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HIGHLY EFFICIENT REMOVAL OF METHYLENE BLUE DYE FROM WASTEWATER USING CaO-$MnFe_2O_4$ NANOPARTICLES PREPARED WITH TEAK LEAF EXTRACT

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Abstract

This research aimed to synthesize a semiconductor photocatalyst CaO-$MnFe_2O_4$ nanoparticles using teak (*Tectona grandis)* leaf extract to degrade methylene blue in wastewater. Nanocatalysts were prepared through the precipitation method, while anthocyanins in extract acted as a reducing and stabilizing agent in this process. The presence of spinel ferrite (Fe-O), and manganese ferrite were indicated by using a Fourier transform infrared (FTIR) spectrometer that showed vibrational peaks at areas 538 cm^{-1} and 872 cm^{-1}, respectively. The crystalline phase of CaO-$MnFe_2O_4$ was confirmed using an X-Ray diffractometer (XRD) that appeared peaks at 2θ: 18º; 29º; 34º; 47º; 52º, while peaks at 2θ: 32º; 37º and 54º indicated CaO. Through the *Debye-Scherrer* equation, the CaO-$MnFe_2O_4$ nanoparticles had an average crystal size of 8.6 nm. The morphology of CaO-$MnFe_2O_4$ nanoparticles was clearly visible in the Scanning electron microscope (SEM) results in the form of fibrous clumps. The CaO-$MnFe_2O_4$ nanoparticles could degrade methylene blue with a degradation percentage of 86% over 240 min**.**

INTRODUCTION

The usage of *methylene blue* in the dyeing process in the textile industry produces carcinogenic and mutagenic water contaminants that are difficult to decompose. Non-biodegradable dyes are decomposed into non-hazardous products using nanoparticles semiconductor photocatalysts through photodegradation [1], [2]**.**

Nanoparticles have more specific properties than large materials because they can penetrate the space between cells [3]. A nanoparticle being developed is spinel ferrite. Spinel ferrite is a particle with the chemical formula MFe_2O_4, where M is a transition metal such as Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+}. Spinel ferrite such as $MnFe_2O_4$ have a narrow band gap and high saturation magnetization so it can be used as semiconductor photocatalysts [4]. The photocatalytic activity of $MnFe_2O_4$ increased when added by supporting materials in the form of oxides such as TiO2 [5]. Moreover, CaO is potentially used as a support material to increase the photocatalytic activity of $MnFe_2O_4$ nanoparticles. CaO is semiconductor material that had a specific crystal size and surface area so it has good catalytic activity [5], [6]. CaO could be produced from environmentally friendly materials containing calcium carbonate such as golden snail shells that potential as catalyst [7].

Metal nanoparticles can be synthesized using top down and bottom up methods, but this method has disadventages, namely hazardous waste pollution, prepared from synthetic chemicals and required high energy [8]. Therefore, an environmentally friendly method was developed by reducing and stabilizing agents from plant extracts. It has been reported that plant extracts such as Sumatra mulberry (*Morus macroura*) leaves [9], aloe vera [10], mangosteen leaves [8], and pelawan leaves [11] were being used to synthesize $MnFe_2O_4$, MFe_2O_4, nanosilver, and SnO_2 nanoparticles respectively. The extracts of these plants contain secondary metabolites used as the reducing and stabilizing agent. Fortunately, teak (*Tectona Grandis)* leaf contains secondary metabolites such as flavonoids (128.69 mg/100 g), anthocyanins (83.89 ppm) and antioxidants (47.61%) [12], so that the current study used red teak leaf extract as a reducing and stabilizing agent to synthesize CaO-$MnFe_2O_4$ nanoparticles. This research conducted the simple method of extract preparation and used abundant and environmentally friendly solvent.

EXPERIMENT

Materials

The samples used in this study were *Tectona grandis linn* and *Pomacea canaliculata* shells from South Sumatra, Indonesia. The chemicals $FeCl_3.6H_2O$, $MnSO_4.H_2O$, NaOH were purchased

from Merck, while aquadest and methylene blue dye was from Pudak Scientific.

Instrumentations

The size, shape and crystal structure of the nanoparticles were characterized using the Arion AquaMate8000 UV-visible Spectroscopy, Bruker's ALPHA II Compact FTIR Spectrometer,Rigaku MiniFlex600 Benchtop X-Ray Diffractometer and Scanning Electron Microscope Tescan Vega3.

Procedures

Teak leaf extract was prepared by boiling 10 grams of clean teak leaves in 50 ml of aquadest. Then cooled and filtered to obtain extract.

Separately, 0.84 g of $MnSO_4.H_2O$ were dissolved in 10 mL of distilled water and 2.70 g of $FeCl_3.6H_2O$ in 10 mL of distilled water, then mixed and stirred at 65 °C for 30 min. The mixture was added by 10 mL of teak leaf extract while stirring and added by NaOH to increase the pH of the mixture, then dropped of CaO solution (10 g of CaO in 40 mL of distilled water) and stirred at 65 °C for 90 min. The mixture was analyzed using UV-visible spectroscopy at range wavelength of 280-800 nm to confirm the formation of nanoparticles. Then the mixture was calcined at 600 °C for 2 h and was used to degrade methylene blue. CaO-$MnFe_2O_4$ nanoparticles were characterized using FTIR, XRD and SEM.

The 50 mL of 5 ppms methylene blue solution was added with 0.03 g of CaO-$MnFe_2O_4$. The solution was irradiated under a UV lamp for 120 min, 180 min and 240 min separately. The solution was measured using UV-visible spectroscopy to determine the amount of degraded methylene blue.

RESULTS AND DISCUSSION

The Synthesis of CaO-$MnFe_2O_4$ Nanoparticles

$MnFe_2O_4$ nanoparticles were synthesized by a precipitation method using $FeCl_3.6H_2O$ as a source of Fe^{3+} ions and $MnSO_4.H_2O$ as a source of manganese. The formation of nanoparticles was done by adding red teak leaf extract which contains flavonoids in the form of anthocyanins. Flavonoids act as reducing and stabilizing agents because they have molecules that have stable active sites [13]. In this study, an oxide support material namely CaO from calcined golden snail shells was added to nanoparticles. The calcination process is carried out at high temperatures to activate the catalyst and to decompose the carbonate groups into CaO [7]. The addition of supporting materials increased the photocatalytic activity of $MnFe_2O_4$. The synthesized nanoparticle was a black powder as shown in **Figure 1.**

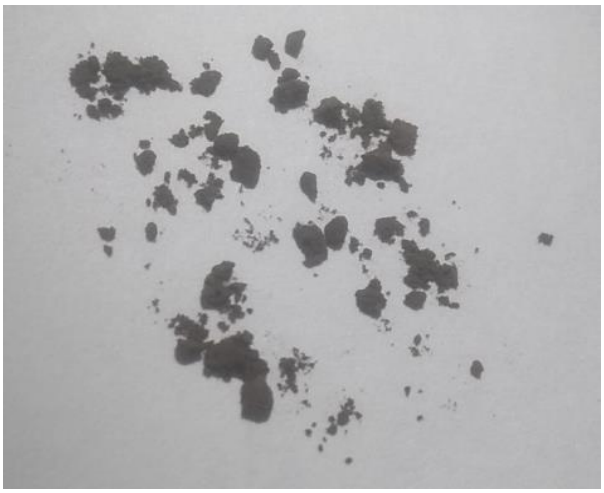

Figure 1. CaO-$MnFe_2O_4$ nanoparticles.

The CaO-$MnFe_2O_4$ nanoparticles were confirmed by the UV-Vis spectrophotometer of Orion AquaMate 8000 at a wavelength of 280-800 nm. The results showed that the CaO-$MnFe_2O_4$ nanoparticles had a peak at 498 nm with an absorbance of 0.232. The wavelength formed is obtained from the calculation of the *Tauc Plot.* The *Tauc Plot* calculation is a linearity equation to determine the gap energy [14], [15]. The band gap energy of the CaO-$MnFe_2O_4$ nanoparticles was 2.49 eV (**Figure 2**). The relation between wavelength and slit energy was formulated in equation:

$$Eg = hc/\lambda \qquad (1)$$

where Eg is the band gap energy (eV), h is Planck's constant (6.63×10^{-34} Js), c is the speed of light (3×108 ms^{-1}), and λ is the wavelength of light (m).

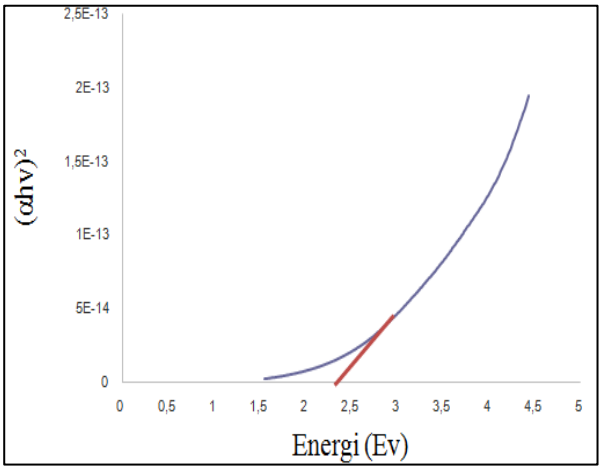

Figure 2. Plot between (αhv)2 and gap energy.

Characterization Results of CaO-$MnFe_2O_4$ Nanoparticles

Fourier Transform Infrared (FTIR)

The functional group analysis is shown in **Figure 3** with a wave number range of 4000-500 cm^{-1}. The spinel ferrite (Fe-O) bond vibration is shown at an area of 538 cm^{-1}. The wave number of 872 cm^{-1} shows the absorption of the manganese ferrite functional group. Senida [15] reported that ferrites were indicated at wave numbers below 1000 cm-1. The vibrations in the area of 1410 cm^{-1} and 872 cm^{-1} were the presence of O-Ca-O and O-C bonds in the CaO-$MnFe_2O_4$ nanoparticles. The vibration at 3644 cm^{-1} shows the presence of OH group. The O-Ca-O, O-C and OH groups in CaO-$MnFe_2O_4$ were observed in the 1450 cm^{-1}, 858 cm^{-1} and 3640 cm^{-1} regions, respectively [16].

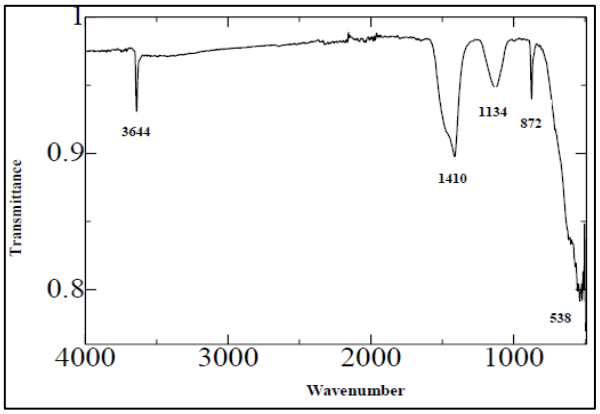

Figure 3. FTIR Spectra of CaO-$MnFe_2O_4$ nanoparticles.

X-ray Diffraction (XRD)

According to the ICSD database standard No. 028666 for $MnFe_2O_4$ and AMCSD No. 0008277 for CaO, diffractogram in **Figure 4** shows an appearing peak of 2θ at 18º; 29º; 34º; 47º and 52º that indicated $MnFe_2O_4$. The presence of CaO in the nanoparticles was shown by the appearance of a 2θ peak at 32º; 37º and 54º. The crystal size of the CaO-$MnFe_2O_4$ nanoparticles was calculated using the *Debye-Scherrer* equation as follows:

$$D = \frac{k\lambda}{\beta \cos\theta} \qquad (2)$$

where D is the crystal size, λ is the wavelength, k is the diffraction constant (0.9) and FWHM (Full-Width Half-Maximum). The CaO-$MnFe_2O_4$ nanoparticles's crystal size is about 8.6 nm.

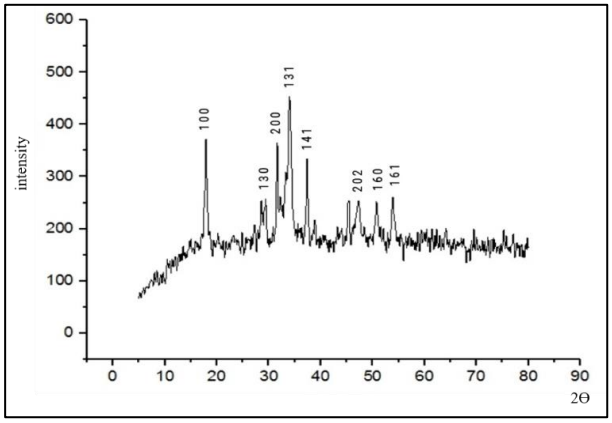

Figure 4. Diffractogram of CaO-$MnFe_2O_4$ nanoparticles.

Scanning Electron Microscopy (SEM)

The morphology of CaO-$MnFe_2O_4$ nanoparticles was characterized using *SEM Tescan Vega 3* with a voltage of 20 kV. **Figure 5** shows the results of characterization using SEM at 10k and 50k magnifications. The characterization results showed that the morphology of the nanoparticles was clearly visible at 10k magnification. At 10k magnification, it is known that the particles are fibrous clumps with various particle sizes. Then at 50k magnification the morphology of the nanoparticles only looks like irregular fibers.

Degradation of methylene blue by CaO-$MnFe_2O_4$ Nanoparticles

Photocatalytic activity of CaO-$MnFe_2O_4$ nanoparticles was applied to degrade methylene blue. The λ_{max} of methylene blue obtained was 664 nm. Degradation was carried out under light and dark conditions to ensure that the catalyst prepared was classified as a photocatalyst. Percent degradation (see **Table 1**), showed that the nanoparticles played a good role in the degradation of methylene blue under a light reaction so that nanoparticles in the current study act as photocatalysts. Kim et.all also reported that methylene blue was degraded by photocatalyst, and no methylene blue was degraded with absence of photocatalyst (in blank test) [17].

Photocatalysts absorb photons due to electrons in the valence band to excite them into the conduction band and produce holes in the valence band. This hole interacts with H_2O on the surface of the photocatalyst to form •OH as a reducing agent. The electrons in the conduction band reacted with O_2 from the air to form superoxide radicals as oxidizing agents. The reducing and oxidizing agents further degraded the methylene blue and produced a simpler product (see **Figure 6**) [18].

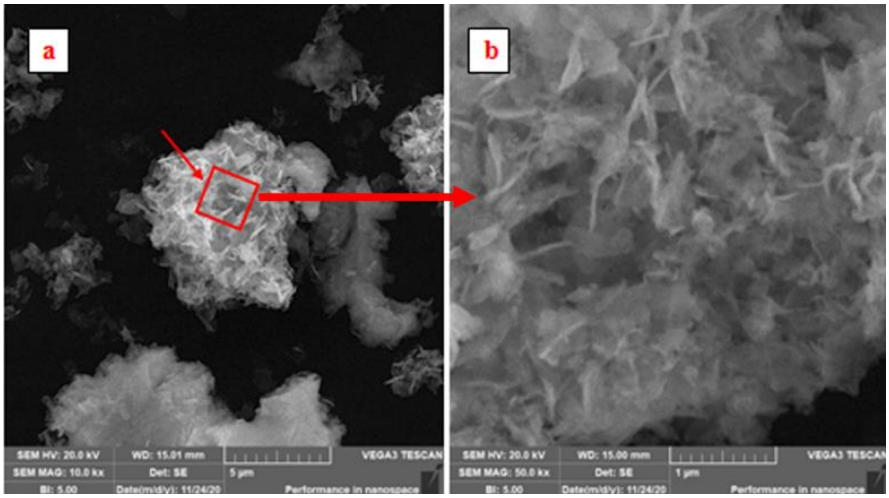

Figure 5. Morphology of CaO-$MnFe_2O_4$ Nanoparticles at magnification: a) 10k; and b) 50k.

Table 1. Calculation of the percent of degradation

Time (Minutes)	Absorbance	Degraded Methylene Blue Concentration	Percent Degradation (%)	Average
The Initial **c**oncentration of methylene blue = 5 ppm				
Light Reaction				
120	0.131	4.1571	83 %	84.67 %
180	0.114	4.2665	85 %	
240	0.110	4.2922	86 %	
Dark Reaction				
120	0.415	2.3295	46 %	48.67 %
180	0.397	2.446	48 %	
240	0.369	2.626	52 %	

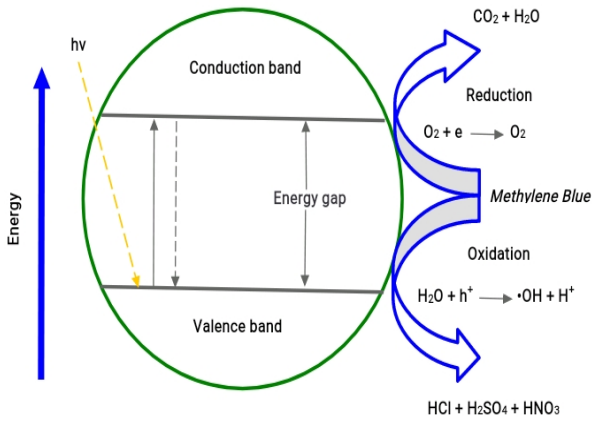

Figure 6. CaO-$MnFe_2O_4$ nanoparticles photocatalyst schematic [18].

The photocatalyst produced •OH which broke the C-S=C bond on methylene blue to become a sulfate ion by forming a sulfoxide which induced the opening of the central aromatic ring. The sulfoxide was attacked again by •OH to form sulfones due to the dissociation of the two benzene rings. The sulfones formed are attacked by •OH to form sulfonic acid compounds. The more increased irradiation time, the lower concentrations of methylene blue that showed methylene blue had already degraded. This provided the catalyst with time to produce •OH which played an important role in the degradation process [18]. Basically, a catalyst solution that is irradiated by light produces pairs of electrons (e) and holes (h+). The photocatalytic activity increases due to retained a large number of these photo-excited holes and the proportion of active surfaces [19], [20].

CONCLUSIONS

Teak (*Tectona grandis*) leaves extract played an important role as a reducing and stabilizing agent for the synthesis of CaO-$MnFe_2O_4$ nanoparticles. The resulting CaO-$MnFe_2O_4$ nanoparticles were black with an average crystal size of 8.6 nm in the form of fibrous clumps. Nanoparticles could degrade methylene blue with the highest percentage of degradation of 86 % for 240 min.

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