

Ground Coffee Waste-Derived Activated Carbon: A Sustainable Adsorbent and Photocatalyst for Effective Methylene Blue Dye Degradation

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ABSTRACT

This study focuses on harnessing the potential of ground coffee waste (GCW) as a valuable precursor to produce activated carbon (AC) through pyrolysis. The objective is to develop an eco-friendly adsorbent and photocatalyst for environmental remediation applications. Preceding pyrolysis at 350°C for 3.5 hours, GCW was subjected to activate using hydrochloric acid (HCl) and potassium hydroxide (KOH). The resulting AC was subsequently combined with titanium dioxide (TiO₂) photocatalyst powder, resulting in the creation of TiO₂-AC composites that functioned both as adsorbent and photocatalyst. The TiO₂-AC composites were investigated for their adsorption and photocatalytic capabilities in the degradation of 10 ppm methylene blue dye under sunlight exposure for 240 minutes. Morphological analysis revealed a sponge-like structure for both HCl-activated AC and NaOH-activated AC, with HCl-AC exhibiting more pronounced and uniform pores compared to KOH-AC. Remarkably, GCW demonstrated the highest removal efficiency, effectively removing 97.34% of methylene blue, outperforming HCl-AC (16.89%) and KOH-AC (10.41%). Nonetheless, the AC-TiO₂ composites, specifically HCl-AC/TiO₂ and KOH-AC/TiO₂, also exhibited considerable removal efficiencies of 93.31% and 92.46%, respectively. These findings underscore the promising potential of utilizing GCW-derived activated carbon as an environmentally sustainable solution for organic pollutant treatment and herald its significance in promoting greener approaches to waste utilization and environmental protection.

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

1. INTRODUCTION

In an era marked by escalating significant attention towards environmental concerns, the researchers all over the world driving the global scientific community to explore innovative approaches to waste utilization and urgency to address sustainable solutions for water pollution, especially in wastewater treatment. Among the numerous environmental challenges faced nowadays, the dye industry has been identified as a significant contributor to water pollution by releasing a harmful synthetic dye, which poses a significant threat to aquatic ecosystems and human health [1,2].

Organic dyes are a hazardous material due to their toxicity and poor biodegradability. Among the organic dyes, Methylene Blue (MB) dye is widely used for various applications in industries, become a matter of considerable environmental concern due to its toxic nature and resistance to natural degradation [2,3].

In the pursuit of sustainable technologies for dye removal, there has been an increasing interest in exploring waste-derived adsorbents and photocatalyst as viable alternatives. Due to this, carbon materials including carbon nanotube, graphene, activated carbon, mesoporous carbon, carbon nanofiber aerogels and carbon nanofiber membranes, have been explored their potential applications due to its unique

properties as efficient adsorbents for the organic dye removal [1].

As the demand for eco-friendly materials and efficient water treatment methods grows, researchers have turned to activated carbon and photocatalysis as promising approaches. In this context, ground coffee waste (GCW), an agricultural by-product of the coffee industry, has emerged as a promising candidate due to its high carbon content, high surface area, abundant availability, low cost and environmental friendliness [4]. Utilizing this waste material provides a sustainable approach to address the challenges of water pollution.

Notably, due to the coffee waste being rich content of carbon, it was a sustainable precursor for the synthesis of activated carbon, arising from the incomplete combustion of coffee beans during roasting for producing activated carbon. Activated carbon is renowned for its remarkable adsorption capacity, offering a reliable method for removing various contaminants from the water. On the other hand, photocatalysis, driven by the utilization of semiconductor photocatalyst under light irradiation, demonstrates excellent potential for dye degradation. Among the photocatalyst, titanium dioxide (TiO₂) is the most promising photocatalyst in photocatalytic process of degrading organic pollutants. This is due to its high efficiency, low cost, chemical stability and non-toxicity [5, 6].

This journal article presents a comprehensive investigation into the potential of ground coffee waste-derived activated carbon as an effective adsorbent and photocatalyst for Methylene Blue dye degradation.

2. MATERIALS AND METHOD

2.1. Materials and Chemical

The ground coffee waste (GCW) was collected from McDonald's Restaurant in Perlis, as source materials. The commercial titanium dioxide (TiO₂) powder was obtained from R&M Chemicals and used as a photocatalyst. The chemicals that were applied in this experiment are hydrochloric acid (HCl) and potassium hydroxide (KOH) which were purchased from HmbG Chemicals which act as acid activators and base activators, respectively. Methylene Blue dye from Sigma-Aldrich was used as an organic pollutant in this research. Distilled water was used for all the experiments.

2.2. Synthesis of Activated Carbon (AC) without Activator

In preparation of synthesis activated carbon without activation, GCW was ground into particle sizes less than 40–60 mesh, which has the range from 0.25 mm to 0.4 mm particles. Then, the GCW was rinsed with distilled water multiple times for contaminant removal. The cleaned GCW was dried at 75±2 °C for 24 hours to remove moisture.

2.3. Synthesis of Activated Carbon (AC) with Activator

For activated carbon with chemical activation sample, a 100g of GCW was soaked in a solution 100mL of acid activator (0.1 M HCl) and basic activator (0.1 M KOH) for 48 hours, respectively. In order to achieve pH neutrality, the sample was then washed with distilled water after the solution had been drained. GCW that has been chemically activated was placed in an oven to reduce moisture content before being placed in a muffle furnace at 350°C for 3.5 hours. The produced activated carbon was sieved through a 80 to 100 mesh sieve and stored in a desiccator. Both samples with acid and basic activator were labelled as Sample HCl-AC and KOH-AC, respectively. The raw sample without activator was also prepared and designated as GCW.

2.4. Synthesis of Titania-Activated Carbon (TiO₂-AC)

For the preparation of the titania-activated carbon (TiO₂-AC) composite, an amount of 10g of Sample HCl-AC was mixed into the 200 ml of titania solution, which was prepared by dispersing 1 g of titanium powder 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 Sample HCl-AC/TiO₂. For different batches of TiO₂/AC composite powder, the process was repeated by replacing Sample HCl-

AC with Sample KOH-AC. The synthesized composite powders were then labelled as Sample KOH-AC/TiO₂.

2.5. Characterization of Prepared Sample

The phase determination of raw sample, sample with chemical treatment, and treated sample with addition of photocatalyst were characterized via X-ray diffraction (XRD D8- Advance, Bruker, USA) over a 2θ range 5° to 80° equipped with a Cu Kα (λ=1.5419 Å) at a scanning rate 5°/min, 2θ with a step size of 0.0131° in powder form. The pattern of XRD was analyzed by X'pert Highscore Plus software with ICDD PDF-2 database.

The surface morphology, topology and pore size of the granular AC and microstructure transformation after chemical activation, also for the sample with the addition of TiO₂ photocatalyst were studied by using a scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDS) (SEM-EDS, TESCAN VEGA, Czech, Republic). It was operated in accelerating temperature voltage of 20 kV, which was used to investigate the original and activated samples. The samples were prepared in powder form and vacuum-sealed for 1 hour to eliminate any entrained gas. Then, the samples are coated with gold in order to eliminate charging and enhance the generation of secondary electrons. This coating procedure is performed using a magnetron sputtering machine from Sputter Coater NS800 for 60 seconds at 18 mA. The samples are then examined by scanning microscopy to observe their characteristics.

The BET surface area and porosity of the raw materials and prepared samples were investigated by using the Brunauer–Emmett–Teller (BET Tristar 3000, Micromeritics, Germany) method. Nitrogen was used as the adsorbate gas. Prior to the analysis, the samples were degassed at 300°C for 3 hours under a nitrogen atmosphere in order to clean up the surface of the sample and to remove the adsorbed water and other adsorbed material.

2.6. Photocatalytic Testing

The decolorization and degradation of the MB dye solution were determined by measuring the MB absorbance at the wavelength of 660 nm by using a UV-Vis spectrophotometer (Lambda 365, Perkin Elmer, USA). The 50mL of MB solution was taken and mixed with the samples by using magnetic stirring at 120 rpm in dark conditions in order to establish the adsorption equilibrium. The MB dye removal efficiency was calculated using Equation 1. The final dye concentration and percentage of dye removal were calculated and tabulated.

$$R = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

While,

R= Removal efficiency of MB (%)

C₀= Initial concentration of the dye solution (mg/L)

C_t= Final concentration of the dye solution at reaction time (t) in hours (mg/L)

3. RESULTS AND DISCUSSION

3.1. Phase Determination

The XRD patterns of the activated carbon (AC), activated carbon that is chemically treated with HCl (HCl-AC), and KOH (KOH-AC) are shown in Figure 3.1. The XRD pattern of AC reveals a semicrystalline structure consisting of both amorphous and crystalline components. This can be seen through a broad hump that was observed between 14° and 22°, which confirms the presence of amorphous carbon in GCW. Additionally, a prominent peak is visible at $2\theta = 21.02^\circ$, corresponding to the (311) plane, primarily originating from cellulose, as stated in [7].

Meanwhile, the XRD patterns of the chemically activated carbon samples, both HCl-activated carbon and KOH-activated carbon exhibit an amorphous hump between 12° and 26° of 2θ degrees. The absence of distinct peaks indicates the presence of amorphous carbon, as observed in the respective XRD patterns. The disappearance peak of cellulose at $2\theta = 21.02^\circ$ as in raw coffee (GCW), indicates that this structure might be decomposed at a temperature higher than 300°C [8].

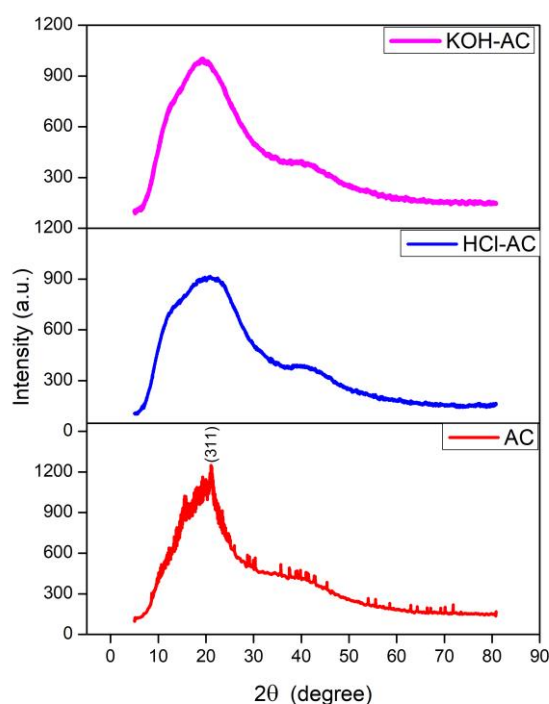


Figure 1. XRD pattern of AC, HCl-AC and KOH-AC.

The XRD patterns of HCl-AC/TiO₂ and KOH-AC/TiO₂ composites are shown in Figure 2 and Figure 3, respectively. As can be seen, those two activated carbon composites show similar diffraction patterns, with most of the peaks appearing at $2\theta = 24.98^\circ, 37.46^\circ, 38.22^\circ, 47.62^\circ, 53.52^\circ, 54.66^\circ, 62.46^\circ, 68.54^\circ, 70.02^\circ,$ and 74.62° corresponding to the planes of (101), (004), (112), (200), (105), (211), (204), (116), (220), and (215) crystallographic phase of tetragonal

structure of anatase, TiO₂ (ICDD No. 01-086-1156). The amorphous humps (15° - 25° of 2θ degree) still can be observed in the composite structures indicating the amorphous phase of the activated carbon.

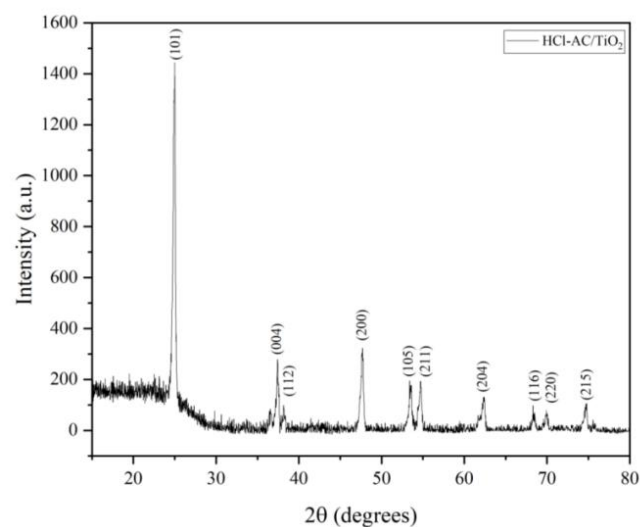


Figure 2. XRD pattern of HCl-AC/TiO₂.

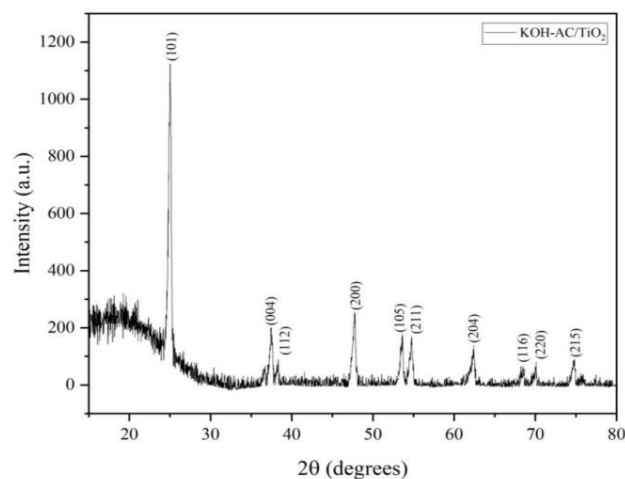


Figure 3. XRD pattern of KOH-AC/TiO₂.

3.2. Morphology

The morphology of GCW was observed under SEM as shown in Figure 4. GCW is an organic powder with a dark brown colour. Upon SEM examination, it was observed that the particles of GCW exhibit irregular shapes and are relatively large. The micrograph in Figure 4 provided insight into the presence of heterogeneous holes in coffee waste, albeit in smaller numbers. However, these holes can still serve as sites for capturing and adsorbing the MB dye, which aligns with the findings in [9].

Additionally, the surface of GCW appears rough, while the pores exhibit an irregular pattern. The irregular surface morphology may be responsible for this characteristic as they adhere to the surface and lead to a reduction in pore size, potentially causing blockages due to the coffee residue.

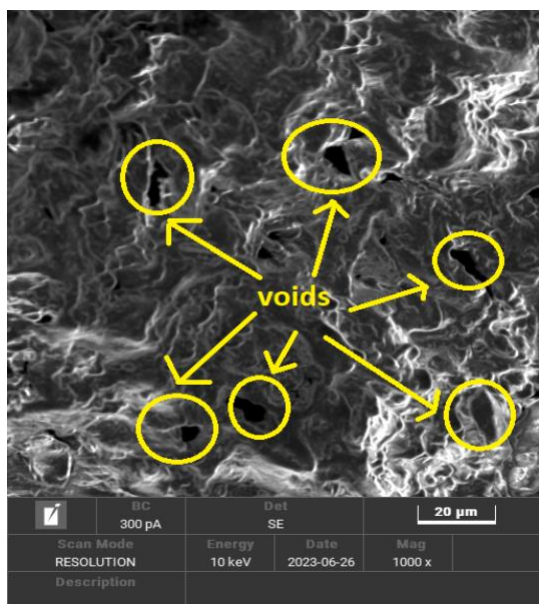


Figure 4. SEM micrograph of GCW.

The surface characteristics of HCl-AC and KOH-AC are shown in Figure 5 (a) and (b), respectively. Both samples exhibit a combination of mesopores and micropores within their internal pore structures. When comparing the surface roughness and porosity of HCl-AC, KOH-AC, and GCW, it is evident that HCl-AC and KOH-AC exhibit rougher and sponge-like structure surfaces compared to GCW. This can be attributed to the removal of water-soluble compounds by using chemical treatment that was cracking the GCW, which leads to an increase in both surface roughness and porosity [10].

The surface of HCl-AC appears rougher, resembling a sponge-like structure, in contrast to the smooth surface of KOH-AC. Additionally, a higher number of pores are evident in HCl-AC compared to KOH-AC. Furthermore, the internal pore structure of HCl-AC contains a greater proportion of micropores, which contributes to its enhanced capacity for adsorbing MB. Conversely, KOH-AC exhibits a relatively smooth surface with slight wrinkles, and the pore size is relatively smaller than that of HCl-AC. This difference may be attributed to the different chemicals used for the activation process, and it matches the finding of [12]. Due to the presence of larger voids in HCl-AC compared to KOH-AC, the removal efficiency of HCl-AC in degrading MB is higher than that of KOH-AC in this study.

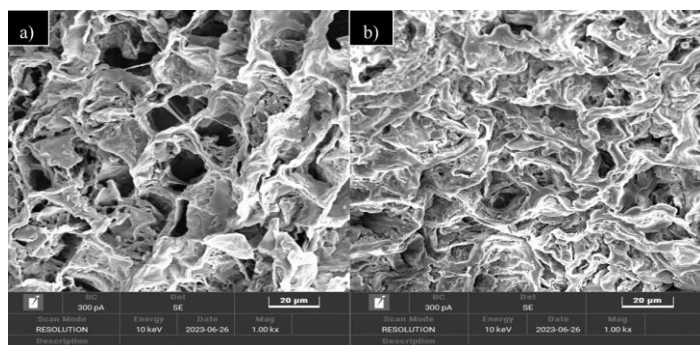


Figure 5. SEM micrograph of (a) HCl-AC and (b) KOH-AC.

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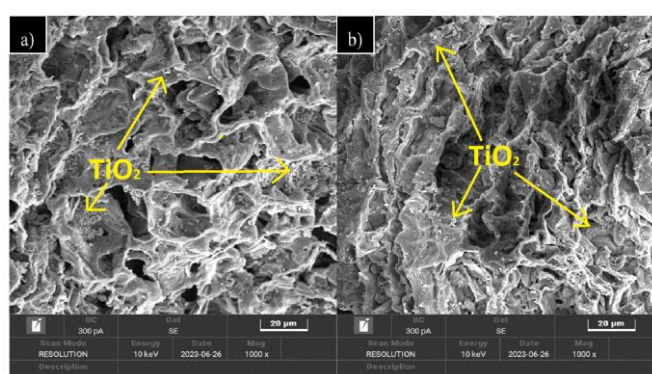


Figure 6. SEM micrograph of (a) HCl-AC/TiO₂ and (b) KOH-AC/TiO₂.

Figure 6 presents the SEM images of HCl-AC/TiO₂ and KOH-AC/TiO₂. The images reveal the presence of numerous small nanoparticles that have become trapped within the micropores on the surface of both treated activated carbon samples. These nanoparticles, identified as TiO₂, have effectively adhered to the surface of the activated carbon. The images reveal the presence of numerous small nanoparticles that have become trapped within the micropores on the surface of both treated activated carbon samples. These nanoparticles, identified as TiO₂, have effectively adhered to the surface of the activated carbon.

Table 1 Average pore size of AC, treated AC and titania-AC

Name of sample	Average pore size (μm ²)
GCW	1.468
HCl-AC	1.673
KOH-AC	1.151
HCl-AC/TiO ₂	0.330
KOH-AC/TiO ₂	0.327

The average pore size of HCl-AC and KOH-AC measured by using Image J software directly from SEM image is presented in Table 1. HCl-AC exhibits the highest pore size of 1.673μm², whereas KOH-AC has a pore size of 1.151μm². This indicates that acid-treated activated carbon has a larger pore size compared to base treated activated carbon.

The larger pore size provides sufficient active sites for MB dye adsorption. However, the pore size decreased after the addition of titania photocatalyst due to the TiO₂ had covered the pores (as shown in Figure 6). This led to the average pore size being reduced.

3.3. Specific Surface Area and Porosity

The details about porosity characteristics including BET surface area and adsorption average pore width for all prepared samples are tabulated in Table 2. This result was measured by BET specific area technique which generates a specific surface area result expressed in units of area per mass of sample (m²/g) in powder form. The sample of activated carbon shows the highest adsorption average pore width which is about 33923.133 nm. This was proved by SEM micrograph in Figure 1, there are a lot of voids that provide a reaction site that act as an adsorbent [11].

Other than that, the average pore width of KOH-AC is higher than HCl-AC. In addition, it is observed that the average pore width of AC containing TiO₂ catalysts is smaller than that of AC treated with chemicals. This is due to the TiO₂ blocking the entrance and depositing on the surface of AC, as shown in Figure 6 [11]. The reduction in the adsorption average pore width can be viewed as the expected consequences of the above conclusion.

Table 2 Porosity characteristics of activated carbon, chemical treated activated carbon and photocatalyst-treated activated carbon

Porosity		
Name of sample	BET surface area (m ² /g)	Adsorption average pore width (nm)
AC	0.015	33923.133
HCl-AC	0.012	1928.217
KOH-AC	0.111	1058.763
HCl-AC/TiO ₂	0.214	62.118
KOH-AC/TiO ₂	0.388	58.380

On the other hand, it is observed that the BET surface area for those of the AC treated with acid is noticeably smaller than those of the AC treated with base. Meanwhile, AC with TiO₂ catalyst recorded high BET surface area compared to other samples. From the result, it can be reasonably assumed that the catalysts are highly dispersed in water, which may be explained by the effect of stirring [13].

3.4. Methylene Blue Degradation Study

In this study, HCl and KOH were selected for chemical treatment to produce activated carbon in order to increase the removal efficiency of MB. This was done because acid and base treatment can increase the porosity of activated carbon by opening the blind pores. As a result of this, chemical treatment activated carbon and activated carbon that had not been subjected to any chemical treatment were both investigated for their ability to remove the MB when subjected to solar irradiation. In addition to this, TiO₂ was

selected as a photocatalyst to mix with treated activated carbon composite as opposed to treated activated carbon without mixing with TiO₂ for the purpose of investigating and comparing the two materials respective removal efficiencies of MB when subjected to direct sun irradiation at several contact times (30, 60, 120, 180, and 240 minutes). Figure 7 shows the removal efficiency of MB by sample GCW, HCl-AC, KOH-AC, HCl-AC/TiO₂, and KOH-AC/TiO₂ under the sunlight within 4 hours. The GCW exhibit the highest removal efficiency, reaching 97.34% compared with the treated AC by chemical, which are HCl-AC (16.89%) and KOH-AC (10.41%) and treated AC-TiO₂ composites which is HCl-AC/TiO₂ (93.31%) and KOH-AC/TiO₂ (92.46%).

This remarkable performance can be attributed to the role of electrostatic interactions between the cationic dye molecules and the surface groups of GCW [14]. Furthermore, the presence of a large number of carbonyl and hydroxyl groups in GCW contributes to enhanced adsorption capacity for cationic dyes like methylene blue [9,15]. These functional groups play a vital role in the surface complexing mechanism between the oxygen-containing functional groups and MB ions [11]. Consequently, GCW, with its abundance of functional groups, exhibits a higher adsorption capacity for cationic dyes through this surface complexing mechanism due to its highest number of average pore widths.

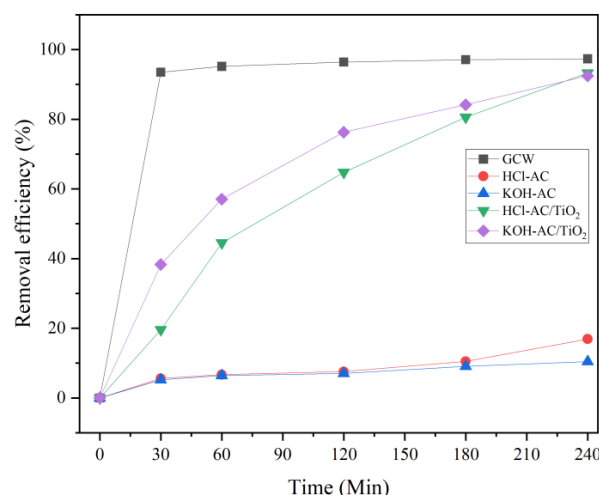


Figure 7. Removal efficiency of MB by using different samples in 240 minutes.

For KOH-AC/TiO₂ and HCl-AC/TiO₂, two mechanisms might have occurred, namely adsorption and photocatalytic degradation. If compared to HCl-AC and KOH-AC, which is without the TiO₂ photocatalyst, the removal efficiency of methylene blue is lower than AC with photocatalyst. This low percentage of the removal is due to the adsorption mechanism only. Nevertheless, as TiO₂ was incorporated in both samples (HCl-AC-TiO₂ and KOH-AC-TiO₂), the removal efficiency increased up to 93.31% and 92.46%, respectively. Besides that, the pore size of HCl-AC is much bigger compared to the pore size of KOH-AC as discussed in the previous section (sections 3.2. and 3.3.), resulting in higher removal efficiency of the HCl-treated sample compared to the KOH-treated sample.

From Figure 7, it can be clearly seen that by using TiO_2 combined with the AC, the removal efficiency increases around 75% compared to AC without using TiO_2 in the experiment. This demonstrates that the concentration of MB is reduced not only by adsorption, but also by photodegradation in the presence of TiO_2 [16]. This is because TiO_2 is a semiconductor and a photocatalyst can improve the removal of methylene blue due to its photocatalytic degradation process.

When under the sunlight, the energy of the UV light (below 387nm) reduces the band gap of the TiO_2 (3.0-3.2 eV), so it promotes energy to photo-excitation and causing the electrons react with the O_2 , and generate reactive oxygen species (ROS), which is hydroxyl radical ($\text{OH}\cdot$), the adsorbed $\cdot\text{OH}$ can be thought of as confined holes involved in a rapid adsorption-desorption equilibrium at the interface between TiO_2 and solution to degrade methylene blue dye [17].

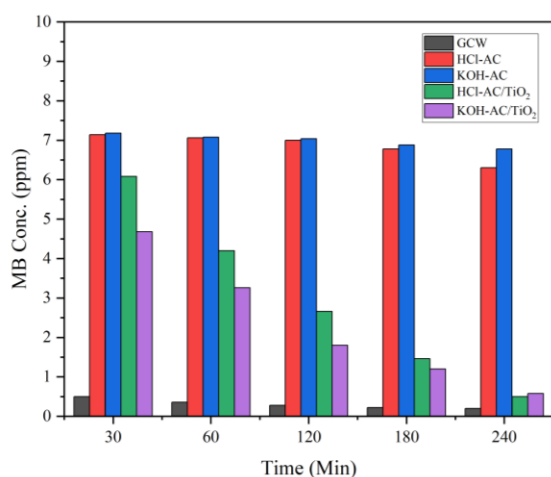


Figure 8. The concentration of MB of different samples.

Figure 8 displays the methylene blue (MB) concentration after 240 minutes of treatment for different samples. The graph clearly shows that GCW exhibited the lowest MB concentration, measuring at 0.20 ppm, while HCl-AC registered 6.30 ppm, KOHAC recorded 6.78 ppm, HCl-AC/ TiO_2 measured 0.50 ppm, and KOH-AC/ TiO_2 showed 0.58 ppm.

During the testing phase, it was intriguing to observe that GCW exhibited the highest removal efficiency of methylene blue (MB) solution, reaching 97.34%, and the lowest concentration of MB solution, measuring at 0.20 ppm, among all the samples. This remarkable performance can be attributed to the role of electrostatic interactions between the cationic dye molecules and the surface groups of GCW, as reported in [14].

Furthermore, the presence of a large number of carbonyl and hydroxyl groups in GCW contributes to its enhanced adsorption capacity for cationic dyes like methylene blue [9,15]. These functional groups play a vital role in the surface complexing mechanism between the oxygen-containing functional groups and MB ions [11].

Consequently, GCW, with its abundance of functional groups, exhibits a higher adsorption capacity for cationic dyes through this surface complexing mechanism.

HCl-AC demonstrates a higher removal efficiency for MB compared to KOHAC, as depicted in Figure 8. This discrepancy can be attributed to the differences in pore size and number of pores on their surfaces. Initially, both materials exhibited similar removal percentages and rates from 0 to 180 minutes. However, a shift occurred at 180 minutes where the removal efficiency of MB by KOH-AC started to decrease and almost stagnant, while HCl-AC continued to remove the MB until 240 minutes. Ultimately, KOHAC only achieved a removal efficiency of 10.41%, whereas HCl-AC reached a removal efficiency of 16.89%, surpassing KOH-AC by approximately 6%.

This difference can be explained by the surface chemistry of the activated carbon. Sample KOH-AC may have fewer interaction sites or functional groups capable of effectively attracting and binding basic dye molecules like MB. Additionally, as revealed in Figure 5, the number of pores on the surface of KOH-AC is relatively lower. Consequently, as the active sites on KOH-AC's surface began to fill with MB molecules, the removal efficiency declined and eventually reached saturation with prolonged exposure time. Consequently, the adsorption capacity and effectiveness of KOH-AC for MB are diminished.

4. CONCLUSION

The following conclusions were reached based on the result analysis as presented in this paper which are, the chemical treatment of activated carbon using HCl, and KOH led to a phase transformation from semicrystalline (GCW) to amorphous structures (HCl-AC and KOH-AC). This transformation occurred due to the degradation of cellulose present in raw coffee during high-temperature heat treatment at 350°C. Besides, HCl-AC/ TiO_2 and KOH-AC/ TiO_2 have a crystalline structure due to the addition of TiO_2 .

In addition, the morphology of chemically treated activated carbon differed from the raw materials (GCW). The treated activated carbon exhibited altered morphology, increased roughness, and greater porosity compared to raw GCW. HCl-AC displayed larger pore size and porosity compared to KOH-AC at 350°C. It can be concluded that, after chemical treatment, both HCl-AC and KOH-AC contained macropores and micropores. HCl-AC exhibited a sponge-like structure, while KOH-AC had relatively smoother surfaces with less roughness. Additionally, the pore size of HCl-AC was larger than that of KOH-AC after high temperature treatment. The presence of these pore structures and micropores contributed to the enhanced removal of methylene blue dye. Furthermore, the presence of TiO_2 particles was observed in AC- TiO_2 composite samples.

In terms of dye removal efficiency, GCW demonstrated superior methylene blue removal efficiency compared to removal efficiency for methylene blue. Notably, GCW

exhibited the highest removal efficiency, which could be attributed to the electrostatic interactions between the surface of GCW and the methylene blue dye. In future investigations, exploring the synergistic effects of GCW and TiO₂ in the removal of methylene blue and other contaminants would be beneficial.

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