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Development of novel catalytic materials for the removal of emerging organic pollutants by Advanced Oxidation Processes (AOPs)

ABSTRACT

Removing pollutants from industrial process water and wastewater is becoming an important area of research as the amount and quality of fresh water available in certain regions of the world is continuously decreasing. There is an increasing concern about the quality and quantity of the freshwater and groundwater resources for life supporting and environmental needs. Disposal of wastewater streams containing highly toxic organic pollutants generated by many industrial processes is a major environmental problem. Pharmaceutical compounds are among the group of emerging pollutants as their toxic effect even at very low concentration has raised a big concern. Persistent pharmaceutical residues are considered as an emerging environmental problem in the recent years due to their harmful effects, such as chronic and reproduction toxicities for human and aquatic systems. Clofibric acid (CFA) is an emerging pharmaceutical pollutant which is pharmacologically active metabolite of the lipid lowering drug, clofibrate which has shown high persistency when introduced in the water. Numerous studies have demonstrated the occurrence of CFA in surface, groundwater and even drinking water. Wastewater discharged from various industrial processes has become a great concern as several organic contaminants in the wastewater are resistant to natural degradation and toxic to animal and human beings. Wastewater contaminated with phenol has drawn much more attention, as it is a basic structural unit for a variety of synthetic organic compounds. Wastewater originated from many industries contains phenol and substituted phenols. Phenols are harmful to organisms and many of them have been classified as hazardous pollutants because of their potential harm to human health. The increasing organic pollution in water sources in last decades promoted the development of new catalytic oxidation technologies for the removal of organic pollutants at the point of origin is highly interesting. The removal of these types of persistent organic compounds from real and urban wastewater cannot be achieved by conventional wastewater treatment. Thus, the oxidative degradation of these types of recalcitrant organic pollutants by heterogeneous catalysis is considered to be one of the most effective techniques for water remediation. Advanced oxidation processes (AOPs) have been assigned an outstanding priority over other wastewater treatment methods, due to their ability to mineralize organic pollutants. AOPs are based on generation of highly reactive oxygen species such as hydroxyl radicals ($\bullet\text{OH}$) which can effectively attack a wide range of organic compounds. Even

though this technology is considered to be powerful regarding contaminant degradation and mineralization, it faces several practical limitations in a large scale. Catalytic ozonation is proved as an effective technology for the removal of organics from wastewater. Also, among the various approaches of generation of hydroxyl radicals, the Fenton reaction is one of the most efficient processes to eliminate toxic compounds present in the wastewater. The aim of this study was to propose new catalytic materials and effective method for the degradation and mineralization of organic pollutants at ambient conditions to extend the applicability of AOPs, whereby the catalytic system plays a key role. The main objective of this research work is the improvement in the advanced oxidation processes for the treatment of industrial wastewater (e.g., pharmaceuticals, recalcitrant organic compounds, etc.) based on ozonation and Fenton-like process. The heterogeneous Fenton-like reactions were performed using commercial H₂O₂ and also in-situ generated H₂O₂ from formic acid and oxygen. The improvements to be introduced in this study are based on the design of new catalytic system and implemented in this process to enhance their performances. Herein, various families of catalysts like hydrotalcite and spinel-type, Lepidocrocite, FeOOH-derived catalyst, Pd-immobilized hydrophilic and hydrophobic Fe-ZSM5 zeolite-based catalysts (for a combined approach of adsorption/oxidation) and Cu-based catalysts were prepared by different synthesis protocols and tested in both type of advanced oxidation processes (catalytic ozonation and Fenton-like process) for the degradation and mineralization of clofibric acid (CFA) and phenol. The physicochemical properties of the prepared catalysts were studied with N₂-physisorption, X-ray Diffraction (XRD), Temperature-Programmed Desorption (TPD), X-ray photoelectron spectroscopy (XPS), Attenuated Total reflection Infrared Spectroscopy (ATR-IR), Inductively Coupled Plasma Mass Spectrometry (ICP) and Point of zero charge (pHPZC). The results of this study have shown that, catalysts tested in ozonation and Fentonlike processes are effective and promising materials for the degradation of clofibric acid and phenol. Among hydrotalcite and spinel-type materials, Fe-hydrotalcite and Cu-spinel are most stable and active catalysts in catalytic ozonation of CFA. Pd/FeOOH is the promising catalyst for the degradation and mineralization of CFA by both types of process (ozonation and Fenton-like process). In Fenton-like process within very short reaction time, achieved higher mineralization degree (60% in 30-60 min) using 0.5%Pd/FeOOH catalyst. Phenol is also effectively degraded by Pd/Fe-ZSM5 catalysts. Hydrophobic zeolite Fe-ZSM5 (236) shows higher adsorption of phenol. Pd/Fe-ZSM5 (236) catalysts also show better performance in in situ generated hydrogen peroxide Fenton-like process. Among all these families of catalysts, Cu-Al oxide catalyst exhibit highest activity and stability for CFA degradation and mineralization, achieving 82% and 96% TOC removal in 2h and 6h respectively. In situ ATR-IR study of this catalyst show that, strong interaction of ozone with

surface acidic sites of catalyst. The reactive active species are generated on the catalyst surface by the interaction of ozone in aqueous solution, which promotes radicals to initiate catalytic reaction. Our catalytic system show the applicability in degradation and mineralization of CFA and phenol by catalytic ozonation and Fenton-like process at ambient conditions