

IRON REMOVAL FOR KINETIC STUDIES ON FENTON TREATMENTS: A NEW APPROACH BASED ON FERROCYANIDE
REMOCIÓN DE HIERRO PARA ESTUDIOS CINÉTICOS EN PROCESOS FENTON: UNA NUEVA PERSPECTIVA BASADA EN FERROCIANURO

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Abstract

A new approach based on ferrocyanide for iron removal in kinetic studies on Fenton treatments was developed and proposed. The influence of iron precipitation using the ferrocyanide treatment on the measured concentration of two model molecules (phthalic acid and meropenem) was studied. For this purpose, different solutions of phthalic acid and meropenem were prepared. Ferrous sulfate was added to the solutions after the adjustment of the pH value. Then, iron was removed by alkalization (traditional) and ferrocyanide treatments, this for phthalic acid. In the case of meropenem, the removal of iron was performed using only the ferrocyanide treatment due to a chemical modification of the molecule at (highly) alkaline conditions. It was found that the precipitation of iron with ferrocyanide can take place at initial pH values below 5.5 and 4.5, for phthalic acid and meropenem, respectively. The pH value of the supernatant solutions after precipitation, in both cases, was 7.0. The results show that the application of ferrocyanide treatment did not affect the measurement of the concentration of phthalic acid and meropenem after the removal of iron. In addition, some considerations are provided to apply this method to other molecules.

Keywords: advanced oxidation processes, phthalic acid, meropenem, wastewater treatment, iron.

Resumen

Se desarrolló y propuso un nuevo enfoque basado en ferrocianuro para la remoción de hierro en estudios cinéticos sobre procesos Fenton. Se estudió la influencia de la precipitación de hierro mediante el tratamiento con ferrocianuro sobre la concentración medida de dos moléculas modelo (ácido ftálico y meropenem). Para este propósito, se prepararon diferentes soluciones de ácido ftálico y meropenem. Se añadió sulfato ferroso a las soluciones después del ajuste de pH. Luego, se eliminó el hierro mediante alcalinización (tratamiento tradicional) y el tratamiento con ferrocianuro, esto para el ácido ftálico. En el caso de meropenem, la eliminación de hierro se realizó utilizando solo el tratamiento con ferrocianuro debido a que la molécula sufre una modificación química en condiciones (altamente) alcalinas. Se encontró que la precipitación de hierro con ferrocianuro puede ocurrir a valores de pH iniciales debajo de 5,5 y 4,5, para el ácido ftálico y el meropenem, respectivamente. El pH de la solución sobrenadante después de la precipitación, en ambos casos, fue 7,0. La aplicación del tratamiento con ferrocianuro no afectó la medición de la concentración de ácido ftálico y meropenem después de la eliminación del hierro. Además, se proporcionan algunas consideraciones para aplicar este método para otras moléculas.

Palabras clave: procesos de oxidación avanzada, ácido ftálico, meropenem, tratamiento de efluentes, hierro.

Advanced Oxidation Processes (AOPs) are promising technologies that are used for the treatment of recalcitrant and non-biodegradable compounds (Alalm *et al.*, 2015; Expósito *et al.*, 2016). Among AOPs, the Fenton process and its modifications (i.e. Fenton-like, heterogenous Fenton) have some advantages over other treatments such as easy operation, simple equipment, and no toxic reagents

(Cihanoğlu *et al.*, 2017). In Fenton process, H₂O₂ reacts with Fe²⁺ ions producing •OH radicals which are strong oxidants ($E_0=2.80$ V) that react with recalcitrant pollutants (e.g., azo dyes, antibiotics, phenolic compounds, pesticides, heavy metals), thus promoting their removal from water (Cheng *et al.*, 2016; Li *et al.*, 2019; Subramanian and Madras, 2017; Subramanian and Madras, 2016; Wang *et al.*, 2016).

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One of the steps required in the kinetic study of a Fenton process is the quenching of the reaction, which could be done by separating one of the reactants involved (pollutant, hydrogen peroxide and/or iron), thus facilitating the measurement of the target pollutant concentration (Amildon Ricardo *et al.*, 2018; Benzaquén *et al.*, 2015; Conte *et al.*, 2017; Perini *et al.*, 2017; Wang *et al.*, 2017). Iron can easily be removed by increasing the pH of the sample because of the generation of insoluble iron hydroxides (Amildon Ricardo *et al.*, 2018; Goi and Trapido, 2002; Li *et al.*, 2018; Maslahati Roudi *et al.*, 2018). This method is frequently applied to quench the Fenton reaction as well as to remove iron from the treated effluent at an industrial scale for its final discharge. However, for kinetic studies, the measurement of pollutant concentrations and their dependence with time, in some cases, might be difficult since some substances could be affected by the increase of the pH value (i.e. some antibiotics) (Elmolla and Chaudhuri, 2010). In these cases, an alternative method is required to remove iron from the solution without interfering the measurement of the pollutant.

In qualitative analytical chemistry, a classic method for the identification of iron is the reaction with ferrocyanide or ferricyanide which produces a precipitate (Dickson, 1965). The idea of using this principle for iron removal from the solution as an alternative method for quenching the Fenton reaction has not been yet explored. In order to do so, phthalic acid and meropenem were chosen as model molecules. Phthalic acid is a well-known water pollutant associated with different chemical industries (Khan *et al.*, 2015). On the other hand, meropenem is an antibiotic and the contact of such substances with environmental microorganism must be strictly controlled to prevent the emergence of resistant strains (Baquero *et al.*, 2008). Since both compounds could resist conventional wastewater treatments (based on biological processes), they are good candidates for the application of AOPs.

The aim of this work is to develop an alternative method for the quenching of the Fenton reaction based on ferrocyanide precipitation of iron. Different assays were carried out to determine whether the application of the proposed method can interfere with the quantification of the selected model molecules or not. Also, some considerations are provided to apply this method to other pollutants.

In the first part of this research, the influence of the proposed method for iron removal on the measured concentration of the pollutant (phthalic

acid or meropenem) was studied. For this purpose, solutions of phthalic acid (99 %; Merck) were prepared with initial concentrations of 0.6, 0.8, 1.0, 5.0, 10.0, 20.0 and 30.0 mg/L. The pH of each solution was regulated to 3.0 which is considered optimum for the Fenton process (Maslahati Roudi *et al.*, 2018; Tarkwa *et al.*, 2019). Then, ferrous sulfate heptahydrate (99 %; Fisher Chemical) was dissolved ($[\text{Fe}^{2+}] = 0.05 \text{ mM}$) and afterward iron was removed from the solution by alkalization or precipitation using a quantitative amount of potassium ferrocyanide trihydrate (98.5 %; Sigma-Aldrich) solution. The concentration of phthalic acid in the supernatant liquid was determined by HPLC (Agilent Technologies 1120 compact LC) equipped with a variable wavelength UV-Vis detector and a Zorbax Eclipse Plus C-18 column from Agilent Technologies (4.6 mm x 150 mm; 5 μm particle size). The mobile phase consisted of a mixture of methanol (LiChrosolv, Merck) and a 5% acetic acid (99.8 %, Merck) aqueous solution (volume ratio of 30:70). The flow rate of the mobile phase was set in 1 mL/min with an isocratic regime. The detection was performed at 280 nm. After the quantification of phthalic acid in the supernatant, this concentration was corrected to consider the addition of potassium ferrocyanide trihydrate solution. The measurements were carried out in triplicate (See Table S1 - Supplementary Material) and the average values were used for comparisons.

In addition, solutions of meropenem with concentrations of 0.5, 1.0, 20.0, 40.0, 60.0, 80.0 and 100.0 mg/L were prepared dissolving meropenem trihydrate (71.6%, Chongqing Pharmaceutical) in Milli-Q water. The pH of each solution was regulated to 3.0 and ferrous sulfate heptahydrate was added ($[\text{Fe}^{2+}] = 0.05 \text{ mM}$). Afterward, iron was removed from the solution using an appropriate amount of potassium ferrocyanide. The concentration of meropenem in the supernatant liquid was also determined by HPLC with the same equipment described above. The mobile phase was a mixture of acetonitrile (LiChrosolv, Merck), methanol (LiChrosolv, Merck) and a buffer solution in a volume ratio of 15:10:75. The buffer solution was prepared by diluting 15 mL of a 20% w/w solution of tetrabutylammonium hydroxide (20%, Merck) to 750 mL. Milli-Q water was used for this purpose and the pH of the solution was regulated to 7.5 by the addition of 10% phosphoric acid (85%, Fisher) solution. The flow rate of the mobile phase was set in 1 mL/min with an isocratic regime. The detection was carried out at 300 nm, and the temperature of the column was set at

25 °C.

After assessing the influence of the proposed method for iron removal on the measured concentration of the pollutants, the applicability of this new method to study a chemical process was evaluated. Therefore, the degradation of phthalic acid by the Fenton process was evaluated. In parallel, the traditional iron removal method (alkalization) and the proposed method based on ferrocyanide were applied and the results compared to each other. A 30 mg/L phthalic acid aqueous solution was treated by the Fenton process at room temperature (~18°C). The initial pH was regulated to 3.0. The concentrations of Fe^{2+} and H_2O_2 (30% w/w; Scharlau) were set at 0.05 mM and 176.1 mM, respectively. Aliquots were taken at 6, 9, 12, 15, 60 and 120 min. The quenching of the reaction was carried out by alkalization of the sample or precipitation using potassium ferrocyanide. When the potassium ferrocyanide precipitation treatment was applied, it was necessary to add manganese dioxide, MnO_2 (89%; Merck) to remove the residual H_2O_2 before the removal of iron. In separated tests, no significant adsorption of phthalic acid over MnO_2 was observed at pH 3.0. All the runs were carried out by duplicate, and the concentration of phthalic acid in each run was determined by HPLC.

The measured phthalic acid concentrations after the application of alkalization and precipitation using ferrocyanide for the removal of iron from the solutions are depicted in Fig. 1. As shown in the Figure, neither alkalization nor the precipitation using the ferrocyanide treatment shows an appreciable influence on phthalic acid concentrations. The aim of these assays was to determine the influence of the proposed method for iron removal on the measured concentration of the pollutant (phthalic acid). As the corrected concentration after the treatment does not show a noticeable difference compared to the initial concentration, the method for iron removal could be considered applicable for the pollutant.

Moreover, an interesting fact is that the sedimentation of the complex iron salt produced by the addition of ferrocyanide is facilitated by the presence of phthalic acid, as shown in Fig. S1 (Supplementary Material), an aspect that makes easy the separation of the aqueous phase.

For meropenem, the application of the alkalization method to quenching the Fenton reaction could result in the hydrolysis of this compound. In fact, when the pH of a meropenem solution was increased to 12 and then returned to 7, partial degradation of this antibiotic was observed (See chromatograms of

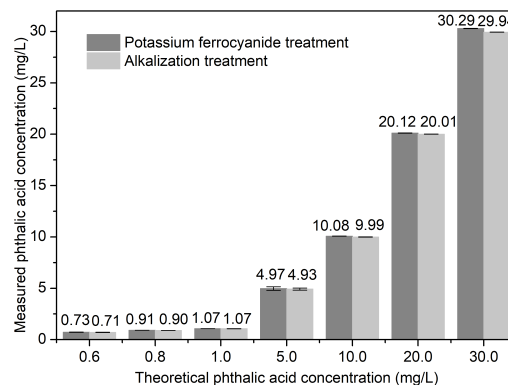


Fig. 1. Measured phthalic acid concentrations after the application of alkalization and precipitation using the ferrocyanide treatment for the removal of iron from the solution as a function of the initial concentration of phthalic acid (before the treatment).

Fig. S2 - Supplementary Material). Therefore, the application of the ferrocyanide treatment for kinetic studies of Fenton processes involving compounds like meropenem may be advisable.

The measured concentrations of meropenem before and after iron removal are depicted in Table 1. In this case, the ferrocyanide treatment did not affect considerably the concentration of the antibiotic. In addition, the sedimentation of the complex iron salt produced by the addition of ferrocyanide was also facilitated by the presence of meropenem. However, it seemed that this effect was weaker for meropenem than for phthalic acid. Consequently, it could be concluded that for some specific molecules the sedimentation of iron could be facilitated. The presence of the molecule of interest (phthalic acid or meropenem) in the structure of the sedimented complex cannot be ruled out, but clearly, this does not imply limitations for the applicability of the iron removal method.

Fig. 2 shows the degradation kinetics of phthalic acid by the Fenton process when both iron removal methods were applied. A similar trend was found when both the alkalization method and method based on ferrocyanide were used for the quenching of the reaction. Slight differences can be observed, and this suggests that the ferrocyanide treatment could be successfully applied for the removal of iron without pH variations. This can be especially important for the study of compounds that can be degraded due to variations in the pH of the solution, such as the case of meropenem.

Table 1. Measured meropenem concentration after the application of precipitation using potassium ferrocyanide for the removal of iron from the solution as a function of the initial concentration of meropenem before the treatment.

Initial concentration [mg/L]	Measured concentration [mg/L]		
	Sample 1	Sample 2	Average
0.5	0.66	0.66	0.66
1	1.17	1.17	1.17
20	19.27	19.07	19.17
40.1	39.12	39.08	39.1
60	57.54	58.11	57.82
80.2	77.92	77.59	77.75
101.4	95.85	97.49	96.67

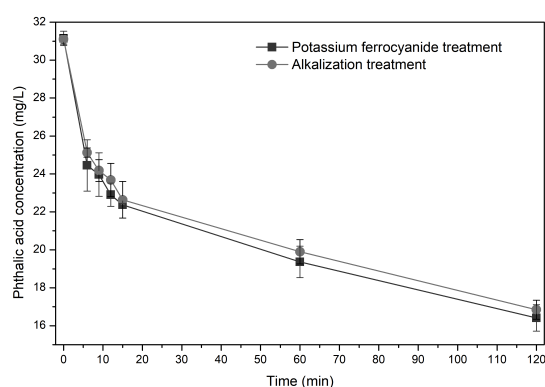


Fig. 2. Phthalic acid degradation kinetics by homogeneous Fenton process ($[\text{Fe}^{2+}] = 0.05 \text{ mM}$; $[\text{H}_2\text{O}_2] = 176.1 \text{ mM}$). The quenching of the reaction was carried out by alkalization and precipitation using the potassium ferrocyanide treatment.

This method could also be applied to other pollutants. In such cases, some aspects should be considered. During the experiments, it was observed that the initial pH of the solution can affect the formation of the complex iron salt. For phthalic acid and meropenem, it was found that the precipitation can take place at initial pH values below 5.5 and 4.5, respectively. Moreover, the addition of ferrocyanide and the subsequent precipitation resulted in an increase of the pH of the supernatant solutions (in both cases, the pH value reached 7.0). It is advisable to consider the final pH of the supernatant solution not only to rule out any degradation/hydrolysis reaction but also to construct the calibration curve at this pH value for quantification purposes.

Although in the case of phthalic acid and meropenem the addition of ferrocyanide did not affect the measurement of the concentration, there could

be other pollutants whose concentration might be affected by the presence of ferrocyanide. For this reason, it is important to verify if the initial and final concentration of the pollutant after the iron removal treatment does not show a noticeable difference. In addition, it must be considered that the iron removal method proposed in this work is based on the use of cyanide species, therefore the pH value is an important issue. Iron-cyanide complexes belong to the group of strong acid dissociable (SAD) cyanide (Donato *et al.*, 2007), therefore the production of HCN at room temperature even at a pH as low as 3 (typical value for Fenton reactions) is unlikely. However, some precautions should be taken to prevent any release of HCN produced by unexpected reactions due to the specific nature of the water sample.

As a final remark, it should be mentioned that the aim of this work is not to propose this method for an industrial wastewater system. Indeed, at an industrial scale, the alkalization method could be one of the best and simple options to remove iron from the effluent. The ferrocyanide treatment is proposed as an option to help in Fenton kinetics studies of pollutants which are not stable at high pH values (a step needed prior to the design of industrial wastewater systems).

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