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Optimized pyrolysis of chicken manure waste in a fixed bed reactor: sustainable production and environmental applications of raw and activated biochar

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Abstract

Managing chicken farming waste is quite difficult due to its potential environmental impacts. To address these issues and promote sustainable poultry farming, effective waste management strategies are essential. In this regard, converting waste into biochar (BC) provides an eco-friendly solution for environmental remediation processes. In this study, chicken manure waste derived biochar was produced within a fixed bed reactor, employing the optimal pyrolysis conditions (440 °C, 7 °C/min, and 115 min) determined through Response Surface Methodology based on Central Composite Design. Subsequently, this solid product underwent activation using two distinct chemical agents (HCl and KOH). Characterized biochar products were investigated for a range of applications, including energy conversion, gas emission control, CO_2 capture, and the removal of dyestuff from aqueous solutions-each of which is vital for protecting water resources, reducing pollution, mitigating climate change, and ensuring compliance with environmental regulations. The CO_2 adsorption capacities of Raw-BC, KOH-BC and HCl-BC products were measured as 27.52, 66.62 and 51.26 mg/g at 25 °C, respectively. The highest CO_2 adsorption capacity of 1.51 mmol/g was achieved with KOH-BC. The Raw-BC had the highest methylene blue removal rate (80%) at 45 °C, pH 4–5, for up to 300 min. When the fuel properties of the raw biochar were compared with different types of coal, it was concluded that this product could be used instead of lignite coal in energy production. As a result, this multifaceted approach showcased the versatility and potential benefits of biochar in diverse environmental and industrial applications.

Keywords Chicken manure wastes · Pyrolysis · Activated biochar · CO_2 capture · Methylene blue

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1 Introduction

Thermal decomposition of biomass with the effect of temperature in an inert atmosphere is the most common method used for biochar production. Biochar that mainly composed of solid carbon, has become focus of interest in recent years with its large surface area, high porosity, high chemical and structural stability and various surface functional groups. This product, which is obtained as a result of the use of waste biomass as a sustainable resource, is an economically suitable and environmentally friendly material (Sakhiya et al., 2020). Thanks to biochar, which has a wide range of application areas, it is possible to improve the properties of low-quality fuels such as plant-based biomass. In addition, biochar applications have an important place in many different areas such as improving soil fertility in agricultural areas and providing some prerequisites for increased activity of soil microorganisms, water purification, energy storage, obtaining catalysts/photocatalysts with high catalytic efficiency, capture of environmentally harmful gases, and production of electrode materials for lithium-ion batteries and super capacitors (Li et al., 2020; Marousek et al., 2018; Panahi et al., 2020; Zhang et al., 2019; Zhao et al., 2020).

The biomass used in biochar production can vary widely, depending on local availability, desired characteristics of the biochar, and the specific goals of its application. Biomass sources for biochar production include wood and forestry residues like sawdust, wood chips, tree branches, and bark, which have high carbon content (Saletnik et al., 2022); lignocellulosic agricultural residues such as rice husks, corn stalks, wheat straw, coconut shells, and peanut shells, which are by-products of farming (Haris et al., 2024); animal manure, including poultry litter, cattle manure, and pig manure (Rathnayake et al., 2023); green waste such as grass clippings and leaves, along with food waste and other organic matter from municipal waste streams; industrial by-products like bagasse (sugarcane residue), olive pits, and paper mill sludge (Abdullah Al Masud et al., 2023); and dedicated energy crops such as fast-growing plants like switchgrass, miscanthus, and bamboo (Kaletnik et al., 2021). However, some contemporary academic perspectives also emphasize the potential of mosses and algae as promising feedstocks for biochar production (Marousek et al., 2024). Especially, locally available biomass is often preferred to reduce transportation costs and carbon footprint. These different biomass types yield biochar with varying properties, such as porosity, nutrient content, and pH, which influence its suitability for specific applications like soil amendment, carbon sequestration, or water filtration. Biochar's effectiveness and characteristics largely depend on the type of biomass used, as well as the conditions under which it is produced.

Especially biomass obtained from animal manure wastes is one of the most reasonable options that can be used for cost effective biochar production. Because such biomass has no economic value and is not in competition with food crops. The use of animal wastes for biochar production not only protects the environment, but also helps to solve the waste problem (Kambo & Dutta, 2015; Panahi et al., 2020). Chicken manure waste, which falls under the category of animal waste, is an ideal candidate to be used in biochar production due to its high biomass production efficiency, storage, high carbon content and continuous growth potential. Evaluation of existing chicken manure waste will enable it to be used as a renewable source on the one hand, and to dispose of large amounts of hazardous wastes safely and economically on the other hand (Mau & Gross, 2018). For this reason, chicken manure, an abundant waste material, was chosen for this study over other biomass samples. Additionally, chicken manure is a natural and renewable biomass material with several advantages, making it a viable and attractive option for wastewater treatment and pollutant removal applications:

1. Availability: Chicken manure is abundantly available as it is a byproduct of the poultry industry. It is a low-cost material that is readily available in large quantities, making it an attractive option for use as an biomass.
2. High Adsorption Capacity: Chicken manure has been found to have a high adsorption capacity for various pollutants, including heavy metals, dyes, and organic compounds. This is due to the presence of functional groups in chicken manure that enable it to adsorb pollutants effectively.
3. Sustainable: The use of chicken manure as an biomass is sustainable as it helps to reduce waste and provides a value-added use for a byproduct of the poultry industry.
4. Low Energy Input: The production of chicken manure as an adsorbent requires low energy input and minimal processing compared to other adsorbents like graphene, which require expensive and energy-intensive production processes.
5. Environmentally Friendly: Chicken manure is a natural material that does not contain any harmful chemicals or additives, making it an environmentally friendly option for the removal of pollutants from wastewater (Dróżdż et al., 2023; Sikder & Joardar, 2019).

The pyrolysis process involves the thermal decomposition of organic biomass materials in the absence of oxygen, leading to the generation of various products like solid char, liquid bio-oil, and combustible gases. The conditions under which the reaction takes place are very important in the pyrolysis process. Biochar product yield through pyrolysis is affected by process parameters such as temperature, pressure, reaction time, particle size and many more. These operating parameters not only control the yield but also affect the quality of the pyrolysis products. The purpose of pyrolysis is to maximize product yield. Therefore, it is important to investigate the effect of processing conditions on biochar production (Tan et al., 2017). Especially the specific heating rate, temperature, and time interval for a successful pyrolysis process depend on several factors, including the type of feedstock, desired product yields, and equipment capabilities. The heating rate can significantly influence the product distribution and properties. Especially in biochar production, the lower heating rate prevents thermal degradation of biomass samples, resulting in greater biochar yield. The effect of heating rate on biochar yield is more pronounced and more effective, at low temperatures. The temperature at which pyrolysis occurs is an other critical parameter. It directly affects the composition of the products and the quality of the end products. The temperature range for pyrolysis can vary widely based on the feedstock and the desired products. Generally, pyrolysis temperatures can range from around 300 °C to 800 °C. Low-temperature pyrolysis (300 °C-450 °C) typically produces more liquid bio-oil and char. Therefore in biochar production, generally low pyrolysis temperature is suitable for high biochar yield. Although there are many literature studies on the effect of pyrolysis temperature on biochar yield, it is not easy to find the appropriate temperature for biochar production (Jerzak et al., 2023). Because the optimized temperature for high biochar production varies depending on the composition and type of biomass. On the other hand, the residence time that the feedstock spends at the elevated pyrolysis temperature is related to the heating rate and the temperature. Longer residence times can lead to more extensive decomposition and cracking of the feedstock, resulting in increased gas and char formation. However, too long a residence time might lead to product degradation or increased energy consumption. Long steam residence time at low temperature is required to produce high yield biochar. Because increasing the steam residence time helps polymerization by providing enough time for the biomass components to react again. If the residence time is reduced, the yield of biochar product also decreases. As a result, the extension of the residence time increases the biochar yield. The residence time not only affects the biochar yield, but also affects the properties and pore size distribution of the biochar product formed by forming micro and macro pores (Tripathi et al., 2016). As a result, the specific combination of these parameters depends on the specific goals of the pyrolysis process. Different feedstocks (animal manure wastes, wood, agricultural residues, plastic waste, etc.) have different chemical compositions, and their optimal conditions will vary. Additionally, the design of the pyrolysis reactor and the intended use of the resulting products will also influence the choice of parameters. It's worth noting that extensive research and experimentation are often required to determine the optimal conditions for a given pyrolysis setup and desired product outcomes. Pilot-scale studies and laboratory experiments are crucial for finding the right balance between temperature, heating rate, and time interval to achieve the desired product yields and qualities.

Experimental design methods have been widely used many applications areas in recent years. Especially in systems with multivariate and more than one dependent variable, various problems can be experienced. In this case, experimental models and statistical analysis methods play an important role. With the experimental design method, great advantages can be achieved in terms of optimizing the ambient conditions, increasing the efficiency and reducing the cost. With the effective use of these methods, it is easier to control transactions. At the beginning of these methods is the Response Surface Methodology (Türk, 2016).

Response surface methodology (RSM) is a statistical technique used to model and optimize the relationship between a response variable and one or more predictor variables. It is widely used in engineering, chemistry, and other fields to optimize processes, products, and designs. Some advantages of RSM in optimization studies include:

1. Reduced Experimentation: RSM allows for the use of fewer experiments compared to traditional optimization methods. By using statistical models, RSM can predict the response of a process or system to different conditions, reducing the number of experiments needed to find the optimal conditions.
2. Improved Efficiency: RSM helps to improve the efficiency of the optimization process by reducing the amount of time and resources required to perform experiments. This results in faster and more cost-effective optimization studies.
3. Increased Accuracy: RSM models are designed to capture the nonlinear relationships between predictor variables and response variables, resulting in more accurate predictions of the response. This helps to identify the optimal conditions more accurately and reliably.
4. Robustness: RSM models can be designed to be robust to changes in input variables, which means that they can still perform well even if the experimental conditions change. This is particularly important when studying complex systems or processes where variables may change over time.
5. Visualization: RSM allows for the visualization of the relationship between variables and the response. This helps researchers to identify trends and patterns in the data, which can be used to refine the optimization process further.

Generally, the advantages of RSM in optimization studies include reduced experimentation, improved efficiency, increased accuracy, robustness to changes, and visualization of the relationship between variables and response. These advantages make RSM a powerful tool for optimizing processes, products, and designs across a wide range of industries (Charusiri & Numcharoenpinij, 2017; Saikia et al., 2018). RSM stands out as a method frequently used in both industrial applications and scientific studies. This method evaluates mathematical and statistical data together and has been frequently used recently to determine the optimum experimental conditions (Ahmadi et al., 2017; Kermani et al., 2019). The most commonly used design type for specifying RMS functions is Central Composite Design (CCD).

Diverse biomass feedstocks and variations in pyrolysis conditions contribute to modifications in the structure and physicochemical properties of biochar. It is crucial to evaluate the influence of operational parameters, including pyrolysis conditions, on biochar's adsorption capacity, as it plays a vital role in designing and managing biochar properties. In this study, it was aimed to convert chicken manure wastes, which were used as raw materials, into solid product by using pyrolysis method in fixed bed reactor. Central Composite Design (CCD) based Response Surface Methodology (RSM) was used for the optimization of pyrolysis conditions in the fixed bed reactor system. The effect of process parameters such as pyrolysis temperature, heating rate and pyrolysis time on the product obtained by reducing the number of available experiments was investigated.

The activation process is essential for enhancing the surface area and porosity of biochar produced under optimal pyrolysis conditions, improving its adsorption capacity and increasing its carbon retention ability. Activation also stabilizes biochar, optimizing its physical and chemical properties for more effective use in environmental, agricultural, and industrial applications. In this process, biomass can be converted into a suitable material for different applications by carbonizing at lower temperatures than in the production of activated carbon, without destroying the surface functional groups, and even by activating functional groups with various physical and chemical activation methods. In literature, various modification methods have been tested and implemented with varying degrees of success (Dissanayake et al., 2020). In order for biochar to be used as an effective adsorbent in the industrial field, these activation processes must be done. In general, these processes are known to increase surface area and porosity. Because the temperature, activation time and activation agent applied both in physical activation and chemical activation process cause changes in the porous structure of biochar, which positively affects the surface area. Although the chemical activation method is performed at higher temperatures than physical activation and is more expensive, it has been widely used in recent years because it allows the production of porous biochar products with higher surface area value (Wang & Wang, 2019). With many alkaline and acidic activation agents used for activation, unwanted metals can be removed from the structure and various functional groups can be attached to the biochar surface. As a result, the functional groups in the biochar structure are increased by activation. Activated biochar products have more adsorption ability due to the presence of enriched oxygen-containing functional groups (C = O, C-O) (Akgül, 2017). There are many chemical activating agents used for activation. These include KOH, NaOH, NH_3, K_2CO_3 and $ZnCl_2$, which are alkaline, and HCl, HNO_3, H_3PO_4 and H_2SO_4, which are acidic stand out. Among them, KOH is particularly effective in creating micropores and increasing the specific surface area (Wang & Wang, 2019). Its alkaline nature enables it to react with biochar, leading to both physical and chemical changes in the material. Because of the reaction between KOH and biochar at high temperatures induces structural changes in the biochar's carbon matrix, leading to the formation of larger pores and an increase in surface area (Lei et al., 2015). On the other hand, when an acidic activation agent such as HCl is used, HCl reacts with biochar's surface functional groups and minerals, causing the removal of surface impurities and the creation of pores and vacancies. This process involves the removal of inorganic components, such as metals and minerals, from the biochar's surface, resulting in the formation of more micropores and mesopores. This significantly increases the surface area and enhances the adsorption capacity. Additionally, HCl treatment introduces acidic functional groups to the biochar's surface, which improves its ability to adsorb certain contaminants or molecules, especially those that are positively charged or polar (Dune et al., 2022).

The use of activated or modified biochar is increasingly recognized for its effectiveness in removing pollutants from water resources and capturing CO_2. As the global population grows and industrialization and urbanization expand, environmental pollution has become a significant issue, driven by factors such as industrial activities, agricultural chemicals, and regional conflicts. This pollution affects air, soil, and water, disrupting ecosystems and posing risks to human health through the food chain. Water pollution, caused by a variety of contaminants including organic and inorganic substances, heavy metals, and pesticides, is particularly concerning. Air pollution, with CO_2 as a major greenhouse gas contributing to global warming, also poses serious health risks (Eslamipoor & Sepehriyar, 2024). Emissions of carbon dioxide are currently 50% higher than they were in 1991, the base year of the Kyoto Protocol, and continue to rise rapidly. To maintain a 50% chance of limiting global temperature increase to 2 °C, the protocol stipulates that by 2050, carbon dioxide levels must be reduced to less than half of the 1990 levels (Eslamipoor, 2024). Thus, the growing application of biochar in environmental remediation is crucial in addressing these challenges (Cha et al., 2016; Mardoyan & Braun, 2014). Active biochar, an environmentally friendly and cost-effective material produced from waste biomass through pyrolysis, is a widely used adsorbent known for its high selectivity for pollutants. Its unique surface properties, porous structure, high surface area, and functional groups that enable hydrogen bonding contribute to its effectiveness. These superior characteristics not only enhance the efficiency of pollution control efforts but also help reduce their cost and environmental impact (Dissanayake et al., 2020; Waqas et al., 2018). In the literature, although there are many studies on the effectiveness of biochar products in the removal of environmental pollutants from water resources, it is seen that there are not many studies on its usability as an adsorbent in CO_2 capture and existing studies have gained acceleration in recent years (Choi et al., 2019; Liu & Huang, 2018; Mau & Gross, 2018). In addition, there are also studies in the literature that analyse the use of biochar as a solid biofuel from a technological and economic point of view (Marousek et al., 2015).

In this study, biochar samples were produced from chicken manure waste under optimal pyrolysis conditions and then activated using HCl and KOH. The raw and activated biochar products were characterized using techniques such as FT-IR, SEM, and BET analysis. Following characterization, the biochar was tested for various applications, including energy conversion, gas emission reduction, CO_2 adsorption capacity, and dye removal efficiency. Commonly used pyrolysis reactors in industrial applications include fixed bed and fluidized bed reactors, each yielding different product qualities and surface properties. Unlike our previous study (Yıldız et al., 2019), which focused on a different reactor type, this study aimed to assess the impact of reactor type on product quality and effectiveness. Experiments were conducted using a fixed bed reactor system with the same biomass and operating conditions, and the resulting products were characterized. By comparing these findings with those of our earlier study, it will be possible to determine which reactor type is more effective for the desired applications.

2 Materials and methods

2.1 Materials

Chicken manure (CM), collected from a poultry farm and with a pH of 6.5 to 8.0, contained high levels of protein (27%) and carbohydrates (31%) and was first subjected to a drying process due to its high moisture content (40%). The samples were dried at 80 °C for 24 h. Dried CM was reduced in size by passing it through a grinder with stainless steel blades (Waring, USA). In order to obtain samples with small grain size to be used in the study, the milled material was sieved. Samples with dimensions less than 250 µm were used in the experiments. In chemical activation processes, HCl (37% purity) and KOH produced by Sigma-Aldrich were used. Characterization of CM was performed according to the methods described in our previous study (Yıldız et al., 2019).

2.2 Design of experiments for optimization

Experimental design is crucial to reduce time and costs (Ghorbani et al., 2020). Therefore, in this study, an experimental design was used to reduce the number of experiments and to examine the effect of process parameters on the product obtained. Response Surface Methodology (RSM) based on Central Composite Design (CCD) was applied using the Design-Expert software program (Version 7.0) for optimization process. In the CCD method, there are two factorial points which are the + (highest) and –(lowest) of a factor consists of levels. One of them is the axial point (α). The values of + α and -α are determine by the program, and these are beyond the two level points specified by the experimenter. The other factorial point is the center point. Center points are points that are repeated to estimate the experimental error. They are the midpoints of the two level/factorial points of the parameters. As a result, there are five levels of each parameter in CCD. These are factorial points denoted by + 1 and −1, axial points denoted by + α and –α, and center point denoted as 0 (Türk, 2016). Experimental results from the CCD model are evaluated using Eq. (1).

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_1 X_i + \sum_{i=1}^{n} \beta_{ii} X_i^2 + \sum_{i=1}^{n} \sum_{j>1}^{n} \beta_{ij} X_i X_j \tag{1}$$

This quadratic model considers the linear effects, quadratic effects and interactions between n variables. In this model, Y is the predicted response, β_0 is constant coefficient, β_i is linear coefficient, β_{ij} describes the interaction effect between i and j variables, and k is the factor number. With the help of this created equation, estimated results for the answers are obtained and the accuracy of the predictions and the adequacy of the model are checked.

In this study, three different operating parameters (reaction temperature, heating rate and reaction/pyrolysis time) were selected for the experiments and were defined as X_1, X_2 and X_3, respectively. The experimental response was defined as Y and this dependent variable was the BET surface area of the biochar products. X_1, X_2, X_3……X_n; independent variable, β_0; fixed value, β_1,β_2,β_3…… βn were expressed as regression coefficients. Each selected variable was encoded in the range of -α and + α. (Achour et al., 2021). The variables and experimental range in this design are presented in Table 1. The Design-Expert software program proposed a series of experiments (20 experiments) based on the combination of the three process parameters. The results are presented in Table 2.

Table 1 Independent variables and experimental range

	Level and Ranges				
Independent variables	-α	−1	0	1	+ α
Pyrolysis temperature (°C)	200	260	350	440	500
Heating rate (°C/min)	5	8	12.5	17	20
Pyrolysis time (min)	30	48	75	102	120

Table 2 RSM matrix and the experimental data

Run	X_1: Pyrolysis temperature (°C)	X_2: Heating rate (°C/min)	X_3: Pyrolysis time (min)	Response (surface area) (m^2/g)
1	350	12.5	75	5.58
2	260	8	48	4.04
3	500	12.5	75	5.31
4	440	8	48	5.33
5	350	12.5	120	5.95
6	200	12.5	75	1.73
7	440	17	102	5.80
8	350	12.5	30	6.19
9	440	8	102	6.88
10	260	17	48	4.69
11	350	5	75	5.63
12	260	8	102	4.87
13	350	12.5	75	4.72
14	440	17	48	6.22
15	260	17	102	4.01
16	350	12.5	75	4.92
17	350	12.5	75	5.88
18	350	20	75	5.01
19	350	12.5	75	6.51
20	350	12.5	75	5.46

2.3 Pyrolysis in fixed bed reactor

The pyrolysis experiments of the raw material were conducted in a fixed-bed reactor system, as shown in Fig. 1. 20 experiments under different conditions determined using the Design Expert program were carried out in this system. CM wastes were placed in an electrically heated fixed bed reactor with a volume of 600 cm^3. Pyrolysis experiments were carried out in an inert nitrogen atmosphere at different temperatures, heating rates and times. The sample amount was weighed as 5 g. The nitrogen gas flow rate was determined as 100 mL/min and was controlled with a flow meter. The reactor temperature was controlled by the thermocouple placed inside the reactor from the top of the furnace. The condensable liquid product was captured in the system with dichloromethane solvent. The biochar sample with highest surface area that produced under optimum conditions in fixed bed reactor was coded as"Raw-BC".

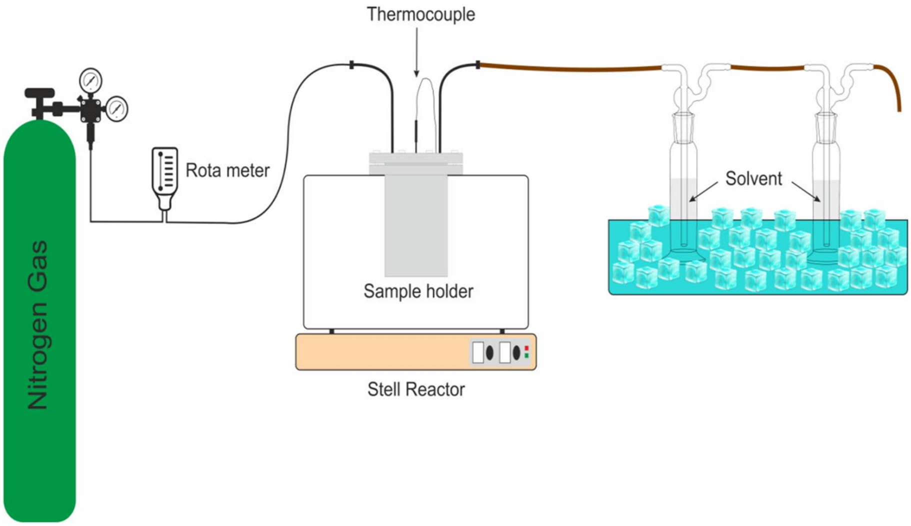

Fig. 1 Schematic representation of fixed bed reactor system

2.4 Activation of raw biochar products

Activation of raw biochar obtained by pyrolysis of chicken manure wastes under optimum conditions was carried out by using KOH and HCl as activation agent in order to method presented in our previous study (Yıldız et al., 2019). The carbonized solid product (raw biochar) produced at the end of the pyrolysis process was separately impregnated with 1 M KOH and 1 M HCl solutions. The impregnation ratio was set at 1:4, based on the weight of the carbonized sample to the weight of the impregnation reagent. The mixture was stirred at room temperature for 24 h. The impregnated biochar samples were then activated at a heating rate of 3 °C/min, with a nitrogen flow rate of 100 mL/min, and a maximum temperature of 700 °C for 1 h. The KOH activated biochar sample was coded as "KOH-BC" and the HCl activated biochar sample was coded as "HCl-BC".

2.5 Characterization of raw and activated biochar products

The characterization of the raw and activated biochar products obtained under optimum pyrolysis conditions in the fixed bed reactor was made using analysis methods such as Fourier Transform Infrared Spectroscopy (FT-IR), Brunauer, Emmet and Teller (BET) and Scanning Electron Microscopy (SEM).

In BET analysis, Micromeritics, Tristar II analyzer was used to determine the surface area and pore volume of the samples. The BET surface area was obtained using nitrogen adsorption isotherms at 77 K. Before gas adsorption measurement, the samples were dried and degassed to remove any moisture or contaminants that could interfere with the adsorption process. Degassed process has been performed under vacuum at 200 °C for 12 h. Adsorption data were obtained at a relative pressure. BET surface area was calculated from N_2 adsorption isotherms using the BET equation. The BET equation is a mathematical model that relates the amount of gas adsorbed to the pressure applied. It is derived from the assumption that gas molecules form a multilayer on the surface and follow a specific adsorption isotherm. The BET equation was used to calculate the surface area by fitting the experimental adsorption isotherm to the equation. The specific surface area was reported square meters per gram (m^2/g) of the sample.

Fourier Transform Infrared Spectrometer (Perkin Elmer, Spectrum Two, USA) device was used to determine the functional groups of samples in their raw and activated form. The FT-IR spectra of the samples were recorded by using ATR in the wavenumber range of 650 cm^{-1} and 4000 cm^{-1}. The samples were prepared as a thin film, a solid pellet, by mixing with a spectroscopically inactive material (KBr). The samples were placed in the sample path of the interferometer, and the instrument generated an IR spectrum by measuring the intensity of transmitted or absorbed light as a function of the wavenumber (reciprocal of wavelength). The resulting spectrum was a plot of absorption intensity (y-axis) against wavenumber (x-axis). Peaks in the IR spectrum corresponded to specific molecular vibrations, such as stretching, bending, and rocking of chemical bonds in the samples. These peaks analyzed to identify functional groups and chemical bonds present in the sample.

In order to determine the three-dimensional surface properties of the biochar products obtained as a result of pyrolysis, Jeol brand (JSM-7001 F) analyzer was used and SEM analysis was performed. Samples were prepared properly to ensure accurate and reliable results. This involved fixing, dehydrating, and coating the sample with a thin layer of conductive material (gold) to prevent charging effects when exposed to the electron beam. Brighter areas in SEM images typically represented regions with higher electron emission or backscattering, provided some information about surface features and material properties.

2.6 Energy conversion applications

The fuel properties (calorific value) of the raw biochar sample produced in fixed bed reactor under optimum conditions was compared with different types of coal (lignite, coke, etc.). CAL e2k brand oxygen bomb calorimeter was used to determine the calorific value of raw biochar product. 0.5 g of sample was placed in the bomb container. Afterwards, oxygen was pumped up to 30 bar pressure and the measurement was made.

2.7 Greenhouse gas emission applications (CO_2 adsorption)

Carbon dioxide (CO_2) is the primary greenhouse gas emitted through human activities. In this study, the CO_2 adsorption capacities of raw and activated biochar products were investigated using thermogravimetric analysis method (Creamer et al., 2016). CO_2 adsorption experiments were carried out according to the method we presented in our previous study (Yıldız et al., 2019). The CO_2 adsorption capacity of raw and activated biochar products was assessed using the thermogravimetric analysis (TGA) technique. Employing a Shimadzu DTG-60 model, a simultaneous TG/DTA analyzer, about 20 mg of the sample was loaded onto the sample holder. To eliminate potential volatile constituents, the sample underwent purification through heating with nitrogen gas at 120 °C for an hour, maintaining a flow rate of 50 mL/min. Following this, the atmosphere was switched to CO_2 at the same flow rate, and the temperature was gradually reduced to 25 °C and held constant for 3 h. The extent of CO_2 uptake was quantified as a percentage based on the weight fluctuations observed in the TG curve. To mitigate the effects of buoyancy, the device was run in an empty configuration under identical test conditions.

2.8 Applications of removal of environmental pollutants from aqueous medium (Dye adsorption)

The usability of raw and activated biochar products obtained under optimum conditions in the fixed bed reactor as adsorbent in dye removal process was investigated. Methylene blue, which is one of the dyestuffs frequently used in many different fields, was chosen as the adsorbate in the adsorption experiments. Especially, methylene blue (MB) is a well-known cationic dye for wood, paper, leather, and silk industry. MB of analytical grade was purchased from Merck and used without further purification. The stock dye solution to be used in the experiments was prepared at a concentration of 25 mg/L. In the adsorption process, 100 mL of this stock solution, which was prepared at the beginning, was taken and placed in separate flasks, and 0.2 g of raw and activated biochar products were added to each flask. In the adsorption studies, the adsorption efficiency (% dye removal) and adsorption capacity (mg/g) values were calculated using the optimum adsorption conditions previously determined in the removal study of the same adsorbate (MB) with a different biomass derived biochar (temperature: 45 °C, contact time: 300 min, pH: 4–5) (Kaya et al., 2018). The pH of the solutions was adjusted using 1.0 M HCl solution and the mixtures were stirred at 250 rpm. After mixing for the specified time, filtration was carried out. To determine the remaining dye concentration in the solution, the filtrates were taken and the absorbance values at the maximum wavelength were measured. The measurements were carried out with a UV–Visible Spectrophotometer (DR2400, Hach Company, USA). Using the equilibrium concentration calculated with the help of the calibration graph, the amount of dye adsorbed per unit mass of the adsorbent (q_e) was calculated according to Eq. 2, while the adsorption efficiency (%) was calculated using Eq. 3.

$$q_e = (C_0 - C) \times \frac{V}{m} \tag{2}$$

$$Dye\ removal\ (\%) = \frac{(C_0 - C)}{C_0} \times 100 \tag{3}$$

q_e; amount of dye adsorbed per gram adsorbent (mg/g), C_o and C; initial and equilibrium dye concentration in solution phase (mg/L), V; volume of dye solution (L) and m is the weight of the adsorbent (g). To ensure the reproducibility of the results, all adsorption experiments were conducted in triplicate using prepared control solutions under identical experimental conditions. The average values were used for data analysis, with relative standard deviations (RSD) found to be within ± 1.5%. RSD is a statistical measure commonly used to evaluate the consistency and reliability of measurements and processes. It allows for the comparison of variability between datasets with different units or scales, providing an indication of the relative precision of the measurements. Therefore, RSD is a valuable tool for interpreting data, making it widely applicable in scientific research, industrial processes, and quality management.

3 Results and discussion

Chicken manure is a type of animal husbandry/farm waste with a complex composition, containing components such as organic matter, nutrients, and moisture. Therefore, determination of the optimal heating rate, temperature, and time interval for the pyrolysis of chicken manure wastes depend on the specific characteristics of the feedstock and the desired products. For chicken manure pyrolysis, a moderate heating rate was often preferred in the literature. A heating rate in the range of 5 to 20 °C/min was commonly used. Because it is thought that in the slower heating rate will preserve the integrity of the organic compounds in chicken manure and therefore increase the yield of bio-oil rather than biochar. In addition, the pyrolysis temperature for chicken manure wastes typically was in the range of 400 °C to 600 °C in the literature. The choice of temperature depends on the desired product distribution and properties. In the lower temperatures (around 400 °C) are more likely to produce higher quantities of biochar, which can have applications in soil improvement and carbon sequestration. Higher temperatures (around 600 °C) tend to favor gas production, including hydrogen, methane, and other combustible gases. The residence time for chicken manure pyrolysis depends on both the heating rate and the temperature. In general, residence times of 15 to 60 min are typical for chicken manure pyrolysis. Longer residence times can lead to further decomposition of organic compounds, potentially increasing gas yields and biochar quality. However, excessively long residence times might result in the degradation of certain valuable components (Cavalaglio et al., 2018; Cely et al., 2015). However, also it's important to note that chicken manure composition can vary based on factors such as diet, bedding materials, and storage conditions. Therefore, conducting initial laboratory experiments and pilot-scale studies is crucial to determine the specific heating rate, temperature, and time interval that would yield the desired product distribution and properties. In this context, in order to obtain the best possible results in terms of product yield, quality and economic viability, the pyrolysis process of chicken manure waste was optimized selecting the parameters compatible with the literature ranges and by using the experimental design and optimization methodology RSM and CCD technique in the first stage of the studies.

3.1 Design of experiments

Response Surface Methodology is a statistical technique that has been widely used in recent years to obtain the optimum values of many variables and to estimate the optimal pyrolysis conditions with a few experiments. In this study, pyrolysis of CM wastes was carried out in a fixed bed reactor system and the effects of process parameters (reaction temperature, heating rate and reaction time) on the surface area were explored.

The effect of pyrolysis conditions on surface area of biochar was determined using the Response Surface Methodology. Pyrolysis temperature (200–500 °C), heating rate (5–20 °C/min), and pyrolysis time (30–120 min) were chosen as independent variables. In this study, 20 experiments were proposed based on the combination of three process parameters. Experimental conditions and surface area results of biochars obtained by pyrolysis are presented in Table 2.

3.2 Variance (ANOVA) analysis

Analysis of statistical (ANOVA) was performed for the surface area of the biochars obtained in the fixed bed reactor and the results are presented in Table 3. The F and P values for the surface area results of the biochar products were calculated as 8.27 and 0.0014,

Table 3 ANOVA analysis of the proposed quadratic model

Source	Sum of squares	df	Mean square	F value	P value	Status
Model	21.01	9	2.33	8.27	0.0014	Significant
A- Reaction Temperature	11.68	1	11.68	41.37	< 0.0001	
B- Heating Rate	0.15	1	0.15	0.53	0.4824	
C- Reaction Time	0.058	1	0.058	0.20	0.6614	
AB	0.000112	1	0.000125	0.00039	0.9845	
AC	0.12	1	0.12	0.43	0.5250	
BC	1.52	1	1.52	5.39	0.0426	
A^2	5.94	1	5.94	21.04	0.0010	
B^2	0.000046	1	0.0000461	0.00016	0.9685	
C^2	0.11	1	0.97	3.44	0.0935	
Residual	4.15	10	0.41			
Lack of fit	0.73	5	0.15	0.35	0.8650	Not significant
Pure error	2.10	5	0.42			
Cor total	23.83	19				
Std. Dev		0.53		R^2		0.8815
C.V %		10.15		Adj R-Squared R^2		0.7749

respectively. For the regression model to be reliable and significant, the P value should be less than 0.05. If P value is greater than 0.05, the effect of parameters on the surface area of biochars is insignificant. According to the ANOVA table, the surface area of biochar was most affected by the pyrolysis temperature. Heating rate and reaction time had little effect on surface area of biochar. Because the parameter with P value less than 0.05 affected the surface area.

A, B and C written in the ANOVA table represent the reaction/pyrolysis temperature, heating rate and reaction/pyrolysis time, respectively. The"Lack of fit"value is an important factor for the regression model. This value should mean insignificant (Spessato et al., 2021). The model is significant since this value is insignificant in the ANOVA table. Regression coefficient (R^2) and adjusted regression coefficient values were determined as 0.8815 and 0.7749, respectively (Table 3). The fact that both values are similar to each other means that the model does not contain statistically insignificant terms. In addition, it is stated in the literature that the calculated R^2 value for the accuracy of the model should be at least 0.80. The R^2 value in the study was found to be 0.8815. Thus, it was understood that the fit of the model was high.

The effect of temperature and heating rate by keeping the reaction time at a fixed point (75 min), the effect of heating rate and time by keeping the reaction temperature at a fixed point (350 °C), the effect of temperature and time by keeping the heating rate at a fixed point (12.5 °C/min) are given in the 3D response surface plot in Fig. 2. These graphs clearly showed that the effect of all independent variables on the surface area of biochar obtained in the fixed bed reactor. It was seen that the surface area of biochar increases with the increase in temperature. When the reaction temperature was kept fixed in the center (350 °C), it was seen that the surface area of the biochar slightly increases with the increase of the reaction time. At the same time, it was concluded that the biochar surface area slightly increases with the increase of the heating rate, but it was not affected much by the reaction time.

3.3 Determining the optimum pyrolysis conditions

Surface Response Methodology and Central Composite Design were used together to determine the optimum pyrolysis condition in the fixed bed reactor. The surface area results of biochar samples varied between 1.73 and 6.88 m^2/g. Analysis of variance (ANOVA) for response is presented in Table 3. "Lack of Fit" of 0.35 showed that it was not significant compared to pure error and the model had good performance. The P value was 0.0014, which proved that the model was significant. The correlation coefficient was greater than 0.8. This result showed that there was an agreement between the calculated and observed results (Chen et al., 2018). When the P values of the three independent variables were compared, it was seen that the reaction temperature was the most important factor affecting the surface area result. In addition, the heating rate also had a small effect on the surface area. Regression analysis was performed by considering all independent variables and their interactions.

The empirical relationship between the surface area and the independent variables can be expressed by the following quadratic polynomial equation (Eq. 4).

$$\begin{aligned} Surface\ area = {} & 5{,}50 + 0{,}92 \times A - 0{,}10 \times B + 0{,}065 \times C + 0{,}00375 \times A \times B \\ & + 0{,}12 \times A \times C - 0{,}44 \times B \times C - 0{,}64 \times A^2 + 0{,}0056 \times B^2 + 0{,}26 \times C^2 \end{aligned} \tag{4}$$

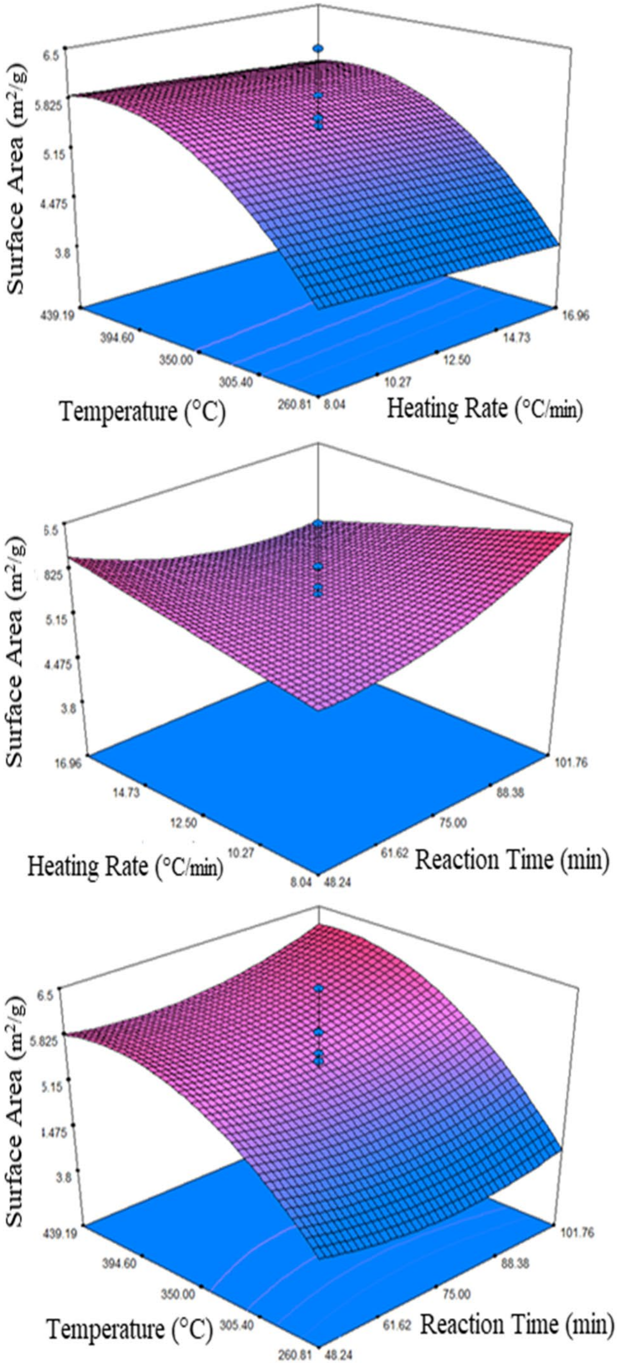

Fig. 2 3D response surface plot

Experimental results showed that the heating rate and reaction time were secondary important parameters on the surface area, while the reaction temperature was highly effective on the product. High temperature and low heating rate caused an increase in surface area values. The reaction time, which was another independent variable, did not have a significant effect on the surface area. The independent variables (temperature, heating rate and reaction time) for determining optimum pyrolysis conditions were selected within the range given in Table 1. Optimization studies were carried out to maximize the surface area of biochar product. When the results were examined, it was observed that the temperature, heating rate and reaction time should be approximately 440 °C, 7 °C/min and 115 min, respectively, to obtain a high surface area (Table 4). As a result, many results have been obtained with a small number of experimental studies by using the Response Surface Methodology in pyrolysis process of CM with more than one variable. In addition, the results were analyzed statistically and the results were evaluated in a healthier way with the graphics obtained.

3.4 Characterization of raw and activated biochar products

In the second stage of the study, biochar produced under optimal pyrolysis conditions was chemically activated to enhance its physical and chemical properties, particularly surface area, porosity, and adsorption capacity. To achieve this, the biochar was treated with KOH and HCl to induce structural changes in its carbon matrix. HCl activation aimed to effectively remove mineral components, heavy metals, and ash content from the biochar, resulting in a purer product with a higher surface area. KOH activation was intended to introduce basic functional groups to the biochar surface and increase surface area by creating deep, well-connected pores. Both activation processes were expected to significantly improve the surface area, pore development, and adsorption capacity of the raw biochar (Wang & Wang, 2019). The structural modifications in the chemically activated biochar were analyzed using widely recognized characterization techniques. Understanding these changes is crucial for predicting how activated biochar will perform in specific applications, such as environmental remediation, water treatment, agricultural use, or energy storage. In particular, surface area and surface chemistry are key factors influencing the interaction between biochar and environmental pollutants in remediation applications. Therefore, this study employed characterization methods such as Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscopy (SEM), and Brunauer, Emmett, and Teller (BET) analysis to assess both raw and activated biochar products.

3.4.1 FT-IR analysis

FT-IR analysis, a powerful tool for non-destructive chemical analysis, was used to gather information on the functional groups, molecular vibrations, and chemical bonds present in the biochar products. To achieve this, FT-IR spectra were generated to

Table 4 Validation of model

Pyrolysis temperature (°C)	Heating rate (°C/min)	Pyrolysis time (min)	Surface area (m^2/g)	
438.18	6.66	114.82	Predicted 7.61	Experimental 4.61

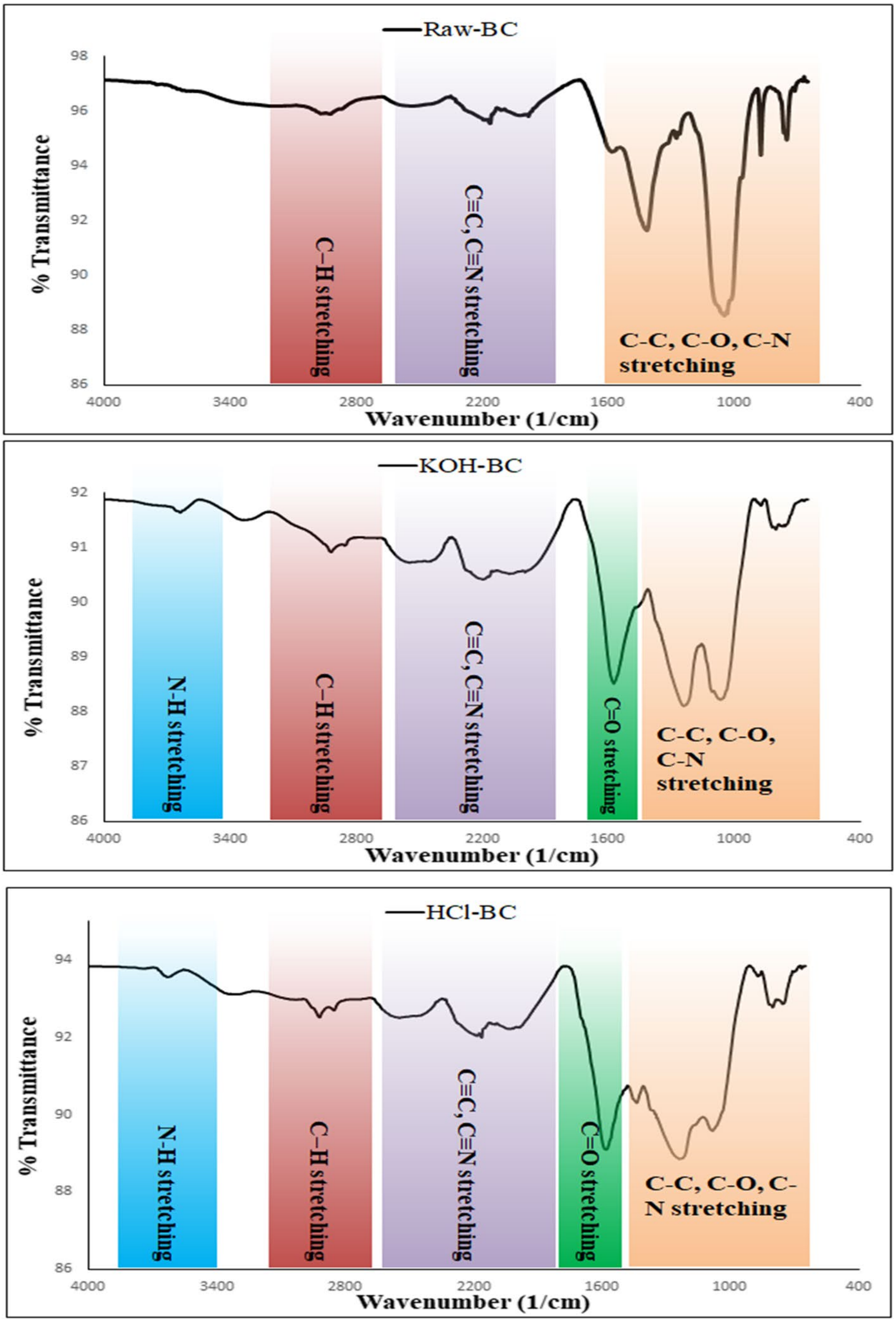

Fig. 3 FT-IR spectra of raw and activated biochar products

Table 5 FT-IR analysis results of raw and activated biochar products

Functional group	Wavenumber (cm^{-1})	Species
Raw BC		
C-H stretching	3000–2969	Aliphatic hydrocarbons
C≡C, C≡N stretching	2250	Nitrile
C–C, C-O, C-N stretching	1000–1500	Ether, alcohol, phenol
KOH-BC		
N–H stretching	3686	Amine
C≡C, C≡N stretching	2250	Nitrile
C-H stretching	2948–2894	Aliphatic hydrocarbons
C = O stretching	1600	Aldehyde, ketone, acid
C–C, C-O, C-N stretching	1000–1500	Ether, alcohol, phenol
HCl-BC		
N–H stretching	3670	Amine
C≡C, C≡N stretching	2250	Nitrile
C-H stretching	2943–2895	Aliphatic hydrocarbons
C = O stretching	1600	Aldehyde, ketone, acid
C–C, C-O, C-N stretching	1264	Ether, alcohol, phenol

identify the functional groups within the structure of both raw and activated biochar products, as illustrated in Fig. 3. The functional groups corresponding to the observed peaks are listed in Table 5.

When the FT-IR spectrum of the product (Raw-BC) obtained as a result of pyrolysis in the fixed bed reactor under optimum conditions was examined, the bands observed around 2250 cm^{-1} correspond to C≡C, C≡N stretching vibrations. The peaks at about 3000 cm^{-1} were C-H stretching vibrations originating from aliphatic hydrocarbons (Mukherjee et al., 2021). In the FT-IR spectrum of the KOH-activated biochar product (KOH-BC), the bands observed at 2250 cm^{-1} correspond to C≡N, C≡C stretching vibrations. The peak belonging to the C= O asymmetric stretching vibration was observed at 1600 cm^{-1}. This peak indicated the presence of compounds with acid, aldehyde and ketone groups in the biochar structure. The peaks at about 2960 cm^{-1} were C-H stretching vibrations originating from aliphatic hydrocarbons. The peak at 3500–3700 cm^{-1} was N–H stretching vibrations originating from amine group compounds. When the FT-IR spectrum of the HCl-activated biochar product (HCl-BC) was examined, C≡N, C≡C stretching vibrations were observed at 2250 cm^{-1} as in the KOH-BC product. In the spectrum, C= O asymmetric stress vibration peak was observed at 1600 cm^{-1}. This peak showed that there were compounds with acid, aldehyde and ketone groups in the structure. Also, the C= O stretching was seen as severe in both spectra. The peak at 3500–3700 cm^{-1} in HCl-BC product was N–H stretching vibrations originating from amine group compounds. In all spectrums, bands belonging to C-O, C-N and C–C stretching vibrations were observed at approximately 1000–1500 cm^{-1}. It can be said that these stresses were caused by compounds such as alcohol and ether (Cuixia et al., 2020; Hossain et al., 2021; Mukherjee et al., 2021). As a result, we can say that functional groups on the surface of biochar products have been improved thanks to the activation of KOH and HCl.

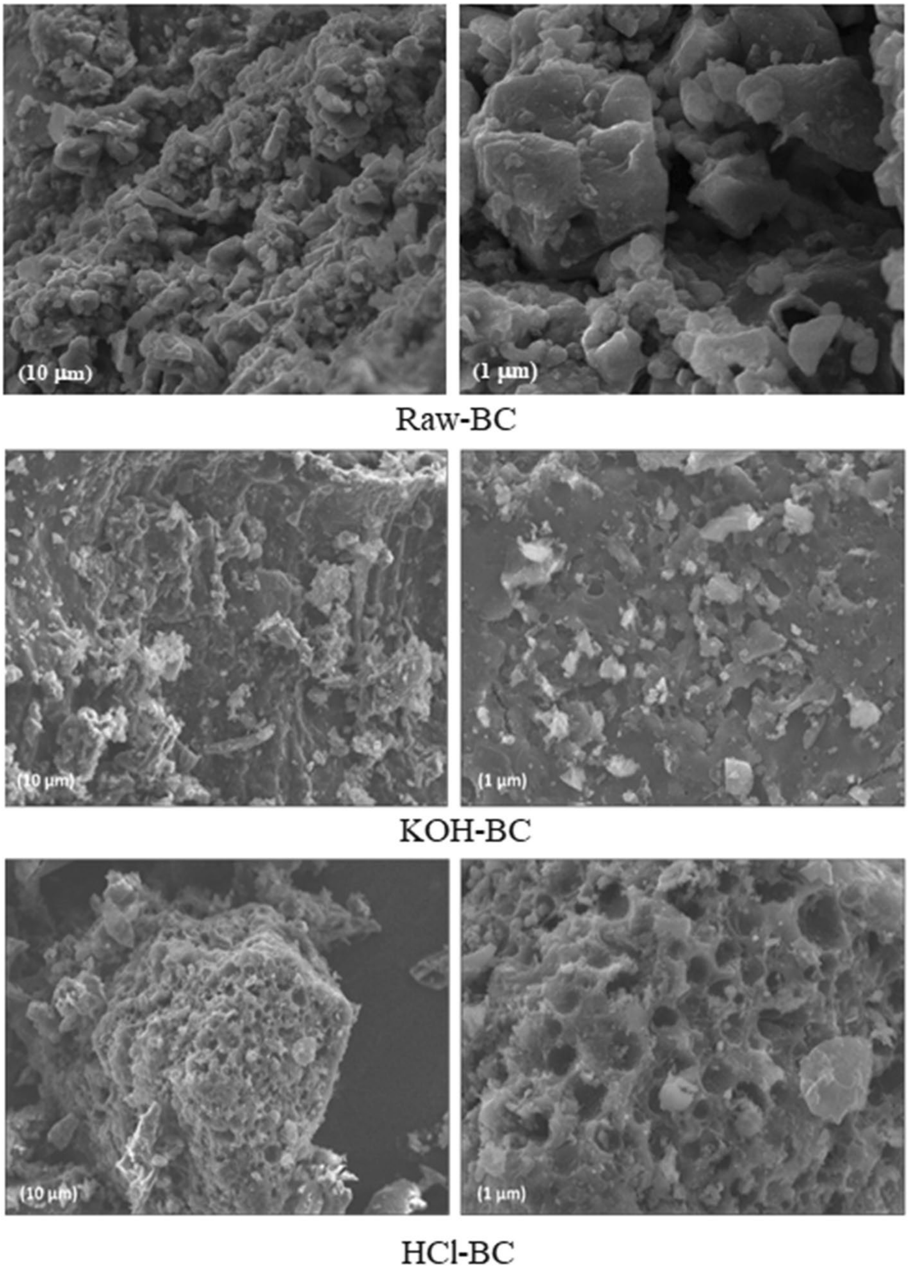

Fig. 4 SEM images of raw and activated biochar products

3.4.2 SEM analysis

In this study, SEM analysis was performed to determine the surface morphology, and structural differences in the pores of the raw and activated biochar products. SEM analysis gave information about the general pore structures and size distributions of the biochar products. SEM images of biochar products were taken at 1 and 10 µm magnifications. SEM images of the samples are presented in Fig. 4. When the SEM images of the raw biochar product obtained from the fixed bed reactor were examined, we can say that there were almost no pores in the structure, with a more oval and spherical structure as well as having a fibrous structure. When we examined the SEM images of activated biochar products, we can see that the HCl-BC product had a porous structure. Although the KOH-BC product had a more fibrous structure, the pore size was smaller compared to the HCl-BC product. Among the biochar products, the product with the most regular and largest pore size was the HCl-BC product.

3.4.3 BET analysis

In this study, surface properties (BET surface area and pore volume) of raw and activated biochar products are presented in Table 6. When the results were examined, the biochar product activated with KOH (KOH-BC) had the highest surface area and pore volume. In the literature, there are some biochar products activated with acid and base and used for different applications. For example, Biswas et al. (2020) used biochar obtained from pine cone at 500 °C pyrolysis temperature as an adsorbent in heavy metal adsorption after activating it with H_3PO_4. The surface area and pore volume values of the raw and activated biochars they obtained were measured as 144.85, 171.85 m^2/g and 0.28, 0.31 cm^3/g, respectively (Biswas et al., 2020). In another study, Choudhary et al. (2020) activated the biochar obtained from Opuntia ficus-indica with NaOH. The surface area and pore volume values of the raw and activated biochars they obtained were measured as 1.15, 32.07 m^2/g and 0.018, 0.093 cm^3/g, respectively (Choudhary et al., 2020). Although the surface area results of biochar are an important factor in adsorption studies, they are not the only effective parameter. In this study, we can say that the pore sizes of biochar have changed and the pore volume and also surface area have increased thanks to the KOH activation. The surface area and pore volume values of biochar did not change much with HCl activation. However, according to the SEM analysis results, the most pores belong to the biochar product activated with HCl. Therefore, it can be misleading to determine the surface properties of biochar just by looking at SEM images. The BET surface area should also be measured and the results should be interpreted together.

Although the surface area values of biochars prepared in this study are low compared to many biochar products in the literature, surface area is not an effective parameter alone in investigating the applicability of the biochar product in different usage areas. Depending on the raw material, the carbon content significantly affects the specific surface area of biochar products. However, high mineral content can close the pores on the biochar surface, reducing the specific surface area (Dissanayake et al., 2020). Especially the high amount of calcium in biochar products obtained from poultry waste can cause a low surface area. When the EDS analysis of the biochar product obtained in this study was performed, it was

Table 6 Surface properties of biochar samples

Biochar	Activation	S_{BET} (m^2/g)	Pore volume (cm^3/g)
Raw BC	–	4.61	0.010
KOH-BC	KOH, 700 °C, 1 h	16.92	0.048
HCl-BC	HCl, 700 °C, 1 h	4.09	0.011

determined that 25.47% Ca was included in its structure. Therefore, this mineral, which is highly present in the structure of biochar products obtained from chicken manure, significantly reduced the specific surface area by closing the pores on the biochar surface. However, the low surface area does not limit the application potential of biochar products. On the contrary, in this study, the surface functional groups of biochars with lower surface area and pore volume compared to biochars produced from plant biomass species were improved by chemical activation and their effective usability in three different application areas was demonstrated.

3.5 Investigations of application areas of biochar products

3.5.1 Energy conversion and gas emission applications

Unlike fossil fuels, the reuse of renewable bio-resources for energy production has gained significant momentum in recent years (Nizami et al., 2017). It is very important to pyrolysis of biomass wastes at a certain temperature in order to obtain value-added products that can be used in energy production. In the current literature studies, biochars produced by pyrolysis have been examined in terms of yield percentages and calorific values. When the limited number of studies in the literature for the biochar product obtained as a result of the pyrolysis of poultry farm wastes used as a biomass source are examined, it has been seen that yield values ranging from 32–54% have been reached in a wide pyrolysis temperature range of 300–800 °C. According to the existing literature, the potential for efficient use of biochar obtained by pyrolysis is due to its high calorific value (12–20 MJ/kg) and energy efficiency (36–68%). Therefore, these results recently show that solid products (biochar) obtained from the pyrolysis of poultry farm wastes have the potential to be used as fuel (Mau & Gross, 2018). For example, Kantarli et al. (2016) was carried out pyrolysis of poultry farm wastes at 250–500 °C, and compared the fuel properties of the obtained biochar with different types of coal (anthracite, bituminous coal, lignite, etc.). They reported that the properties of the biochar obtained after pyrolysis at 300 °C were close to that of bituminous coal (Kantarli et al., 2016). One of the key factors to consider when investigating the use of alternative biomass for energy production is the release of pollutants into the environment that may occur during thermal or thermochemical processes. Pollutants that are released during biomass conversion processes and may cause adverse effects on the environment mainly consist of NO_x, SO_x, CO_2 and CO gases (Dalolio et al., 2017).

In this study, the fuel properties of the biochar product obtained from the fixed bed reactor were compared with different types of coal (lignite, petrocoke, etc.). For this purpose, thermal value comparison was made between the biochar product and different coal types. Considering the results of the analysis, the use potentials of the biochar product as a fuel compared to different types of coal were evaluated. Coal is one of the most important energy sources today. Coal is heterogeneous in structure. At the same time, coal is a rock that consists of organic and inorganic materials and can give off heat when burned (Boylu & Karaağaçlıoğlu, 2018). The characteristics of raw biochar product obtained in the fixed bed reactor under optimum conditions and also properties of different coal types are given in Fig. 5. As can be seen from the figure, raw biochar and other types of coal (lignite and petrocoke) differ in terms of chemical properties. In this study, the properties of biochar and coal types in terms of ash, moisture, volatile matter and calorific value were examined and evaluated. Because it is very important to investigate these parameters, which reduce the quality of coal and cause it to have unfavorable properties. The advantageous situations

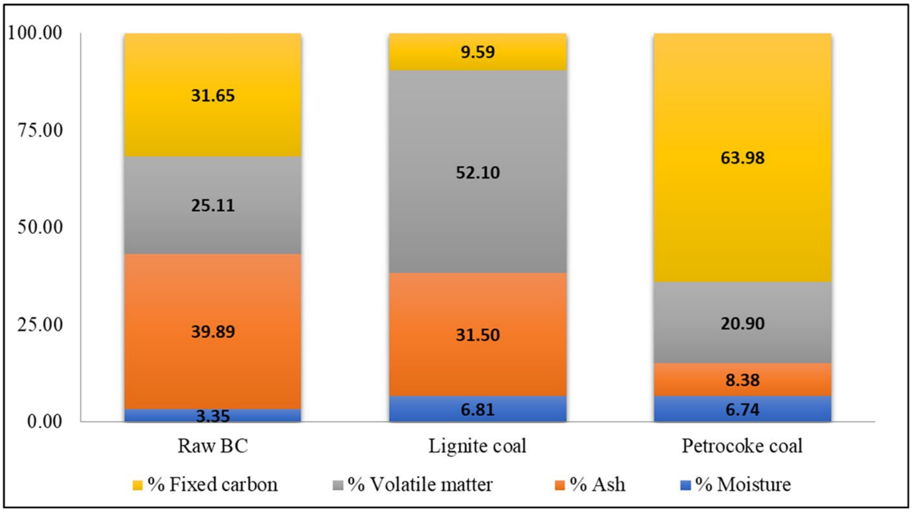

Fig. 5 Characteristics of raw biochar and different coal types

of the raw biochar obtained from the fixed bed reactor in the optimum condition, which can be used instead of other coal types, have been evaluated and interpreted.

As can be seen from Fig. 5, the moisture content of petrocoke coal is generally higher than that of biochar. Humidity is one of the main characteristics that determine the quality of coal (Kopuz, 2011). Humidity reduces the calorific value of coal, since it is not combustible and requires energy for evaporation during combustion. The lowest moisture content belongs to the raw biochar product (Raw-BC) produced from the fixed bed reactor under optimum conditions. The volatile matter content in coals consists of methane, hydrocarbons, hydrogen, carbon monoxide and non-combustible oxidized gases such as CO_2 and nitrogen in the coal (Boylu & Karaağaçlıoğlu, 2018). When comparing the coal types in Fig. 5, lignite has the highest amount of volatile matter. One of the most important features affecting the quality of coal is the ash content. Ash creates inorganic matter in the coal structure and reduces the thermal value of the coal as it is not combustible. Ash is an undesirable component of coal and is discarded at the end of the process (Boylu & Karaağaçlıoğlu, 2018; Dalolio et al., 2017). Petrocoke coal has the lowest ash content among coal types. It is generally accepted that coals containing 18–20% ash can be used as household fuel. The fixed carbon content in the structure of the coal is the solid part that remains after the volatile matter is removed from the coal structure in the combustion unit. Fixed carbon is a guide in determining the composition and amount of the gases released during the combustion of biochar and different types of coal (lignite coal and petrocoke). Fixed carbon consists largely of carbon and compounds such as hydrogen, oxygen, sulfur and nitrogen that are not emitted during combustion (Boylu & Karaağaçlıoğlu, 2018). Pollutants that may cause adverse effects in the environment mainly consist of NO_x, SO_x, CO_2 and CO gases (Kantarli et al., 2016). Based on all these results, we can say that the higher the fixed carbon content of biochar, the less the composition and amount of harmful gases released to the environment. When comparing the coal types in Fig. 5, the type of coal with the highest fixed carbon content is petrocoke (~ 64%). The type of coal with the lowest fixed carbon content is lignite (~ 10%). The fixed carbon content of the Raw-BC product is given as ~32%. Among these products, lignite coal, which has the lowest fixed carbon

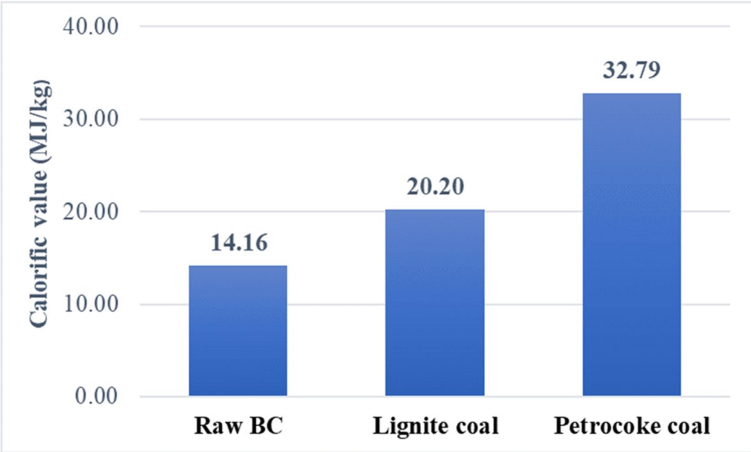

Fig. 6 Comparison of the calorific value of raw biochar and different coal types

content, is less environmentally friendly than others. When evaluated in terms of harmful gases released to the environment, Raw-BC product can be used instead of lignite coal.

The calorific value of coals depends on the amount of non-combustible materials mixed with its organic structure. In general, the calorific value of lignite coal is low. Because the oxygen and moisture content is high. As seen in Fig. 6, the calorific value of lignite coal is lower than that of petrocoke. For this reason, lignite coal produced worldwide is mainly consumed in thermal power plants. Carbon and hydrogen in the coal structure are found in both organic and inorganic structures in coal. The high calorific value of coal types is due to the combustion of carbon and hydrogen in its structure (Dalolio et al., 2017). One of the most important reasons for the high calorific value of petrocoke is due to its high carbon content. It is Raw-BC product, which has the lowest heating value among coal types. However, this value is close to the calorific value of lignite coal. This result shows that biochar can be used instead of lignite coal if it is more environmentally friendly (less greenhouse gas emission value released to the environment). As a result, using chicken manure biochar as an alternative fuel source has the potential to provide several environmental benefits, including carbon sequestration and waste management.

3.5.2 CO_2 adsorption

The increase in CO_2 emissions is the main source of global climate disruption and its impact on the environment has been proven worldwide (Dissanayake et al., 2020). Biochar, a stable form of carbon, plays an important role in CO_2 capture and climate change mitigation. Offering benefits such as carbon sequestration, waste utilization and renewable raw material use, when biochar is used for CO_2 capture, it can store CO_2 for a long time, contribute to the reduction of atmospheric CO_2 levels and help combat climate change (Jung et al., 2019; Waqas et al., 2018). In this study, the CO_2 adsorption capacities of biochar samples were determined under the same conditions and the results are presented in Fig. 7. The maximum CO_2 adsorption capacities of Raw-BC, KOH-BC, HCl-BC samples were measured as 27.52, 66.62 and 51.26 mg/g (0.63, 1.51, 1.17 mmol/g), respectively. As can be seen from the results, KOH-BC has the highest CO_2 adsorption capacity depending on its high surface area and porous structure.

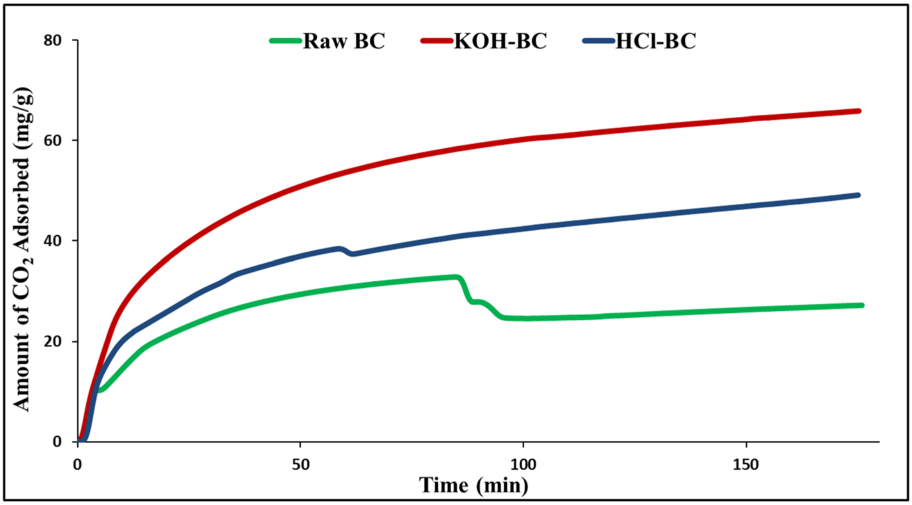

Fig. 7 CO_2 adsorption capacities of biochar products (T = 25 °C, Flow rate of CO_2 = 50 mL/min, Adsorption time = 3 h, Sample weight = 20 mg)

As can be seen from Table 7, the adsorption capacity of the biochar product has increased due to acid activation (H_3PO_4) in the studies in the literature. Adsorption capacities of biochar products activated with KOH are similar according to literature results. All these results showed that the raw biochar obtained under optimum conditions increased its usability in CO_2 capture applications after being activated with KOH. Because in this study, the CO_2 adsorption capacities of activated biochar products are compatible with many other biochar products reported in the literature (Table 7). In particular, the KOH-activated biochar product showed a high CO_2 adsorption capacity, despite its low surface area, compared to the others. As a result, it can be said that activation of raw biochar is necessary for higher CO_2 adsorption. Thanks to the activation, the adsorption capacity of biochars has been increased and has been brought to a level comparable to the adsorption capacities of other biochars reported in the literature.

3.5.3 Investigation of the effectiveness of dyestuff removal from aqueous solution

The rapid advancement of technology and industry has led to a significant increase in environmental problems, particularly through the depletion of natural resources and the unchecked disposal of waste. The growing variety and quantity of domestic and industrial waste, especially in water resources, have resulted in pollution reaching dangerous levels. Industrial wastewater containing dyestuffs is a major contributor to water pollution, as these organic dyes are highly toxic to aquatic life and pose potential health risks to other organisms (Chakraborty et al., 2011; Poon et al., 1999). Due to their complex chemical structures, synthetic organic pigments are resistant to biodegradation and are stable against light and oxidizing agents, making them difficult to remove using conventional treatment methods. Among various treatment techniques, adsorption stands out as the most effective, low-cost, and environmentally friendly method for removing dyes from wastewater. It is particularly favored for its simplicity and efficiency in separating a wide variety of chemical compounds (Gaouar-Yadi et al., 2016). The effectiveness of adsorption

Table 7 Comparison of CO_2 adsorption capacities of activated carbons produced from different biomass

Biomass	Activation method	S_{BET} (m^2/g)	Time	Conditions (°C/v% CO_2)	CO_2 adsorption capacity (mmol/g or mg/g)	Reference
Chicken manure	No activation	4.61	3 h	25/99.9	0.63	This study
Chicken manure	KOH	16.92	3 h	25/99.9	1.51	This study
Chicken manure	HCl	4.09	3 h	25/99.9	1.17	This study
Coffee grounds	KOH	990	1 h	35/99.9	2.67	(Liu & Huang, 2018)
Corncob	H_3PO_4	1038.2	-	15/99.9	130	(Sarwar et al., 2021)
Corncob	$ZnCl_2$	658.7	-	15/99.9	160	(Sarwar et al., 2021)
Corncob	KOH	1222	-	15/99.9	198	(Sarwar et al., 2021)
Walnut shell	KOH	1488.89	10 min	25/10	2.1	(Pu et al., 2021)
Enteromorpha	KOH	60.2	12 min	25/12	0.52	(Ding & Liu, 2020)
Sargassum	KOH	291.8	12 min	25/12	1.05	(Ding & Liu, 2020)
Cashew nutshell	K_2CO_3	521–1126	-	0/20	4.16–6.22	(Garg & Das, 2020)

depends on the surface area of the adsorbent, with materials like activated carbon being ideal due to their high surface area and adsorption capacity (Demiral & Aydın Şamdan, 2016). However, the high cost of commercial activated carbon has driven the search for more affordable alternatives. In general, using biochar for dye removal from wastewater is an important and beneficial approach to address water pollution and improve water quality. Its adsorption capacity, cost-effectiveness, sustainability, and versatility make it a valuable tool in the field of water treatment and environmental protection. Moreover, biochar can be used in various water treatment setups, including batch adsorption processes and continuous flow systems, making it adaptable to different water treatment scenarios. Thus, biochar based dye removal processes can be scaled up for industrial applications, offering a versatile solution for industries that generate dye wastewater (Alade et al., 2012; Aygün et al., 2003; Rafatullah et al., 2010; Savova et al., 2001).

Within the scope of this study, the adsorption capacities of raw biochar and activated biochar products, which are obtained as a result of the pyrolysis of poultry farm wastes (chicken manure) in fixed bed reactor under optimum conditions, in dyestuff removal from aqueous solutions were investigated. For this purpose, raw and activated biochar products, characterized by determining their chemical and surface properties, were used in adsorption studies for the effective removal of methylene blue (MB), an organic dyestuff, from aqueous solution. The methylene blue adsorption capacities and dye removal efficiencies of raw and activated biochar products are shown in Fig. 8. While the adsorption capacity of the raw biochar produced in the fixed bed reactor under optimum conditions was calculated as 10.06 mg/g, the methylene blue adsorption capacities of the biochars activated with KOH and HCl were calculated as 9.57 and 4.98 mg/g, respectively.

In the literature, the maximum amount of methylene blue adsorbed by the biochar samples obtained as a result of the pyrolysis of different biomass has been reported. For example, the maximum amount of methylene blue adsorbed by biochars obtained from the pyrolysis of biomass samples such as pine tree plant, pig manure, cardboard, etc. has been reported as 3.99, 16.30, 1.66 mg/g, respectively (Dai et al., 2019). Therefore, the methylene blue adsorption capacity of the biochar samples obtained in this study is compatible

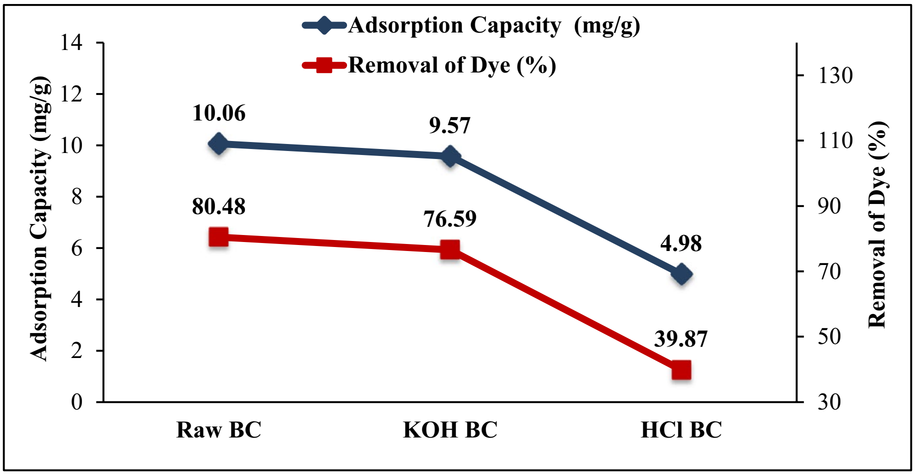

Fig. 8 Comparison of dye adsorption capacities and percentages dye removal of raw and activated biochars (C_o = 25 mg/L, pH = 4–5, T = 45 °C, Adsorbent dosage = 0.2 g/100 mL dye solution, Mixing speed = 250 rpm, Contact time: 300 min)

Table 8 Comparison of adsorption capacities of biochars produced from different biomass in methylene blue removal from aqueous solution

Biomass type	Pyrolysis temperature (°C)	Adsorption capacity (mg/g)	Reference
Chicken manure	440	10.06	This study
Chicken manure (KOH-activated)	440	9.57	This study
Chicken manure (HCl-activated)	440	4.98	This study
Eucalyptus	400	2.06	(Sun et al., 2013)
Wood	600	2.40	(Inyang & Dickenson, 2015)
Palm tree	400	2.66	(Sun et al., 2013)
Pine tree	525	3.99	(Dai et al., 2019)
Pig manure	400	16.30	(Dai et al., 2019)
Straw	500	18.10	(Dai et al., 2019)
Wheat straw	200	46.6	(Li et al., 2016)
Poplar tree	600	85.00	(Zhang & Gao, 2013)
Magnolia tree leaf	500	101.27	(Ji et al., 2019)

with the literature. In particular, the methylene blue adsorption capacity of the raw biochar product is much higher than that of many biochar products in the literature (Table 8). On the contrary, it was observed that the activated biochar samples adsorbed less methylene blue than the raw form. Activating biochars for methylene blue adsorption required an extra process, as well as reduced the adsorption capacity of the products.

Experimental results demonstrated that the effectiveness of characterized biochar in energy applications and pollutant removal is closely tied to its unique physical and chemical properties, which can be modified through the pyrolysis process and subsequent treatments. In energy applications, biochar serves as a solid fuel due to its high carbon content and calorific value, with its efficiency dependent on energy density, which is influenced by the pyrolysis temperature and the type of biomass used. Biochar with higher carbon content and lower volatile matter is more efficient, producing more energy per unit weight. For contaminant adsorption, biochar is highly effective in removing a wide range of pollutants, including organic compounds like dyestuffs and inorganic compounds such as CO_2. This effectiveness stems from its large surface area, porous structure, and surface chemistry, which can be enhanced through careful characterization and optimization. Thus, the performance of characterized biochar in energy applications and environmental pollutant removal is intrinsically linked to its structural and chemical properties. By optimizing these properties, biochar can be made more efficient as a fuel, in CO_2 storage, and in water treatment, making it a powerful tool for environmental remediation.

3.5.4 Reusability of biochar products

Generally, reusability tests involve evaluating the ability of an adsorbent to be regenerated and reused over multiple cycles of adsorption and desorption. These tests may involve exposing the adsorbent to a regenerating agent, such as heat, steam, or a chemical solution, to remove the adsorbed pollutants. The cost of reusability tests can depend on the cost of the regenerating agent, the energy required for the regeneration process, and the labor required for the testing. Therefore, it is of great importance to perform this expensive test in adsorbents with high production cost and high surface area/adsorption capacity. However, in practical application especially for low-surface area adsorbents produced from a cheap biomass, such as chicken farm waste, reusability test is not an economically applicable/feasible and significant test. Because the cost of adsorption/desorption process in adsorbents with low surface area is quite high compared to the production cost of the adsorbent material. For this reason, regeneration of adsorbent produced from a biomass that is cheap and abundant like chicken farm waste is not practically applicable. Because, the cost of reusability process or adsorption/desorption process for adsorbents can vary widely depending on the specific requirements of the experimental procedure and the experimental setup. It's important to carefully consider the costs and benefits of these tests/processes to ensure that they are a worthwhile investment for the specific application and intended use of the adsorbent material.

3.5.5 Mechanism of the dye adsorption

Understanding the mechanism of adsorption is critical in designing and optimizing adsorption systems. The mechanism of the adsorption process involves several steps such as transport, adsorption, surface diffusion, adsorbate–adsorbate interactions and equilibrium. The strength of the adsorption process depends on the nature of the adsorbate, the adsorbent, and the environment (Achour et al., 2021). In this study, to clarify the mechanism of MB dye adsorption onto activated biochar, the interaction between adsorbate and adsorbent was explained with supporting data result obtained from FT-IR analysis. The schematic representation to visualize the mechanisms interactions between MB molecules with the carbon surface are presented in Fig. 9. As can be seen from the figure, the activated biochar product has potential adsorption sites such as C= C, C= O, O–H. It can be said that the adsorption mechanism of MB dye on the activated biochar surface was occurred by two different interaction types. While one of them was hydrogen bond, the other can be said as weak interactions (such as Van der Waals force, π-π interactions etc.). As a result, the possible mechanism for the adsorption process is considered to involve monolayer, chemical adsorption, and the participation of robust intermolecular forces.

3.6 Potential limitations and challenges

Producing biochar from chicken manure waste offers various benefits, such as waste management and carbon sequestration. However, there are also several challenges and limitations associated with this process. Chicken manure's composition can vary widely due to factors like diet, age of the chickens, and management practices. This variability can affect the quality and properties of the biochar produced. Pyrolyzing chicken manure can release ammonia, a potent greenhouse gas and air pollutant. This can contribute to local air quality issues and further environmental concerns. Chicken manure can contain contaminants such as heavy metals, antibiotics, and pathogens. If not properly managed during the pyrolysis process, these contaminants can be concentrated in the resulting biochar, potentially posing risks to soil, water, and crops. The pyrolysis process requires a significant amount of energy to reach and maintain the high temperatures needed for efficient biochar production. This raises production costs and hinders scalability to a commercial level, ultimately impacting the overall environmental sustainability of the process (Marousek, 2014).

On the other hand, the costs associated with collecting, transporting, and processing chicken manure into biochar can be significant. The economic feasibility of such a venture

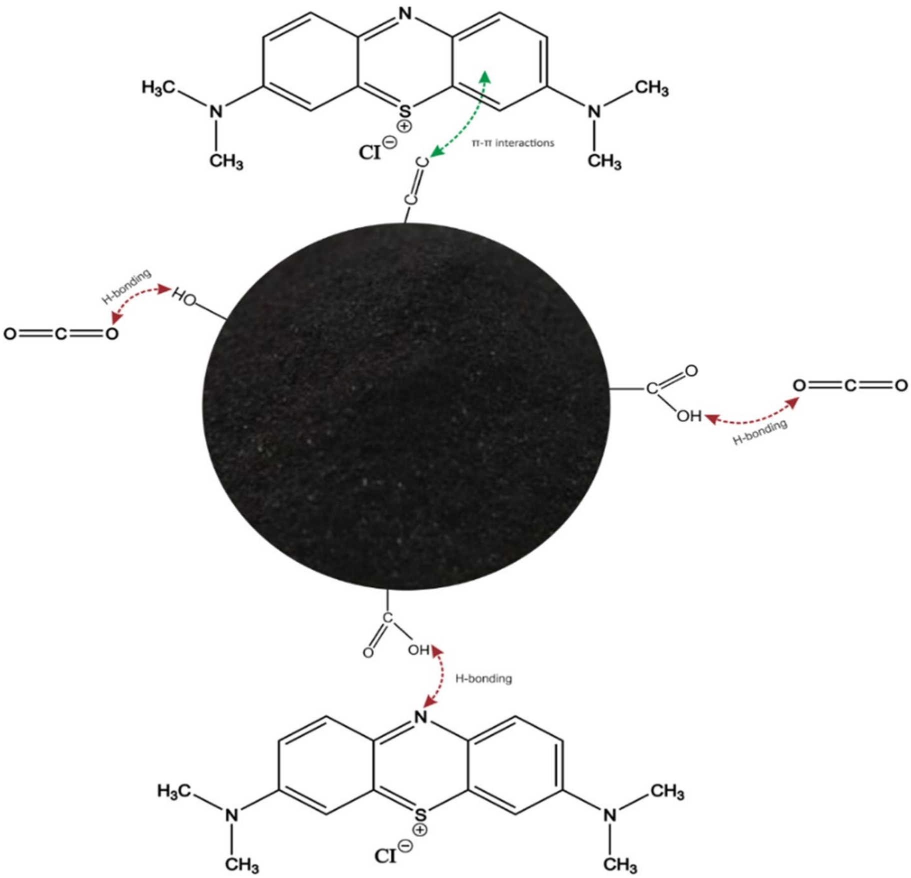

Fig. 9 Schematic diagram of adsorption mechanism of MB onto activated biochar

depends on factors such as the local market for biochar and the availability of suitable waste material. The successful production of biochar from chicken manure waste requires appropriate facilities and equipment. Setting up and maintaining these facilities can be a logistical challenge, particularly for large-scale operations. Waste management and biochar production are subject to regulations and permits that can vary depending on the location. Navigating these requirements can add complexity to the process. As a result, while producing biochar from chicken manure waste has the potential to address waste management, it's crucial to address these challenges and limitations to ensure the environmental, and economic benefits are maximized while minimizing potential negative impacts. Although there are many biochar applications in the literature, produced from many different types of biomass, which have been repeatedly and independently demonstrated to provide a wide range of environmental benefits, the commercial viability of most of the research conducted to date has been limited by the stringent requirements of the biochar used (expensive feedstocks or difficult activation methods). As different feedstocks or production alternatives have increased production costs, this has weakened the financial sustainability of many biochar applications. The production costs of biochar therefore need to be significantly reduced in order for the benefits of biochar to be felt on a global scale (Marosek et al., 2023).

4 Conclusions

This study has been carried out to generate added value product from poultry farm wastes such as chicken manure, and also to minimize the disposal problems of these wastes. Chicken manure (CM) wastes were converted to solid product with application potential in fixed bed reactor by pyrolysis method. In the fixed bed reactor, pyrolysis of CM wastes used as raw material was carried out under optimum conditions. Optimum pyrolysis conditions were determined using Design-Expert software to maximize the surface area of the biochar product. In fixed bed reactor systems, pyrolysis of chicken manure wastes was carried out as a result of a series of experiments. The effects of pyrolysis temperature (200–500 °C), heating rate (5–20 °C/min) and pyrolysis time (30–120 min) on the surface area of the obtained biochars were investigated. The optimum condition was determined as 440 °C reaction temperature, 7 °C/min heating rate and 115 min reaction time. Raw biochar was activated with KOH and HCl, and the usability of the obtained biochar products in energy conversion and gas emission applications, determination of CO_2 adsorption capacities and efficiency of removal of dye were investigated. The CO_2 adsorption capacities of Raw-BC, KOH-BC and HCl-BC products were measured as 27.52, 66.62 and 51.26 mg/g at 25 °C, respectively. The results showed that activated biochars are candidates for CO_2 adsorption. In addition, the raw and activated biochar products were used as adsorbent in the removal of methylene blue (MB) from aqueous solution, and the highest MB removal (80%) was achieved with raw biochar. When the fuel properties of the raw biochar obtained under optimum pyrolysis conditions in the fixed bed reactor were compared with different types of coal, it was concluded that this product could be used instead of lignite coal in energy production. As a result, in this study, the potential of the products obtained by the pyrolysis of chicken manure wastes to be a raw material source for the production of chemicals that can be used as an alternative to commercial activated carbon in the removal of environmental pollutants and energy production were evaluated.

The results obtained from the study show that converting chicken manure waste to biochar offers several important benefits for the environment. Moreover, it is also known that chicken manure is rich in nutrients like nitrogen, phosphorus, and potassium. When it's converted into biochar, these nutrients are captured and stored in a stable form. This prevents nutrient runoff into water bodies, which can lead to water pollution and eutrophication. At the same time biochar can also be used as a soil amendment to enhance soil quality and fertility. When biochar-enriched soils are utilized in agriculture or forestry, they can sequester more carbon from the atmosphere and promote long-term carbon storage. The process of converting chicken manure to biochar also reduces the release of methane and other greenhouse gases that can occur when manure decomposes in conventional waste management systems. As a result, by converting chicken manure into biochar is important for addressing climate change and offers a range of environmental benefits, including carbon sequestration, waste utilization, renewable feedstock utilization, and the potential for carbon–neutral energy generation. It is a valuable tool in the global effort to reduce greenhouse gas emissions and combat the effects of climate change and also in the field of water treatment and environmental protection. Especially, optimizing biochar production is crucial for enhancing its environmental benefits, ensuring economic viability, enabling large-scale implementation, and meeting regulatory standards. These factors collectively make biochar a more effective and sustainable solution for addressing real-world environmental challenges.

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Data availability All data generated or analysed during this study are included in this published article.

Declarations

Ethics approval Not applicable.

Consent to participate Not applicable.

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