

“Vegetable acids” for selective precipitation of metallic cations : a green chemistry application

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The aim of this paper is to propose a green chemistry approach for the synthesis of carboxylic acids from biomass and for the selective precipitation of metallic cations contained in industrial wastewaters. This project allows a new way of non-food valorization of vegetable oils and a metal recovery.

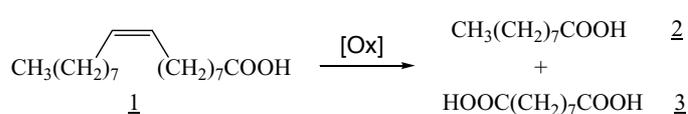
Introduction

Green chemistry¹ is the universally accepted term to describe the movement towards more environment friendly chemical processes replying to sustainable development. It encourages the design of products and processes that reduce or eliminate the use and the generation of hazardous substances. The ideal synthesis should be realized in one step with a simple separation, leads to a quantitative yield and no waste. Moreover it must be safe, environmentally acceptable and based on “atom efficiency”. Nowadays, for chemical industry, the use of renewable raw materials becomes increasingly important not only for economical reasons but also for ecological effects. In oleochemistry, the use of vegetable oils can lead to the synthesis of competitive products^{2,3}. The fatty acid composition determines the use of the oil. For instance, rapeseed and sunflower oils are composed by many long chain fatty acids (C18, saturated and unsaturated acids), which are commonly used for polymers and lubricants. The oxidation of fatty acids leads to mono and/or di-carboxylic acids which can be easily transform to carboxylates, besides we have showed that carboxylates can be used for the precipitation of metallic cations⁴. Surface treatment and hydrometallurgical leaching processes produce industrial wastewaters containing heavy metals, the conventional treatment to remove these metals involve a chemical precipitation. The hydroxide precipitation using lime or caustic is the most commonly used method. This process leads to sludges without any commercial value, indeed they are stored in specialized landfills after solidification/stabilization process using hydraulic binders. Contrary to this method, the selective precipitation of metallic cations by carboxylates⁵ allows the metal recovery. As a consequence, the production of carboxylic acids has been studied in accordance with a green chemistry approach.

1. Fatty acid oxidation

1.1. Oleic acid cleavage

The oxidation of oleic acid **1**, from rapeseed and sunflower oils, leads to pelargonic **2** and azelaic **3** acids (Scheme 1). These carboxylic and dicarboxylic acids are industrially produced by



Scheme 1: Oxidative cleavage of oleic acid

ozonolysis of oleic acid but this is a costly process in energy and low yields of acids are obtained. To oxidize oleic acid many other processes have been developed such

1.3. Oxidation protocol

The general procedure for the oleic acid cleavage is the following : a flask is charged with 7mL of solvents, 282mg (1mmol) of oleic acid, 5mg (2.2%) RuCl_3 and 877mg (4.1eq) NaIO_4 . To this mixture, 2% of Aliquat 336® is added and the reaction is carried out under ultrasounds (20 Hz). The final products are extracted by 3 x 20mL of AcOEt, the combined organic extracts are dried with MgSO_4 and concentrated. The resulting pelargonic and azelaic acids are purified in warm water. After a second purification azelaic acid can be obtained with a purity of 99%¹³.

2. Selective precipitation of metallic cations using sodium azelates

2.1. Theoretical feasibility

In order to predict the feasibility of the separation of metallic cations in mixture by sodium azelate, a theoretical study of the metallic azelate precipitation has been realised. The solubility of Ca, Cu, Ni, Pb and Zn azelates has been determined in pure water at 20°C⁴. The solubility of divalent metallic azelates in water depends of pH. Therefore we established a diagram of conditional solubility of metallic azelates (Fig. 1) using MINQL+ software. With the help of this diagram, it is possible to predict theoretically the separation of metallic cations in a M_1 - M_2 mixture. When $\log([M_2]/[M_1]) > 2$, the separation leads to the precipitation of 99.9% of the cation M_1 without embedding more than 1% of M_2 .

Table 3 shows the calculation results for M_1 - M_2 mixtures. $\log([M_2]/[M_1])$ is determined by researching the highest difference between $\log M_1$ and $\log M_2$ from the diagram. So, from a theoretical point of view, sodium azelate could be use for the selective precipitation of lead for the mixtures Pb^{2+} - Ca^{2+} , Pb^{2+} - Ni^{2+} and copper for Cu^{2+} - Ni^{2+} .

Azelate can precipitate selectively not only divalent metallic cations but also trivalent cations such as Fe^{III} , Cr^{III} . Previous studies have showed the possible formation of hydroxycarboxylate¹⁴. In this case, the precipitation of iron (III) by azelate leads to different species : Fe_2AZ_3 , FeOHAZ , $\text{Fe}(\text{OH})_2\text{AZ}_{1/2}$ or a mixture of all these compounds. The stoichiometry of the synthetized compounds depends of the precipitation pH, that make impossible the calculation of conditionnal solubility. For instance at pH 4,5 the solubility of iron-azelate is equal to $1.58 \times 10^{-6} \text{ mol.L}^{-1}$.

Fig. 1 : Conditional solubility of metallic azelates

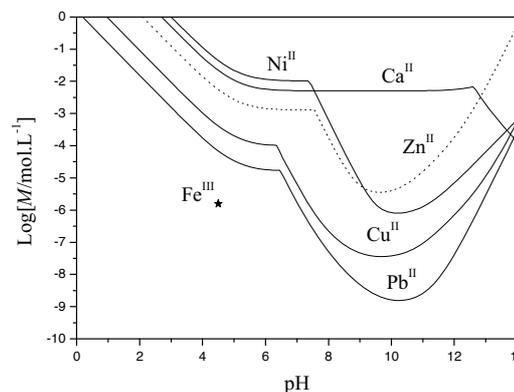


Table 3 : Theoretical selective separation of cations in mixture

Entry	M_1 - M_2	$\log ([M_2]/[M_1])$	pH
1	Pb^{2+} - Ca^{2+}	2,49	6,4
2	Pb^{2+} - Ni^{2+}	2,79	6,4
3	Cu^{2+} - Ni^{2+}	2,03	6,3

2.2. Selective precipitation of iron in a Fe^{III}-Zn^{II} mixture

We have chosen to experiment the selective precipitation on the Fe^{III}-Zn^{II} mixture corresponding to sulphate leach liquors in zinc hydrometallurgy¹⁵. The aim is to remove iron without embedding zinc. Figure 1 shows that this separation is possible ($\log([Zn]/[Fe]) = 3.55$). Different factors have been investigated by using a Design Of Experiment : the pH, the zinc concentration of the solution, the addition speed of the reactant and the precipitate stirring time. The results clearly show that pH is the most influent factor for iron removal. Zinc concentration has a significant effect too. In the best condition (pH = 2), it is possible to remove 99.9% of iron without co-precipitating more than 2.1% of zinc. This process leads to a filtrate with a zinc concentration more than 3.5 g.L⁻¹ and an iron concentration less than 7.3 mg.L⁻¹. From this solution zinc can be recover by electrodeposition.

Conclusion

In conclusion, the oxidation of fatty acids has been performed with a ruthenium/periodates catalytic system : the optimisation of co-solvents has been realised by eliminating CCl₄ which is carcinogen. The oxidative system, 2.2% RuCl₃ / 4.1eq NaIO₄ with 2% Aliquat 336® in H₂O/CH₃CN in ratio 1/1 under ultrasounds 20 Hz, is the most adapted for fatty acid cleavage. The oxidation can be carried out in water with emulsifier and sonication. The final products have been purified in water. The produced carboxylic acids can perform the selective separation of metallic cations. Azelate could be use for the precipitation of lead in Pb²⁺-Ca²⁺, Pb²⁺-Ni²⁺ and copper in Cu²⁺-Ni²⁺. The selective precipitation was realized for Fe^{III}-Zn^{II} mixture. As a result, this process using “vegetable acids” could lead to a selective separation of metallic cations contained in industrial wastewaters: this comes within the context of green chemistry.

The oxidation of other reactants such as olefins, cyclo-olefines etc by the oxidative catalytic system RuCl₃ / NaIO₄ are actually in progress in our laboratory, as well as studies for the selective separation of metallic cations by sodium nonanoate.

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