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Comparing low-cost activated carbon made from coffee waste and bagasse to remove heavy metals and methylene blue dye

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ABSTRACT

Heavy metal contamination from wastewater, mainly iron (Fe), copper (Cu), and methylene blue (MB) dye, presents a substantial risk to both human health and the environment. Biomass-sourced activated carbon, with its porous structure and environmentally friendly adsorption properties, offers a sustainable method for removing these metals. This study investigated the cost-effective removal of Fe, Cu, and MB dye from wastewater by utilizing sugarcane bagasse activated carbon (SCBAC) and espresso coffee waste activated carbon (ECWAC). The study then compared the adsorbents' effectiveness based on variables, for instance, initial concentration, contact duration, pH, and adsorbent dosage. Batch experiments were conducted to assess the adsorption efficiency of SCBAC and ECWAC. The results showed that SCBAC outperformed ECWAC in pollutant removal. Removal efficiencies ranged from 4.8 % to 100 %. Various adsorbent ratios (0.2, 0.4, 0.6, 0.8, and 1) and contact times ranging from 10 to 240 min were investigated. The findings showed that a higher adsorbent dose led to the removal of large amounts of heavy metals and MB dye, with efficiencies reaching 100 %. Kinetic studies were assessed using pseudo-first-order and pseudo-second-order models to clarify the potential copper adsorption mechanism, which indicated a more rapid adsorption rate on the adsorbent, with the pseudo-second-order model exhibiting an acceptable fit for all samples. SCBAC and ECWAC had irregular, cavity-filled surfaces with BET surface areas of 403.1 and 359.1 m^2/g, respectively. The FTIR spectra of SCBAC and ECWAC exhibit unique chemical compositions and functional groups, such as aromatic structures elucidating their structural characteristics and possible applications. SEM images showed that the activated carbon's upper surface was not smooth and had many holes of different sizes and shapes.

Introduction

Water contamination is a growing problem because of urbanization and industrial wastewater production [1,2]. It is essential to find effective and long-term solutions to remove these pollutants so that people can continue to use clean water [3]. Currently, approximately 785 million individuals globally lack access to clean water for drinking. Approximately 1.5 million children under the age of five die as a result of drinking contaminated water [4,5]. Heavy metals and dyes, being major types of contaminants, are particularly durable in water. Their complicated structure and synthetic origin make biodegradation difficult [6,7]. Emissions from industrial waste, particularly those containing heavy metal pollutants, have a significant impact on the environment and life cycles, adversely affecting human health, ecosystems, and marine organisms [8]. Egypt and Sudan release industrial effluents containing heavy metals into the Nile River [9]. The Nile River in Egypt spans 950 km, linking Egypt's agricultural system to a network of 31,000 km of branches, canals, rayahs, and smaller streams that run from Aswan to north Cairo [10]. Nevertheless, the primary Nile River, located near Nasser Lake, is vulnerable to pollution from a variety of sources, including agricultural runoff, industrial emissions from specific locations, diffuse industrial emissions, and untreated discharge of home sewage [10]. Each year, industrial sources release an estimated 2628 million cubic meters of wastewater into the main stem of the River Nile, accounting for 15 % of this volume [11]. The primary industries that produce fertilizers, agrochemicals, pulp and paper, power plants, detergents, fibers, food processing, dyestuffs, textiles, and construction materials are the main sources of pollution in the coastal zone of Alexandria governorate. The daily average discharge from these industries is between 30,000 and 128–261,000 cm^3 of domestic sewage and 1–2

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million cubic meters of agricultural waste per day [12]. The coastal regions of Egypt, especially those near major cities, have significant pollution from several sources [13]. Depending on the specific chemical species and physicochemical parameters, one can find metals in coastal ecosystems either dissolved or deposited on sediment beds [14,15]. Industrialization has resulted in the release of excessive amounts of heavy metals such as lead (Pb), nickel (Ni), cadmium (Cd), copper (Cu), and zinc (Zn) into the aquatic environment via the release of storm water and wastewater [16]. These metals have significant ecological importance because they gather in reservoirs and penetrate the food chain [17]. The primary cause of elevated metal levels in reservoirs is the higher concentrations found in the bottom sediment. This makes the sediment a critical repository for these heavy metals [18,19]. Many different types of industries produce effluents that contain heavy metals and dyes. Some examples of these industries include those that produce batteries, electroplating, leather, tannery, petroleum refining, textiles, pigments, paint, wood processing, and photographic film production [20,21]. Heavy metals are often resistant to degradation and cannot be easily detoxified by biological means [22]. Heavy metals, when deposited and aggregated in the human body, have detrimental effects on several organs, including the liver, myocardium, kidney, pancreas, basal ganglia of the eyes, brain, and bones [23]. Additionally, additional environmental impacts include the lack of ecosystem variety, death of plants and animals, and decreased rates of reproduction in organisms. A previous study focused on measuring the levels of heavy metals, including Fe, Zn, Cd, Cu, Pb, chromium (Cr), mercury (Hg), manganese (Mn), and nickel (Ni), in water samples from six locations in Assiut Governorate, located on the Nile River in Egypt [24]. The findings indicated that the amounts of Zn, Cu, and Fe were the most elevated in the water samples, with Mn, Cd, Ni, Cr, Pb, and Hg following suit in the investigated areas. Sharaf & Shehata [25] evaluated the levels of heavy metals in water samples obtained from two locations (Temsah Lake and Suez Canal, Egypt) which are indicative of contaminated and unpolluted areas, respectively. The findings indicated that the concentrations of the toxic heavy metals (Co, Mg, Pb, Cd, and Zn) in the contaminated region were above the internationally recognized limits for harm. Lasheen (1987) [26] discovered that the levels of Cu in Nasser Lake and Lake Nubia ranged from 0.87 to 13.8 mg/l and 3.38 to 18.92 mg/l, respectively. The data suggest that the average Cu concentrations in Nasser Lake are lower than those in Lake Nubia. Several industries, such as dyestuffs, textiles, paper, and plastics, use dyes to enhance the colour of their products, resulting in a significant production of wastewater containing colorants. Colour is identified as the primary contaminant in wastewater [27]. More than 11 % of worldwide organic dye production is lost in wastewater, presenting a considerable environmental concern due to their potential carcinogenic and toxic properties [28]. Furthermore, they increase the levels of Chemical Oxygen Demand (COD), and Biological Oxygen Demand (BOD) hence posing significant dangers to human health [29]. The elimination of remaining dyes from textile dyeing, for instance methylene blue (MB), and heavy metal ions, such as Cu, is crucial because to their potential impact on human health, aquatic microorganisms, and the environment if not adequately handled prior to being released [30,31]. The textile sector is responsible for 10 % of the world's dye production, with a staggering 0.8 million tons of varied colours produced each year [32]. Literature indicates that MB is the most used cationic dye for dyeing silk, cotton, and wood. Human exposure to untreated MB by ingestion may result in adverse effects such as respiratory distress, vomiting, nausea, and severe diarrhea [21]. Researchers have developed various methods to reduce the harmful effects of organic dyes in water bodies [33]. Traditional methods for removing dyes, heavy metal ions, and other contaminants from water include physical and chemical processes such as adsorption, coagulation-flocculation, membranes, filtration, ion exchange, electrodialysis, and electrocoagulation [34,35]. Most of these operations are expensive, time-consuming, and produce waste, which further complicates the discarding process. Because of its low energy consumption, favourable working conditions, and cost-effectiveness, adsorption is regarded as a competitive option among various approaches [36,37]. Commonly used adsorbents for the removal of heavy metals and dyes include cellulose-based waste, activated carbon (AC), industrial fly-ash, zeolites, silica gels, carbon nanotubes, polymer resins, pillared clays, natural adsorbents, and different minerals [37]. Activated carbon is very effective as an adsorbent due to its micro-porous structure, large surface area, high adsorption capacity, and strong reactivity [38]. Several research have moved their focus to creating the adsorbent from natural materials because of the high cost of carbon active, which is the major restriction. The possibility of creating carbon active adsorbent from locally sourced agricultural waste by converting negative-valued materials into useful ones has recently attracted the attention of several researchers [39]. Previous study has demonstrated that the chemical activation process for AC production is more successful than physical activation. This is because it results in a larger open pore surface area, allowing AC to have a greater surface area and absorb more contaminants compared to the raw materials [40]. Furthermore, the effectiveness of the adsorption process is relies on various parameters, including pH, duration, and the amount of adsorbent used [41]. A lot of different sub-separation methods have been suggested to remove heavy metals and MB out of wastewater and sewage [42]. These include chemical/electro-coagulation, oxidation, photocatalyzed degradation, biodegradation, biocatalytic degradation, and adsorption [43,44]. According to previous studies, most conventional methods are expensive, require a lot of electricity, and generate a lot of harmful waste [43]. Current research has a notable gap in that it doesn't focus enough on low-cost, sustainable solutions that are easily implementable in regions like Egypt, where industrial activity is growing. Considering the health and environmental risks of untreated effluents, eco-friendly and locally adaptable strategies are required. This study focuses on producing activated carbon from biowaste like sugarcane and coffee waste at a low cost, achieving maximum yield for heavy metal and dye removal. The low cost of sugarcane and coffee waste contributes to its cost-effectiveness and commercial viability. The single-step chemical activation method enhances efficiency and minimizes environmental impact, making it a sustainable alternative. This scalability could lead to widespread adoption in textile industries, reducing water pollution and enhancing brand reputation.

Activated carbon as an adsorbent

Activated carbon is a substance that possesses a larger surface area and a high degree of porosity, resulting in a greater capacity for adsorption [45]. AC has a variety of applications in air purification, desalination, water and wastewater treatment because of its distinct qualities [46]. The internal surface area of AC ranges from 500 to 2,000 m^2/g, which is rather significant [47]. Two processes, physical and chemical activation, could be used to produce AC. Physical activation [48] refers to the process of carbonizing a precursor and then activating it. Carbon dioxide (CO_2) or steam were used as gasifying agents for activation purposes. Carbonization occurs within the temperature range of 400 to 850 °C, whereas activation occur within the temperature range of 600 to 900 °C. This approach facilitates the formation of new functional groups that improve the sorption characteristics of the char. Chemical activation involves impregnating the precursor with a chemical agent and then proceeding with activation. A variety of activating agents can be used, including H_3PO_4, $ZnCl_2$, KOH, NaOH, Na_2CO_3, K_2CO_3 and H_2SO_4 [49]. After being cleaned with hydrochloric acid and deionized water, the AC is dried and ready to be used again. Sulphuric acid (H_2SO_4) is a frequently utilized and cost-effective chemical activator for producing carbonaceous adsorbents from diverse lignocellulosic materials [50,51], and it can increase the surface of biomass [52]. Several studies have been conducted to improve the adsorption capacity of AC adsorbents. These studies primarily concentrate on modifying process factors such as the choice of raw material or adsorbent, carbonization, and activation process, ensuring optimal conditions

are achieved [53,54]. Another technique is to modify the composition of activated carbon's surface, resulting in noticeable modifications to the structure of different surface functional groups. These modifications resulted in the addition of atoms, creating a new functional group, and improving the texture of the adsorbent, so increasing its surface area. The enhancement of physical and chemical activation processes significantly enhances the adsorption of contaminants from wastewater, particularly in the removal of industrial colors and heavy metal ions [35]. Currently, AC is derived from both natural adsorbents and waste materials from industries or agriculture. These adsorbents are not only cost-effective but also very efficient in eliminating pollutants. However, the process of activating and modifying at the pilot or industrial scale level suffers significant costs.

Biowaste as carbon-based, green adsorbent alternative

Biomass resources are derived from four main categories: Crop plants are the first generation of biomass feedstock. But second-generation biomass feedstock, which includes lignocellulosic materials, has taken center stage for bioenergy generation because of disruptions to the food supply and the food chain [55]. The problems with the second generation prompted the development and use of biomass feedstocks from the third and fourth generations, which capitalize on microbial communities [55]. The use of biowastes would be beneficial to both the environment and solid waste management. Biowastes such as bagasse [56,57], coffee wastes [58], and fruit shells/peels [59] are often employed as carbon-based, environmentally friendly adsorbents for pollutant removal [60]. Consequently, researchers have extensively studied the use of adsorbents made from local biowastes as a substitute for commercial AC in the process of adsorbing heavy metals and dyes [61]. Biowastes have been used as adsorbents because of their significant adsorptive capacity, improved surface reactivity, and very large specific surface area, which provide great potential for recycling [62]. The choice of adsorbent is crucial to enhance the sustainability and competitiveness of the adsorption treatment process. Utilizing agriculture waste (AW) is a crucial step towards achieving economic and environmental sustainability since AW is abundant in nature and does not cost anything. Its low manufacturing costs make it a promising option, especially for small-scale businesses, and it has recently received a lot of attention as a cheap supply for air conditioners [63]. The primary source of agricultural waste for AC manufacturing is derived from the stones and shells of fruits [64]. A growing amount of focus is being placed on the waste that is generated during the production of cereals such as maize, rice, corn, and coffee. There are both economic and environmental benefits associated with the production of ac from waste materials by the process of pyrolysis [65]. Coffee is an immensely popular and widely consumed beverage, with a worldwide production of 171.9 million 60 kg bags in the years 2020 and 2021 [66]. Within the context of a sustainable economy, coffee derivatives are used for the purpose of bio-energy generation, as well as for use as fertilizers in composting, nutraceuticals, and low-cost adsorbents. Coffee wastes (CW) are lignocellulosic materials that include a complex composition of important components and exhibit excellent physicochemical properties. These characteristics render them highly suitable for use as adsorbents for a variety of pollutants. The current linear economics model dictates that most used coffee grounds be sent to landfills. The circular economy model suggests that it be utilized in the production of high-value materials and energy [67]. The pollutants' molecules that can be adsorbed on the surface can interact with the hydroxyl, carboxyl, and carbonyl groups of CW. Additionally, it is possible to convert CW into a highly porous form of activated carbon (CWAC) that has the capability to adsorb and bind a wide range of contaminants. Both CW and CWAC have previously been used as adsorbents for eliminating diverse organic and inorganic pollutants from water. Recently, researchers have conducted studies on the conversion of used coffee grounds into AC and the removal of dyes [68] and heavy metals [69,70]. In regard to the adsorption of heavy metals, Loulidi et al. [71] used untreated CW to eliminate Cr (VI) and achieved a removal efficiency of around 90 %. Additionally, Edathil et al. developed magnetic CW nanocomposites for the purpose of adsorbing lead, resulting in an adsorption capacity of 41.15 mg/g [72]. Both CW and its derivatives have been shown to be effective in adsorbing organic contaminants. Sugarcane Bagasse (SCB) is the residual fibrous material that remains after the sugarcane is crushed to get its juice [73,74]. Approximately 0.3 tons of bagasse is generated for each ton of sugarcane crushed [75]. Annually, the sugar industry in Egypt produces around 66,000,000 tons of SCB [73]. SCB is a widespread and inexpensive agricultural waste produced worldwide at a rate of 54 million tonnes per year [74]. Egypt contributes around 4.7 million tonnes to this global total [76]. Most of the SCB is burned directly on the sugarcane fields to save money on management costs. Bagasse would end up in landfills if organizations didn't use it and turn it into valuable products[77]. This pollutes the air in a big way [76,78]. As a result, the exploration of practical uses for this waste material is a research area that supports the conservation of the environment. SCB, a kind of waste material composed of lignocellulosic fibers, has garnered significant attention due to its potential as a bio adsorbent in wastewater treatment [41,45]. S. M. Kakom and colleagues [73] conducted a research in which they observed that AC created from SCB pyrolysis had a maximum BET surface area of 431.375 m^2/g, which is equivalent to the surface area of commercial activated carbon. Furthermore, they discovered that the prepared AC entirely removed cadmium from the sample, which thus made it possible to reuse the frying oil without any risk. The untreated SCB waste includes contaminants that often need extensive cleaning and modification in order to enhance the adsorption capabilities of the resultant activated carbons (ACs) [79]. A variety of heavy metal ions are bound to the surface of SCB-based ACs via functional groups known as active adsorption sites [80]. Thus, by reducing the amount of agricultural waste and using SCB waste as ACs source, we can tackle the worldwide wastewater issue. Therefore, SCB is a promising precursor to a sustainable, simple, and inexpensive wastewater treatment technology, which is in high demand [76].

Materials and methods

Materials

All the materials that were required for the fabrication of AC were obtained from local sources. The sugarcane residue used was gathered from the stockyard of an Egyptian sugar factory. The collected SCB was washed, dried under the sun for 2 weeks, and grounded using crushing machine and contained inside a controlled environment at a temperature of 24 °C. The consumed coffee grounds were used to make espresso. They were retrieved from a nearby coffee shop, rinsed with distilled water to remove any dust or other things that may dissolve in water, and then left to dry in the sun for a week. In this study, sulphuric acid (H_2SO_4) (85 %), sodium hydroxide (NaOH) (98 %), hydrochloric acid (HCl) (99 %), methylene blue (MB), Iron (III) chloride ($FeCl_3$) and cupric sulfate ($CuSO_4$) all purchased from Sigma-Aldrich. In the absence of any other indication, all the chemical that was used in the research was of the analytical grade.

Preparation of activated carbon

Two AC sample types were derived from SCB and ECW grounded using a one-step chemical activation method by impregnation with H_3PO_4 in a ratio of 1:3 (W/V), according to Girgis et al [23]. Briefly, the mixture was stirred to ensure acid penetration, heated to 70°C for 2 h, and left at room temperature overnight. After that, the mixture was heated to 500°C at a rate of 5°C/min in a muffle furnace for 1 h. The carbons that were produced were extensively rinsed with hot distilled water and separated until the rinses reached a pH of around 6.5. They were then dried at a temperature of 110 °C for a duration of 2 h.

Adsorption study

The adsorption tests were carried out in 100 mL glass beakers, containing 100 mL of heavy metal, and dye solutions and adding different amounts of AC with constant agitation. The authors obtained the heavy metal solutions by dissolving $FeCl_3$ and $CuSO_4$ in deionized water in a beaker and stirring with a magnetic stirrer to fully dissolve the iron and copper compounds. After the adsorption process was finished, the solution combination was filtered via a filter paper. The filtrate obtained was then analysed using the spectrophotometer iris-HI801 at the absorption wavelengths of copper, iron, and methylene blue (560, 525, and 500 nm, respectively). The pH of the solution was adjusted by adding either HCl or NaOH with the use of a pH meter. The removal efficiency percentage was determined using the following equation:

$$\text{Removal Efficiency}\,(\%) = \frac{A_0 - A}{A_0} \times 100 \quad (1)$$

where, (A_0) the absorbance or transmittance values obtained from the baseline measurement, and (A) the measurement of the treated solution.

Kinetics of absorbing

The adsorption mechanisms of Cu, Fe, and MB dye from the adsorbent were examined by applying pseudo-first order and pseudo-second-order kinetic models to the experimental data. The equation typically used to represent the pseudo-first-order kinetic model [81] is:

$$Ln(qe - qt) = \ln(qe) - k_1 t \quad (2)$$

where, k_1 is the pseudo-first-order rate constant of adsorption, and qt and qe are the amounts adsorbed at time t (min) and equilibrium (mg g^{-1}), respectively. A linear solution is achievable by plotting ln (qe – qt) against time (t), facilitating the calculation of the pseudo-first-order rate constant of adsorption (k_1). In contrast, the pseudo-second-order kinetic model can be expressed by the following differential equation [82]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where k_2 represents the pseudo-second-order adsorption rate constant (g mg^{-1} min^{-1}), which can be obtained by plotting t/qt against t.

Regeneration and reusability of adsorbent

The regeneration of the adsorbent is essential for practical applications [82]. The adsorbent can be reused once adsorption equilibrium of Cu, Fe, and MB dye has been attained. Recent research shows that a simple drying process can reuse activated carbon three times [83]. This approach has the potential to reduce regeneration costs. The adsorbent received a cleaning process using deionized water and was subsequently allowed to air dry overnight prior to its reuse. After the drying of the AC, 0.4 g of activated carbon were dissolved in a heavy metal and MB solution and let for 30 min, after which efficiency was calculated using equation (1).

Characterization of activated carbon surface properties

The surface characteristics of AC were examined to determine its applicability for heavy metal and dye removal. Adsorption capacity is directly proportional to the surface area of carbon-based adsorbents, which provides adsorbates with adsorption sites [84]. The characterization of the activated carbons was assessed by N2 adsorption at −196 ∘C using a surface area and pore size analyzer (Micromeritics, Gemini analyzer) using the BET technique, which measures pore volume, specific surface area, and pore diameter [85]. By using the t-Plot micropore volume, the volume of the pores was determined. In order to find the distribution of pore sizes, the Barrett-Joyner-Halenda (BJH) model was used [86]. Different functional groups of molecules present in activated carbon derived from bagasse and coffee waste were analysed using FT-IR spectroscope (model: Bruker, Tensor-27). IR spectra were recorded in the range 500–4000 cm^{-1}. Scanning electron microscope was utilized to capture high-resolution images of the sample surface. Using an electron beam allowed this apparatus to collect intricate morphological and structural details.

Results and discussion

Factors influencing adsorption

The study examined the impact of various factors, such as pH, concentrations of heavy metals and dyes, time, and dosage of adsorbents, to determine the efficiency of sugarcane bagasse activated carbon (SCBAC) and espresso coffee waste activated carbon (ECWAC) in removing MB and heavy metals, specifically Cu and Fe, from wastewater typically generated by textile factories. The parameters were chosen from a range of factors that impact the adsorption process. This selection was made based on the belief that pH, dose, and duration are crucial elements that need to be modified in order to achieve the highest possible removal of heavy metals from various types of wastewater [87]. In addition, Cu and Fe are considered macro-elements, so they may be very poisonous at elevated doses [41]. The impact of contact time was examined at agitation intervals of 10 min, 30 min, 60 min, 120 min, and 240 min. The removal of Cu and Fe ions approximately have the same result starting from 10 min until 240 min at fixed other parameters, so affixed time of 10 min was used in all experiments. This is because many of the active sites are free at the start of the adsorption process. After a short time, these sites connect with the metal ions [88]. The adsorption of metals is influenced by the characteristics of the surface of the adsorbent and the composition of the solution containing the metals [88,89]. An important factor in determining a material's adsorption capacity is the initial pollutant concentration in the solution. To assess the impact of the initial concentration, experiments were conducted at a temperature of 25 °C, which is equivalent to room temperature. To assess the effect of pollutant solution concentration on removal efficiency, solutions of dye and metal ions ranging from 0.2 to 2 mg/L were examined. The extractability of the heavy metals from water is pH dependent [90]. At a lower pH, hydrogen ions (H^+) and metals both compete for the exchange sites in the system, resulting in the partial release of the metals. Heavy metals are fully liberated in settings of very acidic nature [91]. pH is an important factor in sorption because it influences both the adsorbent's surface charge and the dye molecule's molecular state [92]. In brief, it interrupts the adsorbents' functional groups as well as the dyes' chemistry in the solution. At the same time, it seems that the dye's adsorption ability is pH-dependent [93]. Fig. 1 illustrates the pH and dose effects of ECWAC on the absorption of MB dye after 10 min. Based on the data given in Fig. 1, it was determined that an optimal pH of 8 (dye removal = 63.6 %) was achieved when employing ECWAC, and that this pH was also favourable for MB dye removal [92]. Furthermore, Fig. 1 demonstrated that the elimination of MB dye increased as the dose of ECWAC adsorbent increased. The highest level of MB dye elimination achieved was around 75.1 % while using a dose of 1 g. This phenomenon may arise due to the presence of a high concentration of adsorbents in the solution, which increases the number of exchangeable sites available for the ions [94].

Al-Gheethi et al. [94] made a similar discovery, stating that the effectiveness of adsorption relies on the amount of adsorbent used. After 10 min, the influence of pH and Activated Carbon dose on the Fe absorption efficiency by SCBAC is shown in Fig. 2. The optimal pH for iron removal with SCBAC is within the range of 7 to 8, where only traces from iron were detected after treatment. In the case of acidic pH values, dosage obviously affected efficiency.

The effects of pH and exposure duration on the effectiveness of 0.4 g

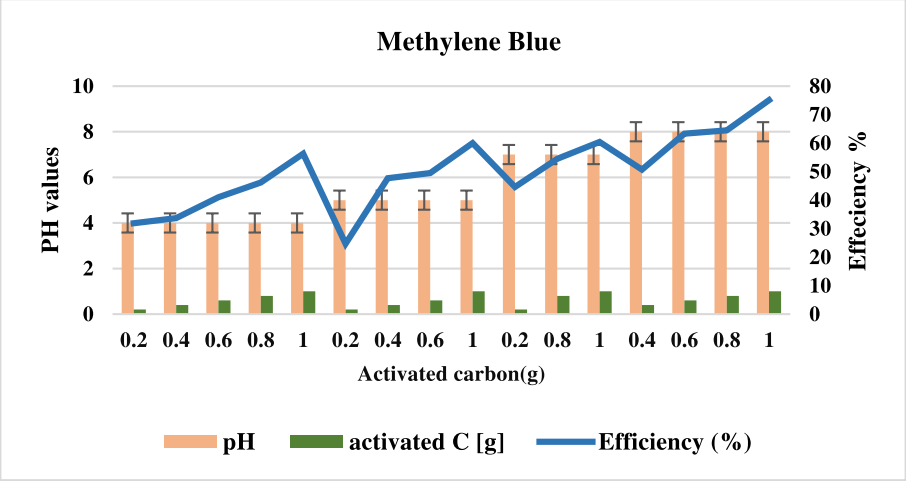


Fig. 1. Effect of pH and Activated Carbon dosage on the absorption efficiency of methylene blue dye by using espresso coffee waste activated carbon after 10 min. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

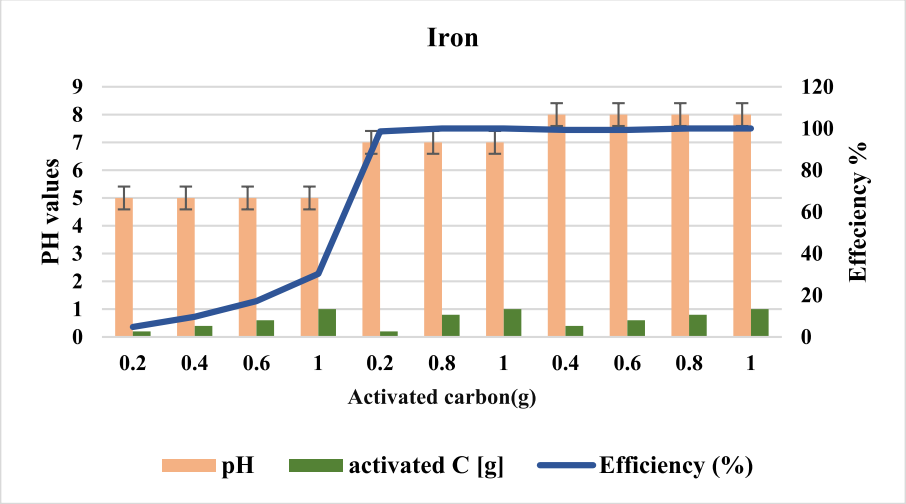


Fig. 2. Effect of pH and dose of bagasse activated carbon on the absorption efficiency of iron after 10 min.

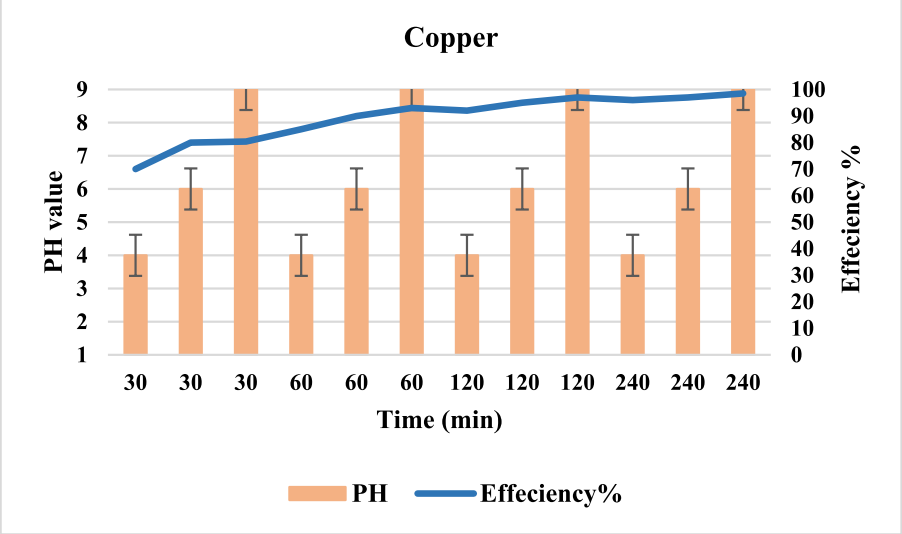


Fig. 3. Effect of pH and exposure time on the absorption efficiency of copper by 0.4 g of bagasse activated carbon.

of SCBAC to absorb copper pollution are shown in Fig. 3. It is shown that the adsorption effectiveness of copper pollutant is significantly influenced by the PH, while the contacting time has a little impact. The optimal efficiency was achieved when the PH was set to 9 and the time value was set to 240 min.

As can be seen in Fig. 4, the comparison between SCBAC and ECWAC demonstrates that SCBAC has the highest efficiency when applied to the removal of all different types of pollutants than ECWAC does.

Kinetics of absorbing

Fig. 5 (a, and b) show the kinetic results of copper adsorption and illustrate the adsorption of copper by SCBAC. The adsorption of copper is also simulated using pseudo-first order and pseudo-second-order adsorption reaction models. Given that the pseudo-first-order model produced a correlation coefficient (R^2) value that was much lower than the expected value, adsorption is not taking place at a single location for each ion involved. In comparison to the pseudo-first-order model, the pseudo-second-order model provided a more accurate description of the data. Indeed, the correlation coefficient (R^2) of all samples was relatively near to 1 (unity), and the chi-square values were lower. Compared to the pseudo-first-order model, the pseudo-second-order kinetic model is preferable when it involves eliminating copper.

Adsorbent regeneration and activated carbon reusability

The reusability process is an important factor to understand for its practicality and economic applications. Fig. 6 shows the removal efficiency of Cu, Fe, and MB using dried sugarcane AC. The impact of different times (10, 30, and 60 min) at constant pH = 9, 2 % concentrations of heavy metals and dyes, and a dosage of 0.4 g adsorbents Cu showed the highest percentage removal (95 %) after 60 min of adsorption. The results from batch adsorption of MB and heavy metals by activated carbon consistently showed that drying is an easy, effective, and practical way to make activated carbon useful again.

Characterization of adsorbent using BET test

Through nitrogen adsorption and desorption, the Brunauer-Emmett-Teller (BET) technique was used to compute the total pore volume (PV) and specific surface area (SSA). The surface area often directly correlates to the adsorption capacity, the defining characteristic of activated carbon. The surface area, and porosity were the main indications of the perfect preparation conditions [95]. The textural properties, surface area, pore volume, and pore radius of sugarcane bagasse and coffee waste activated carbon have been calculated using a variety of methods, including the BET, BJH, and Langmuir methods, as shown in Table 1.

The textural features of activated carbon made from bagasse and coffee waste are shown in Fig. 7a, and b respectively which demonstrates that an increase in relative pressure results in an increase in the amount of material that is adsorbed. The BET analysis results also indicated a well-developed porous structure in SCBAC. The material exhibited a narrow pore size distribution, suggesting uniformity in the pore structure. This uniformity is favourable for efficient adsorption and diffusion of adsorbates within the activated carbon matrix. Based on their size, activated carbon pores can be divided into three groups: micropores (D < 2 nm), mesopores (2 nm < D < 50 nm), and macropores (D > 50 nm). Micropores have a high surface area and adsorption capacity, making them crucial for retaining molecules of similar size. Mesopores serve as intermediaries and can retain molecules between the size ranges of micropores and macropores. Macropores function as pathways, facilitating the transport of adsorbates to smaller pores and retaining larger molecules.

Understanding the distribution and characteristics of these pore sizes in activated carbon is vital for optimizing its adsorption capacity and selectivity for various pollutants. This isotherm is produced by the BET surface area of materials having mesoporous structures, which have pore sizes ranging from 2 to 50 nm [96]. The samples' isotherms have the characteristic hysteresis loop of a Type IV isotherm as classified by the IUPAC, which indicates that the carbon material is mesoporous [97]. Fig. 8 presents a comparison of the pore volumes of two different types of carbons that are created. The data representing the pore volume of activated carbon that was created from bagasse is shown in Fig. 8(a). Better pore volume was seen in the micropore area of the activated carbon that was derived from bagasse, as can be seen in the pore size distribution. The largest pore volume was 0.33 cc/g, whereas the pore radius was around 1.01 nm. Fig. 8(b) displays the pore volume data obtained from activated carbon derived from coffee waste. The pore size distribution of ECWAC exhibited superior pore volume in the micropore range. The highest pore volume recorded was 0.919 cc/g, observed at a pore radius of roughly 3.85 nm.

Surface area of SCBAC was greater than that of ECWAC. The prepared activated carbon's surface area and total pore volume are impacted by the type of waste that is used. While activated carbon derived from sugar cane bagasse had a maximum surface area per unit weight (SBET) of 407.1 m^2/g, AC made from coffee waste had the greatest BJH surface area (399.2 m^2/g) and total pore volume (0.87 cc/g). According to the ratio SBJH/SBET, the mesoporosity character increased with coffee waste derived activated carbon.

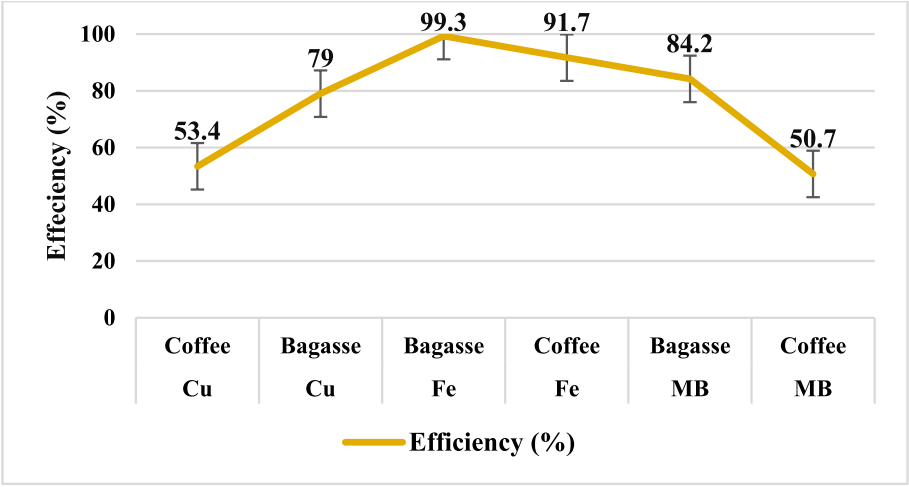


Fig. 4. Effect of activated carbon type on adsorption efficiency.

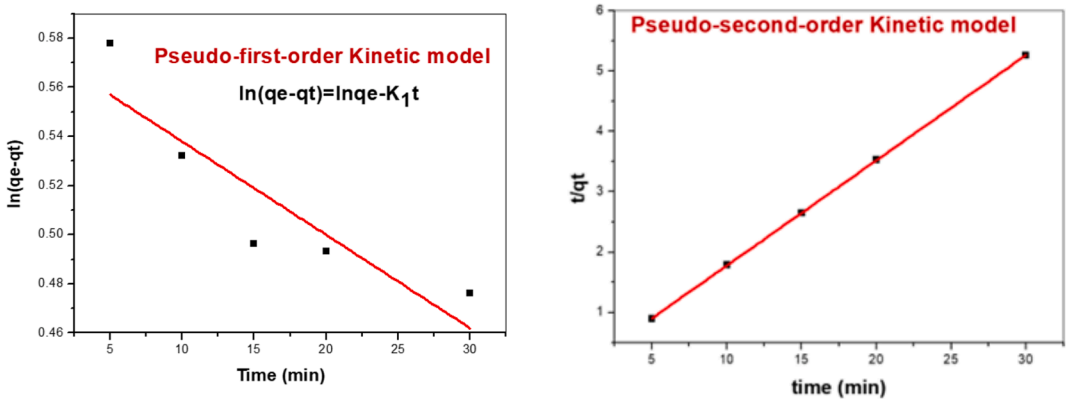


Fig. 5. **(a)** pseudo-first-order kinetic model **(b)** pseudo-second-order kinetic model (best fitting) for copper.

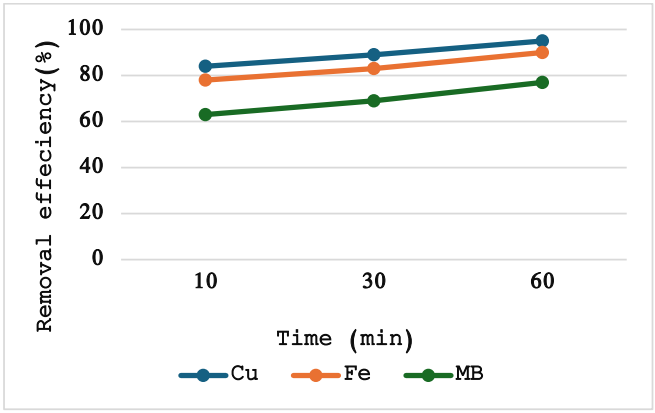


Fig. 6. The impact of time on the adsorption efficiency of recycled AC.

Characterization of adsorbent using FTIR spectroscopy

Fig. 9 (a and b) shows the FTIR spectrum of SCBAC and ECWAC, respectively, which provides valuable insights into its chemical structure and functional groups. The weak band detected at 3468 cm^{-1} in SCBAC indicates the existence of hydroxyl (–OH) groups, linked to the O-H stretching vibrations found in cellulose, hemicellulose, and lignin molecules [98]. This band is quite limited in the AC spectrum and vanishes in the presence of AC coffee waste, attributed to dehydration resulting from the interaction of H_3PO_4 and heat. The peaks at 2930 and 2849 cm^{-1} indicate presence of both methylene (–CH2–) bridges and aromatic C–H stretching vibrations [99,100]. The peaks at 1479 and 1466 cm^{-1} indicate C = C groups present in carbon [100]. Following the activation process using H_3PO_4, residual phosphate compounds may persist on the surface of the activated carbon [101]. The peak observed at around 1018 cm^{-1} corresponds to the C-O vibrations associated with different oxygen-containing groups [102]. The band observed in the range of 934-715 cm^{-1} can be linked to the stretching vibrations of C-H and C = CH2 in aromatic structures [102].

Characterization of adsorbent using SEM analysis

A scanning electron microscope was used to investigate the surface morphology of activated carbon. An indicator of the type of porosity may be obtained via the use of the SEM. SEM, is an electron microscope technology that uses a high-energy electron beam to scan a material [45]. This interaction between the electrons and the atoms of the sample results in the production of signals that provide information on the surface structure of the sample, as well as its composition and other features, such as its electrical conductivity [45]. Figs. 10 and 11 show the SEM images of SCBAC and ECWAC, respectively, illustrating their heterogeneous surface and porous characteristics at several magnifications.

The fractures, gaps, and fissures found in the morphology serve as the entry points for pore channels in the microporous-mesoporous network of AC [103]. The pores found in AC serve as the active locations where adsorption occurs [104]. During the process of adsorption, SCBAC exhibited a morphology characterized by a rough and irregular surface, with irregular cavities and holes of varying sizes. The coffee AC's exterior surface displays a smooth, sponge-like texture due to the dehydration agent's impact during the heat treatment process [103]. As the number of micropores increases in activated carbon, the surface area also increases [104]. The SEM image shows that the activated carbon's

Table 1
Table Comparing the textural properties, surface area, pore volume, and pore radius of sugarcane bagasse and coffee waste activated carbon.

		AC from coffee waste	AC from Bagasse
Surface Area Results	Single point BET	359.1 m^2/g	403.1 m^2/g
	Multipoint BET	390.0 m^2/g	407.1 m^2/g
	Langmuir method	664.7 m^2/g	694.9 m^2/g
	BJH adsorption	399.2 m^2/g	48.5 m^2/g
	BJH desorption	557.6 m^2/g	83.4 m^2/g
	DH adsorption	408.9 m^2/g	49.6 m^2/g
	DH desorption	578.9 m^2/g	86.3 m^2/g
	DFT method cumulative surface area	381.3 m^2/g	556.4 m^2/g
Pore Volume Results	The cumulative micropore volume of BJH adsorption	0.86 cc/g	0.121 cc/g
	The cumulative micropore volume of BJH desorption.	0.92 cc/g	0.138 cc/g
	The cumulative micropore volume of DH adsorption	0.84 cc/g	0.119 cc/g
	The cumulative micropore volume of DH desorption.	0.91 cc/g	0.136 cc/g
	The cumulative pore volume using the DFT approach.	0.84 cc/g	0.326 cc/g
	Total Pore Volume	0.87 cc/g	0.306 cc/g
Pore volume results of coffee waste	BJH adsorption pore radius	5.18 nm	2.13 nm
	BJH desorption pore radius	3.85 nm	1.90 nm
	DH adsorption pore radius	5.18 nm	2.14 nm
	DH desorption pore radius	3.85 nm	1.90 nm
	DFT method pore radius (mode)	4.07 nm	1.01 nm
	Average Pore Size	4.44 nm	1.50 nm
Average Particle Size Summary/ Results	BET Surface area	390.0 m^2/g	407.1 m^2/g
	Average Particle radius	3.5 e + 000 nm	3.4e + 000 nm

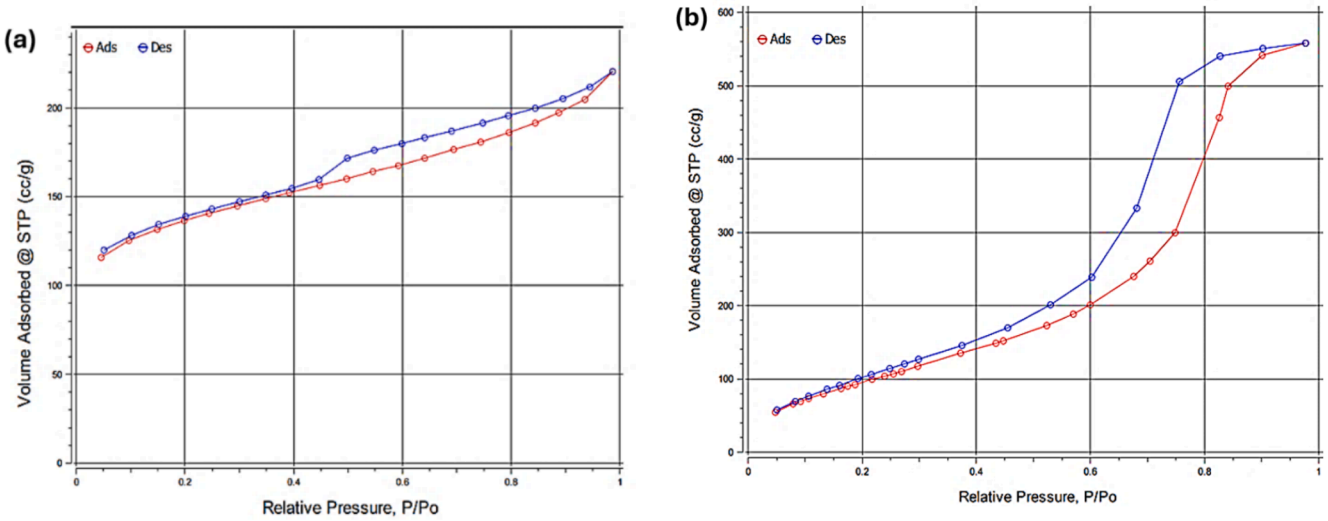


Fig. 7. Comparison of Nitrogen adsorption–desorption isotherms of activated carbon prepared from (a) bagasse, (b) coffee waste.

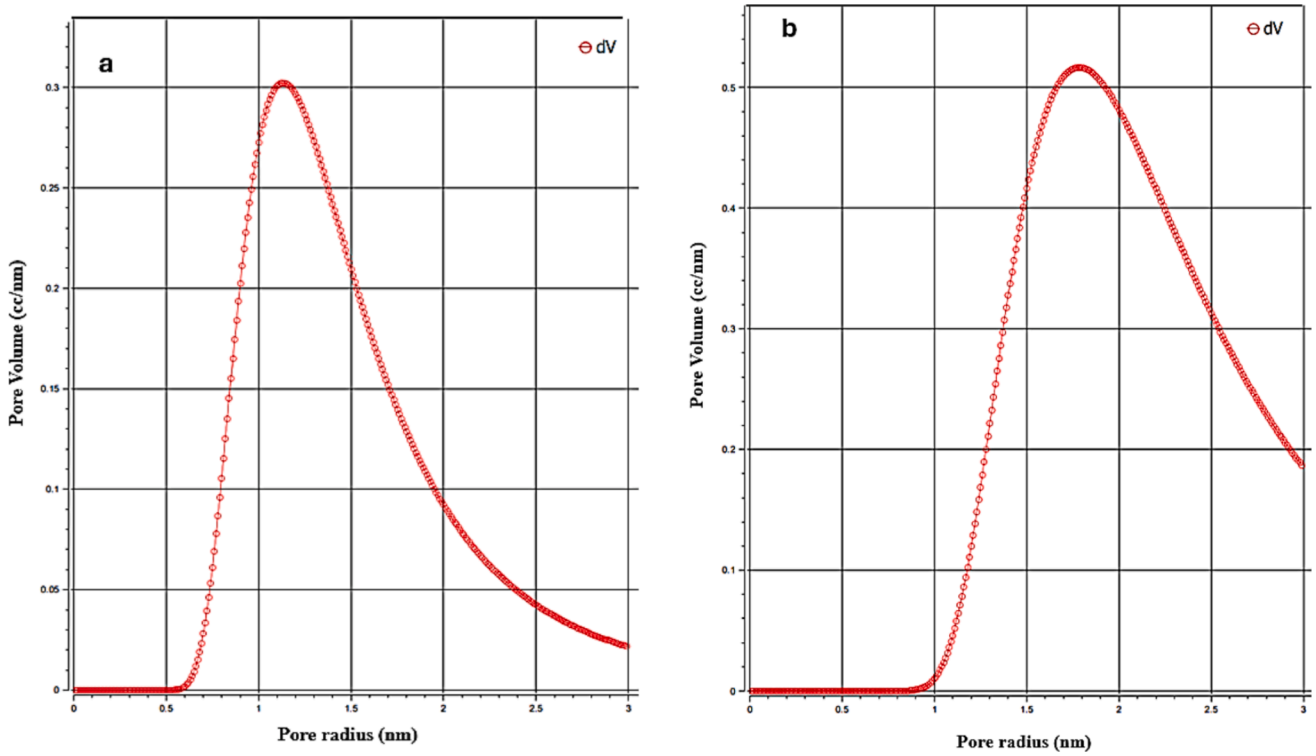


Fig. 8. Comparison of pore volume: **(a)** bagasse activated carbon and, **(b)** coffee waste activated carbon.

outer surface as being uneven and containing a multitude of voids of different forms and sizes.

Fig. 12 illustrates image of sugarcane activated carbon following the removal of copper heavy metal. The surface morphology study clearly indicates that sugarcane bagasse powder has been infused with metal ions, which can be absorbed into the internal walls of the adsorbent surface.

Potential for further improvements

In recent years, advanced treatment techniques such as photocatalysis have attracted considerable attention for the degradation of organic pollutants in water [105]. In chemical reactions, catalysts play a key role by accelerating and directing the reactants to produce the desired end products [106]. Photocatalysis has emerged as a sustainable method, utilizing titanium dioxide (TiO_2) as a photocatalytic material to convert light energy into chemical energy [105]. It produces reactive oxygen species (ROS) to oxidize contaminants into harmless byproducts. In order to enhance the photocatalytic performance, it is essential to study various factors, including organic dye concentration, catalyst content, and catalytic content [107]. Research indicates enhanced removal efficiency and decreases operational expenses relative to traditional methods. The optimization of photocatalytic systems can enhance real-world applications, paving the way for more effective, environmentally friendly solutions across various sectors and promoting a more sustainable climate [34]. To improve photocatalytic processes

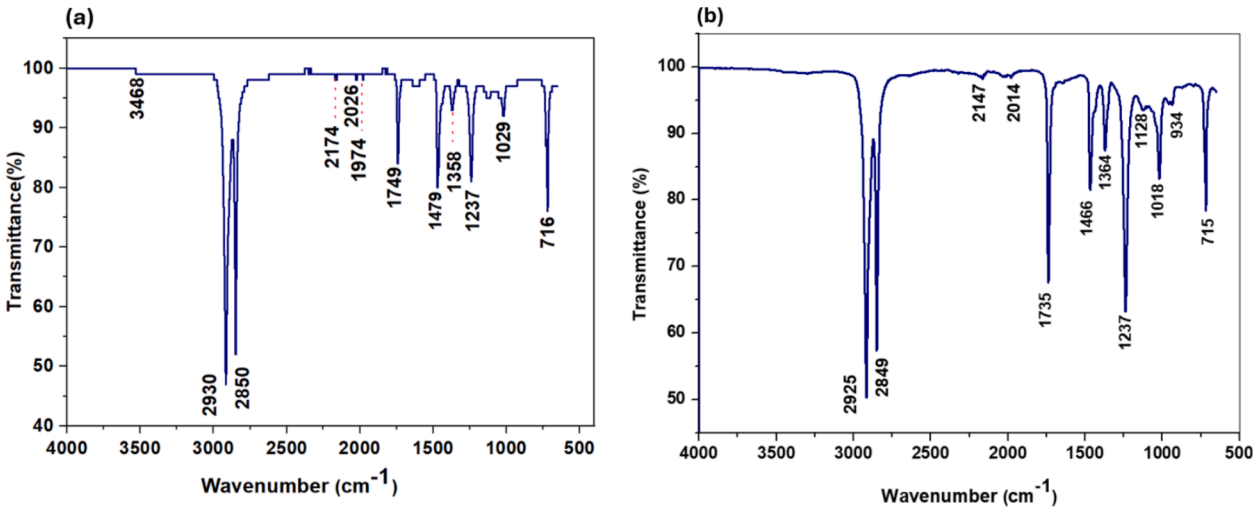


Fig. 9. The FTIR spectrum for (**a**) Bagasse activated carbon, (**b**) Coffee waste activated carbon.

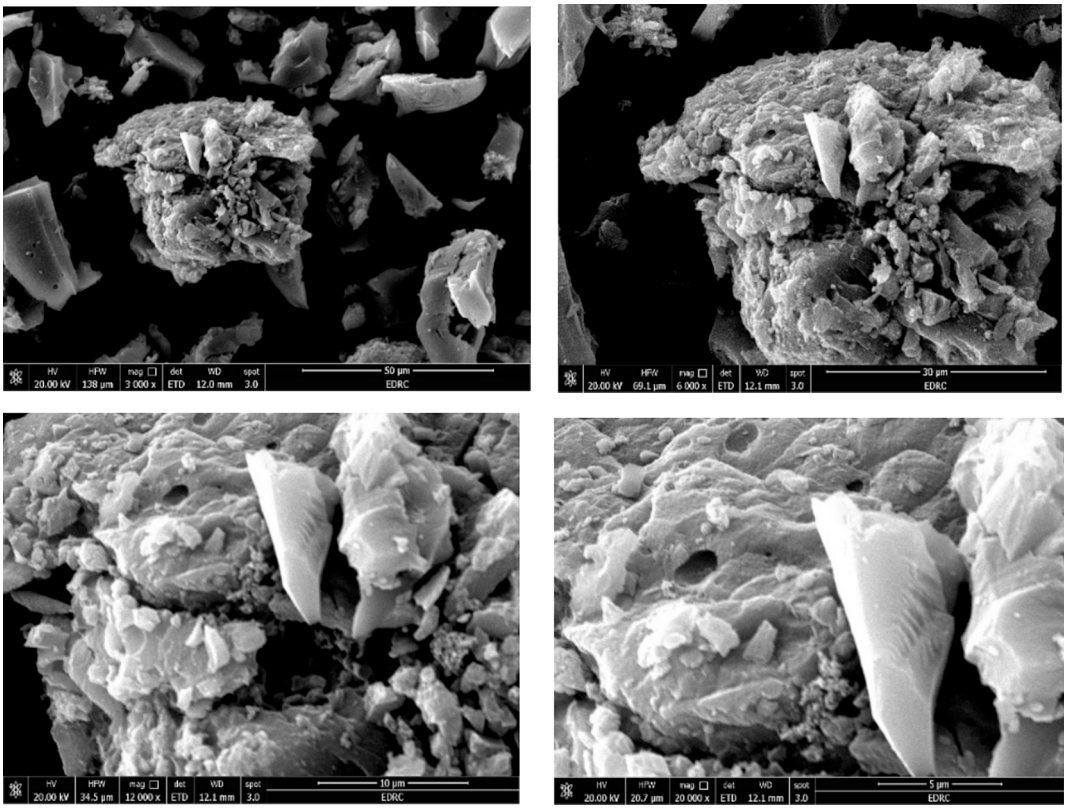


Fig. 10. SEM micrographs of AC from bagasse at different magnifications.

and confirm their effectiveness in practical applications, it is necessary to study stability and recyclability factors [4,108]. Biomass wastes are cost-effective and easily accessible for conversion into AC support material for photocatalysts. The addition of AC changes the acid–base properties of TiO_2, which in turn changes how some molecules interact with the catalyst surface and, in turn, changes how photocatalytic it is. Because the photocatalytic process is essential in treating wastewater, future studies will focus on combining photocatalysis with adsorption methods that use activated carbon from sugarcane bagasse. This involves optimizing photocatalytic parameters, selecting the right photocatalyst, setting the right light source intensity, adding the right catalyst, and adjusting reaction time, pH, temperature, and stirring. We will conduct in-depth studies to understand how pollutants break down quickly under different conditions, find rate constants, evaluate the photocatalyst's regeneration ability, and explore methods to enhance the regeneration process and prolong the catalyst's lifespan for sustainable wastewater treatment applications. Also, future research will focus on studying stability and recyclability factors.

Conclusion

Briefly, sugarcane bagasse activated carbon (SCBAC), and espresso coffee waste activated carbon (ECWAC) were prepared by chemical activation in a single step. This study conducted adsorption experiments

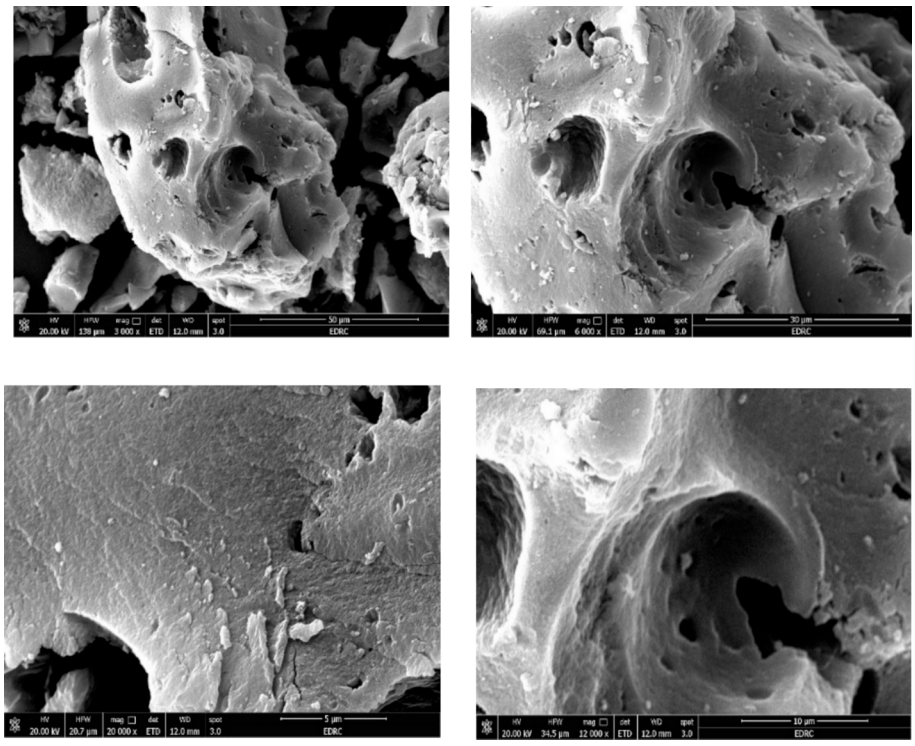


Fig. 11. SEM micrographs of AC from coffee waste at different magnifications.

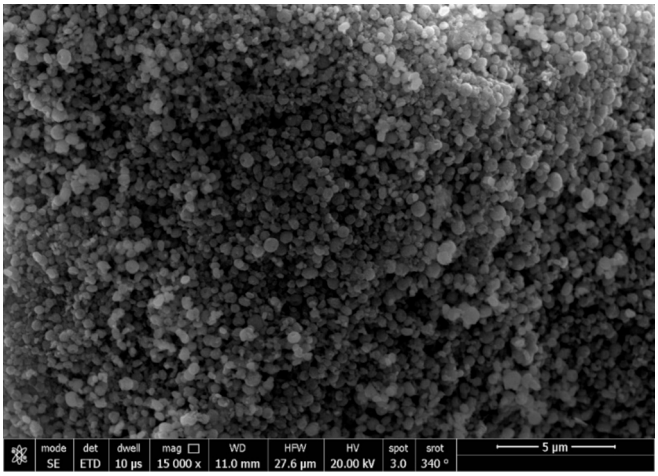


Fig. 12. SEM micrographs of sugarcane AC after Cu adsorption.

for the uptake of iron (Fe) and copper (Cu) heavy metals and methylene blue (MB) from wastewater, utilizing SCBAC and ECWAC as low-cost and naturally available adsorbents. It was found that the removal efficiency of MB dye, Fe, and Cu significantly improved by increasing the dosage of activated carbon. Higher pH values generally lead to higher removal efficiencies for MB dye. SCBAC demonstrated excellent efficiency in Fe removal, leaving only traces for iron at higher dosages and pH values. pH, dosage, and contact time significantly influence the efficiency of pollutant removal. The optimal pH levels for dye removal are found to be pH 8, while basic pH values yield 99.3 % and 100 % Fe removal with SCBAC. Dosage also plays a significant role in removal rates, with a 1 g dose of ECWAC achieving the highest MB dye removal at 75.1 %. SCBAC outperforms ECWAC in pollutant removal across various scenarios. Exposure time and pH also influenced the removal efficiency of these pollutants. Kinetic studies were assessed using pseudo-first-order and pseudo-second-order models to clarify the potential copper adsorption mechanism, which indicated a more rapid adsorption rate on the adsorbent, with the pseudo-second-order model exhibiting an acceptable fit for all samples. The surfaces of SCBAC and ECWAC were irregular and cavity-filled, exhibiting BET surface areas of 403.1 and 359.1 m^2g, respectively. SEM images of SCBAC and ECWAC demonstrated their heterogeneous surface and porous characteristics, thereby confirming their capacity to remove pollution. The comparison between SCBAC and ECWAC further elucidates the superior performance of SBAC in pollutant removal. The results showcase their potential for sustainable water treatment applications.

CRediT authorship contribution statement

Nahla.M. Salatein: Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization. **Mahmoud Shaaban:** Writing – review & editing, Formal analysis, Data curation. **Irene S. Fahim:** Writing – review & editing, Supervision, Project administration, Conceptualization.

Declaration of competing interest

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

Data availability

Data will be made available on request.

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