Silver-Palm Kernel Expeller Ash Formation by Combustion Technique and its Congo-red Removal Activity

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ABSTRACT

This study aims to synthesize silver-palm kernel expeller ash (PKE) composites using in-situ combustion at 600 °C. Compared to previous methods, the novel in-situ combustion was developed to easily obtain composites in the laboratory using simple procedures. The products obtained were characterized with X-ray diffraction (XRD) analysis. The results showed that the composites contained silver metal peaks and some peaks of a mixture of compounds predicted to be calcium phosphate, calcium hypophosphate, and other undetermined metal oxides. In addition, X-ray fluorescence (XRF) analysis showed the presence of several important minerals derived from PKE combustion. Composites obtained in this study showed better activity as catalysts in the removal of congo-red under sunlight irradiation compared to only PKE ash. Based on these results, the by-products of palm oil processing had the potential to be used for advanced materials preparation

Keywords: palm kernel expeller; silver particles; composite; congo red; combustion.

INTRODUCTION

Several studies are known to have explored the use of cellulose-containing biomass as a precursor in bio-based materials manufacturing. For example, various investigations have been conducted on the production of carbon from empty palm bunches and rice husks [1]. A previous investigation also explored the effect of the particle size of activated carbon from bamboo on its function as an adsorbent [2]. A typical example of cellulose-containing biomass is palm kernel expeller (PKE), often produced as a by-product during palm kernel processing. PKE typically shares similarities with grass in terms of its fiber content. According to several reports, the material contains water, fat, and crude fiber [3], which facilitate its use as animal feed. The use of palm residues, particularly PKE, for livestock feed offers various economic benefits and provides high nutritional value. This contributes to the production of lean meat containing digestible nutrients and energy that can be metabolized in the animal body, specifically cattle [4-5]. Another significant application of PKE lies in its potential as a carbon source, which can be activated using phosphoric acid. The activated carbon obtained has been proven to be effective as an absorbent for chromium metal ions in the tanning waste environment [6,7].

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According to previous studies, advancements in science and technology have led to rapid growth in the production of inorganic composites. A typical example of these materials is carbon-silver composites, produced by reducing silver (I) ions with a reductant, followed by impregnation of carbon pores using a solution [8]. Another environmentally friendly production method comprises the use of plant leaves as a carbon source and an internal reducer [9]. Recent reports have also shown the production of silver nanoparticles using *Clitoria ternatea* flower extract, which are subsequently added to a separately synthesized carbon matrix [10]. According to other research reports, silver particles have potential applications in the catalytic process as well as imaging materials [11-12].

Based on results, there are no investigations on the use of PKE for the production of solid materials-silver composites aimed at removing hazardous substances, such as congo-red (CR) through adsorption and photocatalytic mechanisms. Therefore, this study aims to investigate the development of solid materials-silver composites and their application in the treatment of CR in water, as shown in Figure 1. Previous reports have primarily focused on reducing the concentration of toxic compounds in aqueous solutions, such as CR [13-15]. The results showed positive outcomes regarding various alternative catalysts for more efficient treatment. Therefore, the results of this current study are expected to contribute to the development of new materials as catalysts and adsorbents.

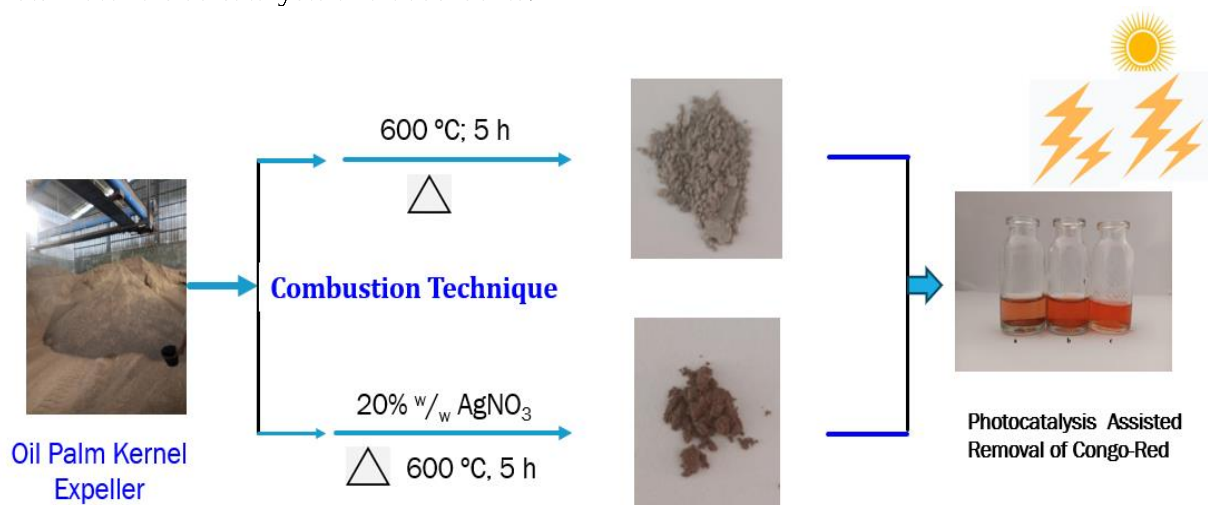

Figure 1. Schematic of recent works

EXPERIMENT

Chemicals and instrumentation

Silver nitrate (Merck), demineralized water, congo-red (Merck), Palm Kernel Expeller (PKE) residue was obtained from a company in Bengkulu (Indonesia). Powder X-ray diffraction (XRD MiniFlex, Rigaku, USA) was used to analyze the crystal phase, and X-ray fluorescence (XRF, NEX DE-Rigaku, USA) for elemental analysis. UV-Vis spectrophotometer (Agilent 60, Germany) was used for congo-red solution analysis.

Procedure

PKE powder was processed by washing the sample using distilled water. A total of 100 grams of the sample was placed into Beaker glass (1000 mL), followed by the addition of 500 mL of distilled water. The mixture was then stirred using a magnetic stirrer and left to stand for 3 hours to enhance contact time between impurities and distilled water. In addition, the distilled water was decanted, leaving behind wet solids. The washing procedure was repeated 3 times, followed by the spreading of wet solids on HVS paper and drying in the sun for 3 days. The dried solids were stored in a desiccator until required for the subsequent procedure.

The preparation of PKE ash was carried out based on the standard procedure for making C_3N_4 graphite [16] by modifying the heating temperature and duration. A total of 5 grams of PKE were weighed, and placed into a crucible, which was covered with a lid. The crucible containing palm kernel cake sample was placed in a furnace, and the temperature was set to 600°C for 6 hours. After the heating process was completed, the sample was allowed to cool and was ready for analysis to obtain characterization information. The preparation of silver-PKE ash composites was conducted based on a procedure carried out in other studies [17] with few modifications. Silver nitrate was prepared by dissolving 0.1 grams in a crucible with demineralized water, and stirred using a magnetic stirrer until completely dissolved. In addition, 5 grams of pre-prepared PKE powder were then added to the crucible. The mixture was stirred using a magnetic stirrer for 30 minutes and allowed to stand for 3 hours at room temperature, where it was protected from light. The sample was then heated at 70°C to slowly evaporate the solvent, leading to the production of sticky solids. The crucible was covered and placed in the furnace, with the temperature set to 600°C for 5 hours. After heating, it was allowed to cool and was ready for analysis. The solid materials produced in this study were analyzed using X-ray diffraction (XRD MiniFlex, Rigaku) and fluorescence (XRF, NEX DE-Rigaku) for elemental analysis, providing information about the material's characteristics. Silver-PKE ash composites were the main material used for the elimination of CR in water.

A total of 10 mg each of PKE ash and silver-PKE ash composite was added to 5 mL of a CR solution (16 ppm). The mixture was exposed to direct sunlight for 3 hours (From 11 a.m. to 2 p.m.), in an open area of the chemistry laboratory at coordinates -3.7562 and 102.2734. The same procedure was also conducted in the absence of light (in the dark). Following exposure, a sample of the solution was collected using a drop pipette and placed into a cuvette for analysis using a UV-Vis spectrophotometer (Agilent Carry 60) across a wavelength range of 200–800 nm. The absorbance obtained was used in a linear regression equation derived from plotting several standard solution concentrations (0; 4; 8; 12; 16; and 20 ppm) against their respective absorbance. The final concentration of the treated solution, compared to the initial concentration, was used for calculating the removal percentage. The % removal was calculated using a commonly accepted equation based on the CR concentration before and after treatments [18].

RESULT AND DISCUSSION

Synthesis and Characterization

Analysis of the combustion products of PKE ash and the $AgNO_3$-PKE ash powder composites using XRD showed distinct differences, as shown in Figure 2. A comparison of the peaks obtained with previous studies showed that the mixture peaks appeared at specific 2θ angles (Figure 2a), showing the composition of PKE ash. These included β-calcium pyrophosphate (β-CPP, β-$Ca_2P_2O_7$, PDF Card: 01-071-2123) and β-tricalcium phosphate (β-TCP, β-$Ca_3(PO_4)_2$, PDF Card: 01-072-7587) [19]. However, there were oxide compounds of other metals present in either major or minor amounts that were not detected in detail in the diffractogram, due to their mixed nature. The combustion products of silver nitrate and PKE powder produced several diffraction peaks (Figure 2b) at 2θ = 38.2°, 44.4°, 64.5°, 77.5 assigned

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as Ag particles phase (JCPDS card number JCPDS 04-0783 for metallic silver (Ag (0)) [20]. Some small peaks corresponding to oil palm-kernel ash were observed. Metallic silver was predictably obtained through a multi-stage mechanism, such as silver(I) nitrate decomposed during combustion, releasing nitrate ions, and simultaneously, silver ions were oxidized into silver oxide at temperatures below 400 °C. As heating continued up to 600 °C, silver oxide was reduced to metallic silver. Some research has already focused on the decomposition of silver oxide, including its mechanisms and kinetics, to form metallic silver [21-24].

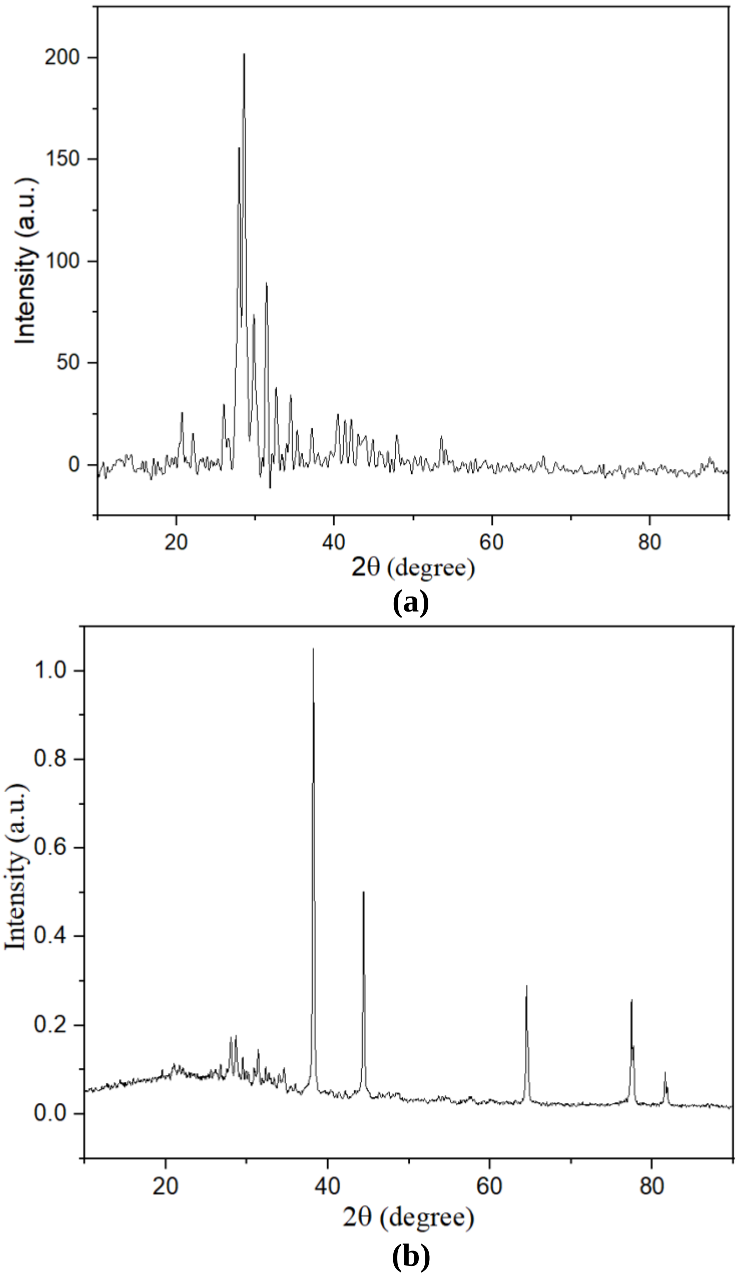

Figure 2. XRD pattern of (a) PKE ash and (b) silver-PKE ash composite

Elemental analysis of PKE product was carried out using XRF, and the results were presented in Table 1.

Table 1. Elemental Detection of PKE ash using XRF Analysis

Element	P	K	Ca	Si	Mg	Al	S	Cl	Mn
%	19.9	16.5	11.1	6.26	4.72	2.47	1.16	0.75	0.71
Element	Fe	Cu	Zn	Sr	Ni	Cr			
%	0.51	0.10	0.047	0.037	0.0035	0.0014			

Based on Table 1, the XRF analysis showed the presence of several elements with a high percentage in PKE ash, such as P, K, Ca, Mg, and Si, along with other detectable elements. These results were consistent with its composition as a precursor, which was identified in previous studies to contain several elements, such as calcium, phosphorus, magnesium, potassium, sulphur, copper, zinc, iron, manganese, molybdenum, and selenium [25]. The results of the XRF analysis of the in-situ combustion product of PKE and silver nitrate mixture are presented in Table 2. The appearance of PKE sample was distinct in the range of 15,000–50,000 keV.

Table 2. Elemental Detection of silver-PKE ash using XRF Analysis

Element	P	K	Ca	Si	S	Cl	Sb	Rb	W
%	8.82	14.6	3.89	3.44	0.88	0.36	0.09	0.01	0.01
Element	Se	Ge	Ga	Br					
%	0.008	0.0003	0.0009	0.0005					

Table 2 showed that composites of PKE ash-metallic silver exhibited several changes in the percentage content of P, K, Ca, and Si. The XRF analysis did not detect the presence of metallic silver, which could be attributed to the potential inhomogeneity of the resulting composites. However, the specific peaks identified in the XRD analysis adequately represented the presence of metallic silver in the sample.

Congo-red (CR) Removal Using Silver-Palm Kernel Expeller Ash

CR was selected as an example of a toxic compound for simulating the utilization of 2 types of materials in the removal process under sunlight. The analysis of the solutions treated with PKE ash and silver-PKE ash under sunlight irradiation was performed using a UV-Vis spectrophotometer, and the results were presented in Figures 3 and 4.

Based on Figures 3, 4, and Table 3, there was a significant difference in the effect of the presence of silver metallic in the photocatalyst. When CR was treated with silver-PKE ash catalyst under sunlight, the removal percentage was 57.8% (Figure 3d), while a value of 20.96% was obtained under dark conditions (Figure 4d). When CR was treated with PKE ash alone, the removal percentages under sunlight and dark conditions were relatively similar, namely 2.70% (Figure 3c) and 2.50% (Figure 4c), respectively. These results were consistent with previous studies reporting the essential role of silver catalysts in the remediation of the water environment from toxic compounds, like CR [26–28].

The role of sunlight in the removal process was showed by the decrease in CR concentration when the solution was exposed (Figure 3b) compared to the solution that kept in dark conditions (Figure 4b). Therefore, the results showed that the removal of CR was primarily due to the catalysis process facilitated by metallic silver-PKE ash composites, rather than the adsorption process.

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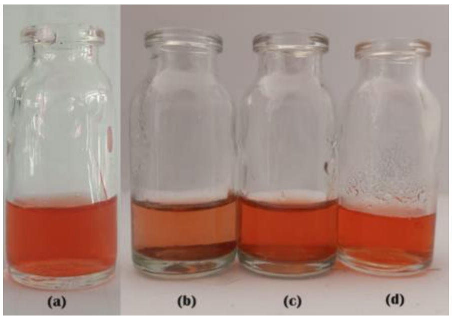


Under Sunlight
Irradiation

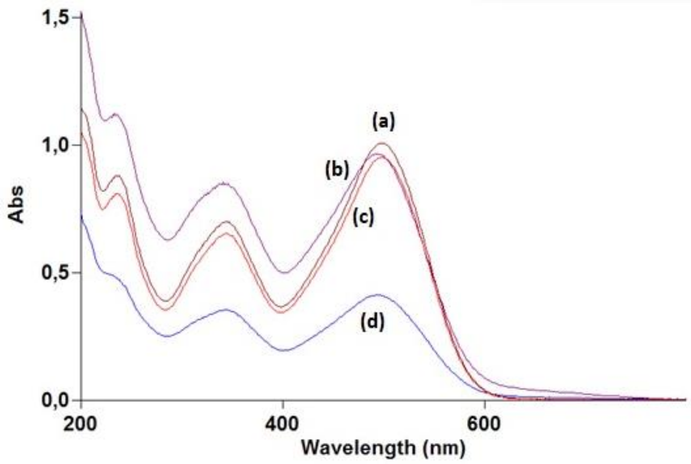
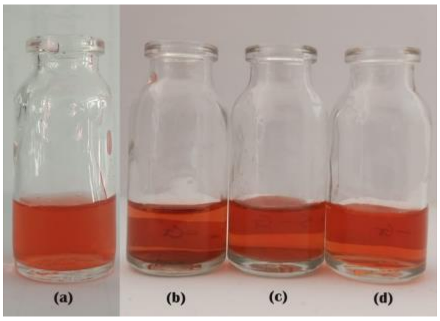


Figure 3. Removal of CR in the presence of PKE ash and silver PKE ash under sunlight irradiation (a) the original of CR; (b) CR treated with no catalyst sunlight irradiation (c) CR treated with PKE ash under sunlight irradiation, and (d) CR treated with silver-PKE ash under sunlight irradiation



Under Dark
Condition

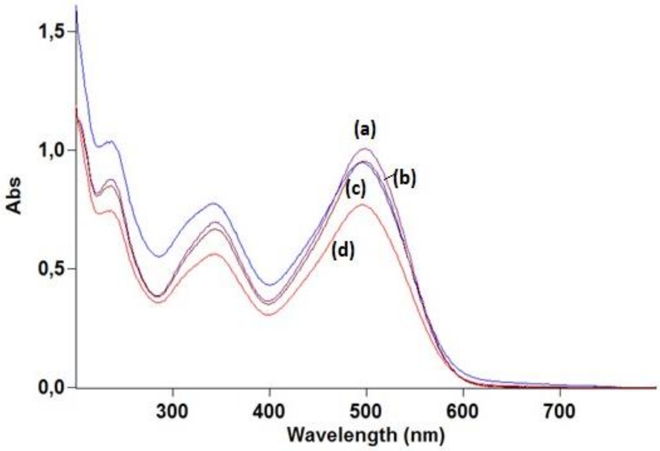


Figure 4. Removal of CR in the presence of PKE ash and silver-PKE ash under dark condition (a) the original of CR; (b) CR treated with no catalyst under dark condition (c) CR treated with PKE ash under dark condition, and (d) CR treated with silver-PKE ash under dark condition

The lack of experimental evidence supporting the catalysis process posed a significant challenge in explaining the reaction mechanism. Previous studies had utilized silver composites with other solid materials to elucidate the CR removal process [29-30]. However, this study did not investigate the presence of silver particles in the reaction system, leaving 2 possibilities, silver either remained attached in the composites or dissolved in the water.

A recent study showed that silver-biomass algae composites could reduce CR by up to 90% [31], compared to other heterogeneous catalysts in aqueous environments. In addition, other reports used $MgAl_2O_4$ to quickly reduce CR concentrations by up to 99% [32]. The results of this study were incomparable to previous results, which suggested the possibility of

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developing new composites for the removal process. Future studies were advised to focus on increasing the amount of silver in composites or combining it with other metals or oxides to enhance its photocatalytic efficiency in lowering CR concentrations.

Table 3. Quantitative analysis results of the CR removal percentage

Material(s)	Condition	% Removal
CR	Sunlight Irradiation	0.96%
CR + Silver-PKE ash		57.8%
CR + PKE ash		2.7%
CR	Dark Condition	0.86%
CR + Silver-PKE ash		20.96%
CR + PKE ash		2.5%

CONCLUSION

In conclusion, this study presented an alternative approach for synthesizing silver-PKE ash composites using an *in-situ* combustion technique. The composites were produced using a mixture of oil PKE as a supporting solid material source and silver nitrate as a metallic source. The results showed the solid material's ability to catalyse CR degradation process, achieving up to 58% removal under sunlight treatment. The obtained material showed potential for further application in CR removal in an aqueous environment.

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