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# Kinetic of oxidation and mineralization of priority and emerging pollutants by activated persulfate

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## HIGHLIGHTS

- Oxidation of prioritary and emerging pollutants with persulphate was studied.
- A radical mechanism for pollutants oxidation and mineralization was proposed.
- A kinetic model for a mixture of pollutants was developed and validated.
- Kinetic parameters were calculated by fitting experimental data.
- Iron addition policy was taken into account in the model (batch or semicontinuous).

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## ABSTRACT

In this work, abatement of diuron (D), (selected as an example of priority pollutant) and nicotine (N), caffeine (C), ibuprofen (I) and phenacetin (P), (chosen as examples of target emerging pollutants), have been carried out by using persulfate activated by $Fe^{2+}$. Reactions were accomplished at room temperature in a batch or semicontinuous (SC) manner, using 5 mg/L of each pollutant.

The effectiveness of the process was measured by attending at the pollutant conversion and TOC removal. Kinetic model for both reaction rates – pollutants oxidation and mineralization – was developed – on the basis of a radicalic mechanism and kinetic parameters calculated. Moreover, the kinetic model discriminated was successfully validated by comparison of predicted and experimental values obtained for pollutant and TOC conversion when mixtures of pollutants were treated at different persulfate and iron concentrations. Iron addition process presented a remarkable effect on oxidation results. It was found that a continuous slow release of $Fe^{2+}$ notably increased the efficiency of the process.



## 1. Introduction

Removal of bio-recalcitrant and toxic compounds (priority pollutants) from wastewaters is a major problem to be solved since coagulation–flocculation processes are generally unable to remove such compounds [1,2] and conventional biological treatment of these pollutants is not effective [3,5]. Moreover, in recent years, abatement of emerging pollutants is receiving an increasing attention [6,7].

Advanced separation processes, such as adsorption by activated carbon [8] and membrane-filtration technologies [9,10] also produce wastes (spent activated carbon and membrane retentates that must be appropriately disposed of). Wet oxidation (catalytic or not) using high temperatures and pressures is not economically viable for heating dilute aqueous solution of these pollutants [11,12].

Therefore, oxidation technologies carried out at mild temperatures and room pressures seems to be more desirable. Among them, Advanced Oxidation Processes (AOPs) as ozonation [13–19], photocatalysis [20–25], electrochemical processes [24,26,27] and Fenton's Reagent [23,28–30], have been successfully used for abatement of priority and, recently, emerging pollutants.

Recently, the oxidant persulfate $\left(S_2O_8^{2-}\right)$ has drawn increasing attention as an alternative oxidant in the chemical oxidation of contaminants at mild conditions. It is a strong oxidizing agent ($E^0 = 2.01$ V), non-selective reactive and stable at room temperature. Its benign end products can also be cited as advantages [31–34]. When persulfate is activated, sulfate free radicals $(SO_4^{\cdot-})$ are generated, which are stronger oxidation species ($E^0 = 2.6$ V) than persulfate itself [35,36]. These radicals are among the strongest oxidants known, much stronger than the oxidants commonly used in industry (permanganate or hypoclorous acid) [14].

Thermal activation of persulfate [32,33,37–39] occurs through Eq. (1):

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