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Magnetite (Fe_3O_4)-Activated Carbon Composite from Ground Coffee Waste for the Removal of Copper Ions (Cu^{2+}) from Solution

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ABSTRACT

The influence of the magnetite addition on the adsorption efficiency of activated carbon (AC) synthesized using different activators was investigated. In this work, the activated carbon from ground coffee waste (GCW) was prepared via activation with phosphoric acid (H_3PO_4) and potassium hydroxide (KOH), followed by carbonization at 500˚C. The magnetite (Fe_3O_4)-activated carbon composites were prepared by mixing the activated carbon with Fe_3O_4 powders. From the X-ray diffraction analysis, both activated carbons produced by H_3PO_4, and KOH are in the form of amorphous structures. Magnetite peaks can be observed from the magnetite-activated carbon composites. KOH-treated activated carbon shows the formation of porous honeycomb-like structures with large pore size (average diameter ±43 μm) compared to H_3PO_4-treated activated carbon where the smaller, non-uniform pore morphology with the average diameter ±32 μm was formed. The copper ions removal efficiency is the highest for biochar (almost 100%). For treated activated carbon, AC-KOH and MAC-KOH shows the highest adsorption removal efficiency (99.7%) compared to the acid-treated carbon (91.9%). Magnetite itself has good adsorption behaviour (93.6% efficiency) due to its nanocrystalline structure (high surface area) and functional groups.

Keywords: *Ground coffee waste, Activated carbon, Photocatalyst, Adsorbent, Methylene blue*

1. INTRODUCTION

The contamination of wastewater by heavy metal ions, such as copper (Cu), lead (Pb), zinc (Zn), cadmium (Cd), chromium (Cr), etc. poses a significant danger to the global ecosystem. Various sectors, including metal plating, mining operations, battery manufacturing, paint and pigment production, and ceramic and glass industries discharge wastewater containing heavy metal ions into the environment. These toxic ions are non-biodegradable and tend to accumulate in living organisms, leading to numerous diseases and disorders [1, 2]. Among those ions, copper is the most toxic in marine life. Copper ions are present in numerous wastewater sources, including semiconductors, electroplating, and the manufacturing of electronic products [3]. Long-term exposure to copper ions can cause negative effects on human health, such as copper poisoning via contaminated food and sources of water [4]. Therefore, removing these ions from wastewater is crucial for maintaining a healthy environment and its effect on human health.

Recent studies have focused on a specific method for removing the copper ions, such as adsorption using synthetic and natural adsorbents, electrocoagulation, coagulation, chemical precipitation, electrolysis, ion exchange, ultrafiltration, lime softening, biosorption, membrane filtration, reverse osmosis, and solvent extraction [2, 3, 5, 6]. Among these methods, the adsorption process is regarded as simple, cost-effective, and the most effective method compared to other alternative approaches [7]. The utilization of the adsorption process is widespread in industry due to its many advantages, including economic efficiency, absence of toxic side effects, and its capability to eliminate organic materials. Various adsorbents are available including activated carbon, chitosan, zeolites, and silica gel. Among them, activated carbon (AC) was found to be extensively used as an adsorbent in wastewater treatment applications due to its effectiveness in managing the release of pollutants. However, since the activated carbon derived from coal is costly, efforts were made to convert inexpensive and abundant agricultural waste into the activated carbon[8]. Agricultural waste such as tea leaves, bamboo dust, pinewood sawdust, sugar cane bagasse, rice husk, and ground coffee waste, are some of the alternative adsorbents used in removing the heavy metal ions [2, 3, 9]. Among them, ground coffee waste (GCW) has become a subject of interest due to their high carbon content and adsorption abilities [2, 4].

The activation of GCW can be conducted either by physical or chemical process. Physical activation involves the carbonization or pyrolysis of GCW in different oxidizing gases (i.e., nitrogen, carbon dioxide, air mixtures or steam) with a temperature range of 800 °C –1100 °C. However, prolonged activation periods that consume high energy with low adsorption capability have become an issue. Therefore, chemical activation has become an option to reduce the processing time, while the development of porous structures in activated carbon is greater. During the process, the starting materials (waste materials) were impregnated with activating agents to enhance the carbon's adsorption properties. The most utilized activating agent are alkaline groups (e.g., potassium hydroxide (KOH), calcium chloride ($CaCl_2$), sodium hydroxide (NaOH), and potassium carbonate (K_2CO_3)) and acidic groups (e.g., phosphoric acid (H_3PO_4), sulphuric acid (H_2SO_4), intermediate metal salts such as zinc chloride ($ZnCl_2$) etc.) [10], [11]. Among them, H_3PO_4 and KOH are mostly used. This is due to the less environmental and toxicological contamination as well as higher dosage of H_3PO_4 created more potential sites in widening and opening the pores. Furthermore, activation with KOH gives a better result and is more efficient in adsorption than other activators due to the formation of functional groups on the carbon surface [10].

The utilization of magnetite (Fe_3O_4) particles for waste-water treatment has become an emerging method due to their good adsorption behavior, ease of separation and reusability of these materials due to their strong magnetic behavior under the application of magnetic field. Hence, the combination of Fe_3O_4 particles and activated carbon (MAC) in the form of composite structure is expected to increase the adsorption efficiency of heavy metal ions, i.e., copper ions. In addition, the spent adsorbents (MAC) and the adsorbed pollutants can be easily separated from the solution under a magnetic field. Thus, additional filtration or centrifugation process can be eliminated, resulting in a simple operation with no additional post-treatment [6].
This paper aims to investigate the influence of the different chemical activators used on the adsorption efficiency of the synthesized activated carbon from ground coffee waste with and without combination with magnetite particles.

2. MATERIALS AND METHOD

2.1. Materials and Chemicals

The raw material, ground coffee waste (GCW) was collected from Starbucks Restaurant in Perlis. Chemicals such as copper (II) sulphate ($CuSO_4$, 99.99%), magnetite (Fe_3O_4, 97%), hydrochloric acid (HCl, 37%), phosphoric acid (H_3PO_4, 85%) and potassium hydroxide (KOH, 90%) were obtained from Sigma-Aldrich. Distilled water was used in all the experiments.

2.2. Chemical Activation Ground Coffee Waste

The ground coffee waste (GCW) was washed with distilled water repeatedly to remove the impurities, followed by filtration, and drying in the oven at 100˚C for 24 hours. For the basic activation process, the dried GCW was first carbonized at 500˚C in the muffle furnace. The carbonized GCW was then impregnated with 1 mol/L of potassium hydroxide (KOH) at a ratio of 1:5 for 24 hours at room temperature. Then, the impregnated GCW was dried in the oven at 105˚C overnight. The sample then was washed with 0.1 mol/L of hydrochloric acid (HCl) to remove the KOH residual and repeatedly washed with distilled water until the impregnated solution reached pH 7, filtered and dried at 105˚C overnight. The sample was labeled Sample AC-KOH.
For the acidic activation process, a similar procedure was applied except the KOH was replaced by phosphoric acid (H_3PO_4). The sample obtained was labelled as AC-H_3PO_4. For comparison, carbon without acidic/basic activation was also prepared labelled as biochar.

2.3. Preparation of Magnetite-Activated Carbon

For the preparation of the magnetite-activated carbon composite, an amount of 10 g of sample AC-KOH was mixed into the 200 ml of magnetite solution (1 g of magnetite was dispersed in 200 ml distilled water) under ultrasonic agitation for 1 hour. Then the sample was filtered and dried in the oven at 105˚C overnight. This composite was labelled as MAC-KOH. Similar method was used to prepare the magnetite-AC-H_3PO_4 (MAC-H_3PO_4) and Fe_3O_4-biochar by replacing the AC-KOH with AC-H_3PO_4 and biochar, respectively. All the prepared samples are summarized in Table 1.

Table 1 Summary of the prepared samples

Sample	Treatment	Activator	Carbonization Temperature
GCW	-	-	-
Biochar	Non-treated	-	500ºC
AC-KOH	Basic activation	KOH	500ºC
AC- H_3PO_4	Acid activation	H_3PO_4	500ºC
Fe_3O_4	-	-	-
Fe_3O_4-biochar	Non-treated	-	-
MAC-KOH	Basic activation	KOH	500ºC
MAC-H_3PO_4	Acid activation	H_3PO_4	500ºC

2.4. Characterization

For the analysis of carbon content, CHNS elemental analyzer (Vario Micro Cube, Elementar, Germany), which followed standard BS EN ISO 16948: 2015 was used. The change in morphology, microstructure, and pore size before and after the chemical activation were observed by using a scanning electron microscope (SEM, TESCAN VEGA). For the sample preparation, the powders were dispersed over the carbon tape and mounted onto an aluminum stub. The sample was then coated with a thin layer of gold using a magnetron sputtering machine from Sputter Coater NS800 for 60 seconds at 18 mA. The surface area of the prepared samples was investigated by using the Brunauer–Emmett–Teller method (BET Tristar 3000, Micromeritics, Germany). Nitrogen was used as the adsorbate gas. Prior to the analysis, the samples were degassed at 250˚C for 4 hours under nitrogen atmosphere to clean up the surface of the sample and to remove the adsorbed water and other adsorbed material. For the phase analysis, X-ray diffraction (XRD D8- Advance, Bruker, USA) was used. The samples were scanned in between 20° to 90° range, equipped with a Cu Kα (λ=1.54178 Å) at a scanning rate 5°/min, 2θ with step size of 0.0131°. Analysis of powder pattern was conducted by using X'pert Highscore Plus software with the ICDD PDF-2 database. The Debye-Scherrer Equation (Equation 1) was used for crystallite size calculation.

$$D = \frac{k\lambda}{\beta \cos\theta} \tag{1}$$

Where,
D = Crystallite size (nm)
K = Scherer's constant (K = 0.94)
λ = The wavelength of X-Ray (1.54178 Å)
β = Full-width half maximum (FWHM)
θ = Angle of diffraction (rad)

2.5. Adsorption Testing

For the adsorption testing of copper ions (Cu^{2+}), 2 g of sample GCW was dispersed in 100 ml of 150 mg/L copper sulphate ($CuSO_4$) solution. The mixture was mixed by using an incubator shaker at a shaken speed of 200 rpm for 60 minutes. The solution was then filtered, and the presence of copper ion was identified by using an atomic absorption spectroscopy (AAS). Flame of AAS was used at the optimized parameters at wavelength 324.8 nm, slit width of 0.7 nm, current 8 mA, and burner height 7 mm for the analysis of copper existence in the filtrated solution.

The adsorption process was repeated by using samples biochar, AC-KOH, AC-H_3PO_4, Fe_3O_4, Fe_3O_4-biochar, MAC-KOH, and MAC-H_3PO_4. The removal efficiency (R) was calculated at the equilibrium conditions from the following equation:

$$R = \frac{C_0 - C_e}{C_0} \times 100\% \tag{2}$$

Where,
Co=initial concentrations before adsorption (ppm) of copper sulphate, $CuSO_4$ solution.
Ce=final concentrations after adsorption (ppm) of copper sulphate, $CuSO_4$ solution.

3. RESULT AND DISCUSSION

3.1. CHNS Analysis

The composition (%) of carbon (C), hydrogen (H), nitrogen (N), and sulfur (S) for ground coffee waste (GCW), biochar and the activated carbon (AC-KOH and AC-H_3PO_4) from CHNS analysis is shown in Table 2. Result shows that the carbon content is the lowest in GCW sample, which is 50.8%. This content increased about 19% after carbonization at 500°C 70.1% (biochar). This is due to the high temperature used during carbonization process caused by the releasing of volatile matters and removing the hydrogen- and oxygen-containing functional groups, which lead to the increment of the carbon content in the samples (which also led to decrement of about 50% of hydrogen content). However, the carbon content slightly decreased for the chemical activated samples, which is 65% for both AC-KOH and AC-H_3PO_4 samples. The decrement in the carbon content is mainly due to the reaction of the activators (KOH and H_3PO_4) and carbon fragments, which consumed certain amount of carbon during the process [12].

Table 2 CHNS analysis for the activated carbon samples

Samples	C	H	N	S	O
	%				
GCW	50.8	6.8	2.2	2.0	38.2
Biochar	70.1	3.0	4.6	1.9	20.4
AC-KOH	65.2	3.0	4.3	1.8	25.7
AC-H_3PO_4	65.3	2.8	4.1	1.8	56.6

3.2. Phase Formation

Figure 2 (A-C) shows the XRD patterns for samples AC-KOH, AC-H_3PO_4, and biochar, respectively. A broad amorphous hump between 20º - 30º of 2θ (degree) can be observed for all samples, showing that the biochar and activated carbon are amorphous materials. Figure 3 (A-E) shows the XRD patterns of the magnetite (Fe_3O_4), MAC, MAC-KOH and MAC-H_3PO_4 samples. The observed peaks in all samples show Fe_3O_4 reflection at 2θ values of 30.3°, 35.6°, 43.3°, 57.3° and 62.9° which correspond to the *hkl* values of (220), (311), (400), (511) and (440), respectively (ICDD No. 01-083-0112). The crystallite size of the prepared samples was calculated using equation (1) and the average crystallite size is 25 nm.

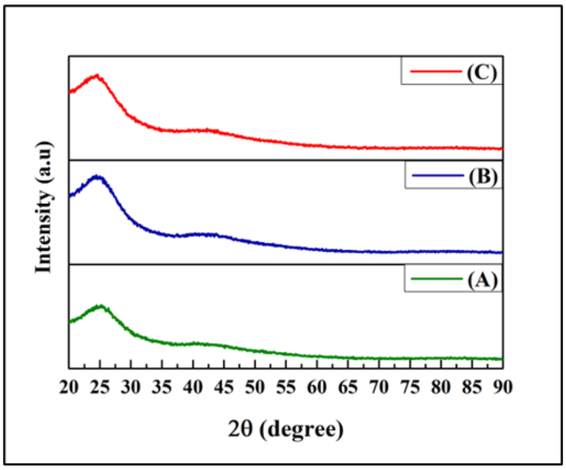


Figure 2. X-ray patterns of samples (A) AC-KOH (B) AC-H_3PO_4 (C) biochar.

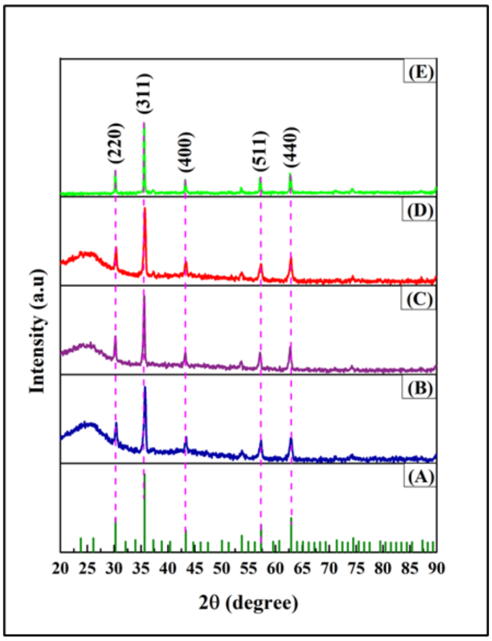
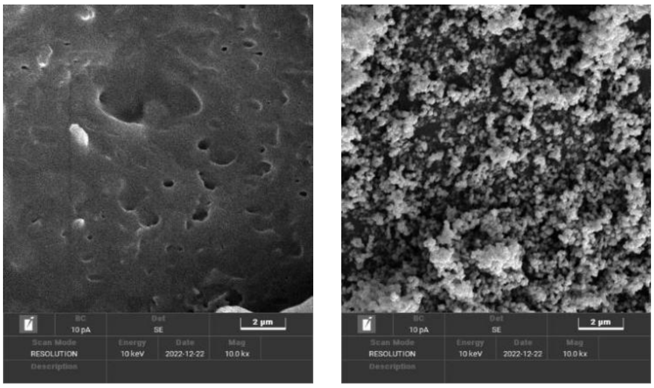


Figure 3 XRD patterns of (A) Fe_3O_4 database (ICDD No. 01-083-0112) (B) MAC-KOH (C) MAC-H_3PO_4 (D) Fe_3O_4-biochar and (E) Fe_3O_4.

3.3. Morphology

The SEM images of GCW and Fe_3O_4 particles are shown in Figure 3 (a) and (b). As can observed from Figure 3(a), even though without carbonization process, the GCW reveals micropores on the surface with an average size of ±0.8 μm. These pores are normally produced during the roasting process of green beans depending on temperature, roasting time, coffee bean size, bean shape and water content [13]. Meanwhile, Figure 3 (b) shows the Fe_3O_4 particles agglomeration due to their nano crystallite size (±25 nm).

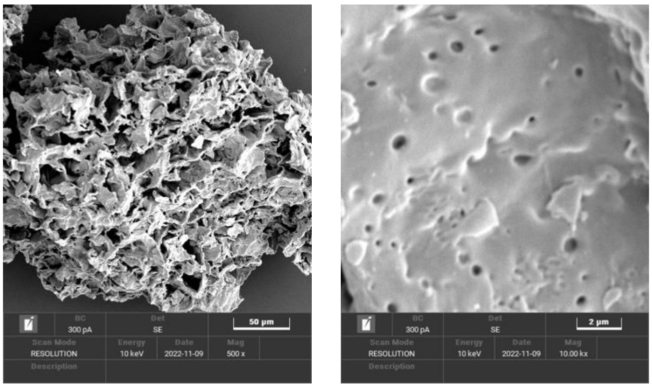


(a) GCW (b) Fe_3O_4

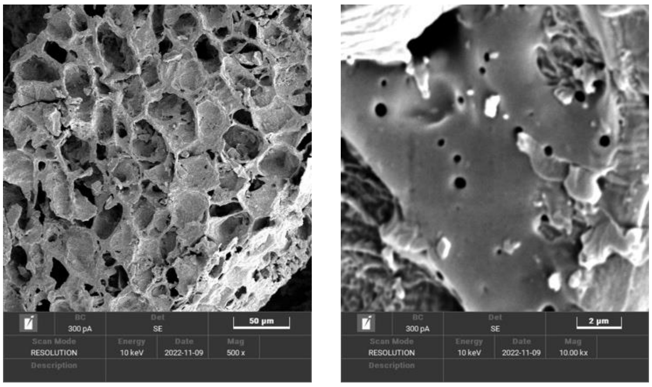
Figure 3. (a) SEM images of (a) GCW and (b) Fe_3O_4.

Figure 4 (a-b) shows the SEM images of biochar, AC-KOH and AC-H_3PO_4, respectively. As observed in Figure 4 (a-b), the biochar exhibits a sponge-like structure. This biochar shows a large porous structure with an average size of ±20 μm. At higher magnification (10kx), the present of micropores (average size ±1.4 μm) can be observed at the biochar surface. These pores might probably be formed by the formation of volatile organic compounds during the pyrolysis process at 500°C [14].

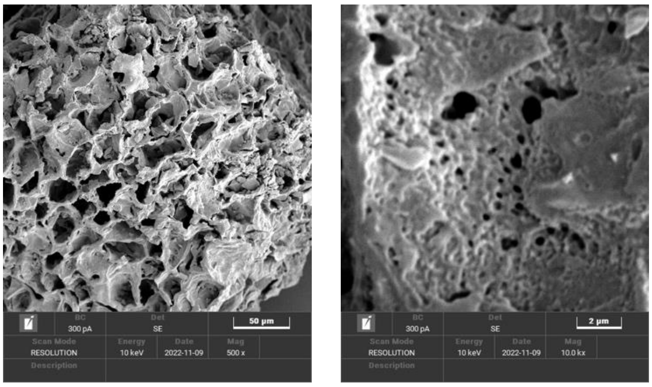
Figure 4 (c-d) shows the surface morphology of AC-KOH sample. The formation of porous honeycomb-like structures can be clearly observed in Figure 4c. The average diameter of these pores is ±43 μm. The existence of micropores (average size ±1.2 μm) also can be observed at higher magnification (Figure 4d). In contrast, the activated carbon produced from basic activation (AC-H_3PO_4 sample), shows the smaller, non-uniform pore morphology, with an average diameter of ±32 μm. At higher magnification (Figure 4f), the formation of micropores becomes more obvious compared to biochar and AC-KOH samples, with average pore diameter of ±0.8 μm.



(a) Biochar (500x) (b) Biochar (10kx)



(c) AC-KOH (500x) (d) AC-KOH (10kx)

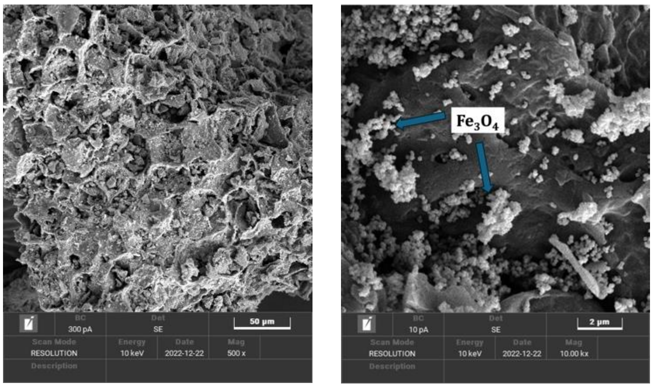


(e) AC-H_3PO_4 (500x) (f) AC-H_3PO_4 (10kx)

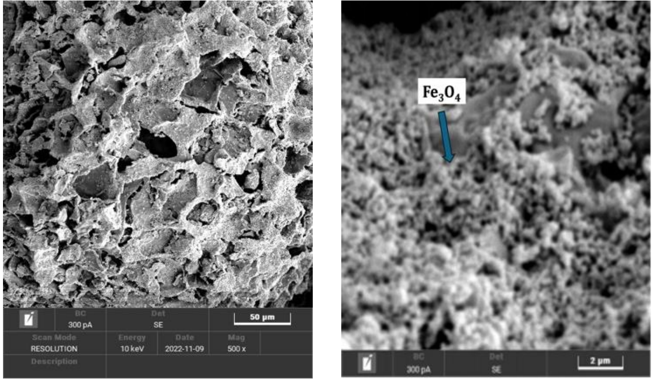
Figure 4. SEM images of (a-b) biochar (c-d) AC-KOH and (e-f) AC-H_3PO_4.

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 forming the active sites onto the activated carbon. However, their mechanism of reaction is different. KOH is a strong base and normally reacts aggressively and has pronounced etching effect onto carbonaceous material that led to the formation of bigger pores (Figure 4c). 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 (Figure 4e) and micropores (Fig 4f) compared to KOH [15].

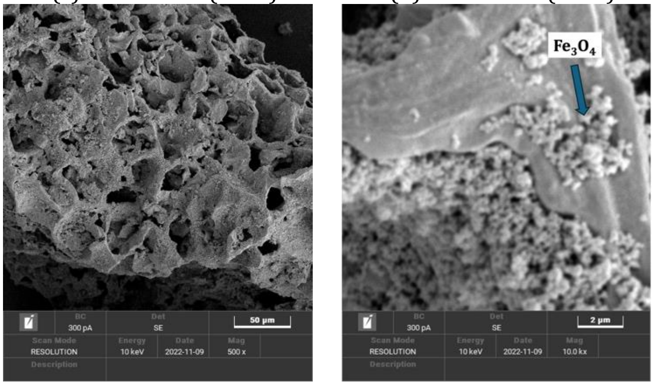
Figure 5 (a-f) shows the surface morphology of Fe_3O_4-biochar, MAC-KOH and MAC-H_3PO_4. The Fe_3O_4 is well-dispersed over the biochar and activated carbon surfaces (Figure 5(b), (d) and (f)) and occupied in the pore structures (Figure 5(a), (c) and (e)).



(a) Fe_3O_4-biochar (500x)
(b) Fe_3O_4-biochar (10kx)



(c) MAC-KOH (500x)
(d) MAC-KOH (10kx)



(e) MAC-H_3PO_4 (500x)
(f) MAC- H_3PO_4 (10kx)

Figure 5. SEM images of (a-b) Fe_3O_4-biochar (c-d) MAC-KOH and (e-f) MAC-H_3PO_4.

3.4. Adsorption Efficiency

Table 3 shows the initial and final concentration (ppm), and the removal efficiency (%) of the copper ions after the adsorption testing process. Based on Figure 6, samples biochar, magnetite-biochar, AC-KOH, and MAC-KOH show the highest percentage of copper ions removal, with more than 99% efficiency. For the biochar sample, even though with the absence of an activating agent, the organic compound in ground coffee waste can contribute to the formation of functional groups such hydroxyl and carboxyl group during the pyrolysis process. These functional groups enhance the adsorption process through the hydrogen bonding or ion exchange process. Furthermore, the pyrolysis of ground coffee waste can lead to a diverse pore structure, including micropores and mesopores. This range allows for effective adsorption of copper ions from the solution and gave almost 100% (99.9%) of the removal efficiency [16]. In addition, based on BET analysis in Table 4, the biochar sample shows the highest surface area value, 78.2 m^2/g compared to other samples which are about 60 m^2/g and below. For magnetite particles, the removal efficiency is 93.6%, indicating that this particle itself has good adsorption behavior. This is due to the high surface area of the Fe_3O_4 nanocrystalline structure, which provides ample sites for copper molecules to adhere. Furthermore, the surface of magnetite contains various functional groups including hydroxyl(-OH) that can interact with Cu^{2+} through electrostatic interactions [17].

Table 3 Percentage of copper ion, Cu^{2+} removal

Sample	**Initial concentration (ppm)**	**Final concentration (ppm)**	**Removal efficiency** (%)
AC-KOH	150	0.4756	99.68
AC-H_3PO_4	150	12.1256	91.92
Biochar	150	0.0891	99.94
MAC-KOH	150	0.2333	99.84
MAC-H_3PO_4	150	12.0927	91.94
Fe_3O_4-biochar	150	0.0884	99.94
Fe_3O_4	150	9.6266	93.58
GCW	150	5.9695	96.02

Table 4 BET surface area of all the samples

Samples	**Surface are (m^2/g)**
AC-KOH	60.2
AC-H_3PO_4	56.3
Biochar	78.2
MAC-KOH	59.8
MAC-H_3PO_4	55.7
Fe_3O_4-biochar	54.6
Fe_3O_4	51.3
GCW	57.8

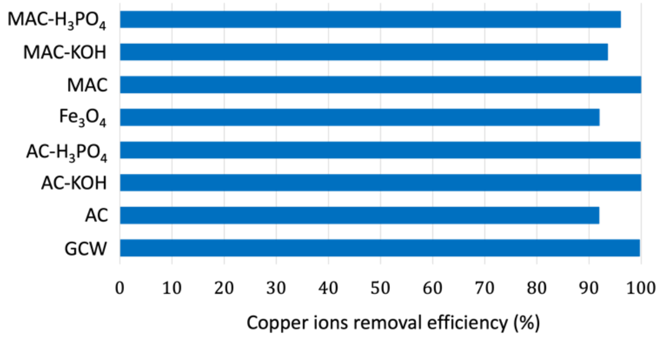


Figure 6. The copper ions removal efficiency (%).

Both samples, AC-H_3PO_4 and MAC-H_3PO_4, exhibit the lowest efficiency of copper ion removal among all samples, which is 91.9%. Even though activation with phosphoric acid can introduce the oxygen-containing functional group (carboxy, hydroxyl) onto the activated carbon surface, which is expected to enhance the adsorption of copper ions through chemical interactions, these functional groups do not guarantee the effectiveness of the adsorption process. The size and distribution of pores that are formed play a crucial role in determining the accessibility of copper ions to the adsorption sites. If the pore structure is not suitable for accommodating the Cu^{2+}, the adsorption capacity maybe limited [10].

In contrast, samples that are treated with potassium hydroxide show high removal efficiency, which is about 99.7% for both AC-KOH and MAC-KOH. After alkaline modification, the surface of the AC-KOH displayed a more developed pore structure as observed in Figure 4 (b), compared to AC-H_3PO_4 (Figure 4 (c)). These pores provide greater surface area and more accessible adsorption sites for target molecules, resulting in higher adsorption efficiency. KOH treatment also tends to introduce higher concentration of oxygen-containing functional groups (carboxyl, hydroxyl) compared to H_3PO_4 treatment, which improved the adsorption efficiency. In addition, treated with KOH resulted in more negatively charged surface compared to H_3PO_4. The differences in surface charge can influence the electrostatic interactions between the activated carbon surface and adsorbates, thus contributing to higher adsorption efficiency [10].

Interestingly, for GCW sample, the removal efficiency is quite high (96%), even though there was no activation or thermal treatment conducted. This might be due to the presence of primary components like cellulose, hemicellulose, and lignin allows the formation of certain surface-active sites such as functional groups of –COOH and –OH that enhanced the removal of metal ions from the solution [18].

4. CONCLUSION

The activated carbon produced by acid (H_3PO_4) and alkaline treatment (KOH) are in the form of amorphous structures. Magnetite reflection can be observed from the XRD pattern of magnetite-activated carbon composites. KOH-treated activated carbon shows the formation of porous honeycomb-like structures with large pore size (average diameter ±43 µm) compared to H_3PO_4-treated activated carbon where the smaller, non-uniform pore morphology with the average diameter ±32 µm was formed. The copper ions removal efficiency is the highest for biochar (almost 100%). Even though without any acid or alkaline treatment, the presence of primary components like cellulose, hemicellulose, and lignin, which allows the formation of certain surface-active sites and porosity due to the thermal treatment might contributed to the high adsorption process. For treated activated carbon, AC-KOH and MAC-KOH show the highest adsorption removal efficiency (99.7%). This is due to the formation of larger pores with more accessible adsorption sites for target molecules compared to the acid-treated carbon (91.9%). Magnetite itself has good adsorption behavior (93.6% efficiency) due to its nanocrystalline structure (high surface area) and functional groups. The results of this work raise new possibilities for synthesizing carbon materials with high Cu^{2+} adsorption capacities from biowastes, via less-toxic, energy-saving conventional chemical activation methods for water-treatment applications.

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