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Cost-effective Synthesis of CeO_2-SiO_2 Based on Oil Palm Leaves for the Removal of Toxic Compounds

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Abstract: Using cerium nitrate as a cerium source and oil palm leaves (OPL) as the main silica (SiO_2) source, CeO_2–SiO_2(OPL) powder was synthesized via calcination at 900 °C under air conditions. An X-ray diffraction analysis of the as-prepared product revealed the formation of CeO_2 supported on cristobalite SiO_2 along with some other minor element oxides. The Fourier transform infrared spectra showed peaks attributable to the Si–O–Si and Ce–O bonds of the binary oxide. According to a scanning electron microscopy analysis, the solid materials produced via calcination were in aggregated form. The solid, which was easily powdered by grinding in a mortar, was studied for the removal of methylene blue (MB) and phenol compounds from aqueous solution. The results showed that the CeO_2–SiO_2(OPL) material could remove MB up to 62.6% but was ineffective for phenol removal under various conditions.

Keywords: ceria; silica; oil palm leaves; toxic compounds; composite

1. Introduction

The combination of ceria (CeO_2) and silica (SiO_2) has attracted much interest owing to its various applications. For instance, a binary CeO_2-SiO_2 material was found to be an effective supporting solid material for nickel catalysts in the dry reforming of methane gas with better results than CeO_2 or SiO_2 alone[1]. Similar results were obtained using nano-sized CeO_2 - SiO_2, which was synthesized via a wetness method and utilized as a pyrolytic catalyst to convert waste engine oil into diesel fuel[2]. CeO_2-SiO_2 has been also prepared by soft chemical routes followed by thermal treatment, achieving an oxygen storage capacity higher than that of cerium oxide (CeO_2)[3], and via thermal decomposition in the presence of PEG-600 to furnish a product that serves as an electrochemical sensor[4]. CeO_2-SiO_2 materials prepared using a precipitation method from tetraethyl orthosilicate (TEOS) and cerium nitrate[5] or cerium chloride and silico fluoric[6] proved to be effective for chemical mechanical polishing. Furthermore, the applicability of CeO_2-SiO_2 as an adsorbent of fluoride ions in solution was also demonstrated[7].

A number of synthesis procedures for CeO_2 - SiO_2 composites with diverse applications have been developed. For example, a CeO_2-SiO_2 composite was prepared as a new type of precursor for the preparation of thin-film indium tin oxide via a sol - gel process[8]. Similarly, a water-in-oil microemulsion of CeO_2-SiO_2 was deposited via dip-coating on a glass or SiO_2 substrate[9]. CeO_2-SiO_2 prepared in a single step using a microwave-induced combustion solution was used as a catalyst for carbon monoxide oxidation[10]. A core-shell CeO_2-SiO_2 structure having high dispersibility was synthesized via chemical precipitation[11]. Other studies have demonstrated the

successful preparation of CeO_2-SiO_2 for methylene blue (MB) degradation using TEOS and cerium nitrate as precursors in the presence of hexadecyltrimethylammonium bromide as a surfactant under microwave irradiation[12].

Using natural SiO_2 or industrial waste SiO_2 instead of commercially available SiO_2 as the precursor for the synthesis of advanced materials is attracting intense research attention from the viewpoint of sustainability[13,14,15]. For example, CeO_2 - SiO_2 was synthesized via a sol-gel method using $CeCl_3 \cdot 7H_2O$ and SiO_2 extracted from rice husk in the presence of sodium dodecyl sulfate. The resulting material was useful in the photocatalytic degradation of the chlorpyrifos pesticide[16]. SiO_2 extracted from blast furnace slag was also used as a precursor in combination with CeO_2 extracted from radioactive cerium nitrate solution[17]. Using rice husk as an SiO_2 precursor also provided a CeO_2-SiO_2 composite that was effective in antibiotic removal[18,19]. In line with these reports, we previously reported the use of oil palm leaves (OPL) as a supporting material in the high-temperature synthesis of Au-SiO_2 composites[20], which is one of the few studies on the utility of OPL as an SiO_2 precursor for the development of advanced materials.

In this work, we further exploit the ready availability of OPL from oil palm plantations and use it as a sustainable SiO_2 source for the synthesis of a CeO_2-SiO_2(OPL) binary oxide via a cost-effective and simple single step sintering reaction between OPL and cerium nitrate salt. OPL are one of the by-products of managing oil palm plantations due to pruning activities. Therefore, the results of this research in general also support environmental sustainability. The obtained product was studied as an adsorbent of toxic compounds including MB and phenol from aqueous environments

2. Materials and Methods

2.1 Materials

Cerium nitrate and methanol were purchased from Merck (Singapore) and used as received. To ensure that the glass material was free from impurities, it was washed with aqua-regia solution prior to use. OPL were obtained from oil palm smallholder farms in the district closest to Universitas Bengkulu (Kota Bengkulu, Indonesia) and subjected to separation from the stem, washing with distilled water, cutting using scissors, air drying for one week, and crushing using a juicer mixer grinder. After cleaning the obtained powder using a sieve, it was ready to be used for the experiments.

2.2 Methods

Cerium nitrate (2 mmol) was dissolved in 50 mL of ethanol in a crucible, and 4 g of dried OPL powder was subsequently added to the solution. The mixture was then allowed to stand for one night for the methanol to evaporate slowly and to mediate the interaction between Si complexes and cerium nitrate. The crucible was then placed into a furnace, which was heated from room temperature to 900 °C for 2 h, followed by maintaining this temperature for 5 h. Then, the mixture was cooled down gradually to room temperature. The obtained powder was subjected to characterization and application experiments. For comparative purposes, SiO_2(OPL) was synthesized following a similar procedure, which involved heating at 900 °C for 5 h. The obtained materials were characterized via X-ray diffraction (XRD; X'PERT Powder-PANalytical PW 30/60), scanning electron microscopy (SEM) coupled with energy dispersive X-ray (EDX) spectroscopy (JEOL JSM 6510 LA), and Fourier transform infrared (FTIR) spectroscopy (Bruker, USA).

To evaluate the performance of the obtained materials in the removal of MB, a series of MB solutions in demineralized water (2, 6, 10, 14, and 200 ppm) were prepared and subjected to ultraviolet–visible (UV–vis) spectrophotometry analysis to obtain the corresponding absorbances, which were used to construct a plot of the MB concentration against absorbance using Microsoft Excel software. The corresponding regression formula was used to calculate the initial and final concentrations of the treated MB solutions. Meanwhile, two bottle samples were filled up with 10 mL of MB solution (16 ppm), and each solution was treated with 25 mg of adsorbent, i.e., SiO_2(OPL) and CeO_2–SiO_2(OPL), at room temperature and without any additional light. The absorbance of the treated and untreated solutions was measured using a UV–vis spectrophotometer. A similar procedure was applied to a series of phenol standard solutions (50, 100, 150, and 200 ppm). For the adsorption experiments, some bottle samples were filled up with 10 mL of phenol solution (150 ppm) and treated with 25 mg of SiO_2 (OPL) or CeO_2–SiO_2 (OPL).

3. Results and Discussion

The OPL powder was obtained following the procedure described in the experimental section. The preparation of the CeO_2-SiO_2(OPL) composite is illustrated in Fig. 1. When the OPL powder (Fig. 1a) was mixed with cerium nitrate salt (Fig. 1b) and subjected to calcination at 900 °C, the product shown in Fig. 1c was obtained. The product is obtained when the organic compounds in OPL are decomposed and cerium nitrate is changed into CeO_2.

Next, the as-prepared material was characterized. The XRD pattern of the product obtained from the reaction of cerium nitrate and OPL at 900 °C is shown in Fig. 2.

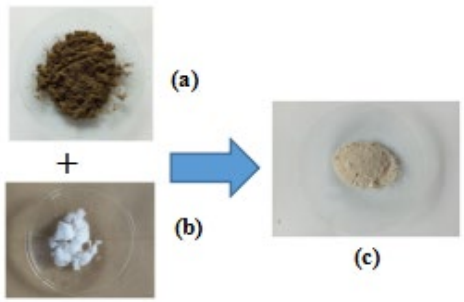


Fig.1: Preparation steps of as-prepared powder; (a) oil palm leaf powder, (b) cerium nitrate, (c) CeO_2–SiO_2(OPL) powder

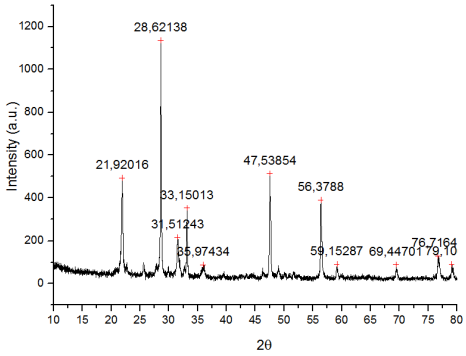


Fig. 2: XRD pattern of CeO_2–SiO_2(OPL) prepared from OPL and cerium nitrate

The sharp peaks at 28.6°, 33.2°, 47.5°, and 56.4° indicated the formation of CeO_2 in the crystalline phase (JCPDS No. 34-0394), and the peaks at 21.9°, 28.3°, 31.5°, and 35.9° revealed the presence of amorphous cristobalite SiO_2[5]. This result demonstrates that the obtained product contained crystalline CeO_2 and cristobalite SiO_2, which was further supported by the FTIR spectra (Fig. 3). Thus, the peaks at 1087 cm^{-1} and 793 cm^{-1} can be attributed to the vibration of the Si-O-Si bonds, and those between 500 and 750 cm^{-1} are related to Ce-O bonds. The latter peaks are very clear due to the formation of crystalline CeO_2. These results are in agreement with those of previous studies[21,22,23].

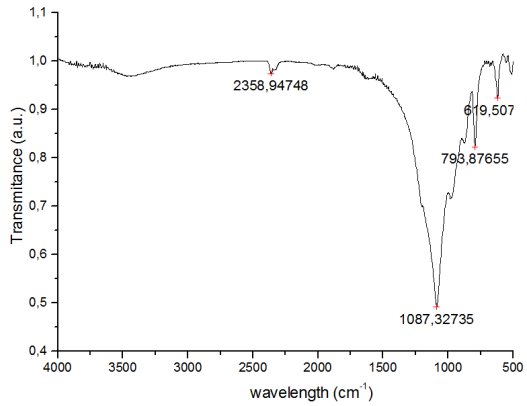
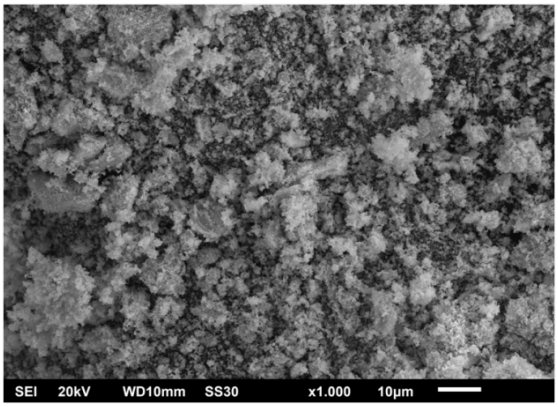
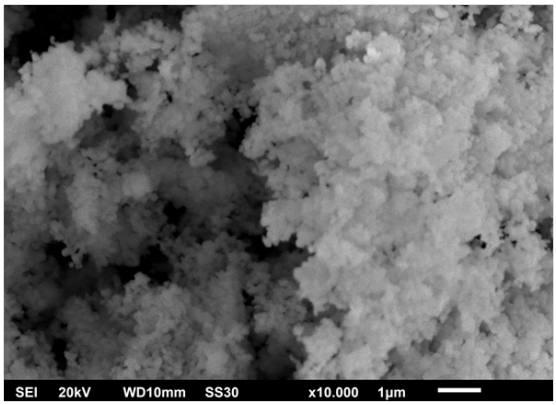


Fig. 3: FTIR pattern of CeO_2-SiO_2(OPL) prepared from OPL and cerium nitrate

The SEM and EDX results shown in Fig. 4 and Fig. 5 reveal the morphology and elemental content of the materials, respectively. Specifically, Fig. 4a displays an SEM image (1000× magnification) of the CeO_2-SiO_2(OPL) product obtained after calcination at 900 °C, showing that CeO_2 particles were combined with SiO_2 particles and distributed in blocks. The higher magnified image shown in Fig. 4b (10000× magnification) revealed the occurrence of aggregation of the CeO_2-SiO_2(OPL) powders. As suggested in previous studies, a high calcination temperature does not necessarily result in clearly separated particles in the powder, and the surface is not always clearly identifiable[24,25].



(a)



(b)

Fig.4: SEM analysis of CeO_2–SiO_2 (OPL) prepared from OPL and cerium nitrate (a) 1000× magnification, (b) 10000× magnification

The presence of Ce and Si elements in the as-prepared material was confirmed by the EDX results shown in Fig. 5 and Table 1, which showed representative peaks for Ce (25%), Si (15%), and O (43%). The presence of minor elements, which are most likely also in the form of oxides, stems from other minor minerals in OPL.

Fig. 6 shows the results of an MB removal experiment performed using the prepared material. Good activity was observed even in the absence of UV-vis or sunlight irradiation.

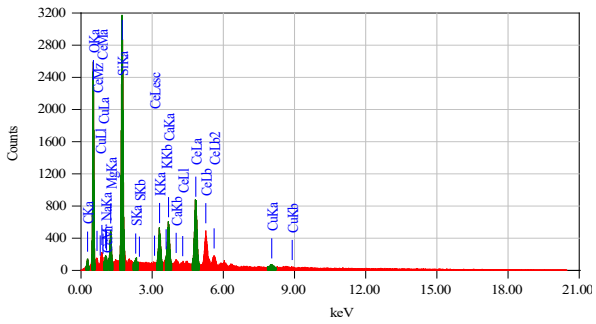


Fig. 5: EDX pattern of CeO_2–SiO_2(OPL) prepared from OPL and cerium nitrate

Table 1. EDX analysis of the prepared CeO_2-SiO_2(OPL)

Element	K(eV)	% mass
C	0.277	6.27
O	0.525	43.41
Na	1.041	0.61
Mg	1.253	2.41
Si	1.739	14.89
S	2.303	0.23
K	3.312	2.72
Ca	3.690	3.19
Ce	4.837	25,22
Cu	8.040	1.04

Using the linear regression equations obtained as described in the experimental section, the final concentration of each solution after treatment was obtained. The removal capacity was then calculated using the initial MB concentration before treatment and the final MB concentration according to the formula:

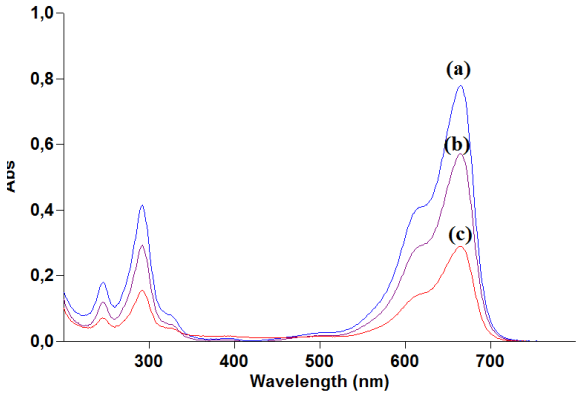


Fig. 6: UV-vis spectrophotometer analysis of (a) untreated MB solution, (b) MB treated with silica (OPL), and (c) MB treated with CeO_2-SiO_2 (OPL)

Using the linear regression equations obtained as described in the experimental section, the final concentration of each solution after treatment was obtained. The removal capacity was then calculated using the initial MB concentration before treatment and the final MB concentration according to the formula:

$$\text{Removal capacity (\%)} = \frac{(\text{Initial concentration} - \text{final concentration}) \times 100\%}{\text{Initial concentration}}$$

CeO_2 - SiO_2(OPL)and SiO_2(OPL) exhibited removal capacities of 62.6% and 26.6%, respectively. This result demonstrates that SiO_2(OPL) produced from the degradation of OPL can remove MB molecules even without the effect of light irradiation, which may be due to the adsorption process that occurs on the surface of the SiO_2 solid materials. The higher MB removal capacity of CeO_2 - SiO_2(OPL) compared with SiO_2(OPL) indicates that there is a synergistic effect on the adsorption of MB molecules between SiO_2 and CeO_2, which could be trapped in the SiO_2 matrix or attached to the surface of the SiO_2 particles. Previous research suggested that adding silica to a nanocomposite could improve MB adsorption because it increases the nanocomposite's surface area[26]. It is also possible that this synergistic effect is achieved through the basicity of the CeO_2-SiO_2(OPL) composite. As previously reported, the basicity of CeO_2 particles depends on their size[27]. The basicity of the reaction medium can accelerate the photolysis of MB molecules in aqueous solution[28]. The presence of minor alkali compounds formed from Ca and Mg might also help achieve the observed performance. This is in line with previous studies showing that doping CeO_2 nanoparticles with alkaline metal ions (Mg, Ca, Sr, and Ba) enhanced the photodegradation of MB compared with that of pure CeO_2 nanoparticles[29]. Furthermore, the high heating temperature used in the preparation of the composite might also affect the adsorption performance of CeO_2-SiO_2(OPL), as was demonstrated in previous works reporting that CeO_2 nanofibers obtained at 800 °C afforded a photodegradation rate of up to 98%, whereas that of the material prepared at 500 °C was 67%[30].

In contrast, the as-prepared material was not effective for the removal of phenol either in the dark or under sunlight irradiation. Only a small decrease in absorbance was observed after treatment, which was indicative of a low phenol removal capacity. This result could be due to inactivation of the CeO_2-SiO_2(OPL) material as a result of a decrease in the basicity of the composite in the presence of acidic phenol. The degradation of phenol has been previously reported to be affected by the solution pH[31,32].

4. Conclusion

CeO_2–SiO_2(OPL) was obtained as a major product by heating a mixture of cerium nitrate and OPL at 900 °C, as demonstrated by means of XRD, FTIR, and EDX analyses. The morphology of CeO_2–SiO_2(OPL) was investigated via SEM, revealing that the powder material was in aggregated form and showed an irregular surface. The as-prepared material could adsorb MB from aqueous

solutions with good activity but was not effective for phenol removal.

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