

THE 13TH INTERNATIONAL INNOVATION, INVENTION & DESIGN COMPETITION 2024

EXTENDED ABSTRACTS

e-BOOK



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ZINC OXIDE PHOTOCATALYST ELECTROGENERATED FROM TEA WASTE FOR THE MITIGATION OF CHLORINATED WATER POLLUTANT IN WASTEWATER

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ABSTRACT

Zinc oxide is recognized for its effectiveness as a photocatalyst in pollutant degradation, but its conventional synthesis involves hazardous chemicals, posing significant limitations. This study introduces an eco-friendly ZnO electrosynthesis method using tea waste or tea leaf residues (TLR). The produced ZnO photocatalysts were analyzed using FTIR, SEM, XRD, and UV-DRS techniques and evaluated for their photocatalytic activity in degrading 2,4-dichlorophenol. Results indicated that the ZnO-TLR sample achieved a higher degradation rate of 2,4-dichlorophenol (90.5%) than commercial ZnO (62.1%). This superior performance of ZnO-TLR is attributed to its narrower band gap (3.20 eV), strong FTIR Zn-O bond signals, and uniform surface morphology. The phytochemical assay showed that the TLR extract had high phenolic contents, which likely contributed to these properties.

Keyword: Green synthesis; Plant extract; Advanced oxidation process; Electrosynthesis; Wastewater treatment

1. INTRODUCTION

With the global shortage of clean water, effective water reclamation has become crucial. Water pollution from organic, inorganic, and microbial contaminants poses serious health risks. Toxic compounds like phenols and chlorophenols, found in industrial waste from petrochemical and chemical manufacturing, are particularly persistent and harmful. The US EPA has identified chlorophenols like 2,4-DCP as a priority contaminant due to their toxicity (US EPA, 2015).

Various methods to clean water, such as adsorption, chlorination, reverse osmosis, and microbiological techniques, have limitations like high costs and secondary pollution. Therefore, attention has turned to advanced oxidation processes (AOPs), which are simpler, safer, and more cost-effective. AOPs use photocatalytic technology to break down pollutants. Photocatalysts like zinc oxide (ZnO), titanium oxide (TiO₂), and others have been effective in this role. ZnO, in particular, is notable for its ability to absorb solar energy and degrade pollutants efficiently (A.A. Mutalib and Jaafar, 2022).

Traditional ZnO synthesis involves harmful chemicals, prompting a shift to green synthesis methods. Researchers are using natural materials like plant extracts, which are environmentally friendly and contain reducing agents that help form ZnO. Plant-based waste, such as tea leaves residue (TLR), are rich in antioxidants and useful for this purpose (Abdeltaif et al., 2018).

This study explores using extracts tea leaves waste to electrogenerate ZnO photocatalysts. The effectiveness of these plant extracts in producing ZnO and their impact on its properties were analyzed. The photocatalytic performance of the ZnO produced was tested for breaking down the pollutant 2,4-DCP under visible light irradiation.

2. METHODOLOGY

2.1 Materials

Tea waste from brewed tea (Camellia sinensis) was collected from local food stalls. Chemicals used in the study included 2,4-DCP (99.2%). Additional chemicals such as sodium carbonate (Na2CO3, 99%), gallic acid (98.0%), and Folin-Ciocalteu reagent (2 N) were obtained from QRECTM. All chemicals used were of analytical grade.

2.2 Electrogeneration of ZnO

Aqueous-based preparation of the plant waste extract was carried out with slight modifications from previous methods (Geetha, 2015). Then, 20 mL of plant waste extract was placed in a glass tube with a platinum (Pt) plate as the cathode and a zinc (Zn) plate as the anode, connected to a DC power supply providing a constant current of 240 mAh. The electrolyte mixture containing Zn (OH)² was collected and heated to 80°C on a hotplate until it became powdery. It was then dried overnight in an oven at 100°C. The dried sample was calcined at 550°C for 3 hours to produce ZnO. The ZnO was labeled as ZnO-TLR. The ZnO sample was then characterized using FTIR, SEM, XRD, and UV-DRS analysis.

2.3 Phenolic evaluation of tea waste extract

The Folin-Ciocalteu method was used to estimate the total phenolic content of the tea leaves residue (TLR) extracts. First, 3.16 mL of distilled water was added to tubes containing 0.2 mL of Folin-Ciocalteu reagent. Then, 0.6 mL of 7.5% sodium carbonate solution and 40 μ L of the sample were added. The mixture was incubated in the dark for 40 minutes before measuring the UV-vis absorbance at 764 nm. The total phenolic content was quantified using gallic acid as the standard, with the results expressed as gallic acid equivalents (mg/L)

2.4 The 2,4-DCP degradation

The photocatalytic performance of the catalysts synthesized from plant waste was assessed by degrading 2,4-dichlorophenol (2,4-DCP) and comparing the results with a commercial catalyst. Before the reaction, the catalyst was stirred for 1 hour in a 100 mL 2,4-DCP solution without light to reach adsorption-desorption equilibrium. The solution was then continuously stirred under visible light from four 9-watt fluorescent lamps placed about 10 cm from the beaker for 480 minutes at room temperature. Samples of 2 mL were taken using a syringe for absorbance measurements at a wavelength of 284 nm with a UV–vis spectrometer (Shimadzu UV–vis 2600i). The degradation percentage was calculated using the formula:

Degradation (%) =($(C_0-Ct)/C_0$)×100

where C_0 is the initial concentration and C_t is the concentration after the reaction

3. FINDINGS

The FTIR analysis of the ZnO electrogenerated from the tea waste demonstrated the involvement of the bioactive components in the plant extract that assist in the formation of ZnO photocatalyst. The functional groups on the ZnO catalysts were identified using FTIR analysis. All samples showed peaks at 3444.21 cm⁻¹, 1621.39 cm⁻¹, 1403.87 cm⁻¹, 1011.42 cm⁻¹, and 487.76 cm⁻¹. The peak at

3444.21 cm⁻¹ is related to hydroxyl groups, while 1621.39 cm⁻¹ indicates Zn-OH bonds. The peaks at 1403.87 cm⁻¹ and 487.76 cm⁻¹ correspond to ZnO and Zn-O bonds. The peak at 1011.42 cm⁻¹ is due to C-O stretching. A band at 1116 cm⁻¹, found only in ZnO-TLR, is likely due to polyphenols in the plant extracts which matches the preliminary phytochemical assay that recorded the significant phenolic content in TLR extract (~1080 mg mL⁻¹ gallic acid equivalent). It is worth mentioning that, the ZnO-TLR showed the highest intensity of ZnO-related bands highlighting the significance of reducing mechanism of the phenolic compounds in tea leaves residue in Zn-O bond growth. Meanwhile, the XRD pattern showed that the biosynthesized ZnO matched commercial ZnO, confirming the hexagonal wurtzite structure. There were no impurities. The calculation based on the Debye-Scherrer equation revealed the small crystallite size for ZnO-TLR (20.05 nm) as compared to commercial ZnO (49.12 nm). The smaller crystallite size of biosynthesized ZnO is due to the capping effect of plant extracts, which control ZnO growth and prevent clumping. The band gap energy (Eg) of the ZnO photocatalysts was calculated using the Kubelka-Munk function from UV-DRS analysis. The ZnO-TLR band gap energy was 3.20 eV, while commercial ZnO had a wider band gap of 3.29 eV. These results align with a study by (Bopape et al., 2022), which also found a narrower band gap in biosynthesized ZnO compared to bulk ZnO. This band gap modification may be due to intrinsic crystal defects caused by bioactive components from plant extracts or the quantum confinement effect from the smaller crystallite size of biosynthesized ZnO (Azizi et al., 2013; Patil & Taranath, 2017). The morphology of the ZnO catalysts was examined using SEM micrographs at 5k magnifications, as shown in Figure 4. The ZnO-TLR displayed a more uniform and less agglomerated structure, compared to the structure of commercial ZnO. The photocatalytic performance of 2,4 DCP (reaction conditions of pH 3, 30 ppm, and 0.019 g catalyst) demonstrated that ZnO-TLR had superior photocatalytic activity (90.5%), than commercial ZnO (62.1%) under visible light illumination. The high activity of ZnO-TLR is attributed to the bioactive compounds in the TLR extract, which enhance the reduction of Zn precursor to ZnO during synthesis. This is supported by the intense ZnO-related FTIR bands in ZnO-TLR compared to ZnO-BP and commercial ZnO. Additionally, vibrational spectroscopy revealed a broad and intense peak around 3444 cm⁻¹ in ZnO-TLR, indicating more surface OH groups. These OH groups suggest a higher presence of hydroxyl species and water absorption at surface defects linked to oxygen vacancies. Moreover, the ZnO commercial exhibited lower photocatalytic activity due to the higher band gap (3.29 eV) compared to the ZnO-TLR sample (3.20 eV). A narrower band gap is preferred because it facilitates electron excitation from the valence band to the conduction band, thereby enhancing the photo response capacity of ZnO.



Figure 1 (A) FTIR (B) XRD and (C) SEM analysis of the ZnO samples

4. CONCLUSION

The ZnO photocatalyst was successfully generated using aqueous extracts from the tea waste. Phytochemical tests showed that tea leaves residue had significant amounts of total phenolic and flavonoid content which assisted the formation of ZnO due to its reducing power ability. This led to stronger FTIR bands linked to Zn-O bonds, lower band gap as well as less agglomerated surface morphology. This resulted in higher degradation efficiencies of 2,4-DCP for ZnO-TLR (90.5%) compared to commercial ZnO (62.1%). This shows that the inclusion of bioactive components from plant extracts was not only beneficial in terms of sustainability and green aspects but also in enhancing the photocatalytic activity of ZnO by improving its surface and optical properties.

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