

Spent Bleaching Earth Supported CeFeO₃ Perovskite for Visible Light Photocatalytic Oxidation of Methylene Blue



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ABSTRACT: Dyes substances from the textile industry wastewater are internationally classified as poisonous substances, and they cause a severe threat to humans being and other living things, even at low concentrations. Therefore, this waste has to be treated before discharge to the environment. One of the most effective processes for degrading dyes is photocatalytic oxidation. Two different pretreatments of Spent bleaching earth (SBE) from palm oil refinery plant were applied to produce catalyst supports. The SBEe support was prepared by extraction using n-hexane, SBEC by calcination at 500 °C, and then used as a support for CeFeO₃/SBEe and CeFeO₃/SBEC perovskite catalyst. Both catalysts were tested for the degradation of methylene blue (MB) using photocatalytic oxidation. The properties of catalysts were characterized using some characterization methods, such as thermogravimetric-differential thermal analysis (TG-DTA), X-ray diffraction (XRD), scanning electron microscope (SEM) equipped with Dispersive Energy X-ray Spectroscopy (EDS), specific surface area (BET) and pore size analysis. CeFeO₃/SBEe catalyst was found more efficient in photocatalytic oxidation for MB compared with the CeFeO₃/SBEC catalyst. CeFeO₃/SBEe catalyst could degrade 99.5% of MB during 120 min, at the condition of 25 mg/L MB, 1.0 g/L catalyst, and pH 7. The effect of pH on the performance of the catalyst followed the order of pH 7 > pH 9 > pH 5. Moreover, the CeFeO₃/SBEe catalyst demonstrated excellent activity in the degradation of MB, displaying that CeFeO₃/SBEe is a favorable catalyst for water purification.

Key words: Perovskite, dyes, water purification, cerium orthoferrite, environment

1. INTRODUCTION

Nowadays, the treatment of wastewater as a source of clean water is vital for society's lives, both from an economic and environmental perspective. Thus, making the development of the wastewater treatment process develop rapidly. One of the most effective methods today is the advanced oxidation process (AOP) [1]. The AOP process relies heavily on the production of highly reactive radical species such as hydroxyl radicals (OH[•]) which have high oxidation potential for the degradation of organic compounds selectively [2]. One process that is relatively attractive for researchers to study is photocatalytic for removing methylene blue (MB) from aqueous solution become less toxic substances, CO₂, and H₂O [3-5].

The solid waste generated in vegetable oil processing, such as spent bleaching earth (SBE), has properties and structures similar to zeolites, which has the main elements of Al₂O₃ and SiO₂ [6]. The bleaching earth is widely used to purify crude oil from undesirable color and impurities [7]. SBE contains more than 20% of oil by weight; it considers hazardous substances and dangerous pollutants to the environment [8, 9]. Disposing of SBE without proper

handling is harmful to the environment due to the degradation of residual oil in SBE and associated with emissions of greenhouse gases in its dumping. The nature of SBE, which has a size of nano/micropores and also zeolite like composition. Therefore, SBE has potential usage after the reactivation process, such as adsorbents, filler, and support catalysis [10].

Over the past decade, the development of semiconductor catalysts for the process of photocatalysis has been increased in wastewater treatment technology. One catalyst that often used is TiO₂ because this catalyst has several advantages, such as inertness, non-toxic, and high chemical stability. However, TiO₂ also has a severe weakness, such as a high energy bandgap (3.0-3.2 eV), thus requiring UV radiation and inhibiting the effectiveness of TiO₂ [11, 12]. This deficiency is overcome by modifying the structure and chemical composition of semiconductor material by emerging new favorable properties. One of the

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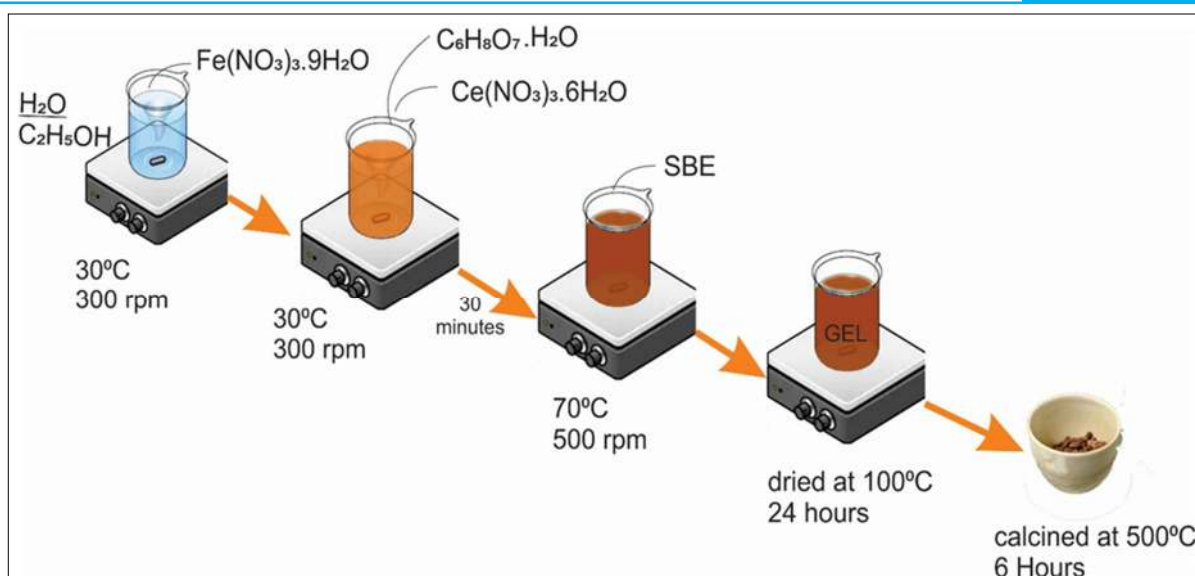


Fig. 1. Schematic of the preparation of $\text{CeFeO}_3/\text{SBEe}$ and $\text{CeFeO}_3/\text{SBEc}$ perovskite catalyst.

impressive materials that have been widely examined is perovskite. Perovskite, with the general AMO_3 formula, has cations A and/or M, which can be exchanged with foreign cations without changing their structure, but changing the oxidation status of the M cation and enter a new oxygen vacancy [13-15]. CeFeO_3 , which is a ferrite spinel nanoparticle material with a narrow bandgap (<1.9 eV), is suitable for photocatalysts. Besides, the stable, non-toxic and magnetic nature of CeFeO_3 makes it easy to separate, making CeFeO_3 suitable for use in wastewater treatment [16, 17]

In this paper, we reported the application of low cost and eco-friendly novel semiconductor catalyst support from SBE, the waste of palm oil industry, for synthesizing $\text{CeFeO}_3/\text{SBEe}$ and $\text{CeFeO}_3/\text{SBEc}$ perovskite catalysts. The photocatalytic performances of both catalysts were compared under visible irradiation. Their physico-chemical properties were also characterized. Furthermore, some critical parameter such as initial pH and the concentration of MB solution was carefully considered in this study. The application of this supports in perovskite catalysts shows excellent performance in degrading MB from wastewater and has a great potential to develop further to be applied in the chemical industry.

2. EXPERIMENTAL SECTION

2.1 SBE Support

SBE sample was obtained from a crude palm oil refinery plant in Riau Indonesia, which has contained ~ 20 % of oil. Before using it as a catalyst supports, two types of SBE were pretreated with two methods, namely solvents extracted and calcined. One SBE sample was extracted by hexane and collected from suspension by filtration, then desiccated in an oven at 120°C for 24 h and represented as SBEe. The other support was attained by calcined at 500°C for three h and denoted as SBEc.

2.2 Preparation of $\text{CeFeO}_3/\text{SBE}$ composite catalyst

The preparation of the $\text{CeFeO}_3/\text{SBEe}$ perovskite catalyst was prepared using a modified method (18). The reactant precursors of the compound are 2.10 g of

$\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ (Merck), 2.02 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Merck), and 2.20 g of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich), while the solvent is 30 mL of mixed $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH}$ with the ratio of 1:2. Furthermore, the solution was stirred homogeneously at room temperature for 30 min. Subsequently, 2 g SBEe were added and stirred at 70°C until the gel was formed. Next, the gel dried at 100°C for 24 hours and calcined at 500°C for 6 h in air. Then the catalyst was put in storage in a desiccator while waiting for usage. The same procedure was also carried out for $\text{CeFeO}_3/\text{SBEc}$.

2.3 Catalyst Characterization

Two materials were characterized by X-ray diffraction (XRD) analysis using SmartLab SC-70, with Cu-K α Radiation of $\lambda = 1.54059\text{\AA}$. Accelerating Voltage and current was 40 kV and 30 mA. The scanning rate was 0.01s^{-1} and 2θ range of 10-90. The morphologies of the catalyst were observed using the field scanning electron microscope (A JEOL JSM-6300F, USA). EDS, energy-dispersive X-ray spectroscopy were also utilized to detect metal particles on supported catalysts. N_2 adsorption-desorption isotherm with the BET (NOVA 4200e, Quantachrome). A thermal gravimetric analyzer was used to collect the thermal stability of materials using a TGA/DSC1 STAR^e system-METTLER TOLEDO.

2.4 Photocatalyst process

The catalytic photodegradation has taken place in a 500 ml beaker glass, in a thermo-controlled water bath, containing 10-40 mg/L of MB solution (250 mL). After that, as much as 0.25 g/L of the catalyst was added. The solution was stirred at 400 rpm in room temperature ($30^\circ\text{C} \pm 2^\circ\text{C}$) and illuminated with a Mercury Lamp 250 W (Phillips). The top of the reactor was located at a distance of 25 cm away from the light source. The solution was a place in darkness for 20 min to reach absorption and adsorption equilibrium. Next, the photocatalytic process started when turning on the light. Every interval time, samples were taken using a 0.45 μm syringe filter from the reactor, and then were 1 mL of suspension liquid collected. For adjusting the pH of the solution, HCl and NaOH solution of 1N was utilization. The

concentration of samples was analyzed using UV-Vis absorption Shimadzu 2600i. Analysis of chemical compositions of the collected SBE was carried out by an X-ray Fluorescence Spectroscopy (XRF, PW 2400, Philips).

3. RESULTS AND DISCUSSION

3.1. Characterization of catalysts

The composition of the collected spent bleaching earth (SBE) are listed in Table 1. As can be observed, SBE mostly consist of silica and alumina with particular iron and calcium oxide.

Table 1 Composition of SBE

Composition	SBE (wt%)
MgO	3.56
Al ₂ O ₃	10.23
SiO ₂	61.51
K ₂ O	1.12
CaO	4.23
TiO	0.64
FeO	4.32
L.O.I	5.40
pH ^a	5.10

^apH was decided by blending 0.1 g solid with 10 mL water.

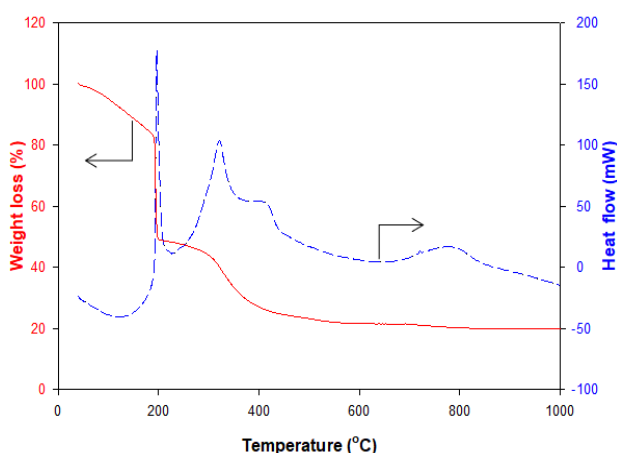
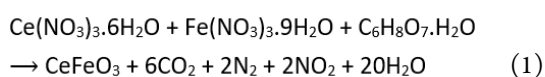


Fig. 2. TGA dan DSC profiles of CeFeO₃/SBEe.

CeFeO₃/SBEe perovskite catalyst was studied by TGA and DSC under the air atmosphere (Fig. 2). The TGA patterns of catalyst show a substantial changed up to 53.5% of weight loss between 30 °C and 200 °C. It corresponds to the loss of water in the crystallization process and thermal transformation (decomposition) of organic, volatile compounds on precursor substances and a trace amount of oxygen. The exothermic peak occurred at 200 °C on the DSC curve due to the vaporization of the volatile component [18, 19]. The Following, at around 250 °C to 500 °C, weight loss of about 21.5% relates to the loss of oxygen from precursor resulting in the phase transformed into perovskite structural compounds CeFeO₃, as shown in the following reaction.



Three of the exothermic peaks appeared between 250 °C and 850 °C (about 320, 420, 850 °C) due to the thermal transformation of citric acid and gradual crystallization of CeFeO₃. Thus, the calcination temperature of 500 °C was chosen to synthesize CeFeO₃ perovskite.

Fig. 3 presents the XRD spectra of supported CeFeO₃ perovskite catalysts, which are the utilization of two different treatments of supports. Overall, two modes of catalysts displayed a weak crystalline phase, as indicated by the observance of a relatively broad peak. CeFeO₃ oxide peaks are observed with diffraction peaks occurred 21.04°, 26.24°, 28.81°, 33.41°, 39.98°, 48.30°, and 57.50°, corresponding to JCPDS standard 00-022-0166 for perovskite crystalline structures. Those XRD results show a successful synthesis of CeFeO₃ perovskite from a sol-gel approach.

N₂ adsorption/desorption of the perovskite catalyst CeFeO₃/SBEe and CeFeO₃/SBEC, as shown in Fig. 4. While the results of the analysis of the two catalysts are shown in Table 2. The S_{BET} of the CeFeO₃/SBEe perovskite catalyst has a higher 20 m²/g than CeFeO₃/SBEC, this caused by differences in the treatment of the SBE. Moreover, both catalysts have a pore radius of less than 20 Å, indicating their microporous nature.

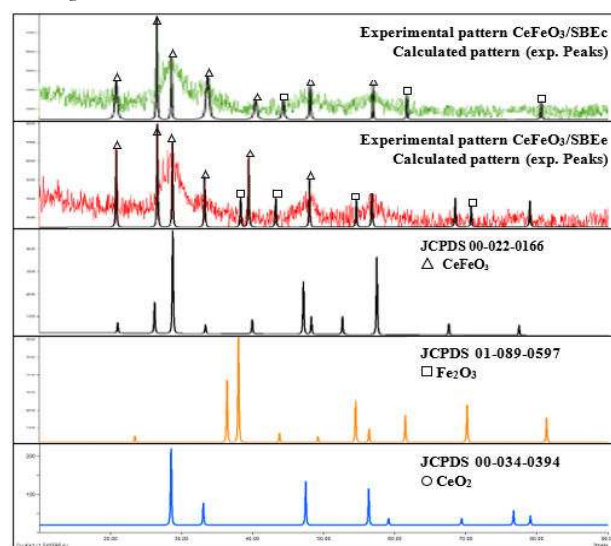


Fig. 3. XRD patterns of spent bleaching earth and their supported CeFeO₃/SBEe and CeFeO₃/SBEC perovskite catalyst.

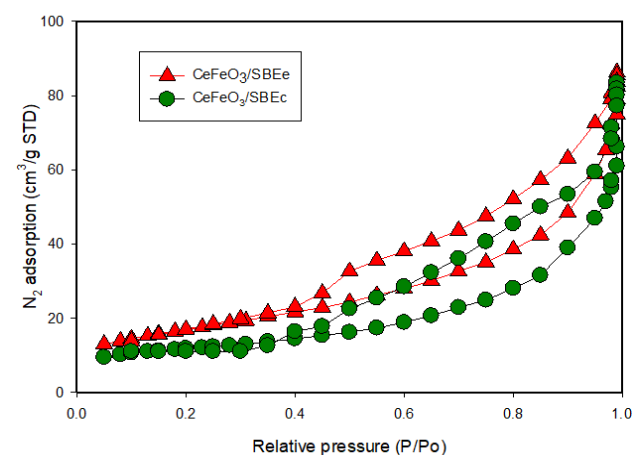


Fig. 4. N₂ adsorption isotherm of the perovskite catalyst CeFeO₃/SBEe and CeFeO₃/SBEC.

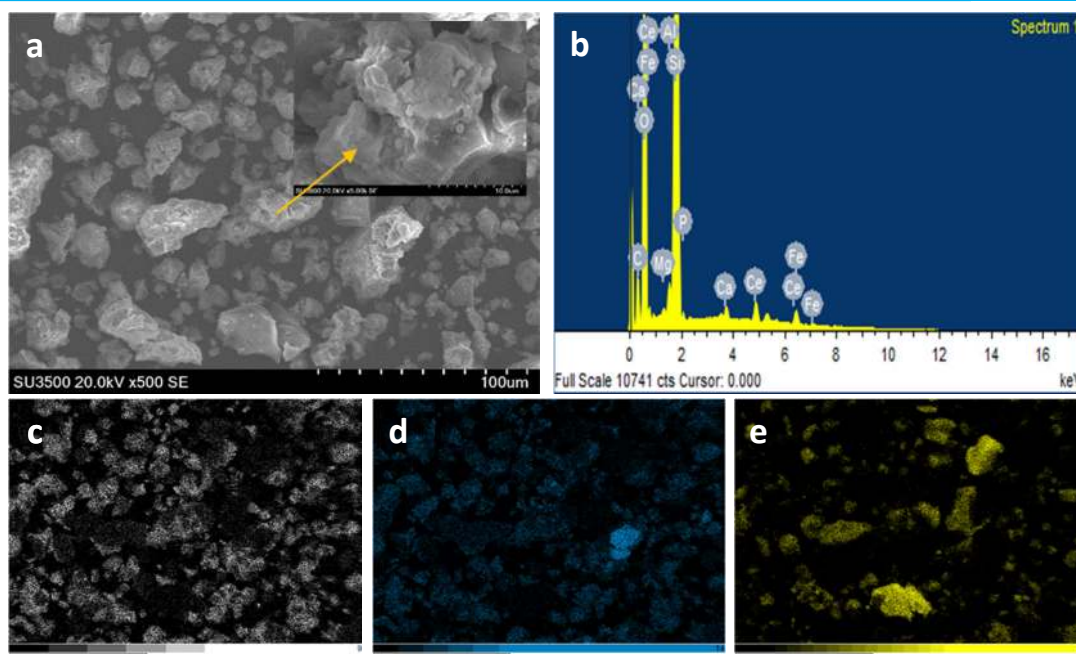


Fig. 5. Morphologies of the CeFeO₃/SBEe perovskite catalyst. SEM images of samples (a), the inset demonstrates the particle magnification, (b) EDS spectrum, and (c, d, and e) the elemental mapping images.

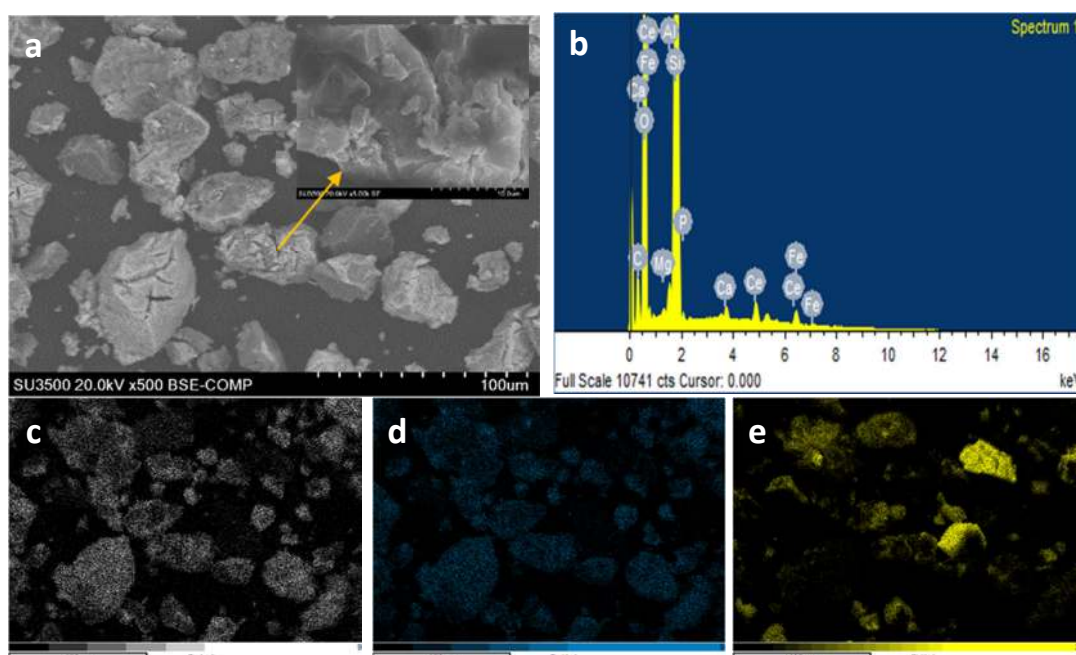


Fig. 6. Morphologies of the CeFeO₃/SBEc perovskite catalyst. SEM images of samples (a), the inset demonstrates the particle magnification, (b) EDS spectrum, and (c, d, and e) the elemental mapping images.

Fig. 5 and 6 present SEM images, EDS spectrum, and mapping images of supported CeFeO₃ catalysts. Most CeFeO₃/SBEe and CeFeO₃/SBEc perovskite catalysts exhibited agglomeration of the particles, and asymmetrical shapes with the average size of CeFeO₃/SBEe particles are 1-30 μm , while CeFeO₃/SBEc are 10-70 μm (Fig. 5a and 6a). It was apparent that the diameter of CeFeO₃/SBEe particles was less than CeFeO₃/SBEc particles. The EDS spectrum of two catalysts is shown in Fig 5b and 6b. Both samples showed the attendance of Ce, Fe, Si, Al, Ca, and Mg. Consequently, the EDS spectra implied the presence of Ce and Fe on two catalysts, conforming XRD patterns. The elemental mapping images of the particle is shown in Fig. 5c,

d, e, and Fig. 6c, d, and e, and it indicates the presence of two elements such as Ce, Fe. Both elements are equally distributed.

Table 2 BET Characterization of Catalyst

Catalyst Type	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Pore Volume ($\text{cm}^3 \text{g}^{-1}$)	Pore Radius (\AA)
CeFeO ₃ /SBE _e	59.44	0.133	19.114
CeFeO ₃ /SBE _c	39.17	0.129	19.175

3.2. Degradation of MB by SBE supported cerium orthoferrite photocatalytic

Fig. 7 displays the photocatalytic performance of catalysts in the removal of MB under visible light irradiations. In general, there is no MB degradation in photolysis using visible light minus the presence of the catalyst. Equally, catalysts showed about 40 % MB removal in dark conditions. UV-vis light could drastically degrade MB. It shows that the efficiency of photocatalytic degradation present of the $\text{CeFeO}_3/\text{SBEe}$ catalyst reached a peak of 99.5% for 120 minutes, while the $\text{CeFeO}_3/\text{SBEc}$ catalyst is reached 90.68% efficiency at the same time. It shows that the efficiency of $\text{CeFeO}_3/\text{SBEe}$ in photocatalytic activity is better than $\text{CeFeO}_3/\text{SBEc}$. That was attributed to several factors, such as surface area, pore size, and the particle size of the catalyst [20]. $\text{CeFeO}_3/\text{SBEe}$ is demonstrated to have better efficiency than $\text{CeFeO}_3/\text{SBEc}$. This is directly related to the S_{BET} of the catalyst used where $\text{CeFeO}_3/\text{SBEe}$ has a larger surface area than $\text{CeFeO}_3/\text{SBEc}$. Specifically, $\text{CeFeO}_3/\text{SBEe}$ had a surface area of $59.44 \text{ m}^2/\text{g}$ while $\text{CeFeO}_3/\text{SBEc}$ had only $39.17 \text{ m}^2/\text{g}$. The highest surface area will give the more active sites of the catalyst. Therefore that the formation of hydroxyl free radicals (OH^\bullet) is more due to the electron-hole recombination process on the surface of perovskite catalyst [21]. Also, smaller particle size tends to disperse more evenly onto the solution and lead to an increase in the activity of the photocatalytic process [22]. The formation of hydroxyl free radicals will direct an oxidation-reduction reaction (redox) of long carbon chains organic compounds (aromatic) (MB, C_{16}) into smaller molecular products such as CO_2 and H_2O [23].

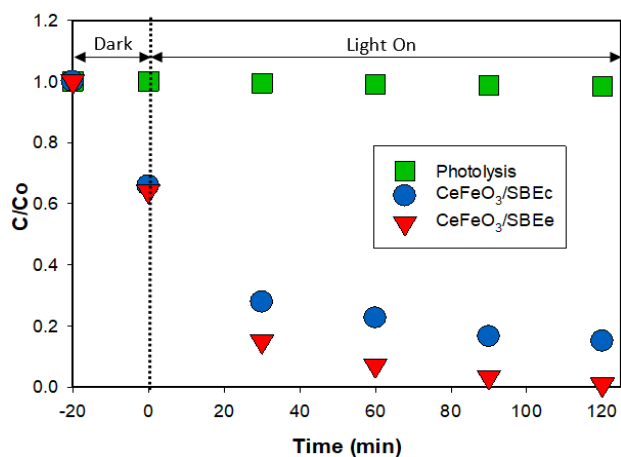


Fig. 7. MB decreased with time in photocatalytic and photolysis. Reaction condition: [MB concentration] = 10 mg/L, [Catalyst concentration] = 1.0 g/L, [pH] = 7

3.3. The effects of reaction parameters on MB degradation on $\text{CeFeO}_3/\text{SBEe}$.

Owing to the high-activity of $\text{CeFeO}_3/\text{SBEe}$, additional investigation on $\text{CeFeO}_3/\text{SBEe}$ was carried out to comprehend the effect of operational conditions. The stability and activity of the catalyst under acidic, neutral, and basic conditions, were investigated under various pH conditions. The effect of pH at 5, 7, and 9 on the photocatalytic degradation is presented in Fig. 8. Overall, the pH of the Methylene Blue (MB) solution affects the

photocatalytic degradation process due to the relationship between the stability of the catalyst nature and the pH solution [24]. At pH 5, MB was degraded 89.60% at 120 min, while at higher pH, which is 7.0 and 9.0, removal would be achieved at 99.5 and 94.45% in 120 min, respectively. Under acidic conditions, OH^\bullet radical ions produced by the catalysis process will react with H^+ to produce H_2O compounds, and reduce the efficiency of degradation. Under higher pH conditions, OH^- ion might be more available to be converted to OH^\bullet radicals. Thus, it will increase the efficiency of MB decolorization. However, at high pH value, H_2O_2 produced from the water catalyzed process would be unstable and could be decomposed into H_2O and O_2 compounds, which cannot perform degradation activities [25-27]. This phenomenon can be seen at pH 9.0; there is a slight decrease in degradation activity compared at pH 7.0. Thus, the efficiency of BM removal toward the effect of pH followed the order of pH 7 > pH 9 > pH 5. The $\text{CeFeO}_3/\text{SBEe}$ perovskite catalyst has high activity at the pH range of 7-9. So, the catalyst that has been synthesized has good activity properties under various pH conditions [28].

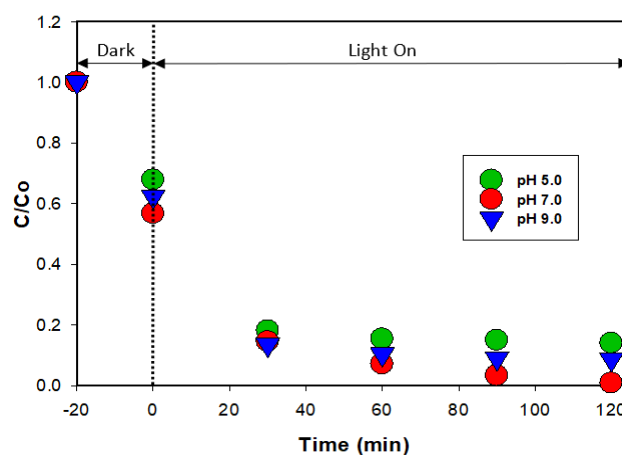


Fig. 8. Effect of pH on the photocatalytic degradation of MB. Reaction condition: [MB concentration] = 10 mg/L, [$\text{CeFeO}_3/\text{SBEe}$ catalyst concentration] = 1.0 g/L

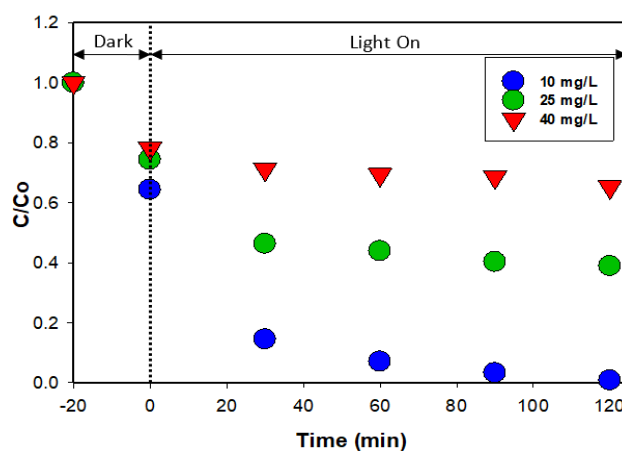


Fig. 9. Effect of MB concentration on the photocatalytic degradation of MB. Reaction condition: [$\text{CeFeO}_3/\text{SBEe}$ catalyst concentration] = 1.0 g/L, [pH] = 7

The effect of initial MB concentration at 10, 25, and 40 mg/L on MB removal is presented in Fig. 9. In broad terms, the MB efficiency of degradation reduced with increasing MB concentration. At a high MB concentration, it means that more number molecules of MB are adsorbed on the surface of the CeFeO₃/SBEe, and the necessity of reactive species such as OH[•] for the degradation of MB also increases, meanwhile the amount of catalyst remains constant [29]. Moreover, increasing the initial concentration of MB will inhibit the intensity of the light that will be absorbed by the catalyst [30]. Because the amount of catalyst used is the same, the rate of formation of hydroxyl radicals (OH[•]) at each concentration of methylene blue is also estimated to be the same. So it will require more time to reach the same degradation rate, therefore reducing MB deterioration in the efficiency [17].

4. CONCLUSIONS

Spent bleaching earth (SBE) was inactive for photocatalytic degradation of MB. However, it could be used as effective support for the CeFeO₃ perovskite catalyst. CeFeO₃/SBEe perovskite catalyst demonstrated a high activity of MB removal in a visible light photocatalytic oxidation. CeFeO₃ was found to be presented on the catalyst, and the dispersion was higher on treated SBE. CeFeO₃/SBEe produced a higher efficiency in MB removal than CeFeO₃/SBEc. The efficiency of MB removal toward the effect of pH followed the order of pH 7 > pH 9 > pH 5. The CeFeO₃/SBEe catalyst can be chosen as a catalyst that is valuable for industrial applications for water purification.

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