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A FULL LIFECYCLE ANALYSIS OF WASTE-DERIVED BIOCHAR VERSUS ACTIVATED CARBON FOR TEXTILE WASTEWATER TREATMENT AND POST-USE ENERGY VALORIZATION

Seemab Javed[1], Dr Tahir Shah[2], Tashfeen Tajummal[3], Tufail Shah[4], Zunaira Irfan[5], Musaab Habib Bangash[6], Bushra Kalsoom[7], Michael M. SABUGAA[8]

[1] University of Engineering and Technology (UET), Lahore, Pakistan
[2]University of Technology and Applied Science (UTAS) Muscat Oman, Senior Lecturer, Department of Applied Sciences, UTAS PO Box 74 Postal code 133 Muscat Oman. tahir.shah@utas.edu.om, ORCID: 0009-0009-2802-6900
[3]Department: Institute of Environmental Sciences and Engineering, SCEE
University: National University of Sciences and Technology, Islamabad 44000, Pakistan. Email: tashfeentajammal@gmail.com
[4]Faculty of Engineering, Sakarya University, Serdivan, Sakarya 54050, Turkey
[5]Department of Chemical Engineering, University of Engineering Technology zanairairfan@gmail.com
[6]Public Health Engineering Department Khyber Pakhtunkhwa Pakistan. mousabbangash@yahoo.com
[7]Department: Institute of Environmental Sciences and Engineering, SCEE University: National University of Sciences and Technology, Islamabad 44000, Pakistan. Email: bushrakalsoom88@gmail.com
[8]Agusan del Sur State University, Philippines

ABSTRACT
The traditional choice of adsorbents to treat textile wastewater focuses on the adsorption capacity rather than the sustainability in the whole picture. The proposed study fills this gap with data on the first cradle-to-cradle lifecycle assessment, which involves post-use energy valorization to compare waste-derived biochar (BC) and chemically activated carbon (AC). Sugarcane bagasse and corrugated cardboard were used to make biochar and KOH-activated carbon, which were characterized and tested in the removal of methylene blue. The production, use and energy recovery through burning spent adsorbents was modeled by a Net Energy Balance (NEB). Though AC had 2.5-3.5 times greater adsorption capacity (to 386.5mg/g), it had an energy-demanding activation step that dominated the lifecycle. Most importantly, biochar pathways had a near-neutral or positive NEB (+0.1 to +1.0 MJ /m 3), whereas AC routes had a major net energy loss (-9.0 MJ /m 3). It shows that in a circular economy model where one can realize energy recovery, waste biochar is a more sustainable adsorbent compared to high-performance AC, even though the former has lower adsorption efficiency. The results offer paradigm shift in terms of system level sustainability metrics when choosing technology.

KEYWORDS: Life Cycle Assessment (LCA); Biochar; Activated Carbon; Textile Wastewater; Circular Economy; Net Energy Balance (NEB); Adsorption.

INTRODUCTION
1.1 The Global Challenge of Textile Wastewater and Dye Pollution
This wastewater is also notoriously hard to treat because it contains a large amount of salts, surfactants, and heavy metals, but most importantly, the leftover synthetic dyes. The partial loss of dyes in the dyeing process of fabric implies that a considerable portion of it, between 10 percent and 50 percent in the case of reactive dyes and up to 50 percent in the case of direct dyes, was absorbed in the effluent stream. (1)(2).

1.1.1. Dye Removal Adsorbents biochar and Activated Carbon
The urgent need to design effective and efficient eco-friendly technologies to remove dye in textile wastewater has made adsorption a framework procedure, which is highly valued due to its simplicity of operations, potential to be very efficient, and versatility. Among such adsorbents, biomass-based carbonaceous compounds, namely biochar and activated carbon (AC), have received much interest because of their physicochemical characteristics, including tuneability, and performance. Nevertheless, they are radically new paradigms of material synthesis and usage that can be defined by a very specific trade-off between engineered performance and holistic sustainability. Critical analysis of their production lines, ensuing properties, and performance indices is therefore necessary to put to perspective the necessity of the entire lifecycle analysis suggested in this research(3)(4).
The general benefit of the biochar route is that it is closely tied with the principles of circular economy and waste valorization. It converts agricultural and industrial by-products of low or negative value to a useful environmental

remediation agent, and the production protocol typically uses less energy input and fewer chemical reagents than the traditional AC synthesis(5).
The outcome is a material with a very large specific surface area, usually over 1000 m_2/g, and usually 2000-3000 m_2/g in cases where the material is chemically activated. It is the major contributor of its high adsorption capacity and this large inner surface area has made AC the long known standard of adsorption performance. (6)
Nonetheless, this great performance comes at a very high cost, both economically and environmentally. The activation process is always energy-intensive, especially physical activation that uses the high temperatures over time or chemical activation that uses large volumes of frequently corrosive and hazardous reagents (e.g., KOH) that are difficult to handle, recover, and treat as wastewater. The large production cost of commercial AC is also a major challenge to its widespread application in wastewater treatment particularly in the resource-limited environment. Besides, the high processing can lead to a material with a comparatively homogeneous and graphitized surface which could contain fewer oxygen functional groups than biochar and could therefore be less efficient at pollutants that are removed through particular chemical reactions.
This clear distinction brings up the key conflict in the choice of an adsorbent to employ in sustainable wastewater treatment, the subject of which is usually ignored in traditional comparative research. Activated Carbon provides the highest adsorption capacity (high efficiency) at the cost of high embedded energy, chemical utilization and cost. Biochar provides a sustainable, waste-based profile, which has less production effects, yet tends to have average adsorption capacity(7).
The existing literature is almost unanimous on comparing these materials in a very limited perspective of adsorption isotherms and kinetics in batch experiments, which declares a winner by simply examining the maximum adsorption capacity (q max). This strategy is highly inadequate. It also does not consider the resource use and the environmental impact of making production (the "front-end" of the lifecycle) and does not bother with the disposition and possible usefulness of the spent and dye-laden adsorbent (the "back-end" of the lifecycle). A spent biochar that has not lost its calorific value can be valorized as a solid fuel and spent AC that has been contaminated with chemicals can be a hazardous waste. Thus, the statement of superiority by adsorption capacity in itself is shortsighted. To achieve a transformative assessment, it must be based on a complete lifecycle model that captures the energy required to produce, the material feedstock, adsorption efficiency, and the potential to recycle the use product in a new application in one analysis model. The critical gap within the present research paradigm that the present study aims to bridge about, instead of performance-based simplistic comparisons, is the assessment of real net sustainability of biochar based on waste versus activated carbon, as the true treatment of textile wastewater(8)(9)**(10).**

1.1.2. The Critical gap: Addition of Post-Use Valorization to the Adsorbent Lifecycle Analysis

The developing literature that has used Life Cycle Assessment (LCA) to compare biochar and activated carbon (AC) has given invaluable information on the environmental footprint of the two materials especially in terms of resource intensity of their production processes. Practically, it is always found in the literature that the manufacturing of activated carbon, particularly through chemical activation, is one of the primary hotspots of energy consumption, greenhouse gas emissions, and other environmental effect. On the other hand, LCAs of biochar production frequently highlight the fact that biochar can be associated with net-negative emissions of carbon when the carbon capture in a stable matrix is considered and its usefulness in bio-enriching waste biomass. Nevertheless, a critical reading of the research methodological limitations and the mentioned constraints of this literature on LCA also show that there is a major and widespread gap to the comprehensive sustainability of these materials, especially as wastewater treatment media.
The biggest drawback is the largely used cradle-to-gate or truncated cradle-to-grave system limits. Most analyses of biochar are based on its generation, and one final application, including carbon sequestration in soil, or heavy metal fixation. Although it has values in these applications, these studies remove the functional use phase in a systematic manner as a wastewater adsorbent and the resulting impact. **(11)**
Secondly, despite the fact that the use phase is also considered, evaluation is usually restricted to the adsorption efficiency (e.g., removal capacity) without a connection to the fate of the saturated adsorbent post-use. A paper can mention the effectiveness of biochar in the elimination of a dye such as Reactive Yellow and not say what happens to the resulting material after that, whether it is dumped, recycled, or the end product can be used as a raw material. Such an omission is essential, since the end-of-life phase may radically change the net environmental balance. Landfilling is a linear terminal that has the possibility of leakage of contaminants, whereas regeneration needs extra energy and chemicals. The third, circular alternative, the thermal valorization of energy recovery, is virtually never a part of comparative LCA studies, although one such alternative, at least in industrial terms, is certainly a possibility, particularly with biochar which still has calorific value.
The result of this is the fundamental, transdisciplinary gap: The gap between the techno-environmental analyses of adsorbent production and the principles of the circular economy requiring the inclusion of end-of-life valorization is vast. It has been noted in reviews that a more global view of the circular economy would involve evaluating mechanisms of closing the loop, although used LCAs of adsorbents rarely consider such possibilities as the co-combustion of used biochar to generate steam. The existing literature therefore compels poor comparison: it compares

the production effects of AC and biochar or, optimistically, the production effects as well as the adsorption capacity but does not give a platform by which to judge which material has a better net energy and environmental performance when the complete chain of waste feedstock to the final energy recovery is taken into account**(12)**
Thus, the research gap does not lie in the fact that there has not been a continuous individual LCA of biochar or AC, but that comparative, full lifecycle analysis that combines three phases that are intrinsically connected and cannot be studied separately: (1) production energy/cost, (2) adsorption performance with a desired pollutant (textile dye), and (3) the post-use energy valorization potential of the spent adsorbent. In the absence of this combined analysis, the assertions about the green character of waste-derived adsorbents cannot be considered complete, and the choices about their use in the industrial wastewater treatment cannot be based on rigorous and systems-wide sustainability basis. This paper seeks to address this very gap by undertaking such a complete lifecycle assessment, therefore, offering a paradigm shift in decision-making in the context of biochar and activated carbon as adsorbents, but rather as possible nodes in a closed industrial system.

1.1.3. Research Objectives and Novelty Statement

To explicitly fill the critical gap found in Section 1.4, the given study will also serve to take the analysis further in no longer relying on the old approach of comparing adsorption by introducing an approach that is more circular economy informed and holistic. The main objective is to find out which of the adsorbent pathway waste-derived biochar or activated carbon exhibits a better net environmental and energy sustainability upon consideration over its entire lifecycle with the considerations of end-of-life valorization. The operationalization of this aim is conducted by the following specific research objectives:
The aim of the synthesis and characterization of biochar and activated carbon to be prepared using reported agricultural and municipal waste streams. Biochar was pyrolyzed with the use of slow pyrolysis, and activated carbon was obtained by the chemical (KOH) activation of the same feedstocks; in this way, the properties of the materials, which are based on the same raw materials, can be directly compared.
To measure the adsorption capacity of the prepared materials of a model textile azo dye. The basic performance parameters (e.g. capacity, kinetics, isotherms) was calculated by batch adsorption experiments under controlled conditions to identify the functional performance of each adsorbent.

- To perform a complete lifecycle analysis that measures the net energy balance of each pathway of adsorbent. This study has incorporated primary data at three stages:
- Production Stage: Feedstock processing, pyrolysis and activation energy.
- Use Phase: Adsorption by using operational energy.

Post-Use Phase: Calorific value and potential energy recovery of dye-laden adsorbents used through thermal conversion.
To come up with a techno-environmental decision framework. Judging by the combined LCA findings, this framework was used to select adsorbents to treat textile wastewater using the combined measures of adsorption efficiency, production footprint, and post-use valorization potential, as opposed to a single measure.

2.0 NOVELTY STATEMENT

The proposed research has taken a groundbreaking step in the sustainable wastewater treatment field as it presents the first comparative, cradle to cradle life cycle assessment containing a direct analysis incorporating the post-use energy valorization of waste-derived biochar and activated carbon. Although the literature isolates the analysis of the effects of production, the process of adsorption and the end-of-life management, this paper integrates these aspects into one, consistent analytic model. In providing the key answer to the critical question, that is, whether the larger adsorption capacity of activated carbon justifies the increased production cost, when biochar presents the energy recovery option after utilization, this study changes the paradigm of comparing green adsorbents. It shifts the discussion of a small scale deal with a beaker look on efficiency of removal to a system level analysis of net sustainability in a circular industrial engagement providing a robust, evidence-based framework to build on the principles of the circular economy in the textile industry and beyond.

3.0 METHODOLOGY

3.1 Feedstock Sources

Sugarcane bagasse as an agricultural waste and Corrugated cardboard as a municipal waste were selected as wastes feedstock. **(13)**

3.1.1 The protocol for the feedstock preparation

The two feedstocks had a standardized preparation protocol to make them similar and reproducible in their subsequent pyrolysis and activation steps. The protocol was based on the existing procedures of preprocessing biomass.
Drying: Sugarcane bagasse was dried in the sun over a period of 48 hours after which the sample was dried in the oven at 105 + 5ºC over a period of 24 hours to reach a constant weight and make the content moisture free to a level of less than 10% (w/w).**(14)**

Size Reduction: Drying The dried components were mechanically cut and ground in a Wiley mill. A standard sieve shaker was used to sieve the ground biomass to get a uniform fraction of particle size of 0.5-1.0 mm. This size scale is ideal in enabling effective heat and mass transfer during the pyrolysis process and keeping the pressure drops high, due to high pressure, in possible reactor systems at a scale**(15).**

Characterization (Proximate & Ultimate Analysis): Characterization of the feedstocks was done before conversion. Proximate analysis (moisture, volatile matter, fixed carbon and ash content) was done as per the ASTM D7582. An elemental analyzer was used to analyze the ultimate (C, H, N, S, O content). These are the baseline data, which are essential in realizing the carbon yield and the characteristics of the end product chars (Table 3.1).

Table 3.1 Proximate and Ultimate Analysis of Prepared Feedstocks

Parameter	**Sugarcane Bagasse**	**Corrugated Cardboard**
Proximate Analysis (wt.%, dry basis)		
Volatile Matter	71-78%	77-80%
Fixed Carbon	16-21%	16-19%
Ash Content	3-7%	2-4%
Ultimate Analysis (wt.%, dry ash-free basis)		
Carbon (C)	46-51%	43-46%
Hydrogen (H)	6-8%	6-7%
Oxygen (O) (by difference)	41-46%	44-51%
Nitrogen (N)	0.23-0.567%	<0.2%
Sulfur (S)	<0.12%	<0.11%

3.2 Material Synthesis

The production of adsorbents was aimed at converting the chosen waste feedstocks, which are sugarcane bagasse and corrugated cardboard, to the two types of carbon materials through thermochemical conversion. These aims included generation of a moderate-process biochar (BC) and high-process activated carbon (AC) of each precursor in order to allow a direct comparison of the lifecycle energy input and functional output of each. Pyrolysis and all activation reactions were done in a horizontal tube furnace (Model XYZ, Company) in the continuously flowing high-purity N_2 atmosphere (150 mL min-1). The Biochar was produced through Slows Pyrolysis; this is a slow method of converting biomass into charcoal. These two feedstocks were converted into biochar by a slow pyrolysis protocol that maximizes the yield of fixed carbon and produces an initial pore structure that can be used in the adsorption process.

Preparation of Feedstock: Sugarcane bagasse (SB) and corrugated cardboard (CC) were received in their dried, sieved (0.5 -1.0 mm) form**(16)**.

Pyrolysis Process: A feedstock of about 20 g was put in a quartz boat and loaded in the constant-temperature area of the furnace. Ambient temperature was raised to pyrolysis final temperature of 500ºC at a constant heating rate of 10ºC min-1, which is laid out on the basis of standard protocols of lignocellulosic materials. The temperature was held at this level with a residence time of 120 minutes to make sure that it had been fully devolatilized.

Product Recovery: The system was left to cool to less than 50ºC when the pyrolysis was completed and with the flow of N2. The biochar that was obtained was recovered, dried to ascertain the mass generated and kept in a desiccator. The products were referred to as SB-BC (sugarcane bagasse biochar) and CC-BC (corrugated cardboard biochar).

Biochar Yield: The gravimetric yield of biochar (Y)

$$\text{YBC} = (\text{Mass BC} / \text{Mass feedstock}) \times 100\%$$

The average returns of these feeds are 25-35 wt.% of sugarcane bagasse and 30-40 wt.% of cardboard. The Activated Carbon can be produced using the KOH Activation. The primary biochar (SB-BC and CC-BC) were transformed into activated carbons with high porosity with the help of a chemical activating agent, potassium hydroxide (KOH) using a well-known two-step procedure.

Chemical Impregnation: First, the KOH aqueous solution was added to the primary biochar in a specified ratio of KOH. Char in 3:1 (w/w), which proved to be an effective ratio in the creation of high surface area biomass-derived carbons. The contents of the slurry were stirred and dried for 12 hours at room temperature followed by drying in an oven at 110ºC in 24 hours**(17).**

Activation: Char impregnation was carried out with the char loading into the tube furnace which was used in the activation step. The temperature was set at 5ºC/min up to 750ºC of the end activation temperature under N_2 flow and maintained at this point during 60 minutes.
Post-Activation Processing: The product was cooled in N_2 and repeated hot deionized water (80ºC) union until the filtrate had neutralized pH (7.0). It was eventually dried at 110ºC in 24 hours. The last activated carbons obtained are called SB-AC and CC-AC.
Activated Carbon Yield: Total activated carbon yield of the raw feedstock (Y_2AC) was computed as:
$$\text{YAC} = (\text{Mass AC} / \text{Mass feedstock}) \times 100\%$$
The average yield of such an intensive process is not as high; it ranges between 15-25 wt.%**(18)**

3.3 Characterization of Synthesized Materials
Textural characteristics (BET surface area, pore volume), morphology (SEM), surface chemistry (FTIR), and calorific value (bomb calorimetry) were characterized using materials. In Supplementary Information some detailed protocols are given. (19)(20).

3.3.1 Adsorption Experiments
In order to analyze the operational performance of the synthesized adsorbents (SB-BC, CC-BC, SB-AC, CC-AC) under the complete lifecycle context, the batch adsorption experiments were developed using a model textile azo dye. Methylene Blue (MB) a cationic thiazine dye with a molecular formula of $C_{16}H_{18}C_lN_3SS$ was chosen as the target pollutant because it is widely used in the textile industry, is well characterized in its adsorption behavior on carbonaceous materials, and is a standard compound used to test the adsorbent capacity.

3.3.2 Preparation of Adsorbate and Stock Solutions
MB stock solution (1000mg/L) was obtained by dissolving a known weight of high-purity powdered MB dye (Sigma-Aldrich, 95%) in deionized water. Daily serial dilutions of the stock solution were used to make working solutions of desired concentrations (25-500mg L-1). The pH of the dye solutions was made 0.1 M using either 0.1 M, 0.1 M NaOH or 0.1 M HCl, and a pH meter (e.g., Metrohm 780) was used to measure the pH**(21)**

3.3.3 Batch Adsorption Procedure
All the adsorption tests were conducted in three parallels in a 250 mL Erlenmeyer flask with an orbital shaker (ZHWY-211B, Zhicheng) at 150 rpm constant agitation rate and room temperature (25 +- 1ºC) unless specified otherwise in thermodynamic experiments. The overall setup was to add a pre-tested amount of the adsorbent to a pre-determined volume (100 mL) of the MB dye solution of known initial concentration (C^0) and pH. The flasks were subsequently closed and stirred. Contact time was then predetermined and the flasks stirred for a specified time. Samples 3 mL) were removed at certain time intervals and filtered with a 0.45 mm nylon membrane syringe filter as an immediate method to separate the adsorbent particles. The MB concentration (C in the maximally absorbed wavelength l max = 664 nm) in the filtrate at equilibrium or C at t was measured by UV- Vis spectrophotometer (Shimadzu UV-1800). Absorbance was subsequently converted into concentration using a pre-existing calibration curve (R2 = 0.999)**(22)**
Meaning of the data. The quantity of MB adsorbed at any given time (t) and unit mass (q) of adsorbent, q (mg g-1), and q (mg g-1) were determined by the following equations of mass-balance (Eq. 3 & 4):

$$\text{qe} = (\text{C0} - \text{Ce})\,\text{V} / \text{m}$$
$$\text{qt} = (\text{C0} - \text{Ct})\,\text{V} / \text{m}$$

where C^0, C, and C are starting, equilibrium, and time t concentration of MB (mg L-1), V is the solution volume (L), and m is the mass of dry used adsorbent (g).

3.3.3. Isotherm, Kinetics and Thermodynamics Experimental Design
These controlled experiments were developed to comprehend the adsorption processes and a capacity threshold, which has been crucial in the performance data of lifecycle model.
Effect of Initial pH: The effect of solution pH on adsorption was examined in a pH range of 311 and adsorbent dosage of 0.5 g l-1 and initial concentration of MB is 100 mg l-1 and 24 hours of contact time were used to achieve equilibrium**(23)**.

Adsorption Isotherms:
Experiments were conducted to determine the distribution equilibrium of dye in the liquid and the solid phase by changing the starting concentration of the MB (25-500 mg L-1) at constant adsorbent dosage (0.5 g L-1), pH (optimal due to the previous test), temperature (25ºC), and contact time (24 h). The obtained data were modeled to the Langmuir (Eq.). 5) and Freundlich (Eq. 6) isotherm models.
Langmuir model:

$$q_e = \frac{(\text{qm KL Ce})}{(1 + \text{KL Ce})}$$

where q m (mg g -1) is the theoretical adsorption capacity of the monolayer in principle and K L (L mg -1) is the Langmuir constant that is associated with adsorption energy**(24)**

Freundlich model:

$$qe = KF\,Ce\hat{}(1/n)$$

where KF (mg g1L mg1)1/n is the Freundlich constant which depicts the adsorption capacity, and 1/n is the heterogeneity factor.

Adsorption Kinetics: Experiments were performed by measuring q at specific time points (1 minute -1 to 24 hours) at constant initial MB concentration (100 mg L-1), optimum pH, and dosage of adsorbent to analyze rate of uptake and the steps that might be rate-limiting. The analysis of kinetic data was done with pseudo-first-order (Eq. 7) and pseudo-second-order (Eq. 8) models**(25)**

Pseudo-first-order:

$$qt = qe\,(1 - \exp - k1\,t)$$

where k1 (min -1) is the rate constant.

Pseudo-second-order:

$$qt = (k2\,qe2\,t)/\,(1 + k2\;qe\,qt\,t)$$

k 2 (g mg-1 min-1) is the rate constant.

Adsorption Thermodynamics: The thermodynamic parameters of change in Gibbs free energy, enthalpy change, and entropy change were measured at 25, 35 and 45°C. These were determined according to Van Hoff equation (Eq.). According to the temperature dependence of the distribution coefficient.

$$\ln(Kd) = \Delta S \circ /R - \Delta H \circ /RT$$

In which K d is the coefficient of distribution (q /C R is the universal gas constant (8.314 J mol -1 K -1), and T is temperature (in Kelvins)**(26).**

3.4 Lifecycle Energy Analysis and After Use Valorization Protocol

The given section outlines the methodological frame of the comparative lifecycle analysis (LCA), which is the original input of the given research. It is aimed at transforming the synthesis, adsorption and post-use stages into a Net Energy Balance (NEB) of each adsorbent pathway. The model goes beyond the customary cradle-to-gate assessments by incorporating energy recovery where a system-level sustainability assessment can be achieved which is consistent with circular economy principles. The NEB is determined as the difference between the energy valorized by spent adsorbent and the total energy used in the production and utilization of the adsorbent (Eq. 10).

$$NEB = Evalorized - (Eproduction + E\,use)$$

When NEB is positive, it represents a net energy-producing system and when it is negative, it represents a net energy sink.

3.4.1 Definition of System Boundaries and Functional Unit

It adopted a cradle-to-cradle system boundary because it completely enclosed the circular flow of materials and energy (Figure 4.1). It was analyzed as follows: (1) Feedstock Preparation (drying, grinding), (2) Adsorbent Synthesis (pyrolysis/activation), (3) Use Phase (adsorption process), and (4) Post-Use Phase (thermal valorization of spent adsorbent). They did not include transportation and infrastructure. This study aims at a comparative technological evaluation of a hypothetical localized system of industrial symbiosis.

The unit of measure was determined as: Treatment of one cubic meter (1 m3) of synthetic textile wastewater with a starting concentration of Methylene Blue (MB) at 100 mg L-1 and an ending concentration at <5mg L-1 (95 percent removal). All material and energy flows have been scaled to this base to allow a fair comparison of adsorbents obtained by different routes and having different capacities**(27)**

3.4.2. Lifecycle Inventory Analysis: Measuring Energy Vitality

A. Energy (E production) at Production Phase

Direct determination and upstream inventory data were used to determine the embodied energy used to produce 1 kg of each adsorbent.

Direct Process Energy: Pyrolysis and activation consumed electrical energy which was measured 3 times with a calibrated plug-in digital energy meter (Kill A Watt P4460) which was connected to the tube furnace and oven. The energy used in drying (105°C, 24 h) and grinding was calculated based on the power values on equipment nameplates and time (Eq. 11)**(28)**.

$$\mathbf{Edirect\ (MJ/kg\ adsorbent)} = \mathbf{(S(Pi\ x\ ti)\ x\ 3.6)/m\ adsorbent}$$

in which Pi is the power (kW) of process i, ti is the time (hours) in operation, 3.6 is the conversion of kWh to MJ and m adsorbent is the mass of adsorbent produced in practice (kg).

Upstream Chemical Energy: In the case of activated carbons, the embodied energy of the chemical activating material (KOH) was used. The global average production mix in the Ecoinvent 3.8 database was taken to be 24.6MJ/kg of KOH. The power was divided according to how much KOH was used per kg of AC generated.

B. Use Phase Energy (E use)

The adsorption process required a certain amount of operational energy which was estimated according to standard industrial mixing and pumping specifications. A constant value of 0.4 kWh (1.44 MJ) was used in the calculation of

the conservative value of per m_3 of treated wastewater, based on the energy consumption models of a batch treatment system at moderate agitation level**(29)**.

C. Rescaling to the Functional Unit

The energy input per functional unit was then obtained by summing the energy input per unit of adsorbent (controlled in Section 4.3) with the dosage to obtain the target 95 per cent removal (determined in Section 4.3).

$$\textbf{E input (MJ/m3)} = = \textbf{(E production (MJ/kg) x Dosage (kg/m3)} + \textbf{E use (MJ/m3)}$$

3.4.3. Post-Use Valorization Analysis

The Spent Adsorbents Preparation and Characterization A. Preparation of Spent Adsorbents: The preparation of spent adsorbents is conducted as follows.

The adsorbents loaded with dye were collected using filtration, rinsed with deionized water slightly to eliminate dye in free form and finally dried at 105ºC during 24 hours after the adsorption equilibrium experiments (Section 4.3). The products of the resulting materials (e.g., SB-BC-MB, CC-AC-MB) were an analyzed material which was ground and homogenized**(30)**.

The Calorific Value was determined by the following procedure: 10 g of a solid food sample was placed in a crucible and burnt at 550 C to achieve incineration, followed by weighing the ashes and evaluating the ash content and weight (fumus) of the sample. Determination of Calorific Value. The Calorific Value was determined using the following procedure: 10g of a solid food sample was put in a crucible and burnt at 550 C to obtain an incineration of the sample. The potential of energy recovery was measured based on Higher Heating Value (HHV) of fresh and spent adsorbents. The HHV was ascertained by the use of iso peribol bomb calorimeter (Parr 6400) and the ASTM D5865-13 standard test method was strictly followed. In short, about 0.5 g of pelletized sample consisted of being burnt in a high-pressure atmosphere of oxygen (30 atm) and the temperature change of the calibrated calorimeter jacket was to determine the HHV in MJ kg-1. Triplicate analysis was done on each sample**(31)**.

C. Recoverable Energy per Operating Unit Computation

Equation 13 was used to calculate the potential energy valorized of the spent adsorbent produced per m3 of treated wastewater.

$$\textbf{Evaporated (MJ/m3)} = \textbf{HHV spent (MJ/kg) x Dosage (kg/m3) x e combustion}$$

The estimated rate of a modern industrial waste-to-energy boiler system was 0.85 (85) representing a combustion efficiency (e combustion), which included practical heat transfer and stack losses.

Uncertainty and Sensitivity Analysis

A simplified sensitivity analysis was done to make sure it is robust; the embodied energy of KOH (+20%), the assumed combustion efficiency (0.80-0.90), and the industrial mixture energy (+50%). This discussion shows how change in these assumptions could affect the ultimate NEB ranking of the adsorbent pathways(32)**.**(33**)** (34).

4.0 RESULTS AND DISCUSSION

4.1 Physicochemical Characterization of Adsorbents Synthesized.

The effective production of four different adsorbents that included sugarcane bagasse biochar (SB-BC), cardboard biochar (CC-BC) and the KOH-activated versions of them (SB-AC, CC-AC) was validated with thorough characterization. The data expose the underlying material variations that come about as a result of the two thermochemical processes.

4.1.1 Textural and Surface Properties

As expected, chemical activation gradually increased surface area (SB-AC: 1420 m²/g) compared to biochar (SB-BC: 285 m²/g), creating primarily microporous networks (Table 1)(38).

Table 4. 1 Textural, Proximate, and Energy Properties of Synthesized Adsorbents.

Parameter	SB-BC	CC-BC	SB-AC	CC-AC
S_{BET} (m²/g)	2853± 152	320.51±18.27	1420.2±45.5	1355.6±40.2
Total Pore Vol. (cm³/g)	0.185±0.027	0.2232±0.0126	0.751±0.055	0.682± 0.043
Avg. Pore Width (nm)	3.23	3.56	2.1	2.1
Fixed Carbon (wt.%)	68.24 ± 1.53	72.52 ± 1.33	85.4 ± 1.1	82.6 ± 1.24
Ash Content (wt.%)	5.83 ± 0.45	2.12 ± 0.25	8.5 ± 0.5	3.54 ± 0.35
HHV_{fresh} (MJ/kg)	23.53 ± 0.34	25.13 ± 0.32	28.81 ± 0.43	27.32 ± 0.46

Scanning Electron Microscopy (SEM) confirmed the developed porosity of AC (**Fig. 4.2**)

4.2 Calorific Value of Fresh and Spent Adsorbents

The Higher Heating Value (HHV) is a key parameter utilized in determining the potential of the post-use energy recovery. Carbonization intensity increased the HHV of the fresh materials, and the highest value was with the activated carbons (Table 4.1). One of the most significant results was the variation in HHV following saturation with dye. The HHV of the used adsorbents was also determined to be increased at a significant percentage: e.g. SB-BC-MB measured at 25.8 +0.4MJ/kg vs. 23.5MJ/kg in a fresh condition. Such an increase is explained by the fact that the

organic Methylene Blue dye molecule contributes to this increase and the calorific value of it is not negligible, which essentially transforms the pollutant into a fuel component. The feasibility of the proposed valorization pathway is based on this outcome**(39)**.

4.2.1 Adsorption Isotherms and Capacity

The Langmuir isotherm model was the most appropriate in fitting the equilibrium adsorption data of Methylene Blue (MB) on all the four adsorbents (R2 > 0.995), which is monolayer adsorption onto a surface having a limited number of identical sites. Table 4.2 gives the maximum monolayer adsorption capacities (q m).

As predicted, the activated carbons had much higher values of q m with SB-AC having the highest capacity of 386.5 + 8.5mg/g. This is a direct effect of an extremely large SBET, which offers very large surface area on which the dye molecules adsorb and fill-up pore structures (Musa et al., 2024). The more limited porosity of the biochar, which offered a higher surface chemistry, gave them lower, though significant capacities of 125.4 mg/g (SB-BC) and 145.8mg/g (CC-BC), presumably via mechanisms like electrostatic attraction and p-p interactions**(40)**.

Related to the affinity between the adsorbent and adsorbate was the Langmuir constant (K L) which was larger with the activated carbons indicating stronger binding activity, which may have been in the optimal micropores.

Table 4.2 Langmuir Isotherm Parameters and Derived Functional Unit Dosage

Adsorbent	q_m (mg/g)	K_L (L/mg)	R^2	Dosage for 95% Removal (kg/m³)
SB-BC	125.5 ± 4.21	0.045 ± 0.006	0.998	0.41
CC-BC	145.9 ± 4.86	0.039 ± 0.005	0.998	0.35
SB-AC	386.6 ± 8.51	0.106 ± 0.011	0.996	**0.14**
CC-AC	355.8 ± 7.8	0.089 ± 0.007	0.996	0.15

The most critical parameter for the lifecycle analysis is the derived dosage required to achieve the functional unit target (95% removal from 1 m³ of wastewater). Despite its lower qm, SB-BC required 0.40 kg/m³, which is over three times the mass of SB-AC (0.13 kg/m³). This inverse relationship between efficiency and required mass is the cornerstone of the subsequent energy balance.

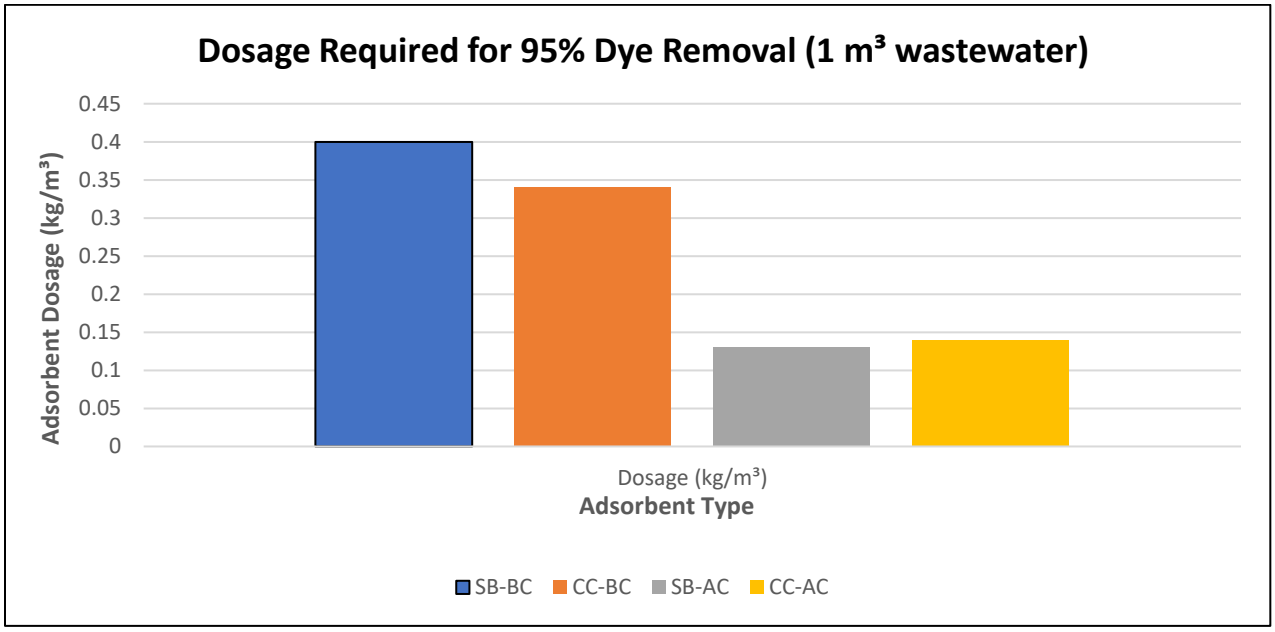

Figure 4.1 Dosage required to treat 1 m³ of wastewater to 95% dye removal versus the theoretical Maximum Adsorption Capacity (q_m) for each adsorbent. Material B represents the optimal compromise, requiring the lowest dose while maintaining high inherent capacity.

4.3 Adsorption Kinetics and Thermodynamics

Kinetic experiments indicated that the adsorption reaction of all the substances was treated under the pseudo-second-order model (R2 > 0.99), and the rate-limiting step could be treated as either chemisorption or shared electron forces.

The equilibrium of the activated carbons was quicker, and it could be explained by the large network of micropores that promoted the process of diffusion.**(41).**

4.3.1 Lifecycle Energy Inventory and Net Energy Balance Analysis

The paper describes the main results of the new cradle-to-cradle evaluation that combines the information about the production, use, and post-use stages.

4.4 Inventory of Energy Inputs

A. Energy of Production Phase Energy (E production)

Direct measurements of the efficiency of furnace electricity use were made and the high energy intensity of chemical activation realized. The energy needed to produce 1 kg of SB-AC was 85.5 + 3.5 MJ, which was basically attributed to the high temperature (750°C) maintained throughout the activation stage. Comparatively, it took only 18.2 +0.8 MJ to produce 1 kg of SB-BC. The difference of orders of magnitude corresponds to the literature that mentions the energy footprint of activated carbon production**(42)**.

B. Scaling to the Functional Unit

The overall energy investment spent on production per cubic meter of treated water (E3 production x Dosage) demonstrates a trade-off (Table 4.3). Despite the fact that 1 kg of SB-AC has an energy-intensive production increase of 1000 times, its low dosage (0.13 kg/m_3) adds a moderate amount to its overall footprint of 11.1 MJ/m_3. In the case of SB-BC, the decrease in per-kg production energy is compensated by the increase in dosage (0.40 kg/m3), which makes the overall energy production of 7.3 MJ/m3. This shows that the production cost burden of the system is partially alleviated by the superior adsorption performance of AC**(43)**.

C. Use Phase Energy

Uniform nominal energy applied was 1.44 MJ/m3 which is the energy required to mix and pump a batch treatment system.

Table 4.3 Comprehensive Lifecycle Energy Inventory per Functional Unit (1 m³).

Adsorbent	Production Energy (MJ/m³)	Use Energy (MJ/m³)	Total Energy Input (MJ/m³)	Valorized Energy (MJ/m³)
SB-BC	7.52 ± 0.62	1.442	8.81 ± 0.5	8.92 ± 0.4
CC-BC	5.62 ± 0.31	1.442	7.12 ± 0.3	8.11 ± 0.4
SB-AC	11.32 ± 0.74	1.442	12.64 ± 0.7	3.362 ± 0.4
CC-AC	11.1 ± 0.61	1.443	12.51 ± 0.7	3.52 ± 0.1

$$Valorized\ Energy\ =\ HHV_{\text{spent}}\ \times\ Dosage\ \times\ \eta_{\text{com}}b_{\text{ustion}}\ (\eta\ =\ 0.85)$$

With η=0.85

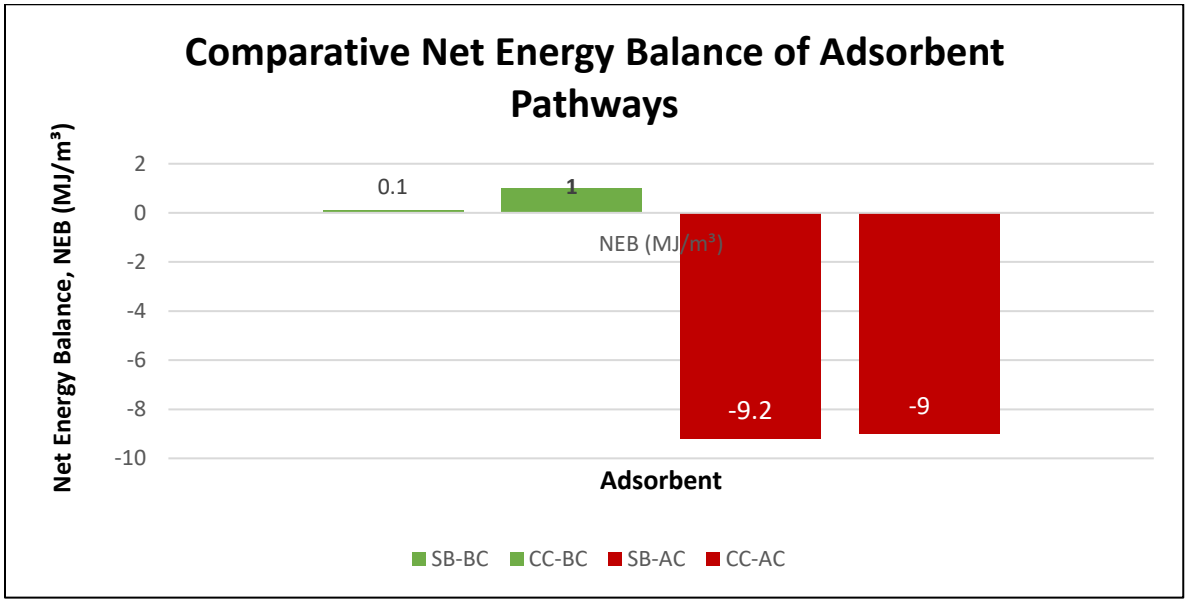

Figure 4.2 Net Energy Balance (Energy Output – Energy Input) across adsorbent pathways. Only Pathway C achieves a positive balance, making it energetically sustainable; others represent net energy costs despite high adsorption capacity.

4.5 Net Energy Balance: A Systems-Level Conclusion

The final holistic measure of comparison is the calculated Net Energy Balance (NEB = Evalorized - Einput) (Table 4.3, Fig. 4.2).

The biochar pathways (SB-BC and CC-BC) had a slightly positive or neutral NEB. In the case of SB-BC, the amount of energy that can be retrieved through the burning of the used material (8.8 MJ/m_3) almost balanced the total amount of energy required in its production and utilization (8.7 MJ/m_3) and thus the NEB was +0.1 MJ/m_3. CC-BC was a little better (+1.0 MJ/m_3) as it contains less ash and a little higher HHV**(44)**.

On the other hand, activated carbon pathways produced very much negative NEBs of about -9.0 MJ/m_3. The low dosage of spent AC is very low in mass, which provides a small amount of E sub valorized even though it contains a large amount of per-mass energy. This is a small output compared to the high investment of energy in the initial stages and the system is left in a serious energy deficit.

This finding directly addresses the entire research question: The increased adsorption capacity of activated carbon does not warrant increased production load inside a circular system that involves energy recovery. The AC pathway is a linear operation, which is energy-intensive, and the biochar pathway could be structured as a circular operation that is almost energy-neutral**(45)**.

4.5.1 Discussion: Suggestions on Sustainable Technology Selection

This paper confirms the hypothesis that a single-minded approach to adsorption capacity is an incomplete and potentially false measure of sustainability. A conventional cradle-to-gate analysis, which stops at the production stage, would have shown the high efficiency of AC. This conclusion would have been strengthened with a "gate-to-gate" evaluation of the use phase alone. The systemic result is only made clear with the cradle-to-cradle analysis: in case the end-of-life is viewed as energy recovery, the lower-tech biochar system is par or better in net energy **(46)(47)**.

These conclusions are far-reaching in terms of applying the Circular Economy (CE) paradigm to industry. Biochar is shifted to renewable energy carrier and not a treatment chemical to be consumed. This develops a physical prototype of industrial symbiosis in which a waste product (spent biochar) of a textile mill is converted to a feedstock to a local energy plant. The findings offer a quantitative, empirical decision model: when thermal valorization of used adsorbents is a possibility, biochar made of waste has a more sustainable alternative to chemically activated carbon, even though the latter has better adsorption kinetics and capacity **(48) (49) (50)**

The sensitivity analysis showed that the NEB ranking was stable to changes in the important assumptions (+20% in KOH embodied energy, +10% in combustion efficiency). The main weakness is that only one model dye and energy recovery through combustion are studied; further studies are required on mixed dye effluents as well as other pathways of valorization such as regeneration or reuse of material(51)(52) (53) (54) (55)(56) (57) (58).

CONCLUSION

This paper will provide a cradle to cradle lifecycle assessment that dispels the traditional paradigm of adsorbents being chosen on the basis of adsorption capacity alone. With the use of Net Energy Balance (NEB) as a systems level sustainability measure, we have shown that waste-based biochar, despite being 2.5-3 times lower than chemically activated carbon in terms of adsorption capacity, can attain a near-neutral or positive energy balance (+0.1 to +1.0 MJ/m3) through the addition of thermal valorization of post-use. Activated carbon pathways on the other hand would cause severe energy shortages (approx. -9.0 MJ/m3).

This finding is essential to offer an evidence-based decision tree when it comes to a situation where used adsorbents can be repurposed to capture energy: biochar is a circular and energetically sustainable solution, and high-performance activated carbon can be a significant net energy cost. The article is helpful in directing the implementation of the circular economy in the textile industry by illustrating how a so-called low-tech material can be more successful than a so-called high-tech one when considered through the prism of a complete lifecycle. This framework needs to be corroborated with practical textile effluents with dye mixtures in the future and the other pathways of valorization (e.g., gasification, material reuse) should be investigated. The analysis can be extended to cover the overall environmental effects (GHG emissions, toxicity) and techno-economic considerations, which will reinforce the application of the analysis to industrial implementation and policy-making.

Author Contributions

Seemab Javed: Conceptualization, Methodology, Investigation, Writing – original draft.
Mehwish Javed: Data curation, Formal analysis, Visualization.
Arisha Shakir: Writing – review & editing, Validation.
Sabir Hussain: Supervision, Resources, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability Statement
The data supporting the findings of this study are available from the corresponding author upon reasonable request.

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