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Aquatic toxicity of dyes before and after photo-Fenton treatment

Luis A.V. de Luna[a], Thiago H.G. da Silva[b], Raquel F. Pupo Nogueira[b,*], Fábio Kummrow[a,c], Gisela A. Umbuzeiro[a]

[a] Faculdade de Tecnologia, UNICAMP – Universidade Estadual de Campinas, Limeira, SP 13484-332, Brazil
[b] Departamento de Química Analítica, Instituto de Química de Araraquara, UNESP – Univ Estadual Paulista, SP 14800-900, Brazil
[c] Instituto de Ciências Ambientais, Químicas e Farmacêuticas, Universidade Federal de São Paulo, Diadema, SP 09972-270, Brazil

HIGHLIGHTS

- Food and textile dyes can be toxic to aquatic organisms in mg L^{-1} levels.
- Vat Green 3 presented the highest acute and chronic toxicity.
- Partial mineralization of dyes may generate more toxic degradation products.
- Photo-Fenton process was effective for the degradation of 4 of the 5 tested dyes.
- Toxicity tests are important parameters in dye treatment evaluation.

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ABSTRACT

This study evaluated the ecotoxicity of five dyes to freshwater organisms before and during their photo-Fenton degradation. EC50 (48 h) of the five tested dyes ranged from of 6.9 to >1000 mg L^{-1} for *Daphnia similis*. In the chronic tests IC50 (72 h) varied from 65 to >100 mg L^{-1} for *Pseudokirchneriella subcapitata* and IC50 (8 days) from 0.5 to 410 mg L^{-1} for *Ceriodaphnia dubia*. Toxicity tests revealed that although the applied treatment was effective for decolorization of the dye, the partial mineralization may be responsible for the presence of degradation products which can be either more toxic than the original dye, as is the case of Vat Green 3 and Reactive Black 5, lead to initially toxic products which may be further degraded to non toxic products (acid Orange 7 and Food Red 17), or generate non toxic products as in the case of Food Yellow 3. The results highlighted the importance of assessing both acute and chronic toxicity tests of treated sample before effluent discharge.

1. Introduction

Pollution of aquatic environment is a concern in modern world. Dyes may be considered emergent pollutants since they are not included in environmental monitoring programs, their environmental fate and toxicological aspects have not yet been completely evaluated, and are continually introduced into the environment due to anthropogenic activities [1,2].

Textile dyes, including Acid Orange 7 and Reactive Black 5, representatives of azo, and Vat Green 3 of anthraquinone, are commonly used for dyeing cotton and polymeric fibers. Food Yellow 3 and Food Red 17 in addition to Food Yellow 4 are used in food, cosmetic and pharmaceutical industry and represent 90% of consumed food dyes in the United Sates [3]. These dyes can reach the environment through the discharge of industrial and domestic effluents. In textile industry, for example, during the dyeing process 10–15% of dyes are released to the aquatic environment, and in case of direct and reactive dyes, almost 30% can be found in the final effluent [4].

Biological treatment is the most commonly used process for treatment of those effluents, however it has proved to be inefficient for complete dye removal [5,6]. When dyes reach the aquatic environment, even at low concentrations, they may interfere in light penetration, inhibiting photosynthesis, and cause other deleterious effects to the aquatic organisms. However, there are still few studies that addressed the ecotoxicity of dyes (Table 1).

Advanced oxidation processes (AOP) may be applied for the degradation of a variety of organic compounds including dyes due the generation of highly oxidizing species, hydroxyl radical [13]. Photo-Fenton process can be applied as pretreatment to

* Corresponding author. Tel.: +55 16 3301 9606; fax: +55 16 33019692.
E-mail addresses: luisvisani@gmail.com (L.A.V. de Luna), dasilvathg@gmail.com (T.H.G. da Silva), nogueira@iq.unesp.br (R.F.P. Nogueira), fkummrow@unifesp.br (F. Kummrow), giselau@ft.unicamp.br (G.A. Umbuzeiro).

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Table 1
Summary of ecotoxicological data of dyes for aquatic organisms.

Dye (C.I.)	Type		Purity (%)	Toxicity tests	Summary of results	References
Basic Red 14 Reactive Red 141	Azo	Textile	– –	*Chlorella* sp. *Moina macropora*	The IC_{50} of Basic Red 14 for the algae *Chlorella* was 10.8 mg L^{-1} and the LC_{50} for *M. macropora* was 4.9 mg L^{-1}. The IC_{50} of Reactive Red 141 for *Chlorella* was 95.5 mg L^{-1} and the LC_{50} for *M. macropora* was18.2 mg L^{-1}.	[7]
Disperse Red 1 Disperse Red 13	Azo	Textile	95 95	*Daphnia similis*	The EC_{50} of Disperse Red 1 was 0.12 mg L^{-1} and for Disperse Red 13 was 0.18 mg L^{-1}.	[8]
Disperse Red 1	Azo	Textile	60	*D. similis*, *Hydra attenuata*	The toxicity of Disperse Red 1 and its chlorination products were assessed. The EC_{50} of Disperse Red 1 was 0.13 mg L^{-1} to *D. Similis* and 1.9 mg L^{-1} for *H. Attenuata*. The EC_{50} of chlorine treated commercial dye was 4.3 mg L^{-1} for *D. similis* and 0.7 mg L^{-1} for *H. Attenuata*.	[9]
HC Orange 1	Phenolic	Hair	>99	*Daphnia magna* *Danio rerio* *Carassius auratus*	The HC Orange 1 was considered toxic for the assessed organisms. The EC_{50} for *D. Magna* was 1.5 mg L^{-1}, for the fishes the lowest LC_{50} obtained was 4.0 mg L^{-1} for *D. rerio* and in the hatchling success assessment the EC_{50} was 0.19 mg L^{-1} for the same fish. The dye also caused behavioral dysfunction in fishes.	[10]
Direct Blue 218	Azo	Textile	–	*D. magna*	The EC_{50} was 3.6 mg L^{-1}.	[11]
Reactive Orange 16 Direct Red 28 Reactive Blue 19 Disperse Blue 3	Azo Antraquinone	Textile	>70 >35 >50 >20	*Vibrio fischeri* *P. subcapitata* *Tetrahymena pyriformis*	The IC_{50} of azo dyes were above 1000 mg L^{-1} for *V. fischeri* and above 300.0 mg L^{-1} for the anthraquinone dyes. In the algae assay, Disperse Blue 3 was the most toxic dye with IC_{50} = 0.5 mg L^{-1}. Disperse Blue 3 also inhibited the protozoan reproduction.	[12]

–, purity not informed.

improve biodegradability [14,15] or as a sole process promoting mineralization. However, if only partial mineralization is achieved, it is important to warrant toxicity removal [16–18].

Hydroxylation of the electron rich azo chromophore group is usually an initial step in the mineralization process using AOP, demonstrated as color removal in many studies [17,19,20]. Further reactions including hydroxylation of aromatic ring, opening of naphthalene ring and desulfonation have also been reported in AOP [21,22]. The toxicity of degradation products of some textile dyes during AOP application has been described (Table 2); however acute and chronic toxicity tests with standardized freshwater organisms are very scarce. Considering that surface waters are the main receiving waters of industrial effluents, the use of freshwater organisms for toxicity evaluation is very important. Furthermore, data about toxicity of food dyes for aquatic organisms such as microcrustaceans and algae are still scarce.

The purpose of the present study was to evaluate the toxicity of textile and food dyes before and during photo-Fenton treatment using acute and chronic toxicity tests with freshwater organisms.

2. Experimental

2.1. Chemicals

We selected three textile dyes, C.I. Vat Green 3, C.I. Reactive Black 5 and C.I. Acid Orange 7 and two food dyes, C.I. Food Yellow 3 and C.I. Food Red 17. Information about common name, chemical structures, purities and suppliers of each dye is presented in Table 3. Hydrogen peroxide (30%, w/v, Synth), iron (III) nitrate (Mallinckrodt) and tartaric acid (Vetec) were used in photo–Fenton experiments, pH was adjusted with 1 mol L^{-1} H_2SO_4 or 3 mol L^{-1} NaOH (Synth). Bovine catalase (0.1 g L^{-1}, Sigma–Aldrich) was used to decompose residual H_2O_2 and consequently interrupt the Fenton reaction. HPLC-grade methanol (J.T. Baker) and ammonium acetate (1.0 mmol L^{-1}, J.T. Baker) were used in the chromatographic analysis.

2.2. Photo-Fenton treatment

Dyes were dissolved in ultrapure water. Photo-Fenton experiments were carried out in a laboratory scale up flow annular photoreactor, with a 15 W black light lamp (average irradiance = 0.53 mW cm^{-2} in the UVA region) inserted in a borosilicate glass tube (optical path = 1 cm) with an irradiated volume of 280 mL [25]. Dye solution (500 mL) was re-circulated through the reactor using a peristaltic pump (Masterflex L/S 7518-12) operated at a flow rate of 50 mL min^{-1} and continuous magnetic stirring. Stock solutions of the dyes (2.5 g L^{-1}) were previously prepared and stored in amber glass at 4 °C.

Photo-Fenton experiments were performed in triplicate under mild conditions, using low concentration of H_2O_2 (3.0 mmol L^{-1}) and iron (0.2 mmol L^{-1}) in the presence of tartrate as iron complexing agent (0.2 mmol L^{-1}) at pH 2.5. Mild conditions were used to allow a better evaluation of the toxicity evolution during treatment process. Based on dyes solubility in water, the initial concentration of Acid Orange 7, Reactive Black 5, Food Yellow 3, Food Red 17 was 60 mg L^{-1} and of Vat Green 3, 50 mg L^{-1}. A chronometer was used to determine the experimental time, 5, 8 and 30 min of treatment, comprising three independent experiments. The pH of samples withdrawn after photo-Fenton treatment was adjusted to 6–7. Bovine catalase was then added and the solution was stirred during 10 min for residual hydrogen peroxide consumption. Samples were filtered with a PVDF membrane (0.45 μm, Millipore) and stored in refrigerator (4 °C) until the ecotoxicity tests. Degradation experiments were performed.

2.3. Chemical analysis

Dye concentrations after the photo-Fenton treatment were monitored using high performance liquid chromatography (HPLC) using a Shimadzu LC-20AT Prominence coupled to a diode array detector SPD-M20A. The stationary phase was the Hyper-Clone C8-DBS column (5 μm, 250 mm × 4.6 mm, Phenomenex) and the mobile phases were 0.1 mmol L^{-1} ammonium acetate and methanol for Acid Orange 7 and 1 mmol L^{-1} for Food Red 17, Food