The Use of Advanced Oxidative Processes and the Toxicity of Textile Effluents

O uso de processos oxidativos avançados e a toxicidade de efluentes têxteis

DOI:10.34117/bjdv6n4-345

ABSTRACT
The textile industries are important in a country's economy due to the generation of resources and constitute industries that consume a lot of water, producing potentially polluting liquid effluents. Among the toxic substances dumped in recipient bodies, dyes stand out. Several studies seek to develop efficient forms of treatment, whether biological or chemical. Advanced oxidative processes are among the most widely researched chemical treatments. Toxicity tests are used in order to verify the effectiveness of these treatments before the discharge of treated effluents into the environment. Effluent toxicity is tested with a number of organisms. In this work, the objective was to verify the efficiency of the Foto-Fenton process and to verify the toxicity using lettuce seeds, before and after the advanced oxidative treatment, the effluent analyzed was from a textile industry for processing jeans from the rough of Pernambuco,
belonging to the Arrangement Local Productive. However, there was a reduction in the toxicity of the textile effluent after treatment.

**Keywords:** Toxicity, Textile effluent, Photo-Fenton; Advanced Oxidative Process

**RESUMO**
As indústrias têxteis são importantes na economia de um país devido à geração de recursos e constituem indústrias que consomem bastante água, produzindo efluentes líquidos potencialmente poluidores. Entre as substâncias tóxicas despejadas em corpos receptores, destacam-se os corantes. Diversos estudos buscam o desenvolvimento de formas eficientes de tratamento, sejam biológicos ou químicos. Os processos oxidativos avançados estão entre os tratamentos químicos mais amplamente pesquisados. Os testes de toxicidade são utilizados com a finalidade de verificar a eficácia destes tratamentos antes do despejo dos efluentes tratados no meio ambiente. A toxicidade dos efluentes é testada com uma série de organismos. Neste trabalho, o objetivo foi verificar a eficiência do processo Foto-Fenton e verificar a toxicidade usando sementes de alface, antes e depois do tratamento oxidativo avançado, o efluente analisado foi de uma indústria têxtil de beneficiamento de jeans do agreste pernambucano, pertencente ao Arranjo Produtivo Local. Contudo, constatou-se a redução da toxicidade do efluente têxtil após tratamento.

**Palavras-chave:** Toxicidade; Efluente têxtil; Foto-Fenton; Processo Oxidativo Avançado

**1 INTRODUCTION**

Industries in different segments discharge a high amount of contaminants into the environment, especially in water bodies. This contamination affects both directly and indirectly living beings along the food chain, which makes pollutants bioavailable contaminating humans. Regarding this, toxicity tests are used to assess the quality of the effluent, as well as, the viability and degradability of domestic and industrial chemicals (BELTRAMI et al., 1999). Mixtures of toxic components form industrial effluents, mainly those from the textile industry. Adding to that, the diversity of the receiving environment makes it difficult to determine each component's toxicities. In addition to the analysis of residues, the toxicity analysis in the aquatic environment is an important parameter in the evaluation of the quality and quantification of the environmental risk associated with pollutants (REEMTSMA, 2001).

Due to the complexity of the means and the characteristics of the toxicity tests, these can be performed by several biological species. Garcia et al. (2013) report a series of applications, notably: plants (CASA et al., 2003; GARCIA et al., 2009), bacteria (OTURAN et al., 2008), cells (COLOVIC et al., 2010), crustaceans (SAUER et al., 2006), Cladocera-Daphnias and ceriodaphnias (RIZZO, 2011) and fish (FERNANDEZ-ALBA et al., 2002).
The water reuse issue has been widely discussed through the current water crisis. Some physical-chemical processes used to this purpose: coagulation, flocculation, adsorption, membrane filtration and advanced oxidative processes (AOP) (GOGATE, 2004; LUSTOSA, 2013; PATEL & RESHMA, 2013). AOPs have been widely applied, efficiently minimizing the presence of aqueous residues (APAYDIN, 2014). Such processes mineralize and eliminate toxic components, destroying polluting organic species (FORGACS, et al. 2004; SHU, et al. 2005; KLAVERIOTI et al., 2009). One of these AOPs is the photo-Fenton process, which consists of the hydrogen peroxide use, iron salts, and light, producing hydroxyl radicals that act in the mineralization of recalcitrant compounds. The toxicity analysis is important since it indicates whether the degradation products are more or less toxic than the original effluent. The average seed length, expressed by the Relative Growth Index (RGI) and the average seed germination forms the germination index (GI), which represents the sample toxicity degree. The RGI is the radicle's average growth during the period of the experiment. According to ASTM (2003), an optimal germination index must have values above 55%. Equation number one and two give the radicle growth and germination rate, respectively (Melo et al. 2009, OLIVEIRA, 2013). This work's goal was to evaluate the toxicity of two effluents, one model and the other a real sample of the textile industry for processing jeans in the municipality of Caruaru, in Pernambuco. The toxicity test, using Lactuca Sativa L. lettuce seeds, was applied before and after treating the effluents with the photo-Fenton process.

2 MATERIALS AND METHODS

The effluent treatment followed a factorial design 2³, whose variables were iron salt (1 mg or 2 mg), peroxide volume 30% (600 µL or 900 µL) and time of exposure to light (30 minutes or 90 minutes), artificial light for the model effluent (Figure 1) and sunlight for the real effluent. The model effluent required three fluorescent lamps with a power of 20 W each.

Figure 1: Bench reactor with a white fluorescent lamp.
An aqueous solution (1000 mg. L\(^{-1}\)) of the red dye drimaren CL-5B, which is widely used in the textile industry, formed the model effluent. The real effluent collection happened before the physical-chemical treatment normally done by the textile industry. The research used a UV-Vis Thermo spectrophotometer (Genesis 10 model), a colorimeter (Hach DR / 2010) and a turbidimeter (2100 P Hach), to verify the oxidation effect on the model and real effluent.

The test using lettuce seeds determined the acute toxicity of liquid effluents. The lettuce seeds of the Lechuga Simpson variety (Lactuca Satica L.) were exposed to different concentrations of the studied liquid effluent, using Petri dishes and filter paper as a support medium. Easily found in sowing, these seeds were used as described in the ASTM E 1963-02 (2003) method that Andrade (2010) described and adapted. The ecotoxicological test was performed for model and real effluents.

For each test is needed 10 (ten) seeds, adding it to the Petri dishes on filter paper. Also, 5 ml of the effluent in natura or diluted in distilled water, varying its concentration by 1%, 3%, 10%, and 30%. All the tests were done twice to confirm accuracy. The negative control was distilled water. The results were expressed in the form of average root growth (in cm), Relative Growth Index (RGI) and Germination Index (GI), such parameters are calculated by equations (1 and 2) below, where RGS is the root growth of the sample, RGC is the root growth of the control, SGS is seeds that germinated in the sample and SGC is seeds that germinated in the control.

\[
RGI = \frac{CRA}{RGR} \quad \text{eq. 1}
\]
\[
GI = RGI \times \frac{SGS}{SGC} \times 100 \quad \text{eq. 2}
\]

The seeds were incubated for seven days, keeping them at a temperature of 20 ± 1°C. A qualitative evaluation of phytotoxicity was performed comparing the toxicity tests of the model, raw and diluted effluents to the toxicity test of the model effluent treated with the photo-Fenton process and artificial light. The seed germination evaluation started from the fifth day (120 h) of seed incubation. The number of seeds that underwent protrusion and the elongation of the roots was measured, considering germination only those that had roots equal to or greater than 2 mm (BAYDUM, 2012). A similar procedure was used to investigate the toxicity of the actual industrial effluent.
3 RESULTS AND DISCUSSION

The analysis of the factorial design indicated that the best condition for the tests was 600 μL of hydrogen peroxide, 2 mg of ferrous sulfate heptahydrate and 90 minutes of exposure to light, in which color reduction and turbidity between 80 and 90% were observed. Therefore, this condition was used in the tests. Table 1 shows the results of seed germination tests.

Table 1: Average number of seeds that germinated and root growth (in cm).

| Seed                  | H₂O | BT* | AT**1% | AT3% | AT10% | AT30% | AT100% |
|-----------------------|-----|-----|--------|------|-------|-------|--------|
| Germination           | 8,0 | 7,5 | 10,0   | 10,0 | 10,0  | 10,0  | 100%   |
| Root growth (cm)      | 2,2 | 1,8 | 2,3    | 2,1  | 2,3   | 1,3   | 0,0    |

*BT – Before treatment; ** AT – After-treatment

Table 1 shows that after-treatment germination, when the effluent concentrations were equal to 1, 3, 10 and 30%, was higher than the one observed for the negative control (distilled water), indicating that the by-products of the degradation have no toxicity to prevent the germination of lettuce seeds at the tested concentrations. However, when the test used raw effluent (100%), no seed germinated, indicating the need for dilution to minimize the toxic effect. This fact corroborates with the work of Palácio (2012), who carried out toxicological tests, with lettuce seeds, in textile effluent after treatment with the photo-Fenton process using artificial light and found that the effluent toxicity did not reduce. The root growth in the effluent before treatment was smaller than the one observed for the negative control. The tests containing 1, 3 and 10% of effluent showed a reduction in toxicity compared to lettuce seeds, since they presented values close to that observed for the negative control. However, the average growth decreased at the highest concentrations, indicating that the by-products formed, when more concentrated, interfere with seed growth and germination. Figure 2 shows the seed's root growth in the effluent before and after treatment.

Figure 2: Lettuce seed toxicity test, a) raw effluent and b) treated effluent
A more detailed analysis was performed based on the relative growth index (RGI) and the germination index (GI), as described by equations 1 and 2. These data are shown in Table 2.

Table 2: GI (%) and RGI values for Lactuca Sativa lettuce seeds.

| Sample | RGI | GI (%) |
|--------|-----|--------|
| BT**   | 0,62| 56,00  |
| AT**1% | 1,05| 105,18 |
| AT3%   | 0,95| 95,24  |
| AT10%  | 1,02| 102,38 |
| AT30%  | 0,59| 59,21  |
| AT100% | 0,00| 0,00   |

*BT – Before treatment; ** AT – After treatment

The analysis of Figure 2 shows that, for lettuce seed, there is better germination and greater root growth after the effluent treatment. Table 2 shows that after the 10% concentration, there is a decrease in both germination and root growth, although the results in 30% concentration are considered optimal, according to ASTM (2003). However, the effluent when mixed to the water body dilutes, resembling the toxicological testing conditions and the effluent concentrations below 100%, thus, root growth mirrors the negative control.

The real effluent treated using the solar photo-Fenton process showed low toxicity in comparison to the bioassays performed with lettuce seeds. The seeds germinated in different concentrations of the real effluent, the tests were carried out in concentrations of 100%, 30%, 3%, and 1%, in all of them there was germination in most of the seeds. Table 3 displays the data from the toxicity test performed for the real effluent.

Table 3: Germination test (average number of seeds that germinated) and root growth (in cm).

| Seed          | H2O | BT** | AT**1% | AT3% | AT30% | AT100% |
|---------------|-----|------|--------|------|-------|--------|
| Germination   | 9,0 | 0,0  | 7,5    | 10,0 | 8,0   | 9,0    |
| Root Growth   | 6,2 | 0,0  | 6,6    | 6,6  | 5,8   | 4,5    |

*BT – Before treatment; ** AT – After treatment;

The data in Table 3 shows the number of seeds that germinated and the respective averages. Before the treatment of the real effluent, no seeds germinated. In all concentrations, including negative control, practically all seeds germinated in duplicate tests. An important fact is that there is no need to dilute the real effluent after treatment because it does not present
toxicity to the environment. It is worth noting that the root lengths were measured in each Petri dish analyzed. The treated effluent at 100% concentration decreased in root growth, although almost all seeds have germinated, as shown in Table 3. Figure 3 shows the seed’s root growth in the effluent before and after treatment.

Figure 3: Seed germination (a) Treated real effluent and (b) raw effluent

Figure 3b shows the real effluent toxicity without treatment and there was no germination of any seed. According to Baydun (2012), germination only happens after a growth greater than 2 cm. Table 4 gives a more detailed analysis of the toxicity test. It shows the relative growth index and the germination index before and after treatment.

Table 4: GI (%) and RGI values for Lactuca Sativa lettuce seeds.

| Sample | RGI  | GI (%) |
|--------|------|--------|
| H2O    | 1,00 | 100,00 |
| BT*    | 0,00 | 0,00   |
| AT**1% | 1,06 | 88,44  |
| AT3%   | 1,07 | 118,92 |
| AT30%  | 0,94 | 83,78  |
| AT100% | 0,82 | 82,09  |

*BT – Before treatment; ** AT – After treatment;

According to Young (2012), GI values below 80% betoken growth inhibition. The germination index values presented in Table 4 are greater than 80%. It indicates that the treatment applied to the real effluent is not toxic (for the variety of lettuce seed used) even at 100% concentration, that is, even without diluting, the sample has no toxicity. According to ASTM (2003), a GI greater than 55% is considered excellent. In the test performed, all germination indexes obtained were above 80%, resulting in exceptional outcomes. The result of toxicity carried out with real effluent after treatment with the solar photo-Fenton process shows that disposal in a water body would not affect aquatic life, due to the low toxicity observed.
4 CONCLUSIONS

This study demonstrated that the photo-Fenton process using artificial and solar light applied to a model and real textile effluent, respectively, results in a treated effluent with low toxicity. The work focused on the evaluation of the final toxicity level after the photo-Fenton treatment, using the seeds of Lactuca Sativa lettuce to indicate it. A significant reduction in the toxicity of raw effluents occurred, proving that lettuce seeds can be used to assess toxicity after the photo-Fenton treatment. In general, the investigation for other types of organisms that indicates toxicity is necessary, as well as the study of ways to treat and reuse effluents, since the water crisis is a reality and cannot be ignored.

REFERENCES

ANDRADE, V. T. ANDRADE, B. G., COSTA, B. R. S., PEREIRA, O. A., DEZZOTTI, M. Toxicity assessment of oil field produced water treated by evaporative processes to produce water to irrigation. Water Science and Technology, v.62, n.3, p.693-700, 2010.

BAYDUM, V. P. A., DANTAS, R. F., TEIXEIRA, A., PACHECO, J. G. A., SILVA, V. L. Pre-treatment of propranolol effluent by advanced oxidation processes, Afinidad, v.69, n.559, p.211-216, 2012.

BELTRAMI, M., BAUDO, R., & ROSSI, D. In situ tests to assess the potential toxicity of aquatic sediments. Aquatic Ecosystem Health and Management, v.2, n.4, p.361–365, 1999.

CASA, R., ANNIBALE, A. D., PIERUCCETTI, F., STAZI, S. R., SERMANNI, G. G., CASCIO, B. L. Reduction of the phenolic components in olive mill wastewater by enzymatic treatment and its impact on durum wheat (Triticum durum Desf.) germinability. Chemosphere, v.50, n.8, p.959–966, 2003.

COLOVIĆ, M., KRSTIĆ, D., PETROVIĆ, S., LESKOVAC, A., JOKSIĆ, G., SAVIĆ, J., et al. Toxic effects of diazinon and its photodegradation products. Toxicology Letters, v.193, n.1, p.9–18, 2010.
Toxicity assays: a way for evaluating AOPs efficiency. *Water Research*, v.36, n.17, p.4255–4262, 2002.

GARCIA, J. C., FREITAS, T. K. F. S., PALÁCIO, S. M., AMBRÓSIO, E., SOUZA, M. T. F., SANTOS, L. B., ALMEIDA, V. C., SOUZA, N. E. Toxicity assessment of textile effluents treated by advanced oxidative process (UV/TiO2 and UV/TiO2/H2O2) in the species *Artemia salina* L. *Environ Monit Assess*, v.185, p.2179-2187, 2013.

GARCIA, J. C., SIMIONATO, J. I., SILVA, A. E. C., NOZAKI, J., SOUZA, N. E. Solar photocatalytic degradation of real textile effluents by associated titanium dioxide and hydrogen peroxide. *Solar Energy*, v.83, n.3, p.316–322, 2009.

MELO, S. A. S., TROVÓ, A. G., BAUTITZ, I. R., NOGUEIRA, R. F. P. Degradação de Fármacos Residuais por Processos Oxidativos Avançados. *Química Nova*, v.32, n.1, p.188-197, 2009.

OLIVEIRA, L. C. A., FABRIS, J. D., PEREIRA, M. C. Óxidos de ferro e suas aplicações em processos catalíticos: uma revisão, *Química Nova*, v. 36, n.1, p.123-130, 2013.

OTURAN, N., TRAJKOVSKA, S., OTURAN, M. A., COUDERCHET, M., AARON, J. J. Study of the toxicity of diuron and its metabolites formed in aqueous medium during application of the electrochemical advanced oxidation process “electro-Fenton”. *Chemosphere*, v.73, n.9, p.1550–1556, 2008.

PALÁCIO, S. M., NOGUEIRA, D. A., MANENTI, D. R., MÓDENES, A. N., QUIÑONES, F. R. E., BORBA, F. H. Estudo da Toxicidade de Efluente Têxtil Tratado por Foto-Fenton Artificial Utilizando as Espécies *Lactuca Sativa* e *Artemia Salina*, *Engevista*, v. 14, n. 2. p. 127-134, 2012.

REEMTSMA, T. Prospects of toxicity-directed wastewater analysis. *Analytica Chimica Acta*, v. 426, n.2, p.12, 279–287, 2001.
RIZZO, L. Bioassays as a tool for evaluating advanced oxidation processes in water and wastewater treatment. *Water Research*, v.45, n.15, p.4311–4340, 2011.

SAUER, T. P., CASARIL, L., OBERZINER, A. L. B., JOSÉ, H. J., MOREIRA, R. F. P. M. Advanced oxidation processes applied to tannery wastewater containing Direct Black 38—elimination and degradation kinetics. *Journal of Hazardous Materials*, v.135, n.1–3, p.274–279, 2006.

YOUNG, B. J.; RIERA, N. I.; BEILY, M. E.; BRES, P. A.; CRESPO, D. C.; RONCO, A. E. Toxicity of the effluent from an anaerobic bioreactor treating cereal residues on *Lactuca sativa*. *Ecotoxicology and Environmental Safety*, v.76, p.182-186, 2012.