Enhanced removal of ciprofloxacin with sludge-based catalysts by catalytic wet air oxidation processes

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Introduction

Sewage sludge is increasingly produced in municipal and industrial wastewater treatment plants. It is a very difficult waste to manage due to its variable composition, its contamination with pathogenic micro-organisms and micropollutants, and its high organic matter and water content.

Current sludge management practices have changed significantly over the last twenty years. Improved biogas production, advanced sludge dewatering processes, controlled landfilling and thermal processes are increasingly implemented. These developments are accompanied by an increase in the cost of sludge management. These costs often represent more than fifty percent of the total cost of wastewater treatment. Due to the high costs, but also the urgent need to develop more sustainable sludge treatment scenarios, research on innovative and more sustainable sludge treatment processes is increasing (Domini et al., 2022).

In this context, an industrial sludge was proposed as promising biomass precursor of chemically activated carbons for catalytic applications. The aim of this work is to characterize and test the efficiency of these green and sustainable iron- and nickel-based catalysts, proposing the mentioned sludge valorization technique as a feasible approach to solid waste management.

Materials and methods

Firstly, the urban and industrial sludge were kindly supplied by a municipal wastewater treatment plant and a local pharmaceutical company, respectively, both located in Spain. These wastes were characterized in terms of the chemical oxygen demand (COD), and the total (TS), fixed (FS), and volatile (VS) solids according to the Standard Methods. The solid fraction was also undergone to elemental analysis and X-ray fluorescence spectroscopy.

For the catalyst synthesis, the sludge was dried in an oven for 24 hours at 105ºC. After a grinding step, the dried sludge powder was chemically activated by using an impregnation technique with $FeCl_3 \cdot 6H_2O$ or $NiCl_2$ as the activating agents. The activation was performed for 24 hours at room temperature, followed by drying for 24 hours at 105ºC. Next, the impregnated sludge was pyrolyzed in a vertical reactor for 2 hours at 800 ºC, maintaining a constant N_2 flow rate of 100 mL/min and a heating rate of 10 ºC/min. The catalyst was washed with HCl 1M solution for the removal of the iron and nickel excess and then with deionized water. Finally, the solid was dried in an oven for 24 hours at 105ºC.

The textural and chemical properties of the iron-based catalysts were determined by using several techniques: Brunauer-Emmett-Teller surface area analysis (BET), X-ray diffraction (XRD), X-ray fluorescence (XRF), thermal gravimetric analysis (TG/DTG), and scanning electron microscope (SEM).

Catalytic wet air oxidation tests of ciprofloxacin 50 mg/L aqueous solutions were carried out in a 100 mL autoclave with a stirrer set at 700 rpm. The experiments were conducted at 140 ºC and 20 bar, using a catalyst dose of 0.68 g/L.

Results and discussion

Among the main macroscopic properties of the industrial sludge, the total solid content was 3.4 wt.%. The high COD and VS values indicated an important organic matter content. This is convenient for the synthesis of biomass derived catalysts as the more organic matter in the precursor, the higher the efficiency. In this regard, VS of 80% and COD of 35.0 g/L was obtained for the sludge.

According to the method mention in the previous section, iron- and nickel-based catalysts were synthesized. The characterization of these carbonaceous catalysts showed favorable properties, as relatively high BET surface area. Figure 1 shows the adsorption-desorption isotherms and SEM images of the catalysts. It can be confirmed that the prepared catalysts are essentially mesoporous (type IVa isotherms) and the supported Fe and Ni particles in the pores of activated carbon are needle shaped.

Promising results were obtained when iron- and nickel-based catalysts were applied to wet air oxidation processes. Figure 2 shows ciprofloxacin conversion for sludge derived catalysts synthesized. An initial removal of the pollutant was observed before the reaction started (zero-time reaction), which is related to the adsorption process until the system reaches the desired temperature. The iron-based catalyst seemed to present considerably higher conversions than the nickel one, oxidizing the emerging pollutant almost completely within 2 h at 140 ºC and 20 bar.

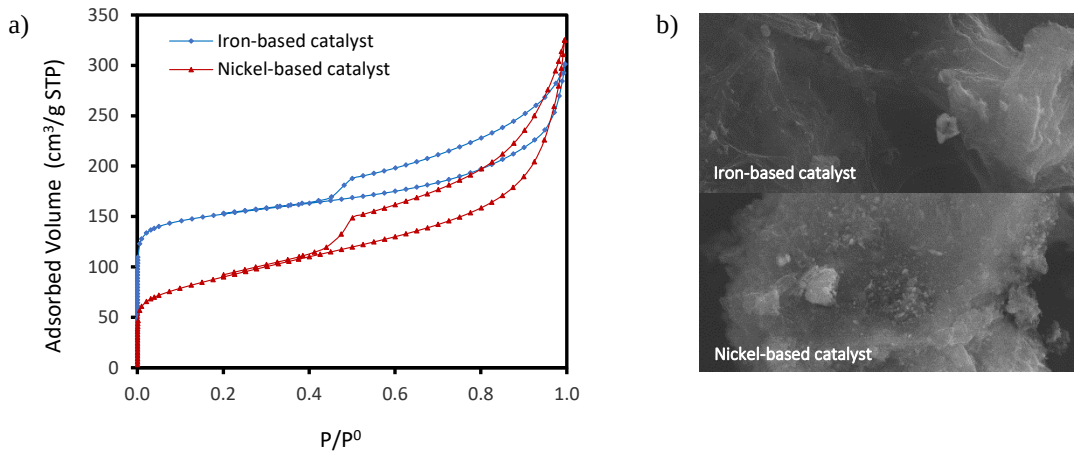

Figure 1. Adsorption–desorption isotherms (a) SEM images (b) of the sewage sludge-based catalysts.

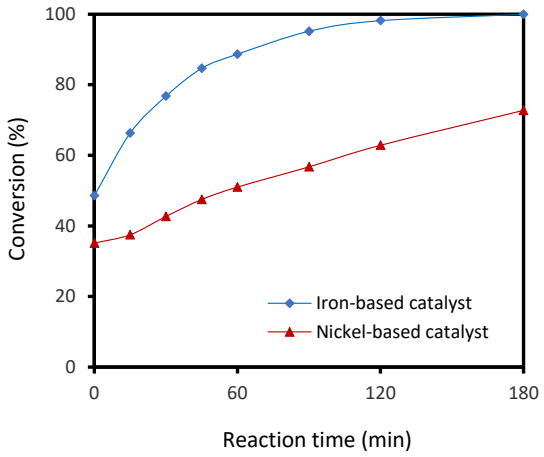

Figure 2. Ciprofloxacin conversion with iron- nickel-based catalysts by catalytic wet air oxidation.

Conclusions

The procedure described in this work allows the valorization of solid waste, contributing to the circular economy in wastewater treatment plants and to the removal of emerging pollutants such as ciprofloxacin.

Catalytic wet air oxidation is capable of degrading ciprofloxacin in aqueous solutions. The results revealed that the iron-based catalyst had high catalytic activity, and the emerging contaminant could be completely oxidized within 2 h at 140 ºC and 20 bar.

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