Technical Note

Effect of intermediate compounds and products on wet oxidation and biodegradation rates of pharmaceutical compounds

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HIGHLIGHTS

- Key role of degree of backmixing and synergism during lab experimentation.
- Differences between lab and industrial rates due to distribution of intermediates.
- Synergism of phenolic compounds during continuous wet oxidation of real wastewater.
- Backmixing favors wet oxidation rate.
- Negative effect of matrix and backmixing on biotreatment specific utilization rates.

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ABSTRACT

Kinetics of pure compounds in batch agitated reactors are useful data to clarify the characteristics of a given reaction, but they frequently do not provide the required information to design industrial mixed continuous processes because in this case the final and intermediate products interact with the reaction of interest, due to backmixing effects. Simultaneously, the presence and transformations of other compounds, frequent in industrial wastewater treatments, adds more complexity to these types of interactions, whose effect can be different, favorable or unfavorable, for chemical or biological reactions. In this work, batch laboratory reactor data were obtained for the wet oxidation and biodegradation of four phenolic compounds present in a pharmaceutical wastewater and then compared with those collected from industrial continuous stirred tank reactors. For wet oxidation, batch laboratory degradation rates were significantly lower than those found in industrial continuous stirred operation. This behavior was explained by a different distribution of intermediate compounds in lab and industrial treatments, caused by the degree of backmixing and the synergistic effects between phenolic compounds (matrix effects). On the other hand, the specific utilization rates during aerobic biodegradation in the continuous industrial operation were lower than those measured in the laboratory, due to the simultaneous presence of the four pollutants in the industrial process (matrix effects) increasing the inhibitory effects of these compounds and its intermediates.

1. Introduction

Increasing interest is being shown in integrating chemical and biological systems to treat polluting pharmaceutical compounds, using a chemical oxidation pretreatment step to convert initially biorecalcitrant organics to more readily biodegradable intermediates (Santos et al., 2003; Kulik et al., 2008; Mandal et al., 2010; Mohapatra et al., 2010). Chemical treatments used to break down toxic and recalcitrant pharmaceutical compounds to molecules suitable for biotreatment include wet air oxidation (WAO), ozonation, photo-oxidation and Fenton's reaction, which are generally termed advanced oxidation processes (AOPs) (Hsu et al., 2004;

Suarez-Ojeda et al., 2007; Mandal et al., 2010). WAO uses temperatures and pressures over 390 K and 1 MPa and air or oxygen as oxidant, being particularly useful for toxic organic wastewater (Bhargava et al., 2006).

A lot of data are available in the literature for the wet oxidation or biological treatment of synthetic waters containing the typical pharmaceutical pollutants at laboratory scale (Quintana et al., 2005; Bhargava et al., 2006). Frequently, these data are obtained from batch experiments with pure compounds, which are usually selected as model pollutants. It is important to bear in mind that the selection of pure compounds as model pollutants, based on their toxicity or high concentration in the real wastewater, implies that the effect of other compounds which are less concentrated or considered not to affect the degradation rate is not taken into account during laboratory experiments.

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It must be also considered that the adequate design of reactors rests on knowledge of two factors: the overall rate at which the reaction proceeds and the extent of backmixing occurring in the reactor. The first factor involves the determination of the rate equation, which for homogeneous reactions may be found most conveniently by using small scale laboratory batch equipment. As backmixing does not occur in such setups, the effect of the reaction rate may be isolated and examined alone. However, real reactors exhibit some degree of backmixing and their behavior should lie somewhere between plug flow (no backmixing) and complete backmix flow. In fact, real hydrodynamic flow in large industrial equipment shows a high degree of backmixing, mainly due to the turbulence generated during the injection of the oxidant (oxygen or air).

In conclusion, the election during the experimentation of a batch operation mode rather than the typical continuous industrial operation with perfect mixing, involves different evolution of the concentration of the intermediates during the wet oxidation and biodegradation. Therefore, it is important to ask how reliable laboratory results are when used as a basis for the design of continuous industrial processes for the treatment of complex wastewaters. The validity of the results obtained at laboratory level when applied to the design of real processes is a topic that has scarcely been studied. This aspect is especially important in free radical reactions, and also in biological systems with many types of inhibitions and interactions between the pollutants.

The aim of this work, arising from the problem outlined above, is to determine the validity of the results obtained at laboratory scale, comparing them with those collected from a real industrial treatment process, in order to analyze the nature of any divergences that might appear, which are expected to be mainly due to variations in the concentration of intermediates associated with matrix effects and backmixing (mixed or batch/plug flow).

2. Materials and methods

Industrial data were obtained from an integrated wet oxidation biotreatment plant in the pharmaceutical industry. This plant treats wastewater generated during the process of acetylsalicylic acid production with a COD of 10 g L^{-1} and mainly composed of phenol, salicylic acid, p-hydroxybenzoic acid and 5-hydroxyisophthalic acid. After the wet oxidation step the wastewater treatment is completed by an aerobic biological process which also treats wastewaters that come from others processes in the industrial plant. Table SM-1 in Supplementary Material (SM) shows average values of inlet concentrations and removal efficiencies for the main pollutants of the industrial wastewater during the wet oxidation and the biological treatment. As it can be deduced from the table, the identified phenolic compounds yield around of 80% of the total COD. The non-identified COD is due to a variety of impurities and subproducts generated during the synthesis of phenol and salicylic acid.

Laboratory wet oxidation experiments were completed in a 1 L capacity reactor. The equipment, charged with the catalyst dissolved in 700 mL of distilled water (Fe^{2+} added as FeSO$_4$), was pressurized and preheated. Once the equipment achieved the desired conditions of pressure and temperature, a predetermined volume of a concentrated solution of the phenolic compound was injected into the reactor. Temperature and pressure were maintained constant during the course of each experiment. The temperature (413 K), pressure (1.0 MPa), concentration of catalyst (800 ppm Fe^{2+}) and initial concentrations were selected in accordance with those employed in the industry (see Tables SM-1 and SM-2). A kinetically controlled regime was ensured for all the experiments.

A more detailed description of the experimental equipment and the analytical methods used was given in Collado et al. (2010a).

Biodegradation experiments at laboratory scale were carried out for 24 h at 250 rpm and 303 K, employing Erlenmeyer flasks (1 L) loaded with 200 mL of buffer solution at pH 7 composed by (in g L^{-1}) Na$_2$HPO$_4$ (8.7), KH$_2$PO$_4$ (5.3), FeSO$_4$·7H$_2$O (0.2) and NH$_4$NO$_3$ (0.3), sludge from the industrial biological reactor (10 g TSS L^{-1}) and the amount of pollutant corresponding to each case. TSS and VSS were determined according to standard methods (APHA, 2005).

A comparison between identical experiments showed that the procedures have a good reproducibility, with standard deviations of the measured value of concentration of phenolic compounds lower than 5% and 9% for lab wet oxidation and biological treatment, respectively.

3. Results

3.1. Lab scale (batch experiments and pure compounds: low concentration of intermediates)

At laboratory scale, the batch degradation experiments conducted with pure compounds allow a low and decreasing concentration of intermediates in the medium, also simulating the behavior of a plug flow reactor for the treatment of the pure compounds.

3.1.1. Wet oxidation

Fig. 1 shows the evolution of the concentrations of the four compounds selected. After 2 h of reaction, the 5-hydroxyisophthalic acid was not degraded and only 30% conversion of phenol and p-hydroxybenzoic acid had been achieved, whereas the salicylic acid almost completely disappeared. The degradation profiles can be divided into two different stages, especially in the case of the more refractory compounds. An induction period can be distinguished, when degradation rates were very low and a second step is then seen, when degradation rates were much higher. These results are in agreement with Mishra et al. (1995), who pointed out the existence of an initial induction period, when the radicals are being formed.

As can be seen in Fig. 1, the COD and compound concentration profiles had similar behavior and the same reactivity order was observed. The salicylic acid was again the most reactive of the four compounds, with 85% COD reduction after 1 h of reaction. COD initially decreased (oxidation of salicylic acid) and then remained approximately constant during the last minutes of the experiment due to the formation of intermediate compounds that were not further oxidized (Collado et al., 2010b).

3.1.2. Biological treatment

In order to determine the capacity of the activated sludge from the biological reactor to degrade pure salicylic acid, 5-hydroxyisophthalic acid or phenol without the matrix effect of the real wastewater, a series of laboratory experiments under aerobic conditions were performed (Fig. 2).

3.1.2.1. Sludge characterization.
Previous to the biodegradation studies on the phenolic compounds considered, the activated sludge from the biological reactor was characterized. TSS and VSS were determined, obtaining a relation of (0.64 ± 0.03) g VSS g^{-1} TSS. The SOUR (specific oxygen uptake rate) test was employed in order to determine the activity of the sludge (APHA, 2005). As expected, the oxygen consumption was proportional to the solids content, obtaining a specific oxygen consumption rate of around 1.5 × 10^{-2} mg O$_2$ g^{-1} VSS min^{-1} (Fig. SM-1).