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Evaluation of Iron-Modified Biochar from Sugarcane Bagasse and Heterogeneous Fenton Process for Batik Dye Removal

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ABSTRACT

Batik is a widely recognized form of clothing in Indonesian society. The batik-making process uses synthetic dyes, which can pollute the environment. This study aims to modify biochar derived from sugarcane bagasse using iron (Fe) synthesis. Biochar was produced through pyrolysis, while iron was sourced from beach sand in Glagah, Yogyakarta. The research involved four stages: (1) production of biochar from sugarcane bagasse, (2) modification of biochar with iron through beach sand synthesis, (3) application of iron-modified biochar (IMB) to methylene blue (MB), and (4) analysis of biochar characteristics. The results show that iron-modified biochar (IMB) affects biochar properties. IMB falls into the micropore category with a micropore surface area of 71.1%. The optimum wavelength was 571 nm with an adsorption level of 0.155. The application of IMB to batik wastewater demonstrated that adding 6% Fe and soaking for 180 minutes achieved the highest reduction in batik wastewater at approximately 69% with an R squared value (R^2) of 0.975. Degradation of batik dye with 6% Fe using the Heterogeneous Fenton method resulted in yellow color degradation of 16%, fast green 3%, methylene orange 4%, red 3%, and methylene blue 23%. These findings highlight the potential of using sugarcane bagasse as a renewable resource for producing adsorbents that contribute to effective batik wastewater treatment.

Keyword: activated carbon, batik wastewater, heterogeneous Fenton, iron-modified biochar (IMB), sugarcane bagasse.

INTRODUCTION

Batik is a masterpiece of the Indonesian Nation which has been recognized by The United National Educational, Scientific, and Cultural Organization (UNESCO) as a Intangible Cultural Heritage of Humanity on October 2, 2009 (Ich.unesco.org, 2009). In addition, batik has also become an important uniform for Indonesian people in various activities. The batik industry in Indonesia can provide benefits to society by providing employment opportunities for the community and supporting the development of micro, small and medium enterprises (MSMEs) (Widjajanti et al., 2022). Batik is created by painting images and adding colour to a piece of cloth. Batik craftsmen typically use synthetic dyes to colour the batik cloth. However, synthetic dyes take a considerable amount of time to decompose naturally that contributed to the environmental pollution. This raises the risk of dangerous chemicals accumulating in the environment, thereby negatively impacting the ecosystem and upsetting the ecological balance (Solayman et al., 2023). Moreover, Synthetic batik dyes containing heavy metals (Cu, Zn, Ni, Al, Fe, and Pb) can have a negative impact on the skin of traditional batik industry workers (Oginawati et al., 2022). Another hazard posed by synthetic dyes is pollution of the aquatic environment caused by high levels of BOD and COD in wastewater (Abdelhameed and Emam, 2019; Sutisna et al., 2017). Synthetic textile dyes represent a large group of organic compounds that have adverse environmental effects and pose risks to humans. Batik liquid waste has attracted the attention of several researchers to overcome the problem of environmental. One of the technologies carried out is to modify the material from activated charcoal. According to (Ahmed et al., 2022) activated charcoal is an environmentally friendly material and can absorb wastewater well (Saravanan and Kumar, 2022). Other technologies that can be used to treat wastewater are adsorption technology, biodegradation technology, membrane technology, and oxidation technology which have been developed to address the problem of water pollutants (Ma et al., 2021). Adsorption technology is the most economical and efficient choice because the adsorption technology uses a simple design and low cost (Yaashikaa et al., 2019). In addition, adsorption technology has been widely applied in the control of antibiotic dyes and water pollution (Jiang et al., 2018). Biochar can be applied for the absorption of organic pollutants from waste water (Qiu et al., 2022). Biochar can be applied for the absorption of organic pollutants from waste water (Qiu et al., 2022). The biochar adsorption mechanism can be carried out by electrostatic interactions, ion exchange, pore filling and precipitation (Ambaye et al., 2021). Biochar efficiency is influenced by the phytochemical characteristics of biochar such as pyrolysis temperature (Pellera et al., 2012), dosage, contact time, initial pH, initial concentration and temperature of the biosorption process (Lam et al., 2016). Studies from (Bayoka et al., 2023) have shown that variation in pyrolysis temperature can lead to biochar with different characteristics and can impact their catalytic activity. Therefore, selecting 300 °C as the calcination temperature might aim to enhance the catalytic activity of the biochar for the specific purpose being investigated, as evidenced by its demonstrated highest catalytic activity for Methylene Blue degradation.. Additionally, the reduced catalytic activity observed in biochar at 500 °C may be attributed to the detrimental effect of potassium, which could deactivate the Cu-Ni alloy present in the bimetallic, thereby influencing the overall catalytic performance.

However, modified chemical activity can increase the effectiveness of biochar (Tomczyk et al., 2023). Chemical activation can be used to improve the absorption quality of biochar such as iron (Fe) (Guo et al., 2023), KOH and KMnO4 (Yue et al., 2023), Mg (Zhu, 2020), and citric-acid assisted (Omiri et al., 2022). Biochar can be produced from biomass such as sugarcane bagasse using a pyrolysis process (Mufandi et al., 2020; Treedet et al., 2020). Bagasse is the residue from sugarcane (*Saccharum Officinarum L.*) milling after the sap is taken. Utilization of bagasse began to be developed for various applications. Sugarcane bagasse has been made of activated carbon and used for the removal of ferrous metals (Fe) and manganese from water (Mn) (Dalai et al., 2015), as well as for the collection of tri-chloro-phenol (Mubarik et al., 2016). In addition, bagasse was also tried to be used for chromium adsorption (Ullah et al., 2013), inorganic phosphate from aqueous solution (Manyatshe et al., 2022), rapid removal of copper ions form wastewater (Li et al., 2022), dan methylene blue adsorption (Dzoujo et al., 2022). The degradation process of methylene blue textile waste was explained from this research (Amelia et al., 2019, 2020; Maryudi et al., 2019). Several reviews (Adegoke et al., 2023; Cheng et al., 2021; Li et al., 2021) have reviewed systematic discussions and stated that surfactant modification, wet treatment, acid and other composite materials are of concern in the use of biochar. An in-depth study on the modification of sugarcane bagasse biochar composite has been carried out by (Bai et al., 2021) using the Fe_2O_3/Fe_3O_4/WBC composite for Cr(V) adsorption. (Jamilatun et al., 2023) investigated the activation of biochar from sugarcane bagasse using 3M HCl soaked and ultrasonicated at 60 °C. (Chen et al., 2021) investigation of biochar modification from sugarcane bagasse using iron-doped base (KOH) activation to remove imidacloprid (IMI) from water. (Pereira Da Silva et al., 2019) conducted research on biochar from sugar cane using iron salts including nitrate, acetate, and a mixture of both to remove colouring substances. (Praipipat et al., 2023) conducted research on the modification of biochar from sugarcane bagasse using iron(III) oxide-hydroxide to remove lead(II) ions. None of the studies mentioned above have explained the modification of biochar composites from sugarcane using iron (Fe) from magnetic separation of beach sand. The combination of Fe (iron) from beach sand and C (Carbon) catalyst from biochar has not been widely explored by previous researchers. The use of iron (Fe) from beach sand as the main material provides a unique dimension to this research because beach sand has not been explored as a source of material in the synthesis of catalytic materials. Meanwhile, Biochar as a catalyst carbon source adds complexity and novelty, because biochar is obtained from wasted biomass materials.

Therefore, the focus of this research is to modify the biochar derived from sugarcane bagasse that combined with iron (Fe) from magnetic separation of beach sand. the combination between the biochar and iron can become advanced materials, namely, Fe/C catalysts that can be applied to the treatment of batik dye wastewater treatment with the Heterogeneous Fenton from the wet impregnation method. By exploring the combination of iron from beach sand and catalyst C from biochar, this research could open the door to further understanding of the potential of these materials in the field of catalysis and sustainable process development.

MATERIALS AND METHODS

Material and biochar preparation

This research was conducted through four stages of the process:

1. Biochar in this research was obtained from sugarcane bagasse by using pyrolysis process. The pyrolysis process of sugarcane bagasse has been completed in previous research (Jamilatun et al., 2023; Jamilatun et al., 2022). Pyrolysis was carried out using 15 g of bagasse in the reactor sleeve. The sleeve was inserted into the fixed bed reactor and tightly closed. Then, it was warmed up with a heating rate of 10–12 °C/min. Pyrolysis temperature was set at (300, 400, 500, 550, and 600 °C) for 60 minutes or until there were no more drips. After each pyrolysis, the equipment was cooled, and the biochar product was retrieved from the reactor. The pyrolysis process is a thermal method at high temperatures that can convert organic material in decomposed sugarcane bagasse into biochar (Wasakorn Treedet, Ratchaphon Suntivarakorn, Ilham Mufandi, 2021). Before pyrolysis process is conducted, sugarcane bagasse is dried under sunlight to reduce the water content. The high of water content in sugarcane bagasse can increase energy consumption in the pyrolysis process. This initial stage is an important parameter for producing biochar with excellent adsorption levels.
2. Iron-modified biochar was conducted with sand synthesis for obtaining Fe particles. this stage is a modified material Fe from sand synthesis and C from biochar. The aim of this stage is to integrate iron particles into the biochar structure and forming a modified Fe/C catalyst.
3. Application of IMB on MB as one of the synthetic dyes used in the batik industry. At this stage it is hoped that IMB can effectively reduce contamination in batik wastewater
4. Analysis of the characteristics of biochar as an adsorbent to reduce pollution of batik wastewater. It should be noted that the Fe/C catalyst was used with the aim of improving the quality of biochar adsorption in batik wastewater (Qin et al., 2022).

Experiment process can be seen in Figure 1. Raw material of sugarcane bagasse was collected from the Madukismo Sugar Factory. BC (Biochar) is obtained from the pyrolysis of bagasse. Preparation of biochar using pyrolysis method refers to previous studies (Jamilatun et al., 2020;

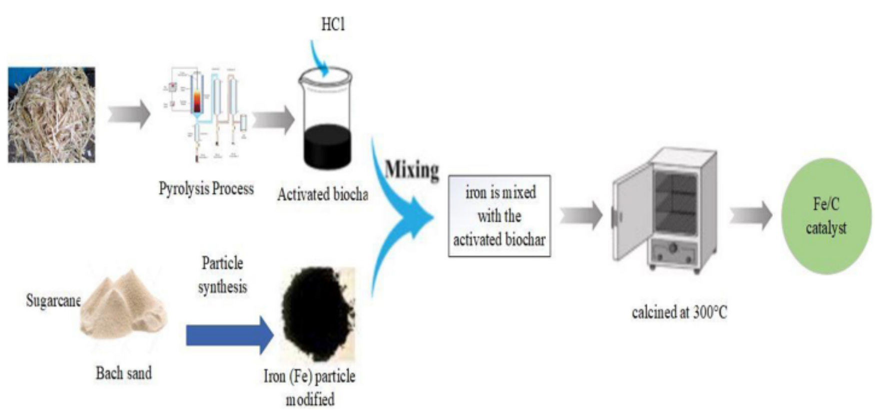

Figure 1. Experimental process

Pitoyo et al., 2022). The activation process is described in detail. The biochar is filtered with a 140 mesh sieve to separate the biochar particles. The activation method is used to increase the ability of biochar as an adsorbent. In this study, 3M HCL solution was used as a solvent for biochar activation. Biochar was soaked with 3 M HCL solution, then the mixed container was covered with aluminium foil and ultrasonicated at 60 °C for 1 hour. last process was washed using distilled water until the pH was neutral (pH 7) and dried in the oven at 120 °C for 2 hours.

Material modification/fabrication of IMB from beach sand

The material modification was applied to prepare the Fe Particle from beach sand. The step of the process to obtained the Fe from beach sand can be seen in Figure 2. Firstly, magnetite crystal was extracted from 500 g of beach sand that extracted by using a magnetic separator. The extracted magnetite was sieved with sized of 140 mesh. Secondly, 10 g of magnetite particles were dispersed in 54 mL of 12 M HCl (37%) and allowed to be ultrasonicated. The frequency used in this process is 30 kHz for 1 hour. The suspension solution was filtered using 0.8 m filter paper to obtain FeCl2 and FeCl3 solutions. Approximately ± 50 mL of the 6.5 M NH_4OH solution was added to the filtered solution one drop at a time into a black deposit was formed. Thirdly, the precipitate was washed repeatedly with ethanol and distilled water into a neutral pH was reached. The precipitate was separated from the solution by centrifugation, then dried in an oven at 60 °C for ± 12 hours. After obtaining the iron magnetic nanoparticles, it was dispersed in isopropyl alcohol at various concentrations including 2%, 4%, and 6%. Subsequently, the solution was mixed with activated carbon and subjected to ultrasonication for 1 hour. The mixture was then dried for 24 hours to allow the isopropyl alcohol to evaporate. Following this, the mixture was calcined at 300 °C for 3 hours. Finally, the Fe/C catalyst was characterized using SEM-EDX, pH, and BET.

Determination of the optimum wavelength

This step is the important in chemical analysis using the spectrophotometric method. The absorbance of the optimum wavelength of blue textile dye was measured from 500–600 nm at 10 nm intervals. Absorbance measurements were carried out at a concentration of 20 ppm using a UV-Vis spectrophotometer.

Waste degradation test with IMB

Schematic of the degradation of methylene blue as a synthetic dye in batik wastewater using IMB can be seen in Figure 3. This scheme illustrates the steps in the adsorption process of methylene blue in water, which will adhere to the carbon surface due to physical and chemical interactions. The duration of contact between wastewater and activated carbon is critical for effective adsorption (Amelia et al., 2020).

A total of 200 ml of blue synthetic waste with a concentration of 20 ppm was put into a glass beaker. Then add 10 ml of 50% H_2O_2, stirred with a magnetic stirrer at 450 rpm. Enter the Fe/C catalyst that was obtained in the previous step as much as 5 mg into the container with stirring

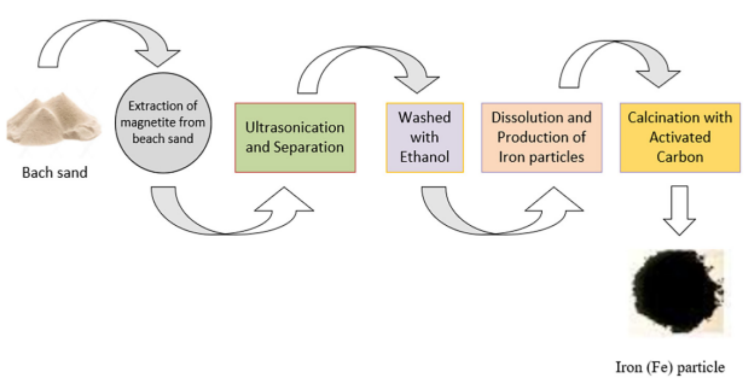

Figure 2. Fe particle process from beach sand

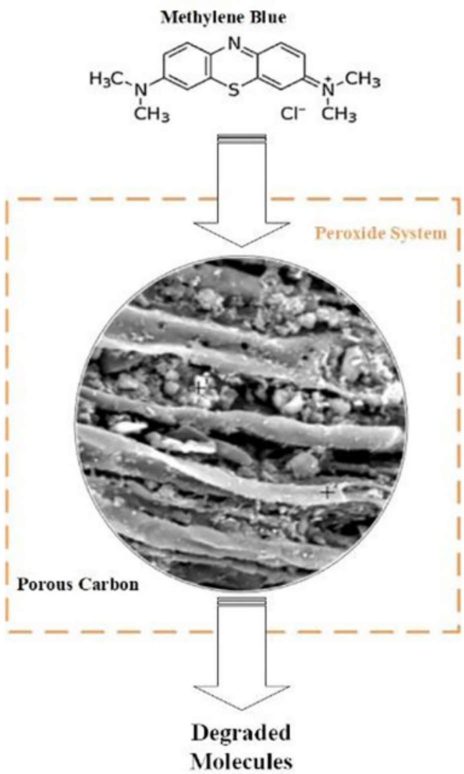

Figure 3. Schematic of the degradation of methylene blue using IM

speed of 450 rpm. For testing the waste degradation, a sample of 5 ml each at a certain time interval was tested with a UV-VIS spectrophotometer. IMB immersion into batik wastewater was carried out in various ways, namely 30, 60, 90, 120, and 180 minutes. The mixture of Fe in IMB varies around 2% Fe, 4% Fe, and 6% Fe. The relationship between degradation of batik wastewater with soaking time and Fe content in IMB has been calculated using the coefficient of determination (R^2) with equation 1. The coefficient of determination (R^2) is used to evaluate how well a linear regression model fits the observed empirical data. The relationship between Batik waste degradation with soaking time and Fe content using the coefficient of determination gives an idea of how much variability in Batik waste degradation can be explained by the model you use. The higher the R^2value, the greater the proportion of variability that can be explained by the model, indicating that the model fits the experimental data excellent.

$$R^2 = 1 - \frac{SST}{SSE} \quad (1)$$

In his calculation, SSE is the square of the number of errors (residual squared). While SST is the sum of the squared variations in the dependent variable. This regression model is used to determine the effect of the independent variable on the dependent variable. the R-squared value is between 0–1. The R squared value of 0.75 belongs to the strong category, 0.50 is the moderate category, and R squared 0.25 is the weak category. The closer to number 1, the better the relationship between the independent and dependent variables (Dziejarski, 2022; Tagbo et al., 2022).

RESULTS AND DISCUSSION

Properties of iron-modified biochar (IMB)

In this study, biochar was obtained from sugarcane bagasse sourced from the Madukismo Sugar Factory. It was dried for 4 days and was heated for 1 hour. Iron is obtained from modification of iron particles from beach sand. The process of the making Fe particles from beach sand can be seen in Figure 2. The IMB was carried out to improve the quality of biochar in absorbing batik wastewater. Biochar from sugarcane pyrolysis is activated using Fe particles from beach sand. Activation process is to break the hydrocarbon bonds. IMB was mixed between Fe Particles modified from beach sand and Biochar from sugarcane bagasse. For knowing the capability of IMB, this research has characteristics including specific surface area, micropore area, total pore volume, micropore volume, and average pore diameter. The properties of IMB can be seen in Table 1.

According to Table 1, IMB was found that the specific surface area (S_{BET}) of 64.983 m^2/gram, micropore area (S_{mic}) of 46.215 m^2/gram, percent S_{mic} of 71.7%, total pore volume of 0.60 cm^3/gram, micropore volume (V_{mic}) of 0.25 cm^3/gram, V_{mic} percentage of 41.7%, and average pore diameter of 2.043 nm. According to the International Union of Pure and Applied Chemistry (IUPAC), pores are categorized into three groups based on their sizes: macro (> 50 nm), meso (2–50 nm), and micropores (< 2 nm) (Sing, 1985; Thommes et al., 2015). The characteristics of IMB in this article demonstrate that it belongs to the micropore category. Microscopic structures are formed as lignin undergoes carbonization, leading to the production

Table 1. Properties of IMB based on BET analysis

Characteristic	Value
Specific surface area (S_{BET}), m²/gram	64.983
Micropore area (S_{mic})	46.215
% S_{mic}	71.1
Total pore volume, cm³/gram	0.60
Micropore volume (V_{mic}), cm³/gram	0.25
% V_{mic}	41.7
Average pore diameter, nm	2.043

of more micropores (Zhang et al., 2022). The value of 64.983 m²/gram shows that biochar has a fairly large specific surface area. This usually correlates with the presence of pores. The micropore area (S_{mic}) value is 46.215 m²/gram and the micropore area (S_{mic}) percentage is 71.1%, indicating that most of the biochar pores are micropores. The total pore volume of 0.60 cm³/gram indicated the total amount of empty space in the biochar. The micropore volume of 0.25 cm³/gram and the V_{mic} percentage of 41.7% reaffirm that this biochar has a significant amount of porosity in the form of micropores. The average pore diameter of 2.043 nm indicated that the biochar pores are mostly microscopic in size (micropore). Micropores are very small in size, so they have a high specific surface area per unit mass. This allows materials with micropores to have a large gas or liquid absorption capacity. Micropore has strong adsorption properties for small molecules, such as gases or organic compounds. This makes micropores often used in applications such as exhaust gas adsorption, water purification, or air pollutant reduction.

The formation of biochar structure is influenced by pyrolysis temperature and activation time. According to [46], [47] the structure and properties of biochar experience significant changes as the pyrolysis temperature increases. These results reflect the influence of pyrolysis temperature on the formation and evolution of biochar. Microporous evolution occurs through three stages including phase separation, migration, and thermal degradation (Chen et al., 2015). Based on the statement above, the results of this research are relevant in that IMB has the microporous category resulting from thermal degradation and phase separation. The pore structure is also affected by an increase in activation time which can cause the carbon structure to break down and cause cross-linking which results in collapsed pores (Borhan et al., 2019). In this study, the micropore surface area was obtained 71.1%. in other words, the surface area of mesopores and macropores are smaller than that of micropores. The percentage of micropore can contribute to the outer surface and volume of the micropore. These findings are relevant to the study (Loc et al., 2022; Phuong et al., 2016). The results of the micropore surface area make a major contribution to the overall surface area of biochar. Surface area with IMB content has a positive correlation as described in the SEM analysis section 3.2.

SEM analysis of IMB

In this part, SEM revealed the pore structure of activated biochar using Fe particles from beach sand. Fe particles have been placed and stabilized in IMB. The presence of Fe particles has also been presented in graphical form. IMB activation uses the impregnation method of the catalyst precursor. Iron (Fe) from the beach sand was put into the biochar pores. In this study, 196 pm iron (Fe) was applied in the IMB because ions can easily enter into the pores of the IMB. The size of the iron is important. The impregnation process is carried out by contacting the metal solution on the surface of the biochar. The next stage is the formation of iron (Fe) oxide using the drying process and calcination process. The distribution of iron oxide on the carbon surface is very important in the impregnation process of iron oxide on the carbon surface. Metal distribution on the carbon surface will maximize the absorption process. In this study, a catalyst morphology analysis was tested by using Scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy. The results of the tests can be seen in Figure 4.

Based on Figure 4, the presence of iron (Fe) from beach sand shows an increase in the pore structure and pore surface area. In addition, the carbon content contained in IMB shows that the higher the carbon content, the better IMB is in absorbing heavy metals in batik wastewater. Four variations of Fe from beach sand include CF-0%, CF-2%, CF-4%, and CF-6% for each variation of the Fe sample that used in this research. The results of the SEM-EDX indicated that the addition of 0% Fe ions (CF-0%) showed irregular surface morphology and no visible pores on the carbon surface. Furthermore, The addition of 2% Fe ions (CF-2%) showed regular surface results and visible pores on the carbon surface, although it had porosity with uneven sizes.”. The addition of Fe ions as much as 4% and 6% resulted in the porous structure of the

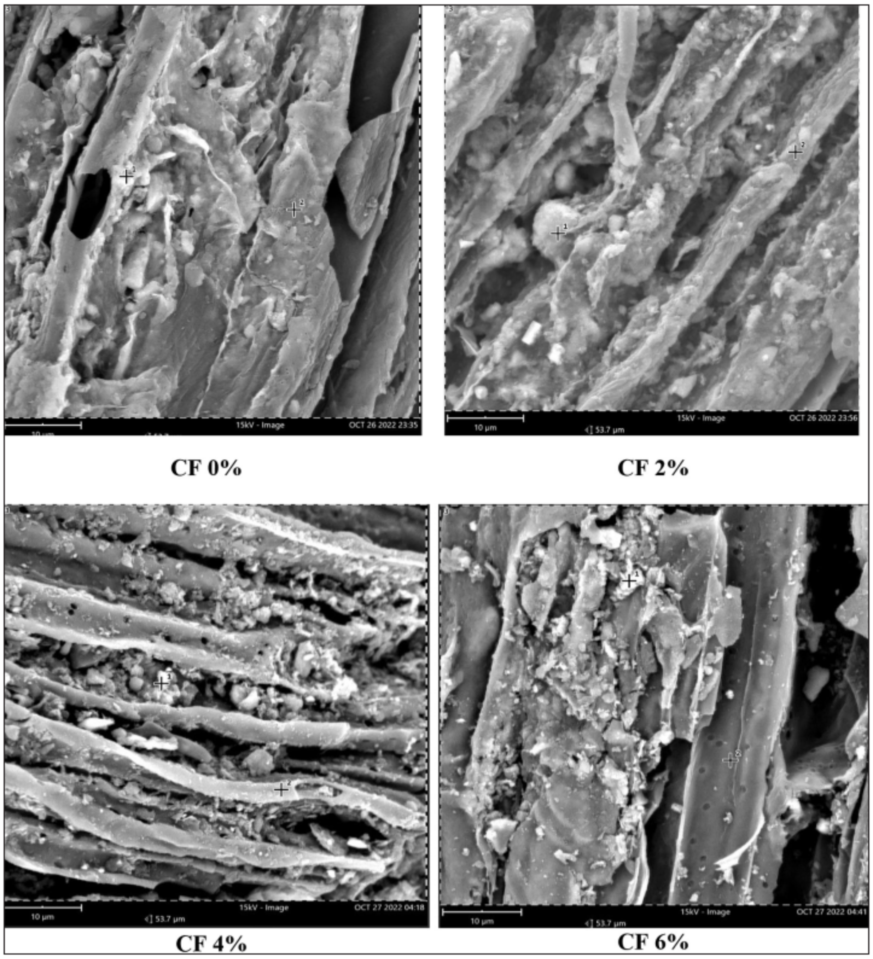

Figure 4. Morphology structure on IMB based on SEM analysis

carbon being clearly visible. This indicates that the mixture of Fe ions has been impregnated by oxidation of iron on the carbon surface. In addition, the difference in Fe and Carbon content in biochar can also be affected by the calcination process for the formation of iron (Fe) oxidation. According to (Leng et al., 2021; Liao et al., 2022) biochar has a different pore structure depending on the pre-treatment process and the operating temperature used. The pore size of biochar can be based on the influence of temperature. The iron content in carbon can affect the absorption process. The distribution of iron oxide on the biochar surface can be seen in Figure 5. the addition of Fe ions to biochar showed an increase in carbon content in biochar. The carbon content in biochar increases in line with the addition of Fe ion levels. The highest levels of Fe and carbon were found in the addition of 6% Fe ions resulting.

Optimal wavelength of adsorption

The determination of the wavelength of adsorption was determined using a UV-Vis spectrophotometer to explain the maximum adsorption quality in batik wastewater. Maximum absorption measurements in this study used the UV-Vis spectrophotometer method. This method is used to measure the absorption or adsorbance power of a liquid (batik waste) against light wavelengths. The UV-Vis spectrophotometer works to send light from a light source through a liquid sample. In principle, this method reflects light which provides information on the concentration

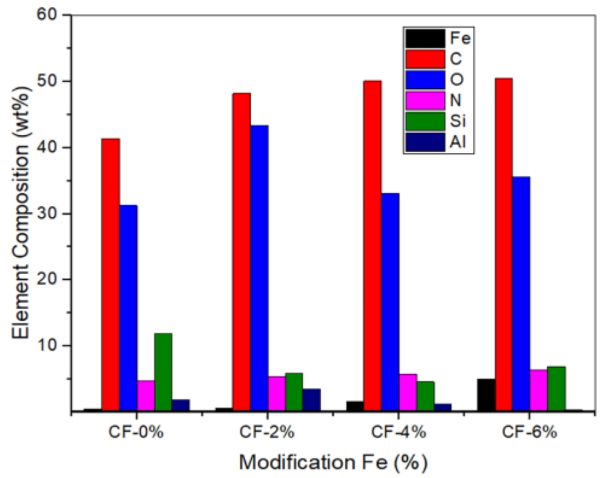

Figure 5. Element composition of IMB based on SEM analysis

of compounds. In this research, batik waste was trapped using biochar which had been modified using iron (Fe) from beach sand. The level of absorption of batik waste water can be seen from the wavelengths produced by the Uv-Vis spectrophotometer test. The wavelength shows the adsorbance reading so that the validation carried out can determine the quality of biochar for absorbing metals in batik waste. Data from wavelength measurements on batik wastewater absorption was measured from 400–600 nm with an interval of 10 nm. The measurement of adsorption was carried out at a concentration of 20 ppm using UV-Vis spectrophotometry. It was seen that the highest adsorption peak of the solution was observed at the optimum wavelength of 571 nm with an adsorption level of 0.155. This wavelength is the complementary colour of the measured solution which has been used to calculate the batik wastewater degradation test using IMB with Fe of 6% in the next section. The determination of the wavelength in wastewater can be seen in Figure 6.

Effect of pH

In this section, the effect of pH on the absorption of methylene blue (MB) with a carbon catalyst from sugarcane bagasse with percentages

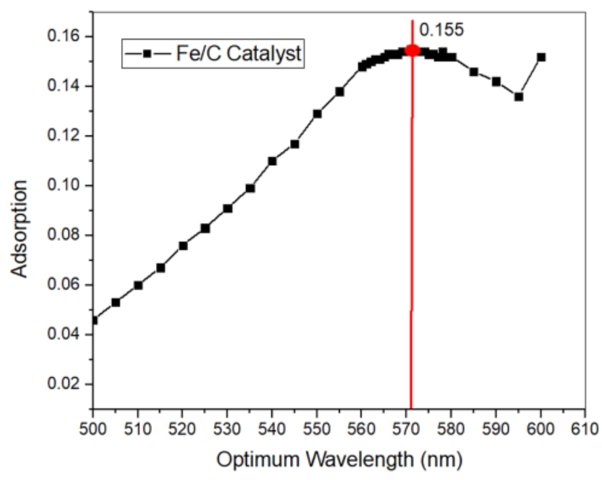

Figure 6. Optimum wavelength of iron-modified biochar (IMB) based on UV-Vis spectrophotometer

of 10%, 20%, and 30%. pH is an important parameter in the adsorption process. The methylene blue solution used was 100 ml with 5 grams of catalyst. Reaction times occurred at varying times from 0, 30, 45, 60, 90, 120, and 180 minutes. The results of research on the influence of pH on MB can be seen in Figure 7.

Based on Figure 7, the initial pH of MB is indicated to be acidic. After immersion or reaction with a carbon catalyst, MB degrades to a neutral or normal pH. In all tests, the carburet catalyst with a percentage of 30% showed more significant changes in pH. The increase in pH over time can be related to the adsorption capacity of activated carbon. A low initial pH (acid) indicated a decreased dye adsorption efficiency. According to (Salahshour et al., 2021), acidic pH has a positively charged adsorbent surface and methylene blue has a cationic charge so that a repulsive force occurs between the cationic surface and the adsorbent surface. This shows that acidic pH cannot be used properly in the methylene blue adsorption process. On the other hand, an increase in pH causes the surface of the adsorbent to be negatively charged so that an attractive force occurs between the surface of the adsorbent and the cationic methylene blue.

This experiment provides significant insight regarding the transformation of MB in acidic wastewater conditions. At the start of the experiment, the pH of the Methylene Blue solution was very low indicating an acidity level that was potentially dangerous for the environment. However, through the degradation process that occurs during the reaction with Activated Carbon, the pH of the solution increases until it reaches a neutral or normal level. These results have very positive implications, indicating that wastewater which originally contained methylene blue in an acidic state can be converted into a solution that is much safer for the surrounding environment.

Removal test of batik wastewater with IMB

The IMB (Iron-Modified Biochar) application was applied to batik wastewater. Batik waste is one of the water pollutions caused by the industry which contains heavy metals Cr and Pb which are toxic from dyes ($CrCl_3$, $k_2Cr_20_7$) or from other substances. The pollution of liquid waste from the batik industry damages the aquatic ecosystem and endangers the surrounding environment. From the experimental results, IMB with a mixture of 6% Fe and soaking for 180 minutes showed the highest decrease in batik wastewater, around 69%. This proves that the mixture of Fe in IMB can significantly reduce batik wastewater pollution. The results of this study are relevant to research conducted by (Ali et al., 2014) that the adsorbent dose or the concentration of the adsorbent used can affect the adsorption of magnetic biochar. The absorption of batik waste experienced a significant reduction within 180 minutes. This study proves that modified Fe obtained from beach sand can increase the absorption of batik waste. The results of absorption of batik waste can be seen in Figure 8. The immersion time of IMB in batik wastewater solution also affects the level of

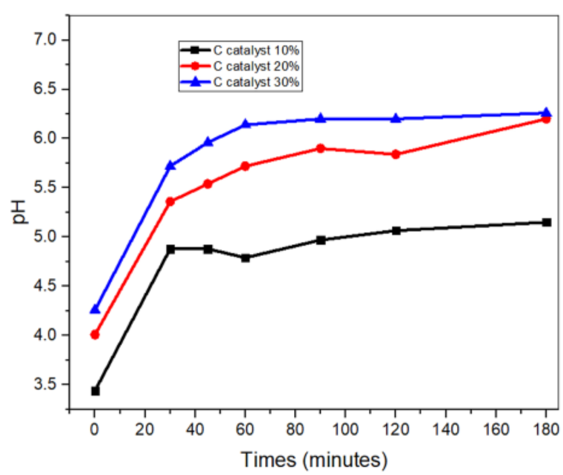

Figure 7. Effect of pH on IMB

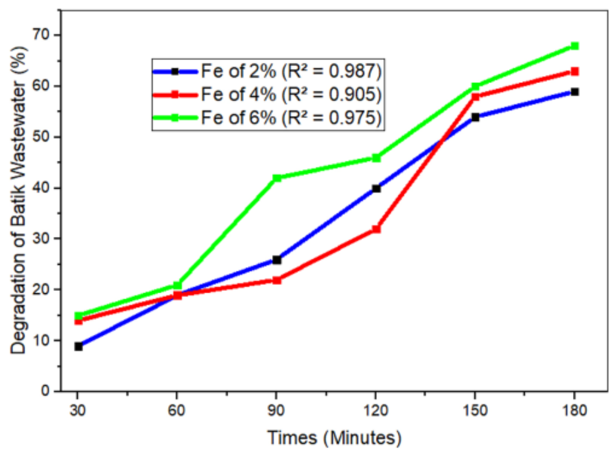

Figure 8. Comparison of Fe concentration on batik waste degradation results

reduction in wastewater pollution. The longer the immersion of wastewater in the IMB, the higher the reduction in wastewater pollution levels**.** The relationship between degradation of batik wastewater with soaking time and Fe content in IMB has been calculated. In this study, the relationship between the degradation of batik wastewater with different mixtures of Fe (2%, 4%, and 6%) was examined with resulting in R^2 values of 0.987, 0.905, and 0.975, respectively. The results of the regression analysis indicate that the residual errors in the regression models are relatively small.

Furthermore, the removal of batik wastewater using IMB with a Fe concentration of 6% has been tested on batik dyes consisting of yellow, fast green, methylene blue, red, and methylene orange that can be seen in Figure 9. This test was carried out using the Fenton heterogeneous method. Based on the research results, degradation of batik dye with Fe 6%/C using the heterogeneous Fenton method showed a significant decrease in concentration. The percentage of removal at 180 minutes using the heterogeneous Fenton method obtained for degradation of dyes yellow of 16%, fast green of 3%, methylene orange of 4%, red of 3%, and methylene blue of 23%. The variation of degradation efficiency in dyes is influenced by the molecular structure. Methylene blue has a simpler chemical structure than fast green or others that can affect the interaction with Fe/C catalytic materials. Methylene blue is a wet dye with cationic properties that tend to be more easily adsorbed on negatively charged surfaces on biochar. Meanwhile, fast green is an anionic dye with a more complex molecular structure, including additional functional groups such as sulfonates, which can inhibit its adsorption and degradation. These results are relevant to research from (Tran et al., 2024) that the cationic nature of methylene blue is more easily adsorbed on the surface of biochar. In addition, the cationic nature of Methylene Blue allows significant electrostatic attraction to negatively charged sites on biochar (He et al., 2024). These colours are often used to make batik, therefore innovation in absorption technology is needed before the wastewater from batik is discharged into rivers.

Method limitations and production challenges

One of the major limitations of the heterogeneous Fenton method used is its sensitivity to pH. Variations in pH in industrial wastewater can result in decreased efficiency, posing a challenge for large-scale applications. In addition, there is a risk of iron ions leaching from biochar which can cause secondary pollution, so the stability of iron-enriched biochar needs to be further evaluated, including the environmental impact of residual iron in treated water. Industrial-scale biochar production also faces significant challenges, such as the need for a consistent and quality supply of raw materials, and high production costs, including energy, labour, and equipment. In addition, optimization of the production process is required to ensure that the biochar properties are maintained as production scales up. The environmental impacts of large-scale biochar production,

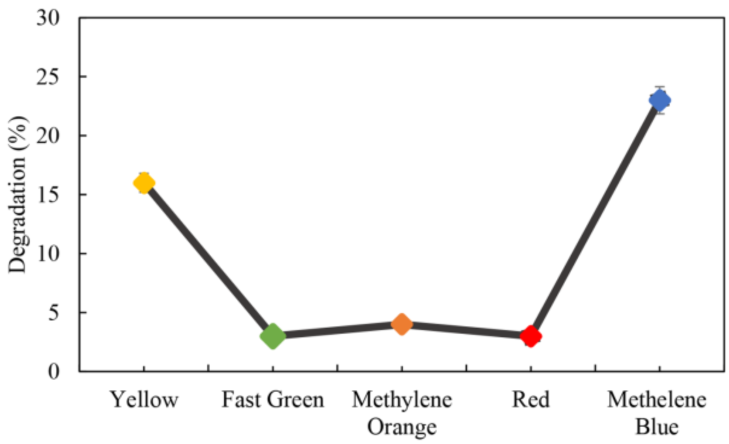

Figure 9. Evaluation of batik waste removal using activated carbon/Fe_2O_3

including energy consumption and carbon footprint, also need to be considered, and a life cycle assessment (LCA) may be required to evaluate these impacts in their entirety.

CONCLUSION

In this research, IMB has been applied to batik wastewater. The formation of biochar structure is influenced by pyrolysis temperature and activation time. The results of this research are relevant because IMB has a micropore category because of thermal degradation and phase separation. The pore structure is also influenced by increasing the activation time, which can cause changes in the carbon structure. The use of IMB with the addition of Fe particles from beach sand can modify the pore structure of biochar, increase porosity, and optimally absorb heavy metals. Additionally, the highest adsorption peak of the solution was observed at the optimum wavelength of 571 nm with an adsorption peak of 0.155. IMB was applied to batik waste with resulting that the highest dye reduction of 2%, 4%, and 6% Fe with removal percentages of 59%, 63%, and 69%, respectively. increasing pH can be considered as a key factor in improving the adsorption efficiency of methylene blue by carbon catalyst from sugarcane bagasse. Furthermore, the degradation of industrial batik waste with IMB using the heterogeneous Fenton method is more effective. The percentage of removals at 180 minutes using the heterogeneous Fenton method obtained for degradation of dyes yellow of 16%, fast green of 3%, methylene orange of 4%, red of 3%, and methylene blue of 23%.

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REFERENCES

1. Abdelhameed, R.M., Emam, H.E. 2019. Design of ZIF(Co & Zn)@wool composite for efficient removal of pharmaceutical intermediate from wastewater. Journal of Colloid and Interface Science, 552, 494–505. https://doi.org/10.1016/j.jcis.2019.05.077
2. Adegoke, K.A., Akinnawo, S.O., Adebusuyi, T.A., Ajala, O.A., Adegoke, R.O., Maxakato, N.W., Bello, O.S. 2023. Modified biomass adsorbents for removal of organic pollutants: a review of batch and optimization studies. International Journal of Environmental Science and Technology, 20(10), 11615–11644. https://doi.org/10.1007/s13762-023-04872-2
3. Ahmed, A.S., Alsultan, M., Hameed, R.T., Assim, Y.F., Swiegers, G.F. 2022. High surface area activated charcoal for water purification. Journal of Composites Science, 6(10), 1–9. https://doi.org/10.3390/jcs6100311
4. Ali, S., Zhu, J., Muhammad, N., Sheng, T. 2014. Science direct effect of synthesis methods on magnetic Kans grass biochar for enhanced As (III, V) adsorption from aqueous solutions.

Biomass and Bioenergy, 71(V), 299–310. https://doi.org/10.1016/j.biombioe.2014.09.027

5. Ambaye, T.G., Vaccari, M., van Hullebusch, E.D., Amrane, A., Rtimi, S. 2021. Mechanisms and adsorption capacities of biochar for the removal of organic and inorganic pollutants from industrial wastewater. International Journal of Environmental Science and Technology, 18(10), 3273–3294. https://doi.org/10.1007/s13762-020-03060-w
6. Amelia, S., Sediawan, W.B., Mufrodi, Z., Ariyanto, T. 2019. Modification of iron oxide catalysts supported on the biomass based activated carbon for degradation of dye wastewater. Jurnal Bahan Alam Terbarukan, 7(2), 164–168. https://doi.org/10.15294/jbat.v7i2.17174
7. Amelia, S., Sediawan, W.B., Prasetyo, I., Munoz, M., Ariyanto, T. 2020. Role of the pore structure of Fe/C catalysts on heterogeneous Fenton oxidation. Journal of Environmental Chemical Engineering, 8(1), 102921. https://doi.org/10.1016/j.jece.2019.102921
8. Bai, L., Su, X., Feng, J., Ma, S. 2021. Preparation of sugarcane bagasse biochar/nano-iron oxide composite and mechanism of its Cr (VI) adsorption in water. Journal of Cleaner Production, 320(July), 128723. https://doi.org/10.1016/j.jclepro.2021.128723
9. Bayoka, H., Snoussi, Y., Bhakta, A.K., El Garah, M., Khalil, A.M., Jouini, M., Ammar, S., Chehimi, M.M. 2023. Evidencing the synergistic effects of carbonization temperature, surface composition and structural properties on the catalytic activity of biochar/bimetallic composite. Journal of Analytical and Applied Pyrolysis, 173, 106069. https://doi.org/https://doi.org/10.1016/j.jaap.2023.106069
10. Borhan, A., Yusup, S., Lim, J.W., Show, P.L. 2019. Characterization and modelling studies of activated carbon produced from rubber-seed shell using KOH for CO_2 adsorption. Processes, 7(11). https://doi.org/10.3390/pr7110855
11. Chen, H., Yang, X., Liu, Y., Lin, X., Wang, J., Zhang, Z., Li, N., Li, Y., Zhang, Y. 2021. KOH modification effectively enhances the Cd and Pb adsorption performance of N-enriched biochar derived from waste chicken feathers. Waste Management, 130, 82–92. https://doi.org/10.1016/j.wasman.2021.05.015
12. Chen, L., Ji, T., Yuan, R., Mu, L., Brisbin, L., Zhu, J. 2015. Unveiling mesopore evolution in carbonized wood: interfacial separation, migration, and degradation of lignin phase. ACS Sustainable Chemistry & Engineering, 3(10), 2489–2495. https://doi.org/10.1021/acssuschemeng.5b00563
13. Cheng, N., Wang, B., Wu, P., Lee, X., Xing, Y., Chen, M., Gao, B. 2021. Adsorption of emerging contaminants from water and wastewater by modified biochar: A review. Environmental Pollution, 273, 116448. https://doi.org/https://doi.org/10.1016/j.envpol.2021.116448
14. Dalai, C., Jha, R., Desai, V.R. 2015. Rice husk and sugarcane baggase based activated carbon for iron and manganese removal. Aquatic Procedia, 4(Icwrcoe), 1126–1133. https://doi.org/10.1016/j.aqpro.2015.02.143
15. Dziejarski, A.M.K.-C. and Dziejarski, B. 2022. Linear and non-linear regression analysis for the adsorption kinetics of SO_2 in a fixed carbon bed reactor-a case study. Energies, 15, 1–22.
16. Dzoujo, H.T., Shikuku, V.O., Tome, S., Akiri, S., Kengne, N.M., Abdpour, S., Janiak, C., Etoh, M.A., Dina, D. 2022. Synthesis of pozzolan and sugarcane bagasse derived geopolymer-biochar composites for methylene blue sequestration from aqueous medium. Journal of Environmental Management, 318(June), 115533. https://doi.org/10.1016/j.jenvman.2022.115533
17. Guo, F., Dong, Y., Dong, K., Xu, L., Liu, S., Qiao, Q., Wei, H., Wang, Y. 2023. Role of biochar-based catalysts in microwave-induced biomass pyrolysis: Structural properties and modification with Fe-series metals. Fuel, 341(September 2022), 127769. https://doi.org/10.1016/j.fuel.2023.127769
18. He, Q., Qi, B., Zhang, D., Yi, X. 2024. Adsorption characteristics of methylene blue onto biochar derived from lavender straws. In D. Han M.J.K. Bashir (Eds.), Environmental Governance, Ecological Remediation and Sustainable Development (ICEPG 2023) 23–36. Springer Nature Switzerland.
19. Ich.unesco.org. 2009. Reference from UNESCO Website: (https://ich.unesco.org/en/RL/indonesian-batik-00170).
20. Jamilatun, S., Amelia, S., Pitoyo, J., Ma'Arif, A., Mufandi, I. 2023. Preparation and characteristics of effective biochar derived from sugarcane bagasse as adsorbent. International Journal of Renewable Energy Research, 13(2), 673–680. https://doi.org/10.20508/ijrer.v13i2.13719.g8737
21. Jamilatun, S., Mufandi, I., Evitasari, R.T., Budiman, A. 2020. Effects of temperature and catalysts on the yield of bio-oil during the pyrolysis of Spirulina platensis residue. International Journal of Renewable Energy Research, 10(2), 678–686.
22. Jamilatun, S., Pitoyo, J., Amelia, S., Ma'arif, A., Hakika, D.C., Mufandi, I. 2022. Experimental study on the characterization of pyrolysis products from bagasse (*Saccharum Officinarum* L.): bio-oil, biochar, and gas products. Indonesian Journal of Science and Technology, 7(3), 565–582. https://doi.org/10.17509/ijost.v7i3.51566
23. Jamilatun, S., Pitoyo, J., Amelia, S., Ma, A., Hakika, D.C., Mufandi, I. 2022. Experimental study on the characterization of pyrolysis products from bagasse (*Saccharum Officinarum* L.) : bio-oil, biochar, and gas products. Indonesia Journal of Science and Technology, 7(3), 565–582.
24. Jiang, B., Lin, Y., Carl, J. 2018. Biochar derived

from swine manure digestate and applied on the removals of heavy metals and antibiotics. Bioresource Technology, 270(August), 603–611. https://doi.org/10.1016/j.biortech.2018.08.022

25. Lam, Y.F., Lee, L.Y., Chua, S.J., Lim, S.S., Gan, S. 2016. Insights into the equilibrium, kinetic and thermodynamics of nickel removal by environmental friendly *Lansium domesticum* peel biosorbent. Ecotoxicology and Environmental Safety, 127, 61–70. https://doi.org/https://doi.org/10.1016/j.ecoenv.2016.01.003
26. Leng, L., Xiong, Q., Yang, L., Li, H., Zhou, Y., Zhang, W., Jiang, S., Li, H., Huang, H. 2021. An overview on engineering the surface area and porosity of biochar. Science of the Total Environment, 763, 144204. https://doi.org/10.1016/j.scitotenv.2020.144204
27. Li, P., Zhou, M., Liu, H., Lei, H., Jian, B., Liu, R., Li, X., Wang, Y., Zhou, B. 2022. Preparation of green magnetic hydrogel from soybean residue cellulose for effective and rapid removal of copper ions from wastewater. Journal of Environmental Chemical Engineering, 10(5), 108213. https://doi.org/10.1016/j.jece.2022.108213
28. Li, Y., Yu, H., Liu, L., Yu, H. 2021. Application of co-pyrolysis biochar for the adsorption and immobilization of heavy metals in contaminated environmental substrates. Journal of Hazardous Materials, 420, 126655. https://doi.org/https://doi.org/10.1016/j.jhazmat.2021.126655
29. Liao, W., Zhang, X., Ke, S., Shao, J., Yang, H., Zhang, S., Chen, H. 2022. Effect of different biomass species and pyrolysis temperatures on heavy metal adsorption, stability and economy of biochar. Industrial Crops and Products, 186(May), 115238. https://doi.org/10.1016/j.indcrop.2022.115238
30. Loc, N.X., Tuyen, P.T.T., Mai, L.C., Phuong, D.T.M. 2022. Chitosan-modified biochar and unmodified biochar for methyl orange: adsorption characteristics and mechanism exploration. Toxics, 10(9). https://doi.org/10.3390/toxics10090500
31. Ma, Y., Li, M., Li, P., Yang, L., Wu, L., Gao, F., Qi, X., Zhang, Z. 2021. Hydrothermal synthesis of magnetic sludge biochar for tetracycline and ciprofloxacin adsorptive removal. Bioresource Technology, 319(September 2020). https://doi.org/10.1016/j.biortech.2020.124199
32. Manyatshe, A., Cele, Z.E.D., Balogun, M.O., Nkambule, T.T.I., Msagati, T.A.M. 2022. Chitosan modified sugarcane bagasse biochar for the adsorption of inorganic phosphate ions from aqueous solution. Journal of Environmental Chemical Engineering, 10(5), 108243. https://doi.org/10.1016/j.jece.2022.108243
33. Maryudi, M., Amelia, S., Salamah, S. 2019. Removal of methylene blue of textile industry waste with activated carbon using adsorption method. Reaktor, 19(4), 168–171. https://doi.org/10.14710/reaktor.19.4.168-171
34. Mubarik, S., Saeed, A., Athar, M.M., Iqbal, M. 2016. Characterization and mechanism of the adsorptive removal of 2,4,6-trichlorophenol by biochar prepared from sugarcane baggase. Journal of Industrial and Engineering Chemistry, 33, 115–121. https://doi.org/10.1016/j.jiec.2015.09.029
35. Mufandi, I., Treedet, W., Singbua, P., Suntivarakorn, R. 2020. Efficiency of bio - oil production from napier grass using circulating fluidized bed reactor with bio - oil scrubber. KKU Research Journal, 20(December), 94–107.
36. Oginawati, K., Suharyanto, Susetyo, S.H., Sulung, G., Muhayatun, Chazanah, N., Dewi Kusumah, S. W., Fahimah, N. 2022. Investigation of dermal exposure to heavy metals (Cu, Zn, Ni, Al, Fe and Pb) in traditional batik industry workers. Heliyon, 8(2), e08914. https://doi.org/10.1016/j.heliyon.2022.e08914
37. Omiri, J., Snoussi, Y., Bhakta, A.K., Truong, S., Ammar, S., Khalil, A.M., Jouini, M., Chehimi, M.M. 2022. Citric-acid-assisted preparation of biochar loaded with copper/nickel bimetallic nanoparticles for dye degradation. In Colloids and Interfaces 6(2). https://doi.org/10.3390/colloids6020018
38. Pellera, F.-M., Giannis, A., Kalderis, D., Anastasiadou, K., Stegmann, R., Wang, J.-Y., Gidarakos, E. 2012. Adsorption of Cu(II) ions from aqueous solutions on biochars prepared from agricultural by-products. Journal of Environmental Management, 96(1), 35–42. https://doi.org/https://doi.org/10.1016/j.jenvman.2011.10.010
39. Da Silva, C.P., Da Guarda Souza, M.O., Dos Santos, W.N.L., Silva, L.O.B. 2019. Optimization of the production parameters of composites from sugarcane bagasse and iron salts for use in dye adsorption. Scientific World Journal, 2019. https://doi.org/10.1155/2019/8173429
40. Phuong, D.T.M., Miyanishi, T., Okayama, T., Kose, R. 2016. Pore characteristics & adsorption capacities of biochars derived from rice residues as affected by variety and pyrolysis temperature. American Journal of Innovative Research and Applied Sciences, 2(5), 179–189.
41. Praipipat, P., Ngamsurach, P., Sanghuayprai, A. 2023. Modification of sugarcane bagasse with iron(III) oxide-hydroxide to improve its adsorption property for removing lead(II) ions. Scientific Reports, 13(1), 1467. https://doi.org/10.1038/s41598-023-28654-5
42. Qin, J., Wang, J., Long, J., Huang, J., Tang, S., Hou, H., Peng, P. 2022. Recycling of heavy metals and modification of biochar derived from Napier grass using HNO3. Journal of Environmental Management, 318(June), 115556. https://doi.org/10.1016/j.jenvman.2022.115556

43. Qiu, B., Shao, Q., Shi, J., Yang, C., Chu, H. 2022. Application of biochar for the adsorption of organic pollutants from wastewater: Modification strategies, mechanisms and challenges. Separation and Purification Technology, 300(June), 121925. https://doi.org/10.1016/j.seppur.2022.121925
44. Salahshour, R., Shanbedi, M., Esmaeili, H. 2021. Methylene blue dye removal from aqueous media using activated carbon prepared by lotus leaves: Kinetic, equilibrium and thermodynamic study. Acta Chimica Slovenica, 68(2), 363–373. https://doi.org/10.17344/acsi.2020.6311
45. Saravanan, A., Kumar, P.S. 2022. Biochar derived carbonaceous material for various environmental applications: Systematic review. Environmental Research, 214(P1), 113857. https://doi.org/10.1016/j.envres.2022.113857
46. Sing, K.S.W. 1985. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity (Recommendations 1984). Pure and Applied Chemistry, 57(4), 603–619. https://doi.org/doi:10.1351/pac198557040603
47. Solayman, H.M., Hossen, M.A., Abd Aziz, A., Yahya, N.Y., Leong, K.H., Sim, L.C., Monir, M.U., Zoh, K.D. 2023. Performance evaluation of dye wastewater treatment technologies: A review. Journal of Environmental Chemical Engineering, 11(3), 109610. https://doi.org/10.1016/j.jece.2023.109610
48. Sutisna, S., Wibowo, E., Rokhmat, M., Rahman, D.Y., Murniati, R., Khairurrijal, K., Abdullah, M. 2017. Batik wastewater treatment using TiO_2 nanoparticles coated on the surface of plastic sheet. Procedia Engineering, 170, 78–83. https://doi.org/10.1016/j.proeng.2017.03.015
49. Tagbo, J., Ositadinma, N., Iheanacho, C., Chiedozie, C., Onu, C.E. 2022. Linear and nonlinear kinetics analysis and adsorption characteristics of packed bed column for phenol removal using rice husk - activated carbon. Applied Water Science, 12(5), 1–16. https://doi.org/10.1007/s13201-022-01635-1
50. Thommes, M., Kaneko, K., Neimark, A.V., Olivier, J.P., Rodriguez-Reinoso, F., Rouquerol, J., Sing, K.S.W. 2015. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). Pure and Applied Chemistry, 87(9–10), 1051–1069. https://doi.org/10.1515/pac-2014-1117
51. Tomczyk, A., Kondracki, B., Szewczuk-Karpisz, K. 2023. modification of biochars as a method to improve its surface properties and efficiency in removing xenobiotics from aqueous media. Chemosphere, 312(P1), 137238. https://doi.org/10.1016/j.chemosphere.2022.137238
52. Tran, H.D., Phuc, H.N., Phuong, P.V.H., Thien, L.N.P., Nguyen, T.L., Tran, U.P.N., Dang, V.-H. 2024. A proposed model for breakthrough curves of methylene blue adsorption on biochar. Chemical and Biochemical Engineering Quarterly, 38(2), 153–164. https://doi.org/10.15255/cabeq.2023.2280
53. Treedet, W., Suntivarakorn, R., Mufandi, I., Singbua, P. 2020. Bio-oil production from Napier grass using a pyrolysis process: Comparison of energy conversion and production cost between bio-oil and other biofuels. International Energy Journal, 20(2), 155–168.
54. Ullah, I., Nadeem, R., Iqbal, M., Manzoor, Q. 2013. Biosorption of chromium onto native and immobilized sugarcane bagasse waste biomass. Ecological Engineering, 60, 99–107. https://doi.org/10.1016/j.ecoleng.2013.07.028
55. Treedet, W., Suntivarakorn, R., Mufandi, I., Singbua P. 2021. Improvement of bio-oil production system by using spray condenser-investigation of yields, Properties, and Production Cost. BioEnergy Research.
56. Widjajanti, K., Prihantini, F.N., Wijayanti, R. 2022. Sustainable development of business with canvas business model approach: empirical study on MSMEs Batik Blora, Indonesia. International Journal of Sustainable Development and Planning, 17(3), 1025–1032. https://doi.org/10.18280/ijsdp.170334
57. Yaashikaa, P.R., Senthil Kumar, P., Varjani, S.J., Saravanan, A. 2019. Advances in production and application of biochar from lignocellulosic feedstocks for remediation of environmental pollutants. Bioresource Technology, 292(August), 122030. https://doi.org/10.1016/j.biortech.2019.122030
58. Yue, T., Cao, X., Liu, Q., Bai, S., Zhang, F., Liu, L. 2023. Enhancement on removal of oxytetracycline in aqueous solution by corn stover biochar: Comparison of KOH and KMnO4 modifications. Chemical Engineering Research and Design, 190, 353–365. https://doi.org/10.1016/j.cherd.2022.12.049
59. Zhang, X., Zhang, X., Zhao, S., Cai, Y., Wang, S. 2022. Sulfurized bimetallic biochar as adsorbent and catalyst for selective co-removal of cadmium and PAHs from soil washing effluents. Environmental Pollution, 314(October), 120333. https://doi.org/10.1016/j.envpol.2022.120333
60. Zhu, J. 2020. Magnetic biochar with Mg/La modification for highly effective phosphate adsorption and its potential application as an algaecide and fertilizer. Environmental Research, 116252. https://doi.org/10.1016/j.envres.2023.116252

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