

DEGRADATION OF PHENOLIC COMPOUNDS. RESIDUE TREATMENT IN THE RESIDUE MANAGEMENT PROGRAM OF AN ANALYTICAL CHEMISTRY LABORATORY

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Abstract — One of the main ideas issued in the Mission of the Centro de Química e Meio Ambiente of Instituto de Pesquisas Energéticas e Nucleares is an integrated management where residues generation is included. Chemical analyses, although necessary to generate knowledge also generate residues. A simple procedure was applied to degrade phenol in aqueous solution based on the reactivity of the produced Fenton's reagent free radicals. As low phenol concentration is expected during the degradation process LC-MS technique was used to carry out the chemical analyses. The results showed that the process is very effective. Phenol aqueous solutions of initial concentration around $70\mu\text{g.mL}^{-1}$ were used in these experiments. After addition of H_2O_2 the phenol concentration decreased to levels not detected by the instrumentation. Nowadays, as a part of the environmental philosophy, academic projects to be developed in our Institute are expected to contemplate a schedule for residue treatment or correct destination.

Index Terms — Fenton, management, phenol, residue.

INTRODUCTION

One of the major concerns of the Instituto de Pesquisas Energéticas e Nucleares, IPEN/CNEN-SP, is to be aligned with the environmental concerns. For many years the activities were almost only related to the nuclear fuel cycle supporting closely the steps of this process. Environmental analyses in order to routinely evaluate the emissions has been carried out. Fortunately, no significant event was found. Nowadays, the environmental studies are broader, not only with nuclear concerns but aiming the public health as a whole. Food, water, air, materials, pharmaceuticals, and many others areas that can be related to the environment are studied. Recently, an institutional integrated management system was adopted as a management tool.

The Centro de Química e Meio Ambiente, CQMA, as a unit of this Institution has been following the precepts of a

quality system trying to minimize the residue generated in its activities. This residue management, already been considered even in the former organizational structure, comprehends among other actions the treatment of most of the solutions not used in the chemical analyses.

Solutions from LC (liquid chromatography) and GC (gas chromatography) analyses are the major ones with organic solvents. Pesticides, herbicides, and pharmaceuticals are some examples of the compounds present in these residues. Other organic compounds such as phenols are present in these solutions, especially old solutions forgotten in the laboratory bench.

Phenolic compounds are very toxic [1]-[2] (phenol dermal LD50, 630 mg/kg, mouse) so 1g can be fatal to Humans and above just $50\mu\text{g.L}^{-1}$ is toxic for some aquatic organisms. Despite of odor of crystals, liquid or very high concentrated solutions, some odorless aqueous solutions can be concentrated enough to cause damages. As phenol is relatively water soluble (1g phenol is soluble in 15 mL of water), the environmental fate can be very complex and dangerous. Phenols are used in applications such as plasticizers, wood preservative, detergents, medicines and dyes, and so on. In environment media, phenol can react with chlorine to produce chlorophenol compounds, which in turn, is more toxic than the former phenol.

In this work, phenol degradation by Fenton's reagent (Fe^{2+} or Fe^{3+} and H_2O_2) was conducted and LC-MS or HPLC UV detection techniques were used to determine the phenol concentration.

Some of the known primary degradation products are resorcinol, catechol, o-benzoquinone, p-benzoquinone and hydroquinone Figure 1, which are results from direct hydroxylation reactions. In the following, muconic acid, maleic acid, fumaric acid, tannin, malonic acid, formic acid, and oxalic acid, Figure 2, are formed in further aromatic ring rupture reaction, [1]-[3]. If complete, CO_2 and H_2O will be the very final products.

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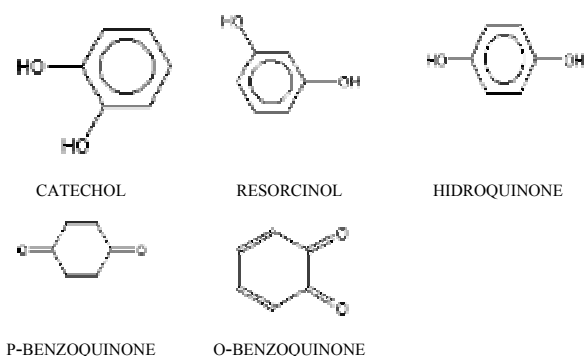


FIGURE 1
PHENOL PRIMARY DEGRADATION PRODUCTS

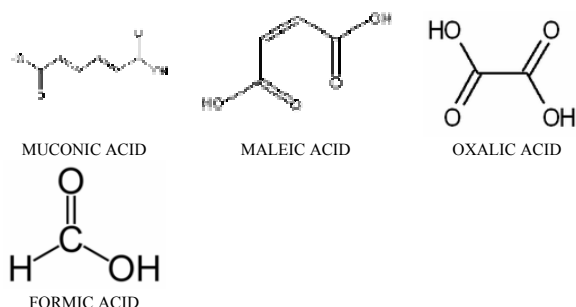


FIGURE 2
PHENOL DEGRADATION PRODUCTS

The Fenton's Reagent Reaction

H. J. Fenton discovered the reaction (1) in 1894, but only after 40 years the mechanism was proposed based on the reactive radical ($\text{HO}\bullet$). Since that, innumerable applications have been developed.

The simplified reaction that represents the formation of highly reactive hydroxyl radicals ($\text{HO}\bullet$) by the Fenton's reagent is



The oxidized Fe^{3+} can be subsequently reduced by H_2O_2 forming the hydroxyperoxyl radical ($\bullet\text{OOH}$).



The second reaction is slower than the first, so the Fe^{2+} added quantity is very important in the initial step. In high concentrated organic solutions, although the high rate of (1), very low Fe^{2+} concentration can not produce observable organic decomposition. So the ratio phenol: Fe^{2+} : H_2O_2 has to be optimized.

EXPERIMENTAL

Reagents

The experiments were carried out using a total volume of 500 mL phenol solution (Sigma, 99%+) around $70 \text{ mg}\cdot\text{L}^{-1}$. The Fe^{2+} was added as $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4\cdot 6\text{H}_2\text{O}$ (Synth) resulting in solutions with nominal concentration of 2,8 and $56 \text{ mg}\text{Fe}\cdot\text{L}^{-1}$.

The initial pH was between 4 and 5 being measured after each H_2O_2 addition and before taking each phenol solution aliquot. The H_2O_2 (Merck, 30%) solution was added in volume of $50 \mu\text{L}$ in intervals of 10 minutes until a total volume of $500 \mu\text{L}$. Solutions were stirred all the time. Although not controlled, the temperature during the reaction was around the room temperature (25°C).

Chromatographic solutions were prepared with acetonitrile (JTBaker, HPLC grade) and sodium acetate (JTBaker). Purified water (Barnsted System) was used thoroughly.

Instrumental

Phenol degradation was monitored by chemical analyses using:

- LC-MS/MS (HPLC, Agilent 1100 Series, Germany/Japan and MS, Applied Biosystem MDS/SCIEX, Canada), measuring phenol in negative mode in single ion monitoring mode. Chromatographic conditions were: C18 column with 50 mm length, aqueous acetate solution (5mM) and acetonitrile as eluents in isocratic run mode.
- HPLC with UV detector (Shimadzu Co., Japan), measuring phenol at 214 nm. Chromatographic conditions were: C18 column (Shimadzu Co, Japan) with 150 mm length, water and acetonitrile (60:40, respectively) as eluents in isocratic run mode.

RESULTS

A first set of experiment was conducted with an initial phenol concentration of $71.4 \text{ mg}\cdot\text{L}^{-1}$. A volume of Fe^{2+} ammonium sulfate solution was added to achieve $56 \text{ mg}\text{Fe}^{2+}\cdot\text{L}^{-1}$. The phenol concentration was measured 10 minutes after each H_2O_2 addition. As one can see in Figure 3, after the addition of H_2O_2 the phenol concentration falls down to low concentrations. The first $50 \mu\text{L}$ decreased the phenol concentration to $0.250 \text{ mg}\cdot\text{L}^{-1}$, the second addition to $0.110 \text{ mg}\cdot\text{L}^{-1}$ and the third and the subsequent additions to less than $0.030 \text{ mg}\cdot\text{L}^{-1}$.

Formation of Degradation Products

As mentioned in the Introduction, the primary phenol degradation products are catechol, resorcinol, and benzoquinone. These compounds were not measured, but as

can be found in the literature [1]-[3]-[4]-[5], they are also easily degraded by the Fenton's reagent in this system.

The formation of catechol enhances the phenol degradation as it promotes the cycle of reduction Fe^{3+}/Fe^{2+} . In fact, other degradation products also promote the referred reduction in the order catechol>hydroquinone>4-chlorocatechol. The sequence of degradation of these compounds is the ring opening forming muconic acid. This acid will be oxidized to form maleic and fumaric acids. If the condition is favorable, CO_2 and H_2O will be the products that will last after the oxidation of oxalic and formic acids.

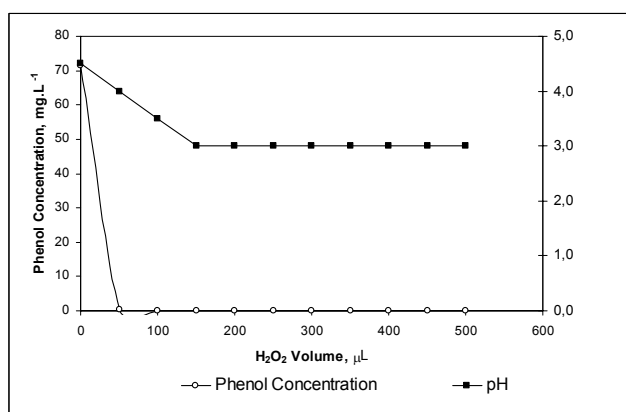


FIGURE 3
PHENOL DEGRADATION AFTER H_2O_2 ADDITION

Decreasing pH

The development of phenol degradation reaction changes the pH of the solution. In Figure 3 and Figure 4, one can see the decreasing of the pH as H_2O_2 is added. This behavior is related to the formation of organic acids due to phenol degradation. This parameter is sometimes essential to monitor the reaction development as no changes (decreasing) in the pH can mean no reaction and, consequently, hazardous H_2O_2 accumulation in the system. On the other hand, an increasing pH can lead to colloidal Fe^{3+} species that can induce reactions with H_2O_2 forming H_2O and O_2 that are undesirable do this process.

In high concentration Fe^{2+} solution (Figure 3, 56 $mg.L^{-1}$) the initial pH 4,5 decreases to 3 in 30 minutes and remains constant even with addition of 500 μL of H_2O_2 . This pH condition is very convenient as the optimum acid concentration to degradate phenol is in the range of 2-5. In low concentration Fe^{2+} solution (Figure 2, 2.8 $mg.L^{-1}$) the initial pH 5 decreases more slowly holding 4.5 - 4 during 60 minutes until decrease to 3. Fortunately, 4.5 - 4 is in the optimum pH range. The reason for the different behaviors may be associated to Fe concentration or, viewing in another way, is due to the quantities of $FeSO_4(NH_4)_2SO_4.6H_2O$ added. There is a possibility of some H_2SO_4 present in the compound that brings the pH to lower values (for high

Fe^{2+} concentration the initial pH 4.5 is lower than the pH 5.0 for low Fe^{2+} concentration solution).

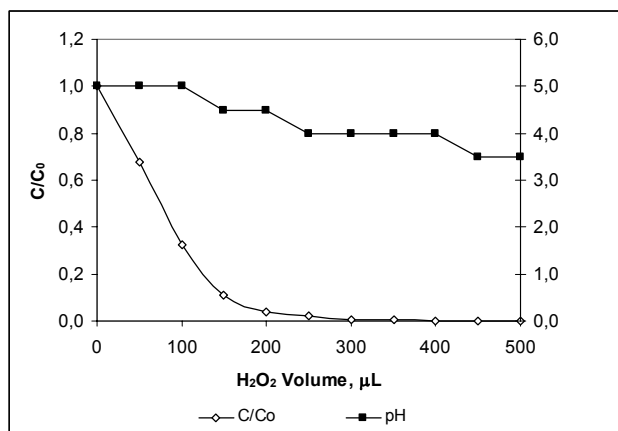


FIGURE 4
PHENOL DEGRADATION. LOW IRON CONCENTRATION

For the both Fe^{2+} concentration the rate of decreasing phenol concentration seems to have a relationship between the rate of pH decreasing.

For high Fe^{2+} concentration the rapid pH decreasing is accompanied by the rapid phenol decreasing. Although not seen in the Figure 3, the phenol concentration after 30 - 40 minutes is less than 30 $\mu g.L^{-1}$, maybe less than 10 $\mu g.L^{-1}$. One can conclude that for a maximum efficiency pH have to be set between 3 and 4.

For low Fe^{2+} concentration the rate of phenol decreasing is low as the same for pH decreasing. The phenol concentration as lower as 10 - 30 $\mu g.L^{-1}$ is only achieved after addition of 300 μL of H_2O_2 .

Unfortunately, the reduced conditions of experiments do not allow to establish an optimized relationship phenol: Fe^{2+} : H_2O_2 . However, as a reference of this work, the conditions of these two experiments were, in mass: 1.3:1:1.8 for high Fe^{2+} concentration, pH 3-4 and 25:1:36 for low Fe^{2+} concentration, pH.

The Time Parameter

The radical reaction, although very fast, does not finish immediately and continues with the consumption of H_2O_2 . The Fe^{2+} oxidized to Fe^{3+} , is re-reduced in a slow rate reaction (2), producing the hydroxyperoxyl radical and has no significant effect in the initial period. In Figures 3 and 4, as one can see, the addition of H_2O_2 is carried out in intervals of 10 minutes. It means that each 50 μL added in those Figures 10 minutes have been passed and a total 140 minute experiments were carried out.

Considering the low Fe^{2+} concentration solution, after 24 hours the phenol concentration have decreased, in comparison to the former aliquots, 40% in the addition of 50 μL of H_2O_2 , 80% in the addition of 150 μL of H_2O_2 and in the addition of 200 μL of H_2O_2 no phenol could be measured

by the analytical procedure adopted. From these results, it is clear that H_2O_2 is not consumed immediately, and maybe even in at very low concentration can still reacts with Fe^{2+} forming radicals.

Although the procedure adopted in this work (addition of H_2O_2 in aliquots at 10 minutes intervals) can difficult the interpretation of the reaction behavior, no doubt remains on reaction time dependence. As it known, the optimized quantity of H_2O_2 can not be added entirely at once. This work shows, considering the conditions followed, the behavior of phenol degradation in intervals of time.

The Quality System

A Quality System to be implemented in a general organization will be certainly faced to a problem – overcomes inrooted traditions in routinely done activities. Since the Institute has also 50 years old, some of technicians presented difficulties to understand the precepts of a quality program and, consequently, the benefits. In the initial periods, frequent speeches were performed by internal and invited specialized speakers trying to make easy the quality program concepts and engage a large number of workers.

The sequence of this initial period was the maintenance of the Quality System. In addition to those routinely done activities some activities are carried out as research. It is very common the idea that a messy desk represents a scientist work place. In this place, nothing can be found unless incidentally. The opposite situation is a methodic person who only does scheduled tasks. These two apparently incompatible behaviors are present in the most of people. In a research institute and in the university, the question ‘Why should I to be submitted to a Quality System?’ is still very common.

All those laboratories that initiated the implementation of the Quality System now, apart from much work, are getting benefits like better organized tasks, more quality results (quantifying uncertainty), accredited methodologies and more.

Residue Management Program

Local treatment can be a solution to residue generation. As a result of this program, a handbook dealing with residue handling, classification, disposing, and treatment was created to be a reference in the CQMA. Successful process like the presented in this work is one of the various that can be used to minimize the pollutants emission. CQMA Residue Management Program is dealing with all chemical analyses residues that are considered hazardous or potentially hazardous. These residues are mainly in solution form but as several different samples are analyzed in our laboratories some solid residue are generated.

The amount of residue generation is not large. Within a period of a year, less than 100 L of generated liquid residue are segregated. Frequently, the generated solutions are in low metal concentration and pH correction or dilution are

applied to discard. Organic solution are disposed in separate containers. Many of the inorganic solutions are treated applying precipitation procedures. Sulfochromic solution is an example. This solution was commonly used for many years to clean laboratory glassware. So, there were volumes of this solution in many laboratories. After the implementation of the CQMA’s Residue Management Program, all but one laboratories replaced the sulfochromic solution with another cleaning solution. These solfochromic solutions were treated in order to precipitate chromium (III) hydroxide, a less dangerous residue to manipulate.

As mentioned in the Introduction, organic solutions are generated by LC and GC analyses and their composition are mainly pesticides, herbicides and pharmaceuticals. The major solvents are water, methanol and acetonitrile. Other quantities of dichloromethane, ethyl acetate and hexane are also present. Of course there is no exact information about qualitative and quantitative nature of these solutions. Two actions were taken to deal with these organic residues.

The first was sending the residue to be incinerated in an adequate process. The company was selected considering, for example, if the proposed process will not produce more dangerous products during the incineration.

The second action was directed to treat the residue in our laboratories. Many processes can be chosen. Two of them were considered: degradation by Fenton’s reagent and by heterogeneous catalytic reactions using TiO_2/UV , both of them exploring the high reactivity of forming radicals ($\bullet\text{OH}$) with pesticides, herbicides, pharmaceuticals, personal care products, fossil fuels and so on.

Inorganic and organic residues are kept in containers identified with expected chemical composition and, as a characteristic of our activities, if it is radioactive or not. Some containers are specially destined to Hg compounds and for cyanide generators. The incineration (oxidizing conditions) of acetonitrile in inadequate conditions can generate cyanide. Periodically, these solutions are analyzed and sent to incineration or locally treated. After 6 years, the actions taken in the CQMA’s Residue Program resulted in more than 500 kg of treated residues (incineration and local treatment).

In the institutional level, as a part of the environmental philosophy, the academic projects and those developed with industry are expected to contemplate a schedule or economic support for residue treatment or correct destination. For long time, many successful projects carried out in this Institute have generated papers and residues. Papers traveled around the world, residues still remains in the laboratory.

Environmental analytical chemistry can be so pollutant as any non-controlled activity. With the implementation of the Quality System and the Residue Management Program, CQMA became aligned to recent attitudes towards the preservation of the environment. In addition, it has to be mentioned that we are not alone in our Mission. Our stakeholders also play important role in this path.

CONCLUSIONS

The Residue Management Program implemented in the CQMA can be considered successful as have diminished the quantities of residues even stored or generated applying these actions:

- Conscientization of technical personnel about environmental concerns
- Using more recent cleaning methods to wash laboratory glassware
- Replacing or developing the analytical methods. Instrumental methodologies are generally less time consuming and use fewer quantities of reagents
- Applying chemical processes to treat (neutralizing or minimizing) the generated residue

The methodology applied to degradate phenol solution is efficient in the conditions presented and

- Fenton's reagent based processes as used in this work are low energy consuming as can be carried out at room temperature
- The pH can be kept within the optimum range just adding H₂O₂ in those conditions mentioned in this work
- A rapid phenol degradation can be achieved using adequate phenol:Fe²⁺:H₂O₂
- Fe²⁺ concentration is significant for the phenol degradation.
- HPLC with UV detector can be used to analyze phenol solutions in these processes. HPLC-MS/MS can also be used but at expenses of higher cost infrastructure

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