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Article

Analysis of the catalytic efficiency of spent coffee grounds and titanium dioxide using UV-Vis spectroscopy

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SUMMARY

Catalysts serve an essential function in manufacturing consumables such as plastic and fuel. However, some of these are scarce, costly, unsustainable, or some combination of the above. Thus, we decided to examine whether an alternative substance that is more environmentally sustainable and economically viable than a conventional catalyst can serve as an effective catalyst support. We investigated the possibility of using spent coffee grounds, given their catalytic properties of conductivity and structural porosity, as a new eco-friendly alternative to titanium dioxide (TiO_2), a catalyst widely used in heterogeneous catalysis. We hypothesized that a mixture of TiO_2 and spent coffee grounds would show a level of chemical efficiency comparable to a catalyst comprised of pure TiO_2. Toward this, we tested the catalytic performance of five mixtures of TiO_2:spent coffee grounds (pure TiO_2, spent coffee grounds, 1:3, 1:1, and 3:1) during the photocatalytic decomposition reaction of methylene blue using an Ultraviolet-visible (UV-Vis) spectrophotometer. The TiO_2:spent coffee grounds mixture at a 3:1 ratio showed the highest efficiency among the spent coffee grounds mixtures, comparable to that of pure TiO_2 catalyst. This finding points to the potential of spent coffee grounds as a sustainable and affordable catalyst support for the costly and unsustainable TiO_2.

INTRODUCTION

Catalysts play an important role in the manufacturing industry. Not only are they essential in the polymerization process for the production of plastics used in everyday life, but they are also key enablers in naphtha reforming to produce fuel as well as in the making of nitric acid needed in the fertilizer and dye sectors (1). They enhance the reaction rate and consequently increase the production rate in chemical processes. Commonly used industrial catalysts, such as nickel, platinum, and titanium, enable manufacturing plants to produce faster with better efficiency (2). Such metal catalysts, however, are scarce resources that come with a high cost of procurement (2). They also have a high environmental impact, producing significant greenhouse gas emissions in the course of their mining, as mining requires energy consumption in the form of fuel or electricity (3).

Due to these shortcomings of conventional industrial catalysts, this study aimed to investigate a more sustainable and economically viable substance that can potentially function as an effective support material for catalysts that may allow reduced amounts of catalyst to be used. We examined the use of spent coffee grounds (SCG) as an eco-friendly catalyst support material. SCG were selected for the experiment as they are readily available in the form of food waste. They also contain conductive carbon material with a porous structure that enables the substance to support the catalytic reaction, and numerous prior studies have demonstrated that porosity promotes the catalytic performance of a substance (4). That a structure is porous means that there is empty space of substantial proportion in the inner dimensions of its solid matrix (5). Air is contained in the pores whose size varies from two nanometers to a much larger fifty nanometers (6). The large surface area of porous substances creates more locations to absorb abundant ions during catalytic processes, enabling faster movement of kinetic mass, thus significantly enhancing catalytic performance (7,8). This porosity of the catalyst essentially provides more reactive sites for adsorption and is conducive to the transfer of charges (8,9). In addition, porous structures also facilitate the transfer of photogenerated electrons and enhance light absorption, which improves the photocatalytic reaction rate (10,11). Thus, all of these characteristics support the function of porous carbon-containing coffee grounds as an effective catalytic material in chemical reactions. Each year, more than 18 million tons of coffee grounds are discarded after consumption (12). Using these abundant substances in a chemical process could also substantially reduce the amount of coffee grounds being thrown away (6). This is why the chemical industry is making an effort to synthesize previously non-existent catalysts by pre-treating coffee grounds (12).

In this study, we aimed to evaluate whether SCG has the potential to work as a catalyst support material by observing its impact on the photocatalytic decomposition reaction of methylene blue. Photocatalytic decomposition reaction of methylene blue is a process that is important and effective for the treatment of wastewater, dyes used in food, as well as for the pharmaceutical industry (13). Photocatalytic processes can help treat organic pollutants in the environment by means of photocatalytic degradation (14). The titanium dioxide (TiO_2) used as a catalyst absorbs photons (15). As the photons have energy that is equal to or greater than the bandgap energy, or energy range with no electrons, of titanium dioxide, electron-hole pairs are generated (15). These pairs start oxidation-reduction reactions, which decompose methylene blue (15). The chemical pathway for the photocatalytic reaction of methylene blue involving TiO_2 is as follows:

$$TiO_2+hv \rightarrow e^-+h^+$$

$$e^-+O_2 \rightarrow \cdot O_2^-$$

$$h^++H_2O \rightarrow \cdot OH+H^+$$

$$MB+\cdot OH/\cdot O_2^- \rightarrow intermediates \rightarrow CO_2+H_2O+NH_4^++SO$$

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The decomposition of methylene blue produces aromatic compounds and amines, including carbon dioxide (CO_2), water (H_2O), sulfate ions (SO_4^{2-}), nitrate ions (NO_3^-), and ammonium ions (NH_4^+) (16).

We used TiO_2 as the reference catalyst and SCG obtained from brewed coffee as our proposed catalyst support material for the photocatalytic decomposition reaction of methylene blue. We selected TiO_2 as the reference catalyst as it is one of the most explored stable materials with strong photocatalytic activity, while at the same time having low toxicity (16).

We hypothesized that a mixture of TiO_2 and SCG at a ratio of 3:1 by weight will show a level of chemical efficiency comparable to a catalyst comprised of 100% pure TiO_2. We observed and compared the reaction performance of the five samples: the pure TiO_2 catalyst, SCG, and three mixtures of the two substances in different ratios (mole percent (mol%) of TiO_2 to SCG) at 12.9% to 87.1% (1:3 TiO_2: SCG by weight), 30.7% to 69.3% (1:1 TiO_2: SCG by weight), and 57.1% to 42.9% (3:1 TiO_2: SCG by weight). Thus, by optimizing the ratio of TiO_2 to coffee grounds, we aimed to identify a catalyst mixture that balances cost and chemical efficiency, offering a more sustainable alternative to pure TiO_2. Results from the experiment showed that the catalyst with 100% TiO_2 had the highest reaction efficiency, while pure coffee grounds had the lowest. The mixtures of TiO_2 and coffee grounds showed varying levels of catalytic performance depending on the ratio in which the two substances were mixed, with the 3:1 ratio of TiO_2 to coffee grounds exhibiting the second highest reactive efficiency, which was comparable to that of pure TiO_2. Hence, this study concludes that a mixture of SCG can work as an effective catalyst and that SCG could be a suitable catalyst support material for the costly, unsustainable titanium dioxide in chemical and industrial manufacturing processes.

RESULTS

We evaluated whether SCG have the potential to work as a catalyst support material by observing the photocatalytic decomposition reaction of methylene blue. The catalytic efficiency of SCG was investigated using TiO_2 as the reference by measuring light absorbance in the photocatalytic decomposition reaction of methylene blue. We used the light absorbance measurements over a period of 40 minutes at wavelength 665 nm, taken with the Ultraviolet-visible (UV-Vis) spectrophotometer, to compare the reaction efficiency of the five samples: pure TiO_2 (100% TiO_2), SCG, and three mixtures of the two substances in different ratios (TiO_2 to coffee grounds at 12.9% to 87.1% (1:3), 30.7% to 69.3% (1:1), and 57.1% to 42.9% (3:1)). The rate of a reaction is correlated to the level of light absorbance of different substances, with lower light absorbance at the end of 40 minutes at 665 nm indicating that less methylene blue is remaining and that the chemical reaction has therefore taken place more quickly (17).

Since the absorbance at 665 nm represents the maximum absorbance of the reactant methylene blue in this experiment, a large decrease in absorbance at this wavelength, when compared at a set time (40 min) among all the samples, directly reflects the faster degradation of methylene blue, remaining in lower concentrations. According to the Beer-Lambert Law, absorbance is proportional to concentration (17). Therefore, we used the absorbance values from the experiment to evaluate the reaction efficiency of the catalyst samples by calculating reaction rates.

Results indicated that the sample containing 0.1 g of TiO_2 catalyst (100% pure TiO_2) showed the highest catalytic efficiency in the photocatalytic decomposition reaction of methylene blue. The absorbance of methylene blue was 0.088 at the wavelength of 665 nm measured at 40 minutes (**Figure 1A**). This absorbance value was the lowest among the five samples, indicating a significant decrease of the methylene blue concentration compared to other catalyst mixtures and demonstrating the high efficiency of the pure TiO_2 catalyst. The reaction rate calculated using initial absorbance, final absorbance, rate constant, and time (**Equation 2**, refer to Methods) was 13.17×10^{-4} M/s.

Using 0.1 g of SCG (100%) alone, presented substantially lower catalytic activity compared to pure TiO_2. The absorbance value of methylene blue in the pure spent coffee grounds sample was 0.108 at 665 nm wavelength at 40 minutes. This is only slightly higher than what was observed from pure TiO_2 as presented in the graph (**Figure 1B**). The reaction rate was 0 M/s. The values for absorbance and reaction rate, however, are theoretical anomalies that could indicate possible interference of coffee color.

The mixture with 0.025g (42.9%) TiO_2 and 0.075 g (57.1%) SCG at a 1:3 ratio showed an absorbance value of 0.248 at 665 nm wavelength at 40 minutes, reflecting the catalytic properties of a combination of both component substances (**Figure 1C**). The methylene blue decomposition reaction efficiency for this mixture was observed to be noticeably higher than pure SCG but lower than pure TiO_2. The reaction rate was 7.34×10^{-4} M/s.

The mixture of 0.05g (69.3%) of TiO_2 and 0.05 g (30.7%) SCG at a 1:1 ratio showed a degree of efficiency higher than that of the 1:3 mixture, with the absorbance of 0.207 at 665 nm at 40 minutes (**Figure 1D**). This suggests that the decomposition of methylene blue occurred more rapidly than in the 1:3 mixture. The reaction rate was 8.13×10^{-4} M/s.

The mixture of 0.075 g TiO_2 (87.1%) and 0.025 g (12.9%) SCG at a 3:1 ratio had an absorbance value of 0.150 at 665 nm at 40 minutes (**Figure 1E**). This was the lowest value among the mixtures that contained SCG. The efficiency observed here was less than pure TiO_2 but notably higher than other mixtures and pure SCG. The reaction rate was 9.36×10^{-4} M/s.

The data presents that while TiO_2 is the most effective catalyst, the mixtures of TiO_2 with SCG showed improved catalyst efficiency compared to SCG alone, with the 3:1 mixture of TiO_2 to SCG providing the best performance among the tested mixtures containing coffee grounds (**Figure 2**). The catalytic efficiency of the five samples (**Figure 3**; TiO_2, pure SCG, and TiO_2 to SCG mixtures at 1:3, 1:1, and 3:1 ratios by weight) can be ranked from high to low according to reaction rates as follows:

$$\underset{(13.17\times10^{-4}\text{M/s})}{TiO_2} > \underset{(9.36\times10^{-4}\text{M/s})}{3{:}1} > \underset{(8.13\times10^{-4}\text{M/s})}{1{:}1} > \underset{(7.34\times10^{-4}\text{M/s})}{1{:}3} > \underset{(0\text{ M/s})}{SCG}$$

DISCUSSION

The conventional metal catalyst TiO_2, widely used in chemical reactions, is a scarce resource that is both costly and unsustainable. To examine whether a substance more environmentally sustainable and economically viable than TiO_2 can serve as an effective catalyst support material, we

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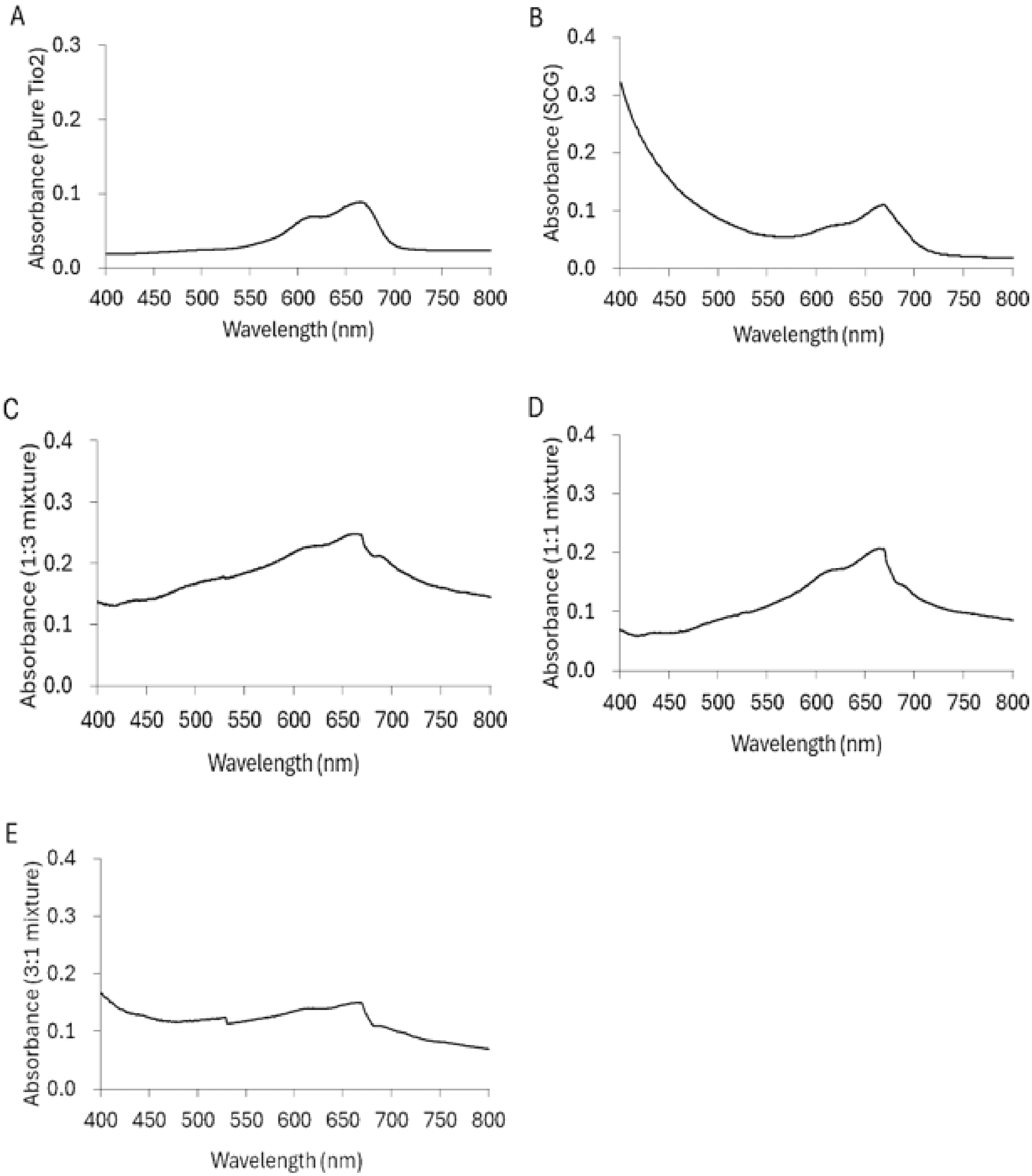

Figure 1. Absorbance for the five catalyst samples. Line graphs showing absorbance of methylene blue solution using (A) pure titanium dioxide (TiO_2), (B) pure spent coffee grounds (SCG), (C) mixture of TiO_2 and SCG at a ratio of 1:3 by weight, (D) mixture of TiO_2 and SCG at a ratio of 1:1 by weight, and (E) mixture of TiO_2 and SCG at a ratio of 3:1 by weight. Measured at 40 minutes using an Ultraviolet-Visible (UV-Vis) spectrophotometer.

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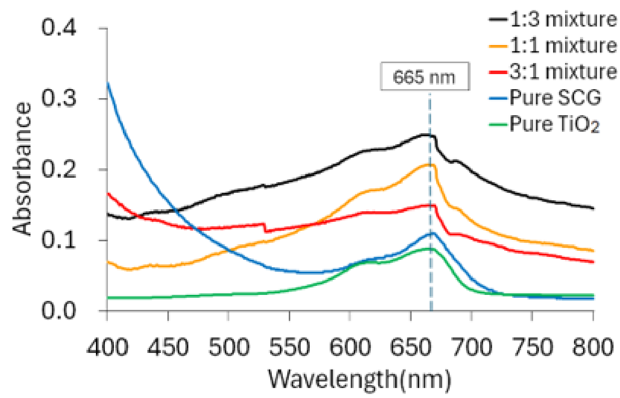

Figure 2. Comparison of absorbance of all five samples. Line graph showing absorbance of methylene blue solution for the five samples containing varying ratios of titanium dioxide (TiO_2) and spent coffee grounds (SCG). Line drawn at 665 nm indicates the absorbance peak for methylene blue. Measured at 40 minutes for pure TiO_2, pure SCG, and mixtures of TiO_2 to SCG at varying ratios by weight (3:1, 1:1, and 1:3) using an Ultraviolet-Visible (UV-Vis) spectrophotometer.

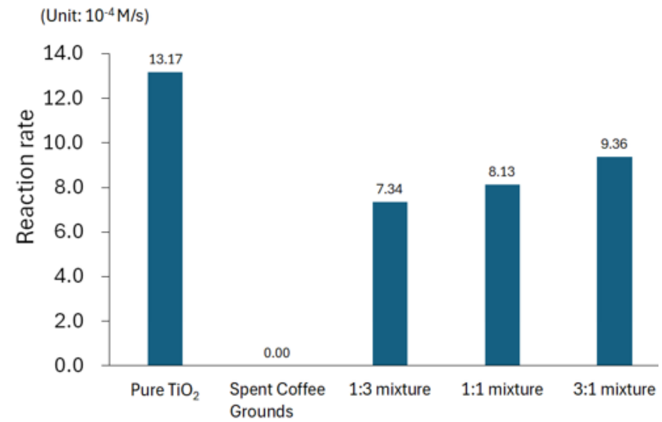

Figure 3. Reaction rates of all five catalyst samples. Bar chart showing the calculated reaction rates for the five samples—pure TiO_2, spent coffee grounds, mixtures of TiO_2 and spent coffee grounds at varying ratios by weight (1:3, 1:1, 3:1).

investigated the possibility of using spent coffee grounds, which are thrown out as food waste in large volumes. We employed a simple mixture method that does not require a doping procedure, which previous methodologies incorporated. We hypothesized that a mixture of TiO_2 and SCG at a ratio of 3:1 by weight would show a reaction efficiency comparable to a pure TiO_2 catalyst. We compared the catalytic efficiency of pure TiO_2, pure SCG, and three mixtures of TiO_2 and SCG in different ratios by weight (TiO_2 to SCG at 1:3, 1:1, and 3:1) through experiments involving the photocatalytic decomposition reaction of methylene blue. Data from the UV-Vis spectrophotometer shows that the methylene blue solution containing pure TiO_2 had the lowest absorbance value of 0.088 among all the samples, indicating that TiO_2 is the most effective catalyst. Among the mixtures that contained coffee grounds, the TiO_2 and SCG mixture at a 3:1 ratio showed the highest efficiency, with an absorbance of 0.150. The 1:1 ratio mixture showed catalytic performance slightly above that of the 3:1 mixture, with an absorbance of 0.207. The absorbance shown by the 1:3 mixture was highest among the mixtures that contained SCG, but its absorbance difference with the 3:1 mixture was not considerably large, which may suggest that the threefold difference in the amount of SCG in these two mixtures does not lead to the same degree of difference in reaction efficiency.

The calculation for the reaction rate of pure coffee grounds produced 0 M/s, which in theory is unlikely. This anomaly for the pure coffee sample may possibly be because coffee ground is a colored compound, a property that may have influenced the color of the upper layer of the solution in the experiment, resulting in identical values for both the initial absorbance and final absorbance. According to literature, the final absorbance should be lower because methylene blue is known to degrade when exposed to light in the absence of interfering color, resulting in a decrease in the absorbance value over time (13). This may also explain the absorbance value of pure coffee grounds at 40 minutes being lower than the other three mixtures containing coffee. To test this hypothesis in future experiments, we could use coffee-colored liquid delicately filtered of solid particles in the reaction and examine whether the color alone would change the absorbance.

The reaction rates of the five samples appear to follow a decreasing trend as the amount of the titanium catalyst in the mixture is reduced and substituted with SCG (**Figure 3**). This decrease in catalytic efficiency could be attributed to decreasing catalyst content rather than increasing SCG, as this increase in the amount of coffee grounds added to replace TiO_2 did not result in an equally proportionate drop in reaction rates. The increase in SCG content produced a proportionately smaller decrease in reaction rates.

As the mixture of TiO_2 and SCG at 3:1 showed the highest reaction efficiency among SCG mixtures, the closest in value to pure TiO_2, this mixture ratio may be an option in formulating catalysts, given the sustainability and cost issues associated with the component substances. While pure TiO_2 provides the best catalytic efficiency, our study shows that decreasing the TiO_2 content by 25% and replacing it with SCG can yield meaningful catalytic efficiency while saving costs and being environmentally friendly. The TiO_2 and SCG in the mixture are essentially complementary since such a mixture provides a balance between chemical efficiency in terms of reactions and the relatively higher cost and environmental impact of titanium dioxide compared to SCG. This study highlights the potential for utilizing SCG as a more sustainable and cost-effective support material for catalysts in chemical reactions, given the fact that coffee grounds are more abundantly available and of lower cost compared to the conventional titanium dioxide catalyst. The results of the 3:1 TiO_2 and SCG mixture in this experiment suggest that combining inexpensive porous materials such as SCG with highly efficient industrial catalysts commonly used today can optimize both cost and efficiency, contributing to a more sustainable chemical manufacturing process. Given that sustainability, together with cost issues, is not a normative standard but rather a choice to be made, the question of industrially relevant efficiency level would depend on the specific priorities of the industry players. The use of SCG as an important catalytic support material presents wider options for the chemical sector in implementing its

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priorities regarding sustainability and efficiency.

The SCG used in this experiment worked as a suitable substitute for the costly, unsustainable titanium dioxide as a catalyst support material due to the presence of carbon substance in the coffee. The sample containing only SCG was not expected to show notable catalytic activity on its own, as the intention was to use the grounds to support the metal catalyst by transporting ions during reactions. This support function is possible as the carbon material in the coffee grounds provides the mixtures with a high degree of porosity that increases the surface area for reactive sites as well as electrical conductivity to facilitate the reaction in the decomposition of methylene blue. Thus, combining porous and electrically conductive coffee grounds with TiO_2 to partially substitute the TiO_2 in the sample produced an effective and more sustainable catalyst mixture whose efficiency was not compromised.

Our study is unique in terms of the simplicity of the test method applied. Previous methodology provides for non-metal doping using SCG and carbon substrates from biomass as a means to improve the photocatalytic performance of TiO_2 for methylene blue degradation (4). This method of doping was designed to overcome the wide band gap of TiO_2 for high light utilization and catalytic activity (4). The experiment we designed involved a simple mixture method for TiO_2 and SCG to compare reaction efficiency with the use of a UV-Vis spectrophotometer. Although the present experiment took longer than previous methods in arriving at the catalytic profiles, the resulting reaction efficiencies delivered meaningful insights.

Future research based on this experiment could uncover other potential catalysts. We could investigate additional ratios besides 1:3, 1:1, and 3:1 of TiO_2 and SCG to identify the combination for various reactions other than the photocatalytic decomposition reaction of methylene blue. Alternative catalyst supplements derived from waste material, such as banana peels or used cooking oil, could also be considered in order to provide more options for improving both chemical efficiency and sustainability. In addition, we could extend the experimental conditions. In our experiment, the analysis was limited to five different samples. We could consider using a blank methylene blue sample without any catalyst as a control to prove whether methylene blue decomposes under light in the absence of catalysts. It would also be meaningful to compare the photocatalytic degradation of the three mixtures used in the present experiment with equivalent pure concentrations of TiO_2 (0.025 g, 0.05 g, and 0.075 g with 1:3, 1:1, and 3:1 mixtures of TiO_2:SCG by weight, respectively) to identify whether there is an augmenting effect of coffee grounds. For example, for a 3:1 mixture, we could add an experiment using only 0.075 g of TiO_2 without coffee grounds to observe the relationship between the absolute amount of TiO_2 and reaction efficiency. The initial hypothesis in this case would be that decreasing the total amount of TiO_2 would result in lower efficiency compared to the 3:1 mixture, since coffee grounds in the mixture serve as supporting material for the original catalyst, although it alone does not function as a catalyst. Furthermore, conducting a pre-treatment process that is identified as simple and low-cost in future experiments could lead to more efficient catalysts. Pre-treatment process removes moisture and organic residues from the catalyst, increasing its porosity and surface area, providing more active sites. Due to these facts, pre-treatment was technically needed for coffee grounds, but was only minimally done in the present experiment due to a lack of access to relevant labs. A catalyst is commonly pre-treated by mixing titanium and carbon activated with nitric acid, air oxidation, or thermal decarboxylation (7). Therefore, pre-treating coffee grounds could enhance their catalytic efficiencies, making them more similar to original traditional catalysts. Another area that could be considered for future experiments is using pre-treated coffee grounds to minimize the potential influence of confounding factors, such as the inherently uneven particle size of coffee grounds that can affect experimental results. Foreign substances present in the coffee grounds should also be removed with more sophisticated chemical procedures involving solutions that could help separate the foreign material. Additionally, since the properties of coffee particles may change depending on the coffee bean variety and brewing method, it would be meaningful to analyze the results based on these factors. Experimenting with industrial catalyst compounds other than TiO_2, such as palladium, rhodium, and iridium, could also produce insightful observations, especially when used with coffee grounds that are pre-treated to serve as supporting material tailored to each specific catalyst.

Additionally, we could consider running statistical tests on the data obtained for absorbance values of the five samples to determine the statistical significance of our results (**Figure 2**). The same would apply for the reaction rates calculated using these absorbance values (**Figure 3**). Addressing the limitation concerning this lack of statistical testing in future analyses would ensure more consistent and compelling results from our research.

This study demonstrates that while TiO_2 remains the most efficient catalyst for the photocatalytic decomposition reaction of methylene blue, SCG offer an alternative when combined with TiO_2. It supports our hypothesis that a mixture of TiO_2 and SCG at a ratio of 3:1 by weight will show chemical efficiency comparable to a catalyst comprised of 100% pure TiO_2. The 3:1 mixture of TiO_2 and coffee grounds proved to be the most effective among the tested catalysts containing coffee grounds, showing promise as a cost-effective solution. These results suggest the potential for reducing the reliance on expensive mineral catalysts and prove that coffee grounds may serve as an effective support material in a catalyst mixture as an environmentally-conscious alternative for use in a sustainable chemical process. With additional experiments under different conditions such as pre-treatment, the mixture may show greater potential as an eco-friendly catalyst support. Further research could lead to the widespread use of low-cost and sustainable catalytic substances at various industrial sites.

As the chemical industry actively searches for more sustainable and cost-effective catalysts that can substitute titanium-based substances, carbon-containing spent coffee grounds with its porous structure have been identified as a promising support material when used in a catalyst mixture. This study found that the mixture of TiO_2 and coffee grounds in the ratio of 3:1 resulted in the highest reaction efficiency among mixture samples tested, signifying a balance between catalytic efficiency and considerations for cost and environmental impact. This finding can pave the way for further research into other sustainable alternatives such as waste material from food sources that can be used in chemical catalysts in

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industrial processes. This re-use of waste substances can contribute to not only mitigating environmental pollution but also supporting a circular economy. The substitution or co-use of sustainable and affordable substances with conventional catalysts can address current global challenges with climate change and reduce reliance on scarce mineral resources.

MATERIALS AND METHODS

Preparation of Samples

The efficiency of SCG as a catalyst was investigated using titanium dioxide as the reference by measuring light absorbance in the photocatalytic decomposition reaction of methylene blue. A series of experiments was conducted with five samples: pure titanium dioxide (TiO_2), SCG, and three mixtures of these two substances in different ratios (TiO_2 to coffee grounds at 12.9% to 87.1% (1:3), 30.7% to 69.3% (1:1), and 57.1% to 42.9% (3:1)).

0.1 mg of methylene blue was measured with an electronic scale and dissolved in 10 mL of distilled water in five beakers, making a 10 mg/L methylene blue dye solution. Then, five catalyst samples were each prepared in separate beakers: one sample containing 0.1 g (100 mol%) of TiO_2, one sample containing 0.075 g (87.1 mol%) of TiO_2 and 0.025 g (12.9 mol%) coffee grounds at a ratio of 3:1 by weight, one sample containing 0.05 g (69.3 mol%) of TiO_2 and 0.05 g (30.7 mol%) coffee grounds at 1:1 ratio by weight, one sample containing 0.025 g (42.9 mol%) of TiO_2 and 0.075 g (57.1 mol%) coffee grounds at 1:3 ratio by weight, and one sample containing 0.1 g (100 mol%) of SCG only. The basis of selecting these sample amounts and ratios was to ensure that only a trace amount of catalysts would be used in order to prevent any interference effect that could reduce the reaction rate. TiO_2 catalyst samples were obtained from the science laboratory at Korean Minjok Leadership Academy, and SCG were collected from TOM N TOMS, a local café that claimed to use Ethiopian Sidamo coffee beans. The coffee grounds were dried and then sifted through a fine mesh to remove foreign material. Each of the five catalyst samples was added at the same time to each beaker containing the methylene blue dye solution. All five beakers were simultaneously placed under UV light (365 nm UV lamp) and stirred to ensure even mixing.

UV-Vis Spectrophotometry

1mL of each sample was collected every 10 minutes for a total duration of 40 minutes while continuously being radiated with UV light from a 4W, 254/365 nm lamp placed at 15 cm above the beakers. The collected samples were put into a cuvette using a pipette. Then the cuvettes containing these samples with varied catalyst ratios, taken at different duration times, were put in the cuvette port. The UV-Vis spectrophotometer was used to detect and measure the absorbance of light by the five samples, over a wavelength spectrum ranging from 400 nm to 800 nm (**Table 1**). The wavelength at which the samples absorbed the light and the light intensity were recorded. Absorbance measurements at 665 nm produced by the spectrophotometer were used because methylene blue presents an absorbance peak around 665 nm (18). These measurements were used to calculate the absorbance values that factor in the Rayleigh scattering effect resulting from mixing TiO_2 with methylene blue (19). Due to the difficulties in finding the exact solution of the wave equations, the Rayleigh scattering effect is an approximate method of solving the scattering problem (20). The Rayleigh scattering effect is the scattering of light by small particles, such as titanium dioxide of 200 nm, that are significantly smaller than the wavelength of the light source (20). Due to this effect, this study used an approximate method of solving the scattering problem, which makes the absorbance lower than its theoretical value. We applied a baseline correction using a reference absorbance measurement of the blank sample containing the catalyst but without the dye. Then we reflected this scattering contribution and calculated the true absorbance of the methylene blue after degradation.

Calculation of Reaction Rates (Pseudo-First-Order Kinetics

Then, for a more direct comparison of catalytic efficiency, reaction rates were calculated for the five samples. This

TiO_2 : SCG (by weight)	A_0 (10min)	Absorbance (20min)	Absorbance (30min)	A_t (40min)	*e* (L·mol⁻¹·cm⁻¹)	*l* (mm)	*k*	*t*	*v* (M/s)
pure TiO_2	0.965	0.866	0.929	0.088	8.20×10^4	10	0.0062	1800	13.17×10^{-4}
3:1	0.809	0.873	0.737	0.150	8.20×10^4	10	0.0037	1800	9.36×10^{-4}
1:1	0.895	0.959	0.937	0.207	8.20×10^4	10	0.0027	1800	8.13×10^{-4}
1:3	0.930	0.900	0.934	0.248	8.20×10^4	10	0.0022	1800	7.34×10^{-4}
pure SCG	0.108	0.08	0.08	0.108	8.20×10^4	10	0.0051	1800	0

Table 1. Absorbance values, reactions rates, and values used in rate calculation. Values corresponding to absorbance of each sample at 665 nm measured at 10 min, 20 min, 30 min, and 40 min. Reaction rates (*v*) calculated using values for final absorbance (A_t), molar absorptivity (*e*), pathlength (*l*), reaction rate constant (*k*), and time (*t*).

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calculation was done with a first-order reaction, as the photodegradation of methylene blue obeys a pseudo-first-order kinetic model, meaning that although the reaction involves more than two reactants, it behaves like a first-order reaction (21). To do this, absorbance was first calculated using the following,

$$A = elc \qquad \textbf{(1)}$$

where A is absorbance, e is the molar absorptivity (8.20 × 10^4 $L \cdot mol^{-1} \cdot cm^{-1}$), l is the pathlength (10 mm), and c is concentration in moles per liter.

Since the molar absorptivity value (e) is an intrinsic property of a substance, it was used based on the values reported in the literature (22). The same e value was applied for all wavelengths. As the absorbance is proportional to concentration (**Equation 1**), we do not have to calculate the concentration when calculating the reaction rate.

Next, the first-order reaction rate was calculated using the following,

$$v = k[C] = (1/t)\ln([C_0]/[C_t]) = (1/t)\ln([A_0]/[A_t]) \qquad \textbf{(2)}$$

where v is the first-order reaction rate in molarity per second, k is the reaction rate constant in per second, C is the concentration in molarity, C_0 is the initial concentration in molarity, C_t is the final concentration in molarity, A_0 is the initial absorbance value, A_t is the final absorbance value, and t is time in seconds (**Table 1**). The calculations for the reaction rates are as follows:

$v = 1/1800 \times \ln(0.965/0.09) = 13.17 \times 10^{-4}$ M/s (pure TiO_2);

$v = 1/1800 \times \ln(0.809/0.15) = 9.36 \times 10^{-4}$ M/s (3:1 mixture);

$v = 1/1800 \times \ln(0.895/0.207) = 8.13 \times 10^{-4}$ M/s (1:1 mixture);

$v = 1/1800 \times \ln(0.930/0.248) = 7.34 \times 10^{-4}$ M/s (1:3 mixture); and

$v = 1/1800 \times \ln(0.108/0.108) = 0$ M/s (only SCG).

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