

## THE EFFECT OF PERSULFATE IONS ON THE HETEROGENEOUS PHOTOCATALYTIC EFFICIENCY OF ZINC OXIDE

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## ABSTRACT

The effective removal of non-biodegradable and biologically active trace pollutants is an urgent problem in water treatment. Application of advanced oxidation processes (AOP) offers a solution. One of the AOPs is heterogeneous photocatalysis, which is based on the excitation of a semiconductor. On the surface of the excited photocatalyst, the reactions of photogenerated charge carriers (holes (h+vb) and electrons (e-cb)) with adsorbed substances result in the formation of radicals that can initiate the transformation of organic materials. However, the combination of heterogeneous photocatalysis with oxidizing agents, such as persulfate ions (peroxymonosulfate (HSO<sub>5</sub><sup>-</sup>, PMS) and peroxydisulfate (S<sub>2</sub>O<sub>4</sub><sup>2<sup>-</sup></sup>, PDS)), can enhance the efficiency due to the formation of SO<sub>4</sub>•<sup>-</sup>. The effect of PMS and PDS (i.e. ZnO/PMS, and ZnO/PDS processes) were investigated in the case of ZnO photocatalyst to remove organic substances from water. The suspensions were irradiated with LED light sources emitting 367 or 398 nm photons. To investigate the contribution of various radicals to the transformation, various substances, i.e. trimethoprim antibiotic (TRIM), hydroquinone (HQ), and nitrobenzene (NB) were selected as target substances.

In the first stage, the effect of ZnO, PMS/PDS dose, and photon flux were studied and optimized. PMS and PDS significantly increased the photocatalytic efficiency of ZnO, even in  $O_2$ -free suspensions, because of the excellent electron acceptor properties of PDS and PMS. The addition of various radical scavengers proved that  $SO_4^{\bullet-}$  had a dominant role in the transformations, besides, the contribution of  $\bullet$ OH and  ${}^1O_2$  was also significant. The relative contribution of these reactive species depended on the organic target substance.

The biologically treated communal wastewater (BTWW) drastically decreased the photocatalytic efficiency. Organic and inorganic components can influence the surface properties of a photocatalyst and the processes taking place there. The competition between the organic substances and inorganic ions for adsorption sites and the photogenerated charge carriers is responsible for decreasing the efficiency. Moreover, matrix components, even inorganic ions, react with •OH and SO<sub>4</sub>•<sup>-</sup> and change the radical set. The individual effect of Cl<sup>-</sup> and HCO<sub>3</sub><sup>-</sup> was also examined and proved that mainly HCO<sub>3</sub><sup>-</sup> was responsible for the lower efficiency because of the hindered transformation of PDS on the ZnO surface.

## Keywords: zinc oxide, heterogeneous photocatalysis, persulfate

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