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Short communication

Adsorption efficiency and photocatalytic activity of silver sulphide-activated carbon (Ag_2S-AC) composites

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ABSTRACT

Background: This study investigates the adsorption efficiency and photocatalytic activity of silver sulphide-activated carbon (Ag_2S-AC) composites derived from ground coffee waste (GCW).
Methods: In this work, GCW was preceding to carbonized at 500 ± 2°C for hours and formed biochar. Then, GCW was subjected to activation using hydrochloric acid (HCl), phosphoric acid (H_3PO_4) and potassium hydroxide (KOH). The mixture was left to soak for 24 h at room temperature, followed by carbonization at 350 and 500℃. In the meantime, the silver sulphide (Ag_2S) was synthesized by using an ion exchange method. Sodium sulphide (Na_2S) was used as sulphur source and mixed with silver nitrate ($AgNO_3$) and sodium citrate (NaCit) for two hours, then dried in oven at 50 ± 2°C for 10 h. Next, the carbonized AC was subsequently combined with synthesized silver sulphide, resulting in the creation of Ag_2S-activated carbon composites that functioned both as adsorbent and photocatalyst. Their capabilities as adsorbents and photocatalyst were studied by using copper ions (Cu^{2+}) and methylene blue (MB) solution.
Significance findings: Based on results, GCW and all the prepared activated carbons are in the amorphous phase, except for the Ag_2S-AC composites, where the Ag_2S peak reflection can be observed from the X-ray diffraction (XRD) pattern. GCW shows rough and dense surface morphology. The AC shows different pore sizes and structures depending on the chemical activators used, where AC-KOH shows the largest pore size (165.31 μm). The existence of micropores can be observed in all the activated carbon samples. For the adsorption of Cu^{2+}, all samples show more than 99 % of the removal efficiency. While for photocatalytic testing, the Ag_2S-H_3PO_4 sample shows the highest degradation rate (97.7 %) of MB solutions.

1. Introduction

Water pollution is a global problem, and industrial activities are major contributors. Industrial wastewater frequently contains heavy metals such as copper (Cu), lead (Pb), zinc (Zn), cadmium (Cd), and chromium (Cr), along with petroleum by-products [1]. The presence of these pollutants in water systems and their discharge from different industrial sectors creates serious challenges for maintaining environmental sustainability [2]. Organic compounds and heavy metals are especially concerning because of their harmful impacts on both human health and the environment. Toxic ions, including non-biodegradable heavy metals, have become a growing global concern due to their tendency to accumulate in living organisms and negatively affect health. Among these ions, copper is particularly toxic to marine life. Copper ions (Cu^{2+}) are commonly found in wastewater from sources like semiconductor manufacturing, electroplating, and electronic product production. Long-term exposure to copper ions can negatively impact human health, leading to copper poisoning through contaminated food

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and water. Additionally, copper ions can also harm several bodily systems, including the brain, liver, kidneys, lungs, cornea, immune system, gastrointestinal system, and blood system [3,4].

In addition to heavy metals, synthetic dyes from the textile industry have also been recognized as major industrial pollutants and significant contributors to water pollution. These dyes have a profound impact on human daily lives and pose harm to the human body [2,5]. Apart from the textile industry, dyes are widely used in the production of cosmetics, pharmaceuticals, and various other products [6]. The ongoing release of effluents contaminated with dyes into the environment poses a substantial environmental challenge on a global scale [7]. This water contamination affects both the natural food chains and the habitats of aquatic organisms [8]. The complex molecular structure and chemical stability of organic dyes make it difficult for them to undergo natural biodegradation [5]. The presence of synthetic dye-based pollutants in the environment has become a serious concern due to their hazardous properties, including toxicity, genotoxicity, mutagenicity, and carcinogenicity. These pollutants pose risks to aquatic environments and human health [2]. Among these pollutants, methylene blue (MB) is a commonly used dye known for its absorption peak at approximately 665 nm. The release of MB into aquatic environments is a significant concern due to both aesthetic and toxicological reasons, as it can have negative impacts on both human and aquatic life [8].

Ground coffee waste (GCW) has gained recognition as a promising and economically viable adsorbent for supplementing traditional methods in the removal of newly identified pollutants from waste streams [9]. It has been found that GCW serves as an effective and cost-efficient adsorbent for the removal of pollutants from aqueous solutions. Previous studies have investigated the adsorption capacity of ground coffee waste and its potential applications in wastewater treatment. These studies have shown that biochar or activated carbon (AC) derived from ground coffee waste can effectively remove synthetic dyes and heavy metals [2,9]. Indeed, activated carbons have been widely utilized as adsorbents for organic pollutants, including synthetic dyes. This is due to their exceptional ability to adsorb a wide range of organic compounds. Activated carbons are also effective in the removal of inorganic pollutants and heavy metals from wastewater. In addition, they can be used as catalysts in various catalytic processes [2,10].

Various techniques are employed to tackle pollutants, including reverse osmosis, ion exchange, chemical precipitation, ultrafiltration, flocculation, and nanofiltration. However, these methods often have drawbacks such as high operational and maintenance costs, significant energy requirements, and complex management. As a result, there is a growing interest in developing cost-effective and efficient approaches for managing aquatic pollutants. Adsorption techniques have gained considerable attention due to their effectiveness in treating pollutants, including both heavy metals and dyes. This adsorption method is characterized by its simple design, user-friendly operation, and high efficiency in removing pollutants. To achieve an effective adsorption process, it is essential to utilize adsorbent materials that possess superior performance and a strong affinity for pollutant compounds. Researchers have developed a wide range of organic, inorganic, and hybrid materials to facilitate efficient adsorption processes. Among these materials, carbon-based adsorbents have attracted significant attention due to their favourable characteristics. Carbon-based adsorbents offer appealing attributes for adsorption applications, prompting researchers to further explore and advance their development. The interest in carbon-based adsorbents arises from the favourable characteristics of carbon precursor materials, including their abundant natural availability, high renewability, and cost-effectiveness. The efficiency of adsorption in composite materials depends on various factors such as surface properties, pore structure, and chemical composition. Activated carbon, with its large surface area and numerous adsorptions site, proves effective in capturing pollutants through physical and chemical interactions [2]. Moreover, the incorporation of silver sulphide nanoparticles onto the surface of activated carbon enhances the adsorption capacity by introducing additional active sites and promoting surface reactions.

Photocatalysis refers to a process where the rate of a chemical reaction is altered or initiated by exposure to ultraviolet, visible, or infrared light. This occurs in the presence of a photocatalyst, a substance that absorbs the light and participates in the chemical transformation of the reactants involved [24]. The photocatalytic process, driven by the photoredox properties of photocatalysts, which facilitate both oxidation and reduction reactions. In photocatalysis, the oxidation of organic contaminants into non-toxic by-products such as carbon dioxide and water are typically achieved by photogenerated holes or various free radicals (i.e. hydroxyl radicals (•OH) and superoxide anions ($\bullet O_2^-$)), which are produced by the conversion of solar energy. The photocatalyst absorbs light photons, which leads to the creation of electron-hole (e^-, h^+) pairs. These excited charge carriers (e^- and h^+) then separate and move. The electrons in the conduction band (CB) reduce protons to form hydrogen, while the holes participate in the oxidation of water [27–29].

Silver sulphide (Ag_2S) is a well-known semiconductor photocatalyst widely recognized for its favourable properties in photocatalytic applications. It possesses a narrow bandgap, thermal and mechanical stability, high photochemical stability, and can be easily synthesized. Recent research has extensively focused on silver sulphide due to its broad range of applications in fields such as biosensors, infrared detection, optoelectronics, and catalysis [8]. In this context, photocatalytic degradation is considered an emerging and environmentally friendly technology that utilizes renewable, clean, and readily available solar energy to convert pollutants into less harmful substances without causing secondary pollution. Over recent years, several techniques have emerged to address organic wastewater pollution, including adsorption, membrane filtration, chemical or electrochemical oxidation, and photocatalysis. Among these methods, photocatalysis stands out for its notable advantages in terms of efficiency and environmental friendliness. It utilizes abundant sunlight to degrade organic pollutants in wastewater without generating additional pollution. Ag_2S, one of the most promising photocatalysts, has gained substantial attention due to its affordability and ease of preparation. It is extensively employed to enhance the photocatalytic characteristics and stability of semiconductor photocatalysts [5,11].

Activated carbon (AC) is widely recognized for its remarkable surface area and porosity, which enable effective adsorption of organic molecules and metal ions from aqueous solutions. Both adsorption and photocatalysis play crucial roles in the efficient elimination of organic pollutants, and these techniques often work in synergy in various applications. The achievement of efficient pollutant adsorption is essential for enhancing the process of photocatalytic degradation. Degradation primarily occurs at the surface of the photocatalyst, and adsorption is a surface phenomenon as well. Adsorption facilitates the interaction between the photocatalyst and organic pollutants at the interface, thus contributing to the successful removal of pollutants [7].

In recent years, there has been significant attention towards developing efficient adsorbents with enhanced photocatalytic activity to tackle this challenge. To address the health and environmental concerns associated with Cu (II) and MB, new materials with improved photocatalytic properties have been synthesized. Among these materials, composite materials that combine activated carbon with semiconducting metal sulphides have emerged as a promising approach. This research focuses on the design of a dual applicable nanocomposite that demonstrates efficiency in both Cu (II) adsorption and the photodegradation of MB. The composite, named silver sulphide-activated carbon (Ag_2S-AC), combines these two materials to synergistically which creates a multifunctional material with superior adsorption and enhance photocatalytic properties. The unique combination of adsorption and photocatalysis in this composite material shows great promise for practical environmental applications, particularly in the degradation of complex pollutants under visible light. The integration of Ag_2S with activated carbon derived from ground coffee waste offers several advantages in environmental applications. The presence of silver sulphide

imparts antimicrobial properties, making it effective in disinfection processes. Additionally, the material's low cost, renewable nature, and potential for reuse further contribute to its appeal as a sustainable solution for water purification and treatment technologies. This sustainable approach not only adds value to waste biomass but also provides a cost-effective solution for addressing water pollution.

However, based on the literature studies, production of the activated carbon derived ground coffee waste with incorporation of synthesized silver sulphide as photocatalytic materials is not widely explored. Thus, this research aims to investigate the potential impact of silver sulphide nanoparticles as a photocatalyst on the adsorption properties and photocatalytic activity of the Ag_2S-AC composite derived from ground coffee waste when exposed to direct sunlight. The study aims to contribute to the development of sustainable solutions for water purification and environmental remediation.

2. Materials and method

2.1. Materials and chemicals

The ground coffee waste (GCW) was collected from a Starbuck Restaurant in Perlis, Malaysia, as the source material. The chemicals used in this experiment consist of hydrochloric acid (HCl, 37 %) phosphoric acid (H_3PO_4, 85 %), potassium hydroxide (KOH, 90 %), copper (II) sulfate ($CuSO_4$, 99.99 %), sodium sulphide (Na_2S), sodium citrate (NaCit), silver nitrate ($AgNO_3$) and methylene blue (MB) powder. All the chemicals were purchased from Sigma-Aldrich and used without prior purification. Distilled water was used for all the experiments.

2.2. Synthesis of activated carbon derived ground coffee waste

In the preparation of activated carbon (AC) derived from ground coffee waste (GCW) using chemical activation, the following steps were performed:

- Washing and Filtration: The GCW was repeatedly washed with distilled water, drained, and filtered to remove impurities.
- Drying: The washed GCW was dried in an oven at 100 ± 2°C for 24 h to eliminate moisture.
- Carbonization: The dried GCW underwent carbonization in a furnace at a temperature of 500 ± 2°C, resulting in the formation of carbonized GCW powder, biochar.
- Chemical Activation (alkaline activation): The carbonized GCW powder was immersed in a solution of potassium hydroxide (KOH) with a concentration of 1 mol/L. The ratio used was 1:5 (g of GCW per (mol/L) of KOH concentration). The mixture was left to soak for 24 h at room temperature.
- Drying: Subsequently, the mixture was dried in the oven overnight at 105 ± 2°C to remove excess moisture. Acid Treatment: The resulting product, labelled as Sample AC-KOH, was treated with hydrochloric acid (HCl) at a concentration of 0.1 mol/L. It was repeatedly washed with distilled water until the pH of the solution reached pH 7.
- Filtration and Final Drying: The slurry obtained from the acid treatment was filtered, and the solid material was dried overnight in the oven at 105 ± 2°C.

For the preparation of the sample treated with acid activators, the following procedures were applied:

1. AC-H_3PO_4: The procedure used for AC-KOH was followed, except that phosphoric acid (H_3PO_4) was used as the activating agent instead of potassium hydroxide (KOH). The resulting sample was labelled as AC-H_3PO_4.
2. AC-HCl: In this case, 100 g of GCW was soaked in a solution of 100 mL of 0.1 M hydrochloric acid (HCl) for 48 h. After draining the solution, the sample was washed with distilled water until achieving pH neutrality. Next, the sample was dried in an oven to reduce moisture content. Subsequently, it was placed in a muffle furnace at 350 ± 2°C for a duration of 3.5 h to activate the carbonization process. The resulting activated carbon was sieved through an 80 to 100 mesh sieve and stored in a desiccator. This sample was designated as AC-HCl.
3. Biochar: A sample without any activator treatment was prepared and labelled as biochar. This sample used as a control to compare the properties and performance of the activated carbon samples derived from different activators.
4. GCW: The raw sample of ground coffee waste was labelled as GCW and used as the starting material for the synthesis of activated carbon.

2.3. Synthesis of silver sulphide

The silver sulphide (Ag_2S) was synthesized by using sodium sulphide (Na_2S) as sulphur source. Initially, 4.3 g of silver nitrate ($AgNO_3$) and 6.5 g of sodium citrate (NaCit) were each dissolved in 500 mL of distilled water. These solutions were then mixed using a magnetic stirrer for one hour. Separately, 6.1 g of Na_2S was dissolved in 1000 mL of distilled water. Thereafter, the prepared Na_2S solution was added to the mixture of $AgNO_3$ and NaCit at intervals of 10 mL every minute. After two hours of stirring, the resulting mixture was allowed to settle for 24 h. The precipitate was washed with acetone and distilled water until reaching a pH of 7. Finally, the sample was dried in an oven at 50 ± 2°C for 10 h. The synthesis of silver sulphide can be summarized by following reaction:

$$2AgNO_3 + Na_2S \rightarrow Ag_2S + 2NaNO_3 \quad (1)$$

2.4. Synthesis of silver Sulphide-Activated carbon composite

For the preparation of the silver sulphide-activated carbon (Ag_2S-AC) composite, 5 g of activated carbon treated with potassium hydroxide (Sample AC-KOH) were mixed with 100 mL of ethanol containing 0.5 g of Ag_2S powder under ultrasonic agitation for 1 h. The resulting mixture was then filtered and dried at 105 ± 2°C overnight in the oven, yielding the composite labelled as sample Ag_2S-KOH.

Then, the process was repeated for different batches of Ag_2S-AC composite by replacing sample AC-KOH with activated carbon treated with phosphoric acid (AC-H_3PO_4) and activated carbon treated with hydrochloric acid (AC-HCl). The synthesized composite powders were labelled as Ag_2S-H_3PO_4 and Ag_2S-HCl, respectively.

2.5. Characterization of prepared sample

The phases present in the raw sample, sample with chemical treatment, and treated sample with the addition of Ag_2S were determined using X-ray diffraction (XRD) analysis. In this experiment, a XRD analysis was used to confirm the phase formation and crystalline structures of the composite samples. The analysis was conducted using an XRD D8-Advance instrument from Bruker, USA. The XRD measurements covered a 2θ range of 20° to 90°, with a scanning rate of 5°/min. The selection of the 2θ range between 20° and 90° for XRD analysis of raw Ag_2S and Ag_2S-AC derived from ground coffee waste is based on the diffraction peaks corresponding to both Ag_2S and activated carbon AC are typically observed within this angular range. This range allows for the identification of the main diffraction peaks for silver sulphide while also capturing any interactions between Ag_2S and the activated carbon matrix. A Cu-Kα X-ray source with a wavelength of 1.5419 Å was utilized, and the samples were in powder form. The step size for the measurements was set to 0.0131°. To analyse the XRD patterns, the X'pert Highscore Plus software was used. This software utilizes the ICDD (International Centre for Diffraction Data) PDF-2 database.

A scanning electron microscope (SEM) equipped with an energy

dispersive X-ray spectrometer (EDS) was used to study the morphological features, surface properties, and pore size of the raw sample, biochar, and the microstructure transformation after chemical activation, including the sample with the addition of Ag_2S photocatalyst. The specific instrument used for this study was the SEM-EDS system from TESCAN VEGA, Czech Republic.

The BET surface area and porosity of both the raw materials and prepared samples were investigated using the Brunauer–Emmett–Teller (BET) method with a BET Tristar 3000 instrument from Micromeritics (Germany). Nitrogen was employed as the adsorbate gas. Prior to analysis, the samples underwent degassing at 250 °C for 4 h under a nitrogen atmosphere. This process was aimed at cleaning the sample surfaces and removing any adsorbed water and other materials.

2.6. Adsorption testing

An adsorption test was performed in order to investigate the potential of the silver sulphide-activated carbon derived ground coffee waste composite to remove heavy metal. For this experiment, copper ions (Cu^{2+}) have been chosen as heavy metal due to abundantly present in wastewater as one of the toxic materials. In these experiments, the Ag_2S-AC samples were exposed to aqueous solutions containing copper ions (Cu^{2+}) to assess their ability to remove the metal from the solution.

Firstly, the copper ion solutions were prepared by dissolving 150 mg/L of copper sulfate ($CuSO_4$) with a purity of 99 % in 100 ml distilled water. For each adsorption experiment, 2 g of prepared sample Ag_2S-AC composite was added to a series of copper ion solutions at 1 M concentration. The initial concentrations of Cu^{2+} before adsorption of copper sulphate solution was taken. Next, the mixture was then subjected to 60 min of mixing using an incubator shaker set at a constant speed of 200 rpm to ensure adequate mixing and contact between the adsorbent and the metal ions. After the mixing period, the solution was filtered, the concentration of Cu^{2+} is analysed using atomic absorption spectroscopy (AAS). The equilibrium time was determined through observation that no significant change in the adsorption of copper was occurring. The time at which the adsorption capacity became stable was considered the equilibrium time. For the Ag_2S-AC composites, the equilibrium reached within 60 min. Then, the final concentrations of copper sulphate, CuSO4 solution after adsorption was recorded. Each experiment was repeated at least three times to ensure the reproducibility of the results. To evaluate the efficiency of copper ion removal, the percentage removal of copper ions from the solution, removal efficiency (R) was calculated under equilibrium conditions using Equation (2):

$$R\% = \frac{C_0 - C_e}{C_0} x100\% \quad (2)$$

where,

R = Removal efficiency (%).

Co = Initial concentrations before adsorption (ppm) of copper sulphate, $CuSO_4$ solution (mg/L).

Ce = Final concentrations after adsorption (ppm) of copper sulphate, $CuSO_4$ solution (mg/L).

2.7. Photocatalytic testing

A photocatalytic testing was conducted in order to study the ability of the prepared silver sulphide-activated carbon derived ground coffee waste to be functioned as an organic pollutant removal material. In this research, the methylene blue (MB) dye was used since it is water-soluble, and its discoloration is caused by the calorimetry effect. The MB also has little sensitivity to the alkalinity of cementitious materials, and its chemical structure (polycyclic aromatic hydrocarbons) is similar with compounds that typically exist as pollutants in urban environments [15]. Hence, methylene blue is chosen to be used as organic dye for photocatalytic test. MB was in powder form was diluted and prepared for 300 ppm for photocatalytic degradation testing. The degradation of the MB dye solution was assessed by measuring the absorbance of MB at a wavelength of 660 nm using a UV–Vis spectrophotometer (Lambda 365, Perkin Elmer, USA). To determine the degradation efficiency, a 50 mL solution of 30 ppm MB dye was prepared. The prepared samples were then mixed with the MB solution using magnetic stirring at 120 rpm in a dark environment for 60 min. The purpose of this mixing process was to establish adsorption equilibrium between the samples and the dye solution. After equilibrium was achieved, the solution was exposed under direct sunlight up to 360 min. During the sunlight exposure, about 10 ml of the MB solution was taken every 30 min for the degradation behaviour analysis. The degradation rate of MB dye was calculated using Equation (3)

$$A_t = \frac{I_0 - I_t}{I_0} x100\% \quad (3)$$

where,

A_t = Degradation rate of methylene blue (%).

I_o = Base absorbency.

I_t = Absorbency after time t.

3. Results and Discussion

3.1. Phase Determination

Fig. 1 **(a)** illustrates the XRD analysis of silver sulphide (Ag_2S). The diffraction pattern confirms that Ag_2S is crystalline in nature. The major peaks observed at the interval 25.9° and 53.3° of 2θ degree indicate the presence of Ag_2S crystalline structure (PDF #00–014-0072). [17]. Fig. 1 **(b)** displays the compilation of XRD patterns for GCW, biochar, and activated carbon-Ag_2S. For GCW, the observed peaks between 10° and 30°, corresponding to the plane (101) and (002), respectively, primarily attributed to the presence of hemicellulose, lignin, and amorphous cellulose [12]. While for biochar, a broad diffraction peak between 20.0° to 30.0° (plane (002)) corresponds to the amorphous carbon [10]. The Ag_2S peaks reflection can be observed for all Ag_2S-activated carbon composites, correspond to the plane (002), (100) and (101) at peak between 25.0° to 45.0°. Those peaks suggest the successful loading of silver sulphide particles onto the activated carbon derived from GCW. From Fig. 1**(b)** almost absence of distinct peaks for amorphous region was observed as a general trend in the XRD spectra of biochar and the pretreated in both acid and base of Ag2S-activated carbons samples. The difference in the crystalline nature of the pretreated Ag_2S-activated carbon samples can be attributed to the reduction in amorphous components, as amorphous carbon consists of aromatic carbon sheets. Furthermore, the broad diffraction peak around 2θ = 45° is characteristic of the graphite structure [10].

3.2. Morphology

Fig. 2 **(a)** displays the scanning electron microscope (SEM) image of GCW. The image reveals that GCW possesses a rough surface with fungi-like structure with the absence of pores. Fig. 2 **(b)** illustrates the Ag_2S agglomerate particles. This agglomeration occurred might be due to the small size of Ag_2S particles, which can increase their surface energy. These particles then tend to minimize their surface energy by coming together and reducing the total surface area, leading to the agglomeration to occurred. The formation of porous honeycomb-like structures of biochar can clearly be observed in Fig. 3. Upon closer examination at higher magnification, it becomes evident that a significant number of mesopores are uniformly distributed throughout the surface of the biochar. This porous structure is due to the thermal decomposition that occurred during the pyrolysis of GCW [13]. The average diameter of the pores for sample biochar and Ag_2S-AC treated with H_3PO_4, HCl and KOH

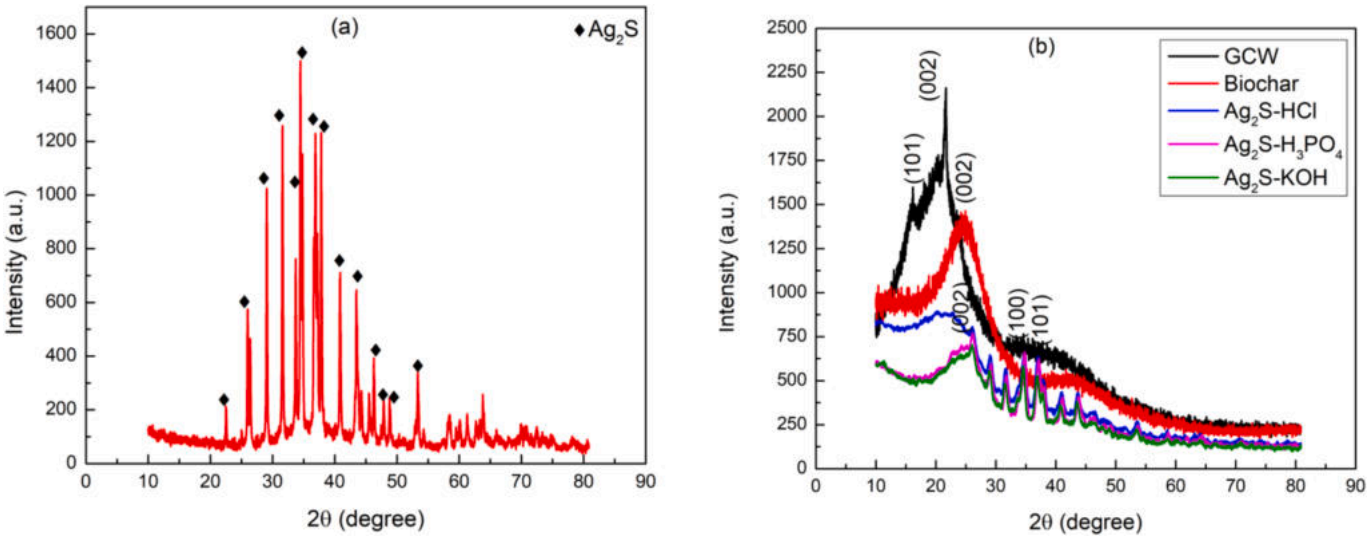

Fig. 1. XRD analysis of; (a) Ag_2S and (b) GCW, biochar and Ag_2S-activated carbons.

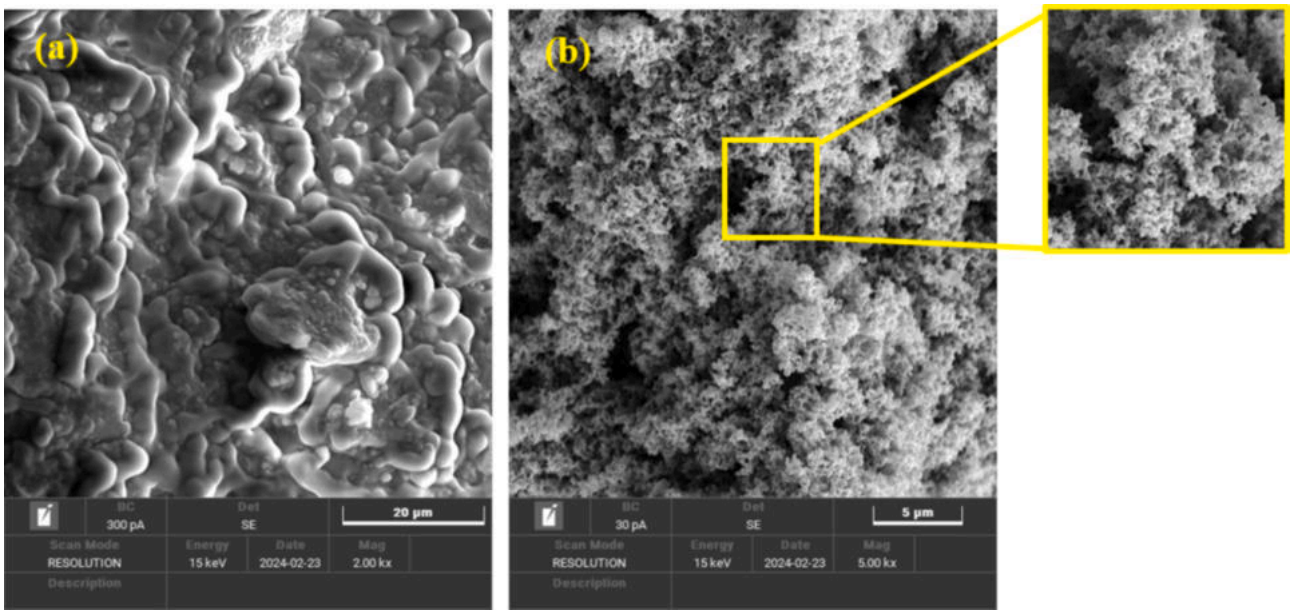

Fig. 2. SEM image of (a) GCW and (b) Ag_2S particles.

are summarized in Table 1. The average diameter of pore for biochar sample about 95.33 µm (µm). The average pore sizes of biochar are quite high, even though without using any chemicals for activated the carbon derived GCW, because due to the pyrolysis method [25].

The morphology of Ag_2S-activated carbons is shown in Figs. 4-6. In term of morphology, Ag_2S-H_3PO_4 (Fig. 4) shows a honeycomb-like structure with the average pore size of 81.52 µm. While for Ag_2S-HCl (Fig. 5), sponge-like structure with irregular pore size and shapes can be observed. The average pore size for Ag_2S-HCl is the lowest, which is about 75.59 µm. This is due to the HCl as an activation agent that affects the surface properties and pore formation in activated carbon. HCl is known to induce the removal of oxygen-containing groups from the surface of the carbon, which leads to the formation of a more hydrophobic and less acidic surface. The activation with HCl creates a significant number of mesopores, as well as enhances the overall surface area of the carbon material. HCl treatment helps to reduce the presence of heteroatoms, which could otherwise disrupt the carbon's electrical properties. The chlorine ions (Cl^-) introduced by HCl might also interact with metal ions, promoting the formation of metal chloride complexes, which could be beneficial in the context of adsorption of certain heavy metals. For Ag_2S-HCl composites, HCl activation may lead to a more pronounced mesoporous structure, which is beneficial for the adsorption of larger ions of heavy metal (e.g. lead and cadmium). This indicates a reduced adsorption of MB molecules in the cavities and pores of the adsorbent [26,30].

For alkaline treated activated carbon, Ag_2S-KOH (Fig. 6) shows similar morphology as in Ag_2S-H_3PO_4, except bigger average pore size, which is 165.31 m. The reason for these changes is due to the activation effects of H_3PO_4, HCl and KOH, respectively, which significantly influences the formation and development of pore structure, also their effects onto physical and chemical properties of the resulting activated carbon. Potassium hydroxide is widely regarded as a strong base used for the activation of carbon materials. KOH treatment promotes the formation of both micropores and mesopores by introducing basic functional groups onto the surface of the carbon. The activation process with KOH typically involves the chemical decomposition of the precursor

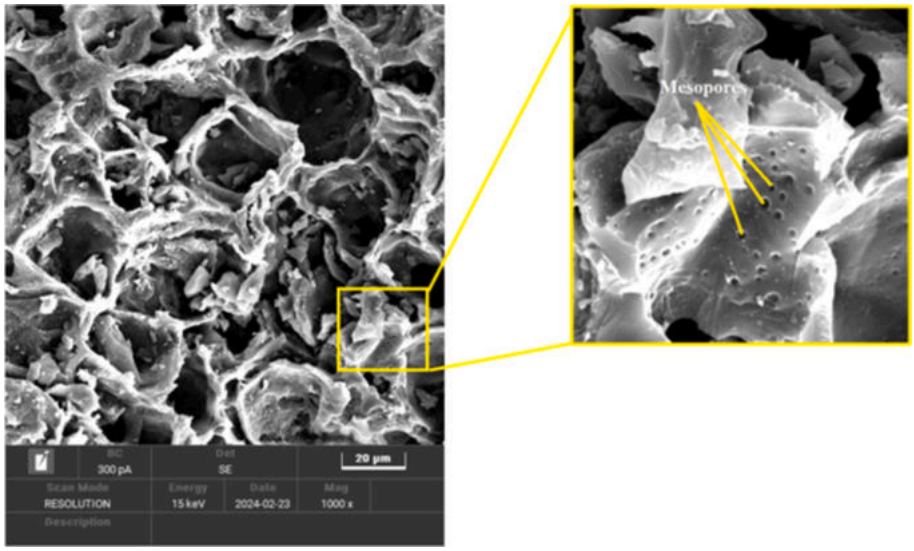

Fig. 3. SEM image of biochar.

Table 1
Average pore size of biochar, Ag_2S-AC treated with H_3PO_4, HCl and KOH.

Name of sample	Average pore size (µm)
Biochar	95.33
Ag_2S-H_3PO_4	81.52
Ag_2S-HCl	75.59
Ag_2S-KOH	165.31

material, which results in an increased number of surface oxygen groups and a highly developed porous structure. The KOH-mediated activation process also leads to the creation of more open and interconnected pores, which is beneficial for the accessibility of metal ions to the surface of the activated carbon. In the case of Ag_2S-KOH composites, KOH activation tends to generate larger pores compared to H_3PO_4 and HCl activation, thereby enhancing the capacity of the material to adsorb a wide range of heavy metals, including copper, lead, and cadmium. Moreover, KOH activation can also improve the conductivity of the material due to the increase in the surface concentration of oxygenated groups that facilitate charge transfer [14,25].

Meanwhile, the role of H_3PO_4 as an activation agent is primarily based on its ability to introduce acidic functional groups, which aids in the creation of micropores within the carbon structure. During the activation process, H_3PO_4 reacts with the organic carbon matrix, breaking down the complex molecules and facilitating the formation of small, highly distributed pores. This acid also assists in stabilizing the surface area of the activated carbon by limiting the collapse of pores during high-temperature treatments. The interaction between H_3PO_4 and the carbon structure may also lead to partial graphitization, which could increase the conductivity of the material. As a result, Ag_2S-H_3PO_4 composites activated with H_3PO_4 typically exhibit a high surface area and a large number of micropores, making them particularly effective in applications such as adsorption of small ions of heavy metal, including copper. The heterogeneous and partially porous structure could provide suitable active sites for the adsorption of Cu(II) ions [14,25,30].

On the other hand, the Ag_2S particles can be observed in the pore structures of all the composites. The elemental analysis conducted through energy-dispersive X-ray spectroscopy (EDX) confirms the presence of high peaks corresponding to silver in the white spots observed in

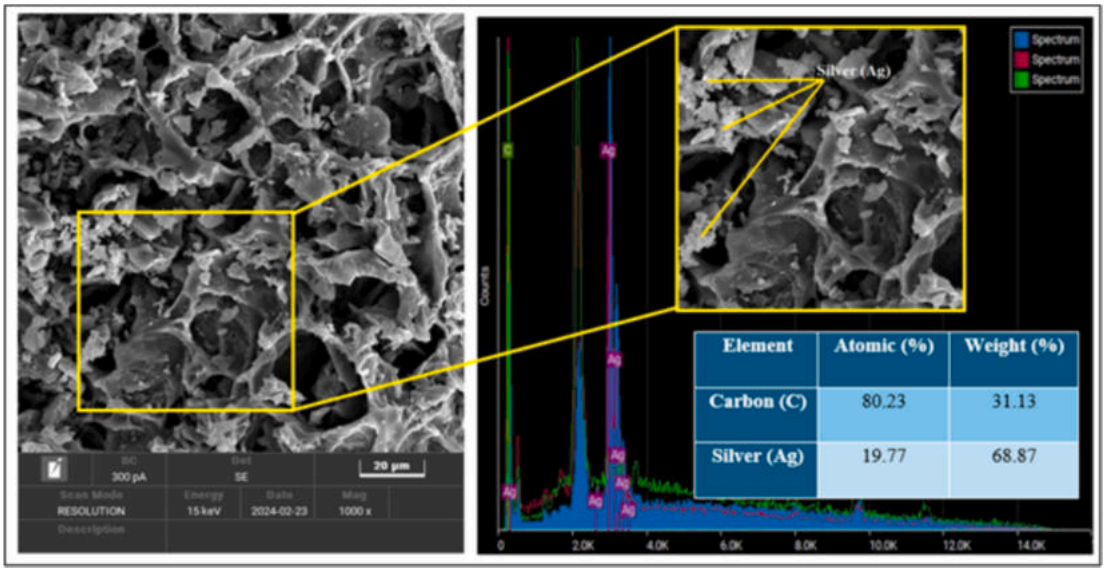

Fig. 4. SEM image of Ag_2S-H_3PO_4.

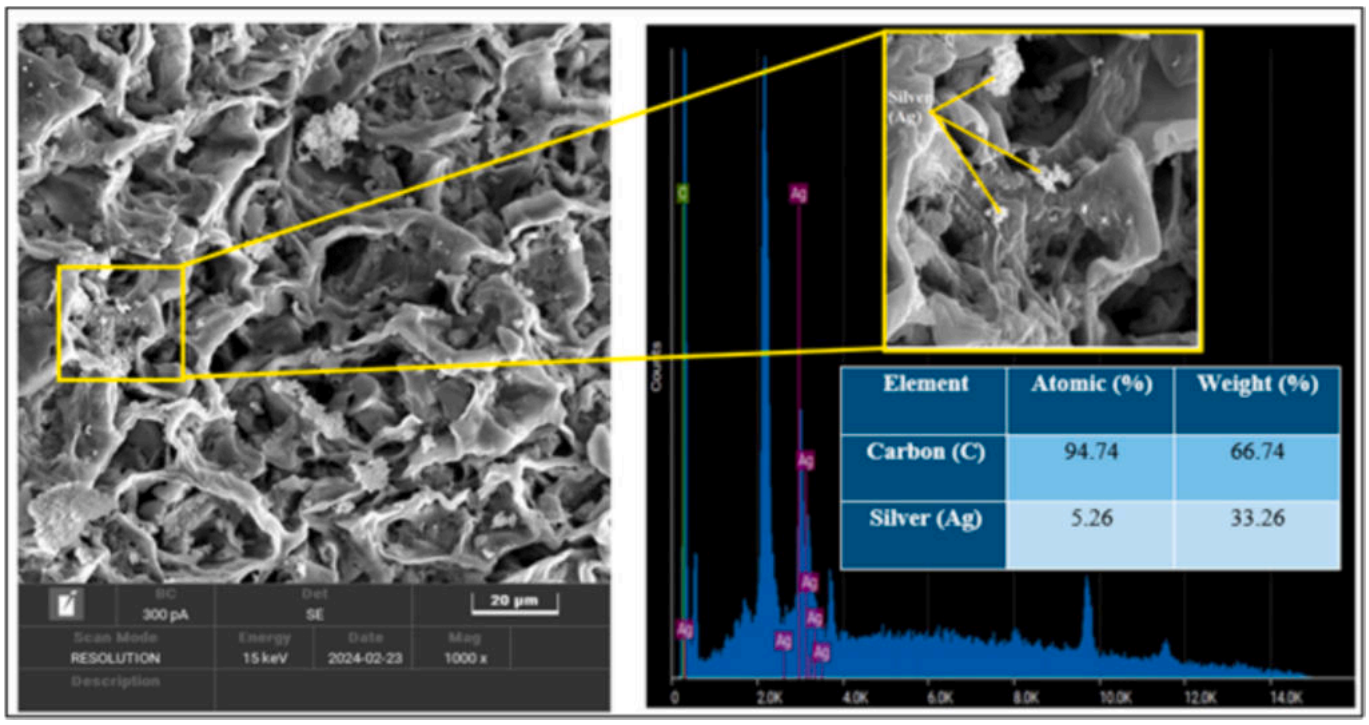

Fig. 5. SEM image of Ag_2S-HCl.

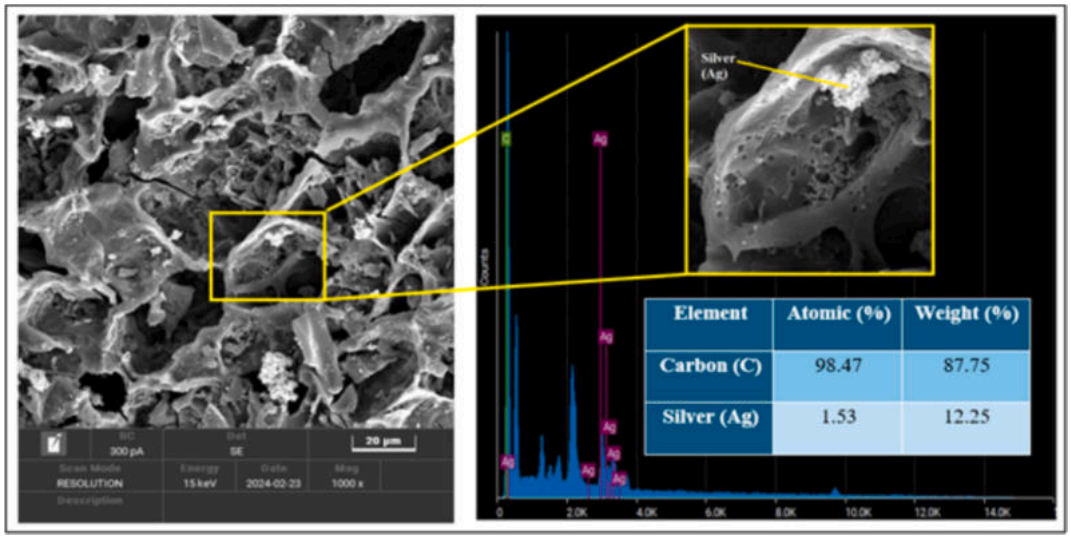

Fig. 6. SEM image of Ag_2S-KOH.

the SEM images (Fig. 4 – Fig. 6). This suggests that silver is successfully integrated into the structure, likely contributing to the material's functionality. In addition, the existence of micropores also can be observed on all the Ag_2S-activated carbon composite surfaces. The findings of EDX analysis reveal the successful deposition of silver sulfide particles in the carbon matrix composite, with a clear distribution across the porous structure. Looking closer at the elemental composition, other than silver, the EDX results also highlight carbon element. These results not only provide insight into the material's elemental composition but also align with other research in the field, while also offering a deeper understanding of how the pore structure and silver content influence the composite's overall properties and its potentially influencing the composite's properties for adsorption and photocatalytic applications.

When compared to similar studies, such as those investigating metal deposits on activated carbon or other porous substrates, the findings in this study are consistent with the literature. For example, in a study by Xie et al. (2024), the authors observed similar silver deposits on carbon-based materials, which were confirmed by EDX spectroscopy, showing high silver peaks in the spectra [31]. However, the current study goes further in noting the specific presence of micropores, which may play a role in the dispersion and stability of the silver sulfide particles. This difference in microporosity could potentially improve the interaction of the composite with various environmental factors, enhancing its efficiency in practical applications such as water purification or catalysis [31].

Acid (H_3PO_4) and basic (KOH) activators are both chemical agents used for carbon activation, which results in destroying the carbon walls, opening the pores and form the active sites onto the activated carbon.

However, their mechanism of reaction is different. KOH is a strong base and normally react aggressively and has pronounced etching effect onto carbonaceous material that led to the formation of bigger pores. Meanwhile, H_3PO_4 is a weak acid, thus the etching effect onto the carbonaceous material during activation process was mild, led to smaller pore formation [14]. For Ag_2S-HCl, even though both Ag_2S-H_3PO_4 and Ag_2S-HCl are acid-treated activated carbon, the non-similarity in pore size and morphology might be due to the differences of these acids interact with GCW. HCl-treated activated carbon has more aggressive and uneven chemical action of hydrochloric acid on the carbon surface. This treatment resulted in selective removal of impurities and the introduction of surface defects, which contributed to a less uniform and more irregular morphology compared to the more controlled and uniform structure achieved with phosphoric acid treatment [15].

3.3. Adsorption efficiency

Table 2 shows the initial and final concentration (ppm), and the removal efficiency (%) of the copper ions after the adsorption testing process. Based on the presented data, it can be observed that the highest removal efficiency of copper ions (Cu^{2+}) was achieved by almost all the samples, with removal efficiency almost 100 %. For GCW sample, even though the sample shows the non-porous structure (as shown Fig. 2a), the presence of primary components in GCW such as cellulose, hemicellulose, and lignin allows the formation of certain surface-active sites or surface functional groups (–COOH and –OH). These metal adsorbing or ion-exchanging functional groups of –COOH and –OH enhanced the removal of copper ions from the solution, thus giving almost 100 % of the removal efficiency [16].

For biochar sample, the porous structure with micropores (as shown in Fig. 3) contributed to the high adsorption rate. In addition, biochar from ground coffee waste is rich in functional groups such as hydroxyl, carboxyl, phenolic, carbonyl, and ether linkages, all of which contribute to its high adsorption capacity for copper ions [17]. For Ag_2S sample, even though only Ag_2S particle was used an adsorbent, the adsorption efficiency was still higher and exceed 100 %. This is because, other than surface activity, the ion exchange process might become the primary adsorption mechanism. The surface of Ag_2S can exchange its silver ions (Ag^+) with copper ions (Cu^{2+}) from the solution. This process can be represented by the following reaction:

$$Ag_2S + Cu^{2+} \rightarrow CuS + 2Ag^+ \quad (4).$$

This ion exchange is driven by the relative solubility and stability of the resulting compounds, where copper (II) sulphide (CuS) is generally less soluble and more stable than Ag_2S in certain conditions, favouring the adsorption process [4]. Hydrochloric acid and phosphoric acid are commonly utilized as chemical activating agents in the preparation of activated carbon from ground coffee waste due to their distinct roles in enhancing the material's porosity and surface chemistry. These acids are effective in facilitating the breakdown of complex organic structures in coffee waste, leading to a highly porous activated carbon material that exhibits a larger surface area and increased active sites for adsorption [14]. The adsorption capacities of the adsorbent decreased as the particle size of the adsorbent increased. This occurs because adsorption is a surface process, and smaller adsorbent particles provide a relatively larger and more accessible surface area [26].

Other than, high porosity structures, the incorporation of Ag_2S particles into the activated carbon composites (Ag_2S-KOH, Ag_2S-HCl and Ag_2S-H_3PO_4) enhances the adsorption capacity by introducing additional active sites and promoting surface reactions. This explains why all the Ag_2S-activated carbon composite samples also exhibits almost 100 % removal efficiency of copper ions.

By comparing the performance in removing copper ions, the silver sulphide-activated carbon composites derived from ground coffee waste showed remarkable potential in removing copper ions from contaminated water, with its effectiveness against other heavy metals, such as lead (Pb^{2+}) and cadmium (Cd^{2+}). Copper ions were chosen for their toxicity and widespread occurrence in industrial effluents. The Ag_2S-AC composite demonstrated a higher affinity for copper ions. This can be attributed to the unique physicochemical interactions between the composite material and copper. Silver sulfide has a high affinity for certain metal ions, and this may explain the superior adsorption capacity for copper compared to other metals like lead and cadmium. Additionally, copper ions might interact more strongly with the sulfur groups present on the surface of the activated carbon, further facilitating the adsorption process. The presence of silver sulfide in the composite material likely enhanced the adsorption process, possibly through the formation of silver-copper complexes or the high surface area provided by the activated carbon [3,4,32].

The removal of lead and cadmium ions was somewhat lower than that of copper, which could be due to the size and charge differences between these metals. Copper ions, being smaller and more easily hydrated compared to lead and cadmium, might more easily penetrate the pore structure of the activated carbon [3,4,32]. Furthermore, the electrostatic interaction between the positively charged copper ions and the negatively charged sites on the Ag_2S-AC composite might play a more significant role in copper removal.

In comparison with other traditional adsorbents, such as activated carbon without silver sulfide, the Ag_2S-AC composite exhibited higher metal removal efficiency for copper ions. This suggests that the silver sulfide component provides a synergistic effect, enhancing the adsorption capacity of the activated carbon. Furthermore, the use of ground coffee waste as a precursor for activated carbon is an environmentally friendly approach that not only recycles organic waste but also offers an economically viable solution for water purification.

Table 2
Removal efficiency of copper ions.

Sample	Initial concentration (ppm)	Final concentration (ppm)	Removal efficiency (%)
GCW	50,000	157.00	99.7
Ag_2S	50,000	0.21	99.9
Biochar	50,000	153.80	99.9
Ag_2S-HCl	50,000	38.97	99.9
Ag_2S-H_3PO_4	50,000	0.13	99.9
Ag_2S-KOH	50,000	16.69	99.9

3.4. Photocatalytic activity

For the photocatalytic activity, the degradation rate of the methylene blue (MB) solution was examined as a function of time for the prepared samples before and after irradiation under natural sunlight, as illustrated in Fig. 7 and data was tabulated in Table 3. Based on the Fig. 7, the degradation rate of MB is directly proportional to time, regardless of sunlight exposure. During the non-exposure time, the degradation rate for all prepared samples ranged between 40 % and 80 %, even after 1 h of experimentation. However, when the same samples were exposed to sunlight, the degradation rate of MB significantly increased, reaching 87 % to 98 % within 5 h.

Ag_2S-H_3PO_4 sample exhibited the highest photocatalytic performance with a degradation rate of 97.7 % after 360 min of exposure, compared Ag_2S-KOH (95.9 %), Ag_2S-HCl (80.4 %) and biochar (97.2 %). This result suggests that there is a chemical reaction occurring with Ag_2S nanoparticles that exhibit photo reactivity under sunlight [8]. As can observed, sample Ag2S-HCl shows the lowest degradation rate. This is due to the HCl playing a critical role in the removal of impurities, including inorganic compounds and mineral salts, from the raw carbon material. This purification process not only cleanses the surface but also exposes more functional groups that are essential for adsorption. The presence of HCl in the activation process leads to the formation of a more

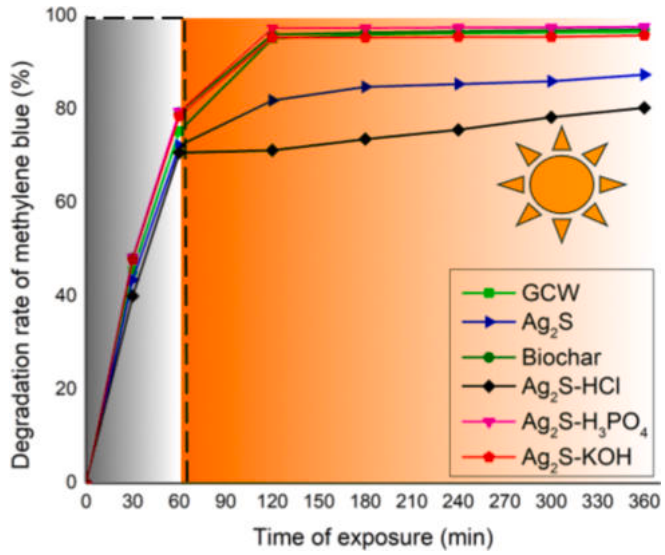

Fig. 7. The degradation rate of methylene blue solution as a function of time at with and without sunlight exposure.

Table 3
Degradation rate (%) of methylene blue solution for Ag_2S-AC derived ground coffee waste under sunlight with a function of time.

Degradation rate of methylene blue (%)						
Name of sampleTime of exposure (min)	GCW	Ag_2S	Biochar	Ag_2S-HCl	Ag_2S-H_3PO_4	Ag_2S-KOH
30	45.5	43.6	48.3	40.1	48.4	47.9
60	75.4	72.3	79.4	70.8	79.6	78.6
120	95.2	82.0	96.1	71.3	97.5	95.4
180	96.1	84.9	96.5	73.7	97.5	95.4
240	96.4	85.5	96.8	75.7	97.6	95.6
300	96.5	86.1	97.0	78.4	97.6	95.6
360	96.6	87.5	97.2	80.4	97.7	95.9

porous structure by etching the carbon surface and enhancing the development of micropores and mesopores (as discussed in section 3.2). This increase in pore volume significantly improves the adsorption capacity of the activated carbon, allowing it to interact more effectively with a variety of contaminants in water, such as organic pollutants and heavy metals. Moreover, HCl activation contributes to the development of acidic surface functional groups, which further enhances the material's affinity for certain pollutants, especially those that are basic in nature [14,15].

HCl playing a critical role in the removal of impurities, including inorganic compounds and mineral salts, from the raw carbon material. This purification process not only cleanses the surface but also exposes more functional groups that are essential for adsorption. The presence of HCl in the activation process leads to the formation of a more porous structure by etching the carbon surface and enhancing the development of micropores and mesopores (as discussed in section 3.2). This increase in pore volume significantly improves the adsorption capacity of the activated carbon, allowing it to interact more effectively with a variety of contaminants in water, such as organic pollutants and heavy metals. Moreover, HCl activation contributes to the development of acidic surface functional groups, which further enhances the material's affinity for certain pollutants, especially those that are basic in nature [14,15].

Activated carbon, on the other hand, serves as an efficient adsorbent for pollutants. The high surface area and the presence of functional groups on the activated carbon surface enhance the adsorption of organic molecules, making them more accessible for the photocatalytic degradation process. Additionally, the porous structure of activated carbon can facilitate the transport of reactants to the catalytic sites, improving the overall degradation efficiency. In the case of Ag_2S-AC composites, the activated carbon not only supports the silver sulfide particles but also assists in electron transfer processes, thereby promoting charge separation and reducing recombination rates of the photogenerated electron-hole pairs [29,33].

On the other hand, the presence of semiconductor nanoparticles, specifically Ag_2S, within the activated carbon establishes the photocatalytic activity under sunlight exposure. This activity arises from the formation of electron-hole pairs, which act as reducing and oxidizing ions on the catalyst's surface. These pairs contribute to the degradation of MB dye solution, leading to nearly complete discolouration and engaging in redox reactions with adsorbed pollutants [8,18]. The nanostructures of Ag_2S possess a narrow band gap and a high absorption coefficient, making them capable of significant light absorption within the range of 200 to 600 nm [8]. During the process of light irradiation, photons with energy equal to or higher than the band gap of Ag_2S (approximately 1.06 eV) are absorbed by Ag_2S, leading to the promotion of an electron (e-) from the valence band (VB) to the conduction band (CB). Simultaneously, a hole (h^+) is generated in the valence band, resulting in the formation of electron-hole pairs. These electron-hole pairs play a crucial role in reduction and oxidation processes.

The electrons on the surface of Ag_2S react with dissolved oxygen (O_2) in the aqueous solution, generating anionic superoxide radicals ($\bullet O^{2-}$). Additionally, the photogenerated holes react with water molecules, producing hydroxyl radicals ($OH\bullet$). Both the anionic superoxide radicals and hydroxyl radicals participate in the oxidation of dye molecules, leading to the decomposition of MB dyes into CO_2 or H_2O and their intermediates [19]. The photocatalytic degradation mechanism can be explained by following chemical reaction:

$Ag_2S + hv \rightarrow e^- + h^+$ (5).

$e^- + O_2 \rightarrow \bullet O_2^-$ (6).

$h^+ + H_2O \rightarrow \bullet OH + H^+$ (7).

Methylene Blue $\rightarrow \bullet O2^- \bullet OH \rightarrow$ intermediates + $CO_2 + H_2O$ (8).

These characteristics of Ag_2S nanoparticles, including high stability and low toxicity, contribute to their excellent photocatalytic capabilities. The photocatalytic process facilitated by Ag_2S nanoparticles leads to the degradation of organic compounds and the reduction of metal ions, resulting in the detoxification of contaminated water [8]. Moreover, the Ag_2S-AC composite exhibits photocatalytic activity, offering a complementary mechanism for pollutant removal. As mentioned in section 3.2, the sample Ag_2S-H_3PO_4 possesses a high specific surface area, which significantly impacts the photocatalytic performance by providing ample reaction sites [6].

For Ag_2S-AC samples, it is important to note that MB degradation did not occur by photocatalytic process only but was accompanied by the adsorption process. In the case of samples loaded with Ag_2S, both photocatalytic degradation and adsorption processes take place simultaneously. The combination of these mechanisms, adsorption, and photocatalytic processes, contributes to the degradation of pollutants into useful and harmless materials [7]. The incorporation of Ag_2S into activated carbon leads to an increase in the MB degradation efficiency, almost fully degrading the pollutants. This indicates that the concentration of MB is reduced not only through photodegradation, but also through the adsorption process since both Ag_2S and AC can act as adsorbents [20]. Fig. 7 clearly demonstrates that the use of Ag_2S combined with the treated activated carbon results in higher removal efficiency compared to using Ag_2S alone. This improvement can be attributed to the role of Ag_2S as a semiconductor and photocatalyst, enhancing the MB removal through its photocatalytic degradation process. Additionally, the activated carbon-derived ground coffee waste, being a carbonaceous material, together with Ag_2S itself contributes to the adsorption of MB.

However, it is worth mentioning that without energy from sunlight, the reduction–oxidation reactions involved in the photocatalysis process will not occur. Consequently, only the process of adsorption of MB dyes

takes place, without the described degradation process [19].

Ground coffee waste demonstrates remarkable photocatalytic degradation of MB, achieving approximately 96.6 % removal. This exceptional performance can be attributed to the electrostatic interactions between the cationic dye molecules and the surface groups of GCW [21]. Moreover, the presence of a significant number of carbonyl and hydroxyl groups on GCW contributes to its enhanced adsorption capacity for cationic dyes like methylene blue [18,22]. These functional groups play a vital role in the surface complexing mechanism between the oxygen-containing functional groups on GCW and the MB ions [23]. As a result, GCW, with its abundance of functional groups and higher average pore width, exhibits a greater adsorption capacity for cationic dyes through this surface complexing mechanism. Comparatively, the removal efficiency of methylene blue is also higher when using activated carbon without the Ag_2S photocatalyst. In this case, the high percentage of removal is solely due to the adsorption mechanism. The higher surface area of activated carbon, as discussed in the previous section (section 3.2), provides more active reaction sites, resulting in a higher removal efficiency of MB.

Several factors can influence the stability of Ag_2S-AC composites. One of the main factors is the physical integrity of the activated carbon matrix, which provides support for the silver sulfide particles. During repeated cycles of adsorption and desorption, mechanical stress or chemical interactions with the contaminant solution could potentially cause the activated carbon structure to break down or undergo chemical modification. The silver sulfide particles, though generally stable, may also undergo some degree of aggregation or dissolution, especially if exposed to aggressive environmental conditions such as acidic or basic solutions [33].

In the case of the Ag_2S-AC composites, studies have shown that the presence of activated carbon plays a stabilizing role by preventing excessive agglomeration of silver sulfide particles. The high surface area and porous structure of activated carbon help maintain the dispersion of silver sulfide, thereby preventing its leaching or significant loss during multiple cycles. Furthermore, the hydrophobic nature of activated carbon may reduce the tendency for silver sulfide to dissolve in water, particularly in neutral or slightly acidic conditions, ensuring that the composite remains stable and retains its ability to adsorb and degrade pollutants [33].

3.5. Mechanism of adsorption efficiency and photocatalytic activity process by Ag_2S-AC composite

The mechanism underlying the adsorption efficiency and photocatalytic activity of silver sulphide-activated carbon (Ag_2S-AC) derived from ground coffee waste material can be explained through the synergistic interaction between Ag_2S and the carbon matrix in Fig. 8. Activated carbon serves as an ideal substrate due to its high surface area, porous structure, and large number of active sites, which significantly enhances the adsorption of contaminants from aqueous solutions. Ground coffee waste, when processed to create AC, provides a sustainable and cost-effective source of carbon.

Ag_2S nanoparticles play a critical role in the photocatalytic process by generating electron-hole pairs when exposed to light, particularly in the visible range. These charge carriers drive the redox-reactions necessary for the degradation of heavy metal (copper ion) and organic pollutants (MB). The carbon component, due to its high conductivity, facilitates the separation of these charge carriers, preventing their recombination. This increases the lifetime of the electrons and holes, thereby enhancing the photocatalytic activity of the composite.

The adsorption efficiency is influenced by the strong interaction between the surface of Ag_2S-AC and the target molecules. The porous structure of the activated carbon offers multiple adsorption sites, while the presence of Ag_2S can introduce additional active sites that improve the interaction with MB or Cu (II) ions. Furthermore, the surface chemistry of Ag_2S-AC can be modified through the introduction of functional groups, such as hydroxyl or carboxyl groups, that further increase its affinity towards different pollutants [24].

Photocatalytic activity depends not only on the formation of electron-hole pairs but also on the generation of reactive oxygen species (ROS), such as hydroxyl radicals (•OH) and superoxide anions (O_2•−), which are highly reactive and capable of breaking down complex organic compounds into simpler, non-toxic molecules (as mentioned in section 3.5). Silver-sulphide being a semiconductor with a narrow band gap, is able to utilize visible light more effectively compared to other photocatalysts, such as TiO_2, which mainly absorb UV light. This allows for a more efficient photocatalytic degradation of pollutants under natural light conditions [19].

The application of sunlight in photocatalytic processes offers several advantages over conventional methods of pollutant degradation. Sunlight is a clean, renewable energy source that is freely available, unlike other catalytic approaches that rely on energy-intensive heating or chemical additives [10]. In the case of Ag_2S-AC composites, sunlight

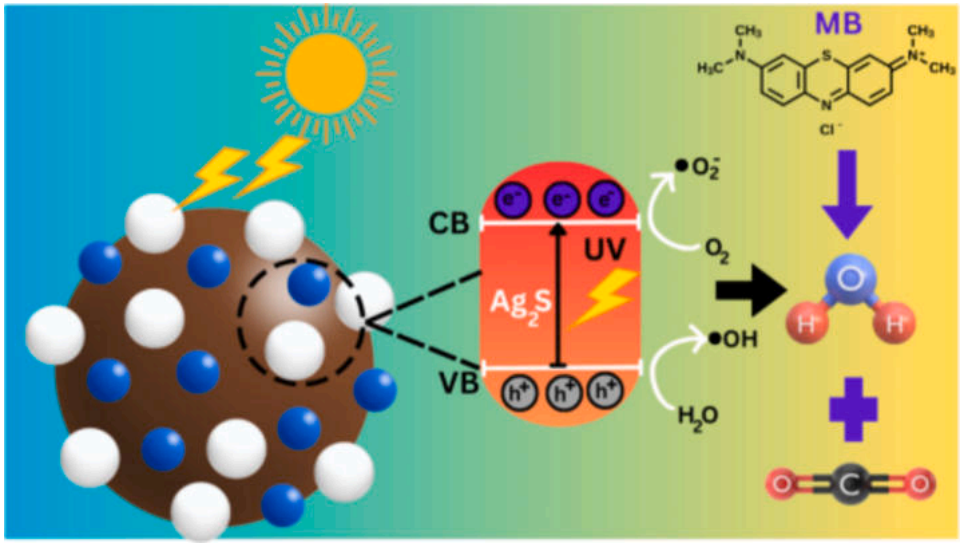

Fig. 8. The mechanism of adsorption efficiency and photocatalytic activity process by Ag_2S-AC composite.

provides the energy necessary to excite electrons in silver sulfide, initiating the photocatalytic reactions. This makes sunlight-driven photocatalysis a sustainable alternative for environmental remediation, as it reduces both the environmental impact and operational costs associated with pollutant removal.

The efficiency of sunlight-driven photocatalytic degradation is influenced by factors such as the intensity of sunlight, the surface area of the catalyst, and the concentration of the organic pollutants. The Ag_2S-AC composite's ability to absorb light in the visible spectrum, due to the narrow bandgap of Ag_2S, makes it particularly advantageous over other photocatalysts, such as TiO_2, which primarily absorbs ultraviolet light. This allows Ag_2S-AC composites to efficiently utilize a broader portion of the solar spectrum, which contributes to enhanced photocatalytic activity under natural sunlight conditions.

In contrast to sunlight-driven photocatalysis, non-solar catalytic methods, such as thermally activated processes or chemical oxidation, often require external energy sources or chemical reagents to initiate the degradation process. Thermal catalysts, for instance, operate by heating the catalyst to high temperatures, which can be energy-intensive and costly. While these methods can be effective in degrading pollutants, they are less sustainable and less suitable for large-scale, low-cost applications, especially in regions with limited access to energy. Chemical catalytic approaches, such as the use of ozone or hydrogen peroxide, also face challenges related to the cost and handling of reagents, as well as the potential formation of harmful by-products. Moreover, these methods may not be as effective for all types of contaminants, and they generally lack the simplicity and scalability of solar-powered processes [29].

The advantage of sunlight-driven photocatalysis, particularly with Ag_2S-AC composites, lies in its ability to degrade a broad range of organic pollutants without the need for additional chemicals or excessive energy input. The ability of Ag_2S to absorb visible light and facilitate the production of highly reactive ROS makes it an ideal candidate for environmental cleanup applications. Moreover, the synergistic effect of silver sulfide and activated carbon in the Ag_2S-AC composite provides an effective pathway for pollutant adsorption and degradation under natural sunlight, a feature that is not found in many non-solar catalytic methods.

4. Conclusion

The activated carbon produced by acid and alkaline activators such as phosphoric acid hydrochloric acid and potassium hydroxide are in the form of amorphous structures. Silver sulphide reflection can be observed from the XRD patterns of all Ag_2S-activated carbon composites. Ground coffee waste exhibit the non-porous structure, while porous honeycomb-like structure can be observed in biochar sample. The acid-treated activated carbon shows different pore size and structures depending on the chemical activators used, where basic-treated activated carbon, AC-KOH shows the largest pore size (165.31 μm). The existence of micropores can be observed in all the activated carbon samples. For the adsorption of Cu^{2+}, all samples show more than 99 % of the removal efficiency. While for photocatalytic testing, the Ag_2S-H_3PO_4 sample shows the highest degradation rate (97.7 %) of MB solutions. The synergistic combination of Ag_2S particles and AC in the form of the Ag_2S-AC composites show great promise for the efficient removal of organic pollutants and heavy metal ions from the wastewater systems. Carbon-based materials, such as ground coffee waste, are particularly advantageous due to their non-toxic nature, eco-friendliness, photostability, and widespread availability. To be summarized, the combined properties of the Ag_2S and AC in the composite material derived from ground coffee waste result in enhanced adsorption and photocatalytic performance. This makes Ag_2S-AC an effective material for water purification applications, utilizing both the adsorption capacity of activated carbon and the visible light photocatalytic properties of Ag_2S. The results underline the potential of utilizing agricultural waste in the development of low-cost, environmentally friendly adsorbents. Furthermore, the findings emphasize the practical use of waste materials in producing functional adsorbents, presenting valuable opportunities for large-scale applications and advancing the principles of green chemistry and circular economy.

In evaluating the study on Ag_2S-AC derived from ground coffee waste, there are several limitations that need consideration. One of the limitations involves the potential variability in the chemical composition of coffee waste due to different cultivation and processing methods. Such variability may affect the consistency and reproducibility of the Ag_2S-AC material, which could lead to variations in the experimental outcomes. Another limitation might be related to the scalability of the synthesis process. While laboratory-scale production of Ag_2S-AC could demonstrate promising results, translating these processes to larger-scale applications may present challenges in terms of cost-effectiveness, material handling, and maintaining uniform product quality. The interaction between Ag_2S-AC and different pollutants or contaminants was possibly explored under controlled conditions, but real-world environments are often more complex, and the material's performance may differ in such settings. These factors could affect the generalizability of the results regarding practical applications.

One of the primary strengths of Ag_2S-AC composites is their dual functionality, where activated carbon enhances the adsorption of pollutants, while silver sulfide contributes to photocatalytic degradation, especially under sunlight. This synergy allows for higher pollutant removal efficiency compared to materials that rely on only one of these processes. Additionally, the use of ground coffee waste, a low-cost and widely available by-product, contributes to the sustainability and cost-effectiveness of the composites, offering an attractive alternative to synthetic or more expensive materials.

However, several weaknesses need to be addressed for Ag_2S-AC composites to reach their full potential. Despite their promising performance, their efficiency can decline after multiple cycles of adsorption and desorption, primarily due to the leaching or agglomeration of silver sulfide particles and potential changes in the structure of the activated carbon support. Although these materials show reasonable recyclability, optimization of desorption and regeneration techniques is necessary to enhance their long-term stability and performance. Furthermore, the stability of silver sulfide under prolonged exposure to reactive species or harsh environmental conditions, such as UV light or extreme pH levels, must be carefully evaluated to ensure the composites' sustained functionality.

When compared to other waste-derived materials used for similar applications, such as biochar or composites made from agricultural residues, Ag_2S-AC composites offer distinct advantages in terms of photocatalytic efficiency. Biochar, for instance, is effective in adsorption but lacks photocatalytic properties, thus limiting its effectiveness for degrading organic pollutants in situ. Additionally, many other waste-derived materials lack the synergistic properties provided by the combination of activated carbon and silver sulfide. However, Ag_2S-AC composites may face competition from alternative materials that offer greater mechanical stability or better recyclability, such as those made from clay or metal–organic frameworks (MOFs). These materials may also demonstrate higher performance under a wider range of conditions, but they often come with higher production costs or environmental concerns associated with their synthesis.

Future research could focus on addressing these limitations by investigating the consistency of the material across various sources of coffee waste. It is also suggested that long-term stability tests under diverse environmental conditions are conducted to better understand the durability and potential leaching of the material. Furthermore, research into the economic feasibility and potential upscaling of Ag_2S-AC production is recommended. Finally, exploring the effectiveness of Ag_2S-AC in more complex, real-world environmental systems, where multiple pollutants coexist, may provide more insights into its practical applications. Additionally, this study suggests the potential for scaling

up the production of this material for broader industrial applications, contributing to circular economy initiatives.

Author Contributions

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Siti Norsaffirah Zailan, Norsuria Mahmed, Aissa Bouaissi, Zahra Ramadlan Mubarokah, Mohd Natashah Norizan, Ili Salwani Mohamad, Nurfina Yudasari and Siti Salwa Mohammad Shirajuddin. The first draft of the manuscript was written by Siti Norsaffirah Zailan, Norsuria Mahmed and Aissa Bouaissi, all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

CRediT authorship contribution statement

Siti Norsaffirah Zailan: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Norsuria Mahmed:** Visualization, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization. **Aissa Bouaissi:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Formal analysis. **Zahra Ramadlan Mubarokah:** Software, Resources, Project administration, Investigation, Formal analysis, Data curation. **Mohd Natashah Norizan:** Software, Resources, Methodology, Investigation, Data curation. **Ili Salwani Mohamad:** Resources, Investigation, Formal analysis, Data curation, Conceptualization. **Nurfina Yudasari:** Supervision, Software, Resources, Methodology, Data curation. **Siti Salwa Mohammad Shirajuddin:** Resources, Methodology, Funding acquisition.

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Declaration of competing interest

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

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Data availability

No data was used for the research described in the article.

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