

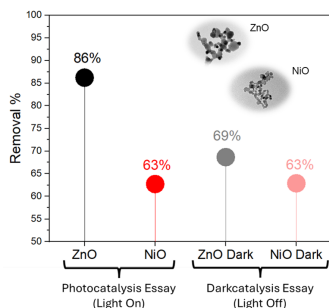
Comparison Between ZnO and NiO Prepared by SCS Synthesis and their Mechanism for the TC – HCl Photocatalytic Removal

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S.Alves, A. Lucena, T. Pigosso, L. Evangelista, T. Bendo, C. Binder. (1) Universidade Federal de Santa Catarina, Florianópolis, Brazil, sofia.silva@labmat.ufsc.br



This study is focused on comparing the potential of zinc oxide (ZnO) and nickel oxide (NiO) produced via solution combustion synthesis as photocatalysts in the degradation of the pollutant model TC-HCl. It highlights the correlation of the chemical and physical properties of these materials and their effectiveness on removing the pollutant from water. The synthesis of nanoparticles (NPs) is performed through a solution combustion synthesis (SCS) technique, followed by characterization using various analytical techniques. The NPs produced via the SCS method exhibited high porosity and a large surface area, as evidenced by our BET and MEV results. This structural characteristic leads to a significant capacity for adsorption of TC-HCl molecules. For the ZnO NPs, photocatalysis occurs in addition to adsorption, leading to an improved system. However, for the NiO nanoparticles (NPs), the higher band gap prevents activation under the illumination conditions provided in this study. Thus, TC-HCl removal in the presence of NiO NPs is predominantly due to adsorption, leading to a less efficient system.

Introduction

The growing chemical industry in laboratories and medical products creates a significant challenge between continuous scientific development and preserving water sources for human well-being [1]. To degrade antibiotics detected in water, advanced oxidation processes, such as photocatalysis, allow the degradation of pollutants into non-toxic components. Zinc oxide (ZnO) has relevance among semiconductor oxides owing to its proven degrading activity and low cost, having a bandgap of 3.2 eV [2]. Nickel oxide (NiO) also has performance as semiconductor metallic nanoparticles due to its chemical stability. With a bandgap between 3.2 and 4.0 eV, it has favorable electrical and optical properties, making the material have an excellent ability to absorb contaminants and pigments [3]. Many different synthesis methods have been studied; among these methods, Solution Combustion Synthesis (SCS) has the advantage of short reaction time, simple instrumentation, and more energy/time saving owing to the lower temperatures used when compared to chemical vapor deposition or sol-gel. SCS depends on the use of an oxidizing agent, fuel, and solvent. This method is based on propellant chemistry and generates an abundant amount of gases and heating during a short period. Such a process leads to crystalline high-temperature stable phases that are maintained as small individual particle sizes, usually aggregated in a very porous nanostructured architecture [4]. The composition plays an important role in the surface area of the synthesized product; hence, it has an important contribution to the pollutant removal ability of the material. The focus of this study is to compare the pollutant removal ability of ZnO and NiO synthesized by the same method, which allows for a comparison of the effectiveness of the almost pure

adsorption mechanism (NiO) to a synergistic approach of adsorption and photocatalysis phenomena (ZnO). Using a simple simulated photocatalytic removal system to quantify the efficiency of the nanoparticles (NPs) produced, the antibiotic tetracycline hydrochloride (TC-HCl) was selected as the model pollutant. Each nanoparticle has been shown to have a characteristic in which pollutant removal is improved.

Material and Methods

To compare the morphological characteristics of the oxides, a fuel/oxidizer ratio of $\phi=0.6$ was selected. The nanoparticles were synthesized using 3.567g of zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) as the oxidizing agent and 0.456g of sucrose ($C_6H_{12}O_6$) as the fuel, generating the ZnO sample. Similarly, NiO used 3.48g of nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) and 0.513g of sucrose. To fully combine the reactants, 3mL of distilled water was used and stirred until it was homogenous. The mixture was placed inside a muffle furnace that had been preheated to 500 °C. The set time for both NPs was 10 min. The structure was then broken using a glass rod and kept in a muffle furnace for another 20 min. The final product was a fine dark gray powder of NiO and a white powder of ZnO. To support this study, a variety of material characterization techniques were carried out, such as XRD, SEM, UV-vis spectral analysis, and TEM. To analyze the photocatalytic performance, the removal of 10 ppm TC-HCl was investigated under both light irradiation by a fluorescent lamp (cold white 85 W spiral lamp with 6500K color temperature) that simulates natural daylight and complete darkness. The essays were carried out under standard times reported in the literature for photocatalysis, ranging up to 120 min.

Results and Discussion

Table 1 displays the results of the physicochemical properties of both samples of NiO and ZnO. Owing to the large formation of gases obtained from combustion synthesis, the nanoparticles acquire a large surface and porous area. NiO stands out with particles that exhibit the largest surface area and pore volume, which are expected to contribute to the absorption of tetracycline. Figures 1 (a) and 1 (b) show that ZnO has a wider pore size than NiO. In Figure 1 (c) and (d), it is possible to see in more detail the aspects of both nanoparticles acquired by TEM, which compose the agglomerates in a flake structure of the NiO and ZnO, respectively, in Figures 1 (a) and (b). According to XRD, it was possible to identify the hexagonal phase of ZnO (ICSD no. 31052) and the cubic phase of NiO (ICSD no. 246910). In addition, the band gap of both materials plays an important role in the efficiency of photocatalysis. The band gap between the valence band of electrons and the conduction band in NiO is larger than that in ZnO Fig. 1 (e), making it easier for the electrons to recombine on the ZnO system. However, only the ZnO NPs can be activated when exposed to fluorescent light, leading to a system with synergy of adsorption and photocatalysis. Consequently, zinc oxide has better pollutant removal performance, as shown in the Graphical Abstract, combining absorption with degradation when exposed to light, reaching up to 88% of the total removal compared to only 66% observed for nickel oxide. For the NiO NPs, the TC-HCl removal is predominantly due to adsorption. The substantial surface area of NiO results in a prolonged time to reach adsorption equilibrium, which explains the continued decrease in TC-HCl concentration during the illuminated period (Fig. 1 (f)).

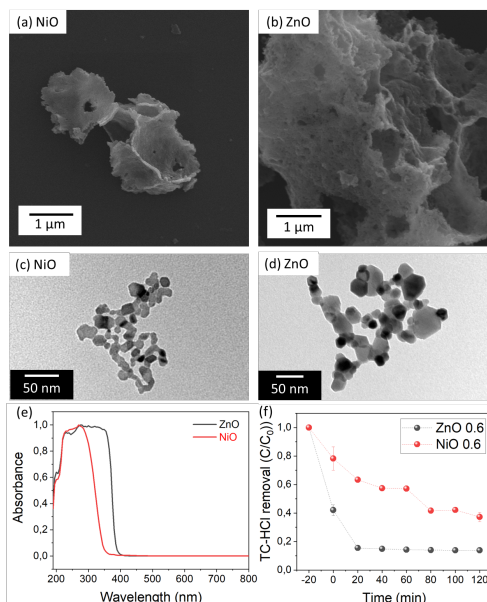


Figure 1. (a) and (b) SEM micrographs of NiO and ZnO, respectively. (c) and (d) TEM analysis of both specimens. (e) the absorbance spectra and (f) the photocatalysis essay.

Table 1. Physicochemical properties of the NiO and ZnO. nanomaterials produced by the SCS method.

Property	NiO	ZnO
Band gap (eV)	3,75	3,28
Surface area (m ² /g)	46,49	17,19
Pore size (nm)	25,5	37,97
Pore volume (cm ³ /g)	0,29	0,16
Crystallite size (nm)	27,1	27,6

Conclusions

Despite the reduction in the surface area when compared to nickel oxide, the zinc oxide nanoparticles synthesized by SCS presented a better performance for TC-HCl removal, which was attributed to a synergy between adsorption and photocatalysis. Additionally, ZnO also presented higher removal of TC-HCl even in the absence of light, which remains to be further investigated in future works.

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