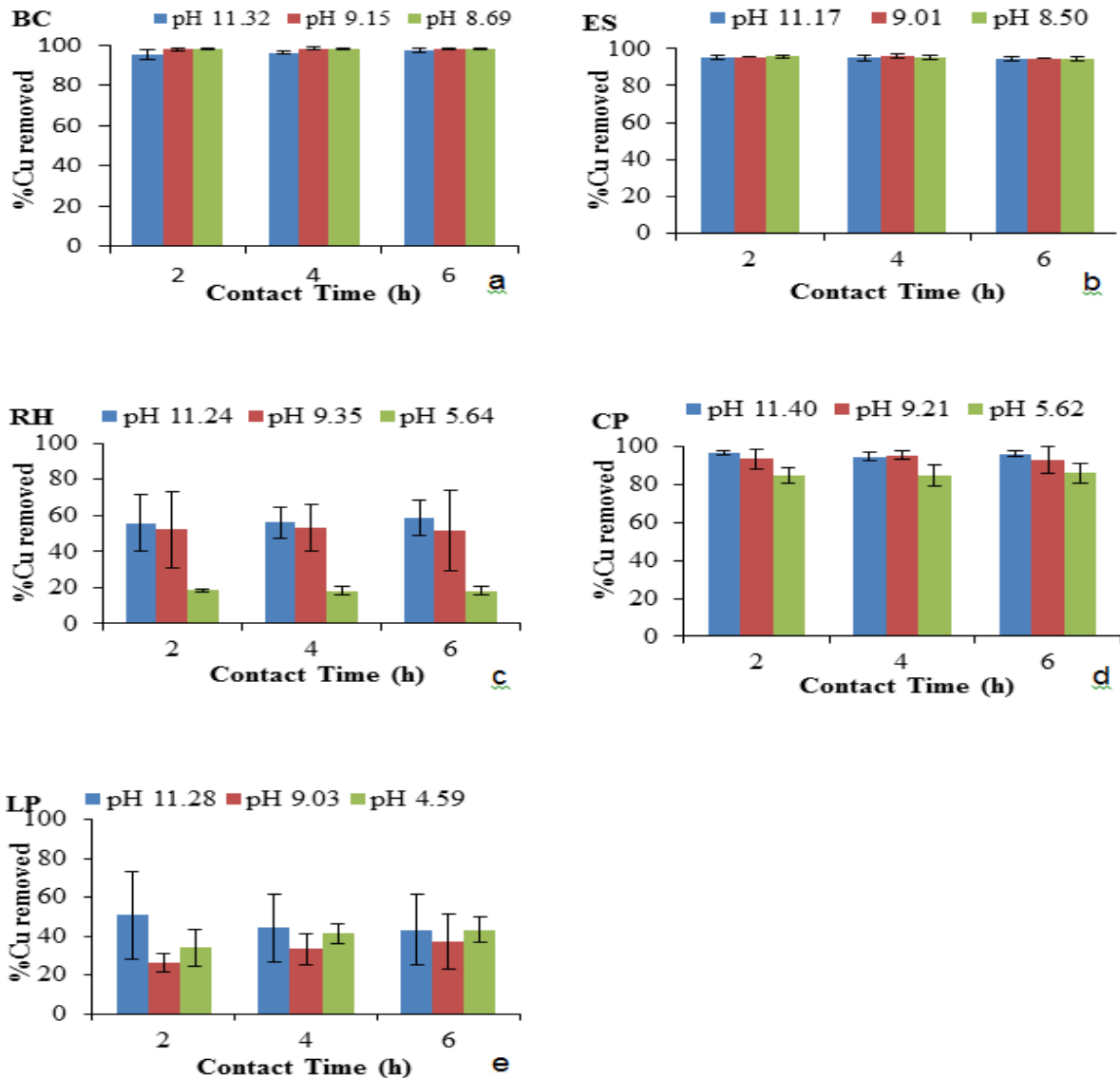


Figure 3 shows the effect of contact time on % removal of Cu by: (a) BC compared (b) ES (c) RH (d) CP and (e) LP

On the other hand, Figure 4 (a) and (b) showed that about 100% of Fe ions was removed by BC and ES after 2 h, same with CP as illustrated in (d). Thereafter, the adsorption rate became practically constant through the remaining period. ES and CP respectively after 2 h; further contact time did not have any significant effect.

Likewise, Figures 5 (a), (b) and (d) demonstrate that over 90% of Pb(II) was removed by BC. It can then be concluded that the rate of metal binding with adsorbent was more rapid during the initial stages (2 h), and this may be due to the presence of large number of active sites for metal binding, which became saturated with time and gradually decreased



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and remain constant. Observation on the effect of contact time on adsorption in this study is supported

by other researchers that examined and heavy metals removal by biomass wastes.

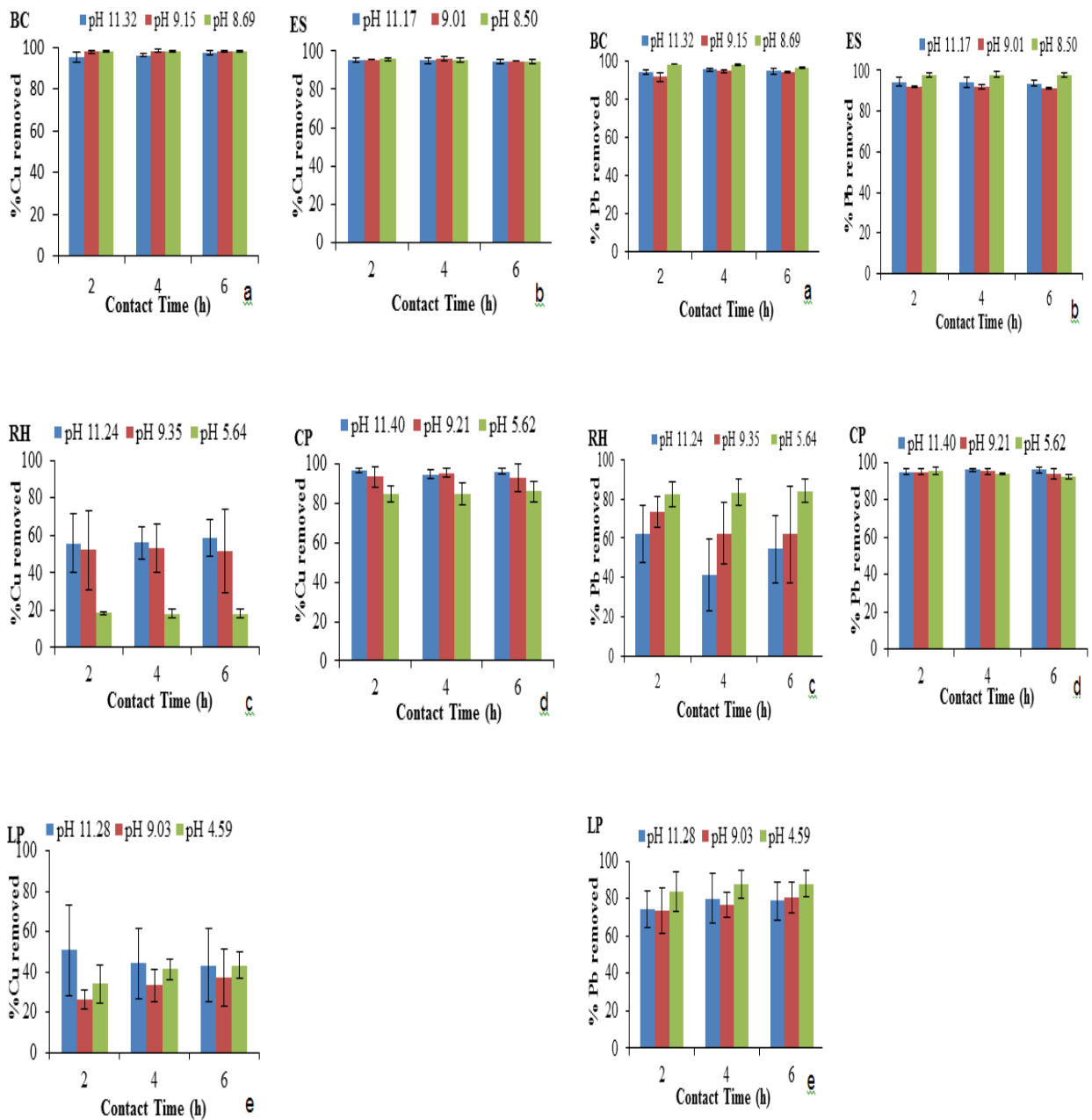


Figure 3 shows the effect of contact time on % removal of Cu by: (a) BC compared (b) ES (c) RH (d) CP and (e) LP

Figure 4 shows the effect of contact time on % adsorption of Fe by (a) BC compared (b) ES (c) RH (d) CP and (e) LP





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Seemingly, based on the trend observed from Figures (2 – 5), The % removal of metal ions by different adsorbents (raw biomass waste) increased after 2 h. This may be due to availability of large active sites for binding, which becomes saturated with time and subsequently reducing in decreasing efficiency with time. In conclusion, findings from this study is in agreement with those reported by Azouaou *et al.*(2010) and Han *et al.* (2017).

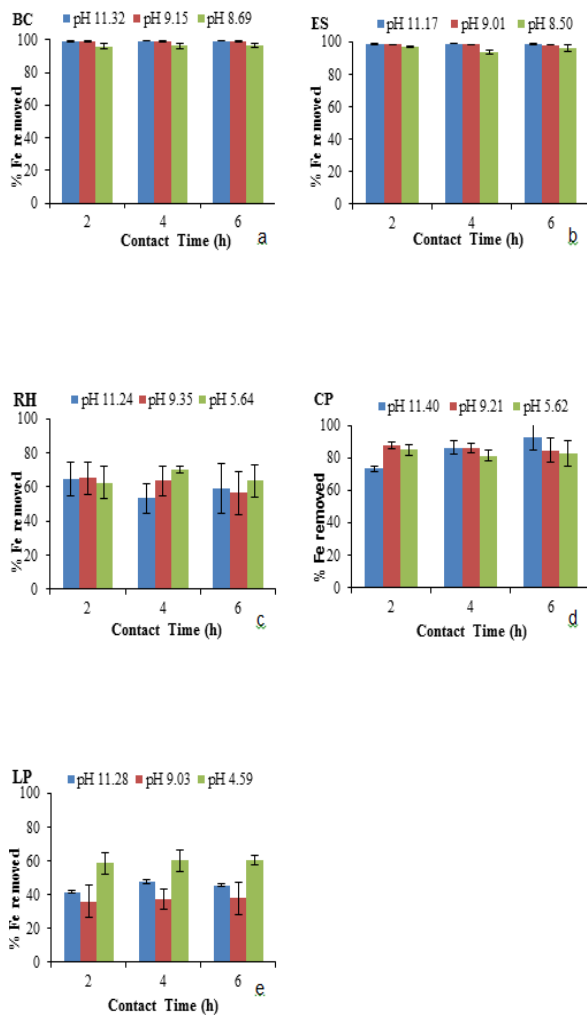


Figure 5 shows the effect of contact time on % removal of Pb(II) by: (a) BC (b) ES (c) RH (d) CP and (e) LP

### 3.2 EFFECT OF pH ON METAL ADSORPTION BY RAW BIOMASS WASTE

As expected, the varying pH considered in this study appears to have influenced on adsorption rate, since it governs the speciation metal ions and dissociation of the active sites of the sorbents. The effect of pH on removal of Cr(VI), Cu(II), Fe(II) and Pb(II) ions by BC and raw biomass of the following: ES, RH, CP and LP was investigated and results linked to Figure 8 to Figure 11. By observing Figure 8, the natural pH5.62 which indicates acidity, appears to explore the potentials of CP by removing over 90% of Cr(VI) ions. The sterling observation made on CP, revealed a better adsorption when compared to the reference adsorbent BC, which is barely 90% at pH8.69 (slightly basic). However, in Figure 8, pH4.59 and pH5.64 were only able to favour the removal of 40% and 20% of Cu(II) by LP and RH respectively. At pH9.01 and 11.0, ES and CP were able to remove about 100% of Cu(II) relatively better than the BC. On the other hand, at natural pH8, adjusted pH 9 and 11, ES was able to remove 100% of Fe(II); hence, equating the performance pollutant adsorption BC. Furthermore, almost 100% of Pb(II) were completely adsorbed by CP, ES compared BC irrespective of their media pH conditions which ranged from weakly acidic pH5.62 through pH8.69 to pH11.32. At high pH values, the surface of these adsorbents become negatively charged (anions); hence, resulting in very high affinity for cations attraction. The effect of pH on metal adsorption found in the present study are in agreement with the results obtained by other researchers that used biomass wastes such as coffee residues (Oliveira *et al.*, 2008), orange waste (Azouaou *et al.*, 2013), tea waste (Amarasinghe and Williams, 2007), banana peel (Anwar *et al.*, 2010) and coconut shell (Pino *et al.*, 2006).

Surmise to the above, the lemon peel used in its raw state in this work did not perform well in the adsorptions of Cr(VI), Cu(II) and Fe(II) at different pH conditions. This may be due to the presence of lipids, fats, oils and lignin in the peels, and when in aqueous media, these constituents are released into the solution. Therefore, to effectively utilise LP for adsorption, it is essential to subject the peels to a



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thermochemical treatment in order to denature the organic constituents and increase its surface area for adsorption. The thermochemical process is termed hydrothermal carbonisation (HTC), which produces a product called hydrochar.

#### 4 CONCLUSIONS

Biomass wastes consisting of coco-peat (CP), coconut shell (CS), rice husk (RH), lemon peel (LP) and eggshell (ES) were hydrothermally treated at 200 °C for 20 h in order to investigate their sorption ability for pollutant adsorption. The study demonstrated that the raw biomass wastes have the potential to be used as adsorbents. However, hydrochar would be better due to changes in surface characteristics of the adsorbents. The SEM images showed that the hydrochars have more porous structures, which resulted from denaturing of biomass structures due to carbonisation. The surface area of the hydrochars were significantly higher than the corresponding raw biomass, with CS hydrochar having the largest surface area (21.82 m<sup>2</sup>/g), whilst ES hydrochar the smallest (0.5 m<sup>2</sup>/g). The enhanced porosity and surface area of the hydrochars result in more characteristics active sites for sorption of pollutants. Therefore, the abundance of these biomass waste materials in developing countries and the moderate HTC temperature required make these produced hydrochars suitable for potential practical applications, especially in developing countries.

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