Degradation of cyanotoxins (microcystin) in drinking water using photoelectrooxidation

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Abstract

The discharge of sewage and industrial effluents containing high concentrations of pollutants in water bodies increases eutrophication. Cyanobacteria, some of the organisms whose growth is promoted by high nutrient concentrations, are resistant and produce several types of toxins, known as cyanotoxins, highly harmful to human beings. Current water treatment systems for the public water supply are not efficient in degradation of toxins. Advanced oxidation processes (AOP) have been tested for the removal of cyanotoxins, and the results have been positive. This study examines the application of photoelectrooxidation in the degradation of cyanotoxins (microcystins). The performance of the oxidative processes involved was evaluated separately: Photocatalysis, Electrolysis and Photoelectrooxidation. Results showed that the electrical current and UV radiation were directly associated with toxin degradation. The PEO system is efficient in removing cyanotoxins, and the reduction rate reached 99%. The final concentration of toxin was less than 1 µg/L of microcystin in the treated solution.

Keywords: microcystin, cyanotoxin, advanced oxidation process, photoelectrooxidation.

Degradação de cianotoxinas (microcistinas) em água potável aplicando fotoeletrooxidação

Resumo

A descarga de esgotos e efluentes industriais contendo altas concentrações de poluentes nos corpos d'água aumenta a eutrofização. As cianobactérias, são organismos cujo crescimento é promovido por concentrações elevadas de nutrientes, são resistentes e produzem vários tipos de toxinas conhecidas, como cianotoxinas, altamente prejudiciais para os seres humanos. Os sistemas atuais de tratamento de água para o abastecimento público de água não são eficientes na degradação destas toxinas. Processos oxidativos avançados (POA) foram testados para a remoção de cianotoxinas, e os resultados têm sido positivos. Este estudo avalia o processo de fotoeletrooxidação (FEO) na degradação de cianotoxinas (microcistinas). Foi avaliado o desempenho dos processos envolvidos separadamente: fotocatalisis, eletrólise e fotoeletrooxidação. Os resultados mostram que a potencia da radiação UV e da corrente elétrica estão diretamente associados com a degradação de toxinas. O sistema de FEO é eficiente na remoção de cianotoxinas e a redução foi de 99%. A concentração final de toxina foi inferior a 1 g / L de microcistina na solução tratada.

Palavras-chave: microcistina, cianotoxinas, processo de oxidação avançada, fotoeletrooxidação.

1. Introduction

The growing eutrophication of water bodies, a result of human activity, artificially enriches ecosystems. Chemical fertilizers and manure, treated or untreated urban sewage discharges, and agricultural and industrial effluents significantly increase the amounts of nutrients, which run out of control and produce blooms of algae, such as cyanobacteria (Lemes and Yunes, 2006). Cyanobacteria, also known as blue-green algae, are a family of single-celled algae that proliferate in water bodies, such as ponds, lakes, reservoirs, and slow-moving streams when the water is warm and nutrients are available. Many cyanobacteria species produce a group of toxins known as microcystins, some of which are toxic.

The occurrence of cyanobacterial blooms and the presence of cyanotoxins in water samples from the Armando Ribeiro Gonçalves reservoir, located in the state of Rio

Grande do Norte, in the semiarid region of northeastern Brazil was reported (by Costa et al. (2006). In the State of Rio Grande do Sul, southern Brazil, cyanobacterial blooms, particularly *Microcystis aeruginosa*, have been described in the Patos lagoon and its estuary at irregular time intervals in the last two decades (Yunes et al., 1996). The toxicity of these blooms reached lethal doses (LD50), from 22 to 250 $mg.kg^{-1}$ in tests with mice (Yunes et al., 1996). Several studies demonstrated the toxic effects of cyanobacteria on zooplankton organisms, particularly microcrustacean (DeMott et al.,1991). Tests with the juvenile pink shrimp, a very important economic fishing resource in the region of the Patos lagoon, showed that LD50 was 2.9 $mg.mL^{-1}$ (Minillo et al., 2000). The main toxic cyanobacteria genera are Anabaena, Aphanizomenon, Nodularia and Microcystis, which produce a hepatotoxin that is hazardous for human beings and responsible for animal deaths (Moreira et al., 2011). Microcystins are cyclic-heptapeptides, characterised by an unusual amino acid residue, which is affects the toxicity of the heptapeptide (Almeida et al., 2006).

Toxic cyanobacterial blooms and the lack of efficient water treatment systems to remove cells and toxins produced by cyanobacteria may result in environmental catastrophes. In 1996, in Caruaru, in the Brazilian state of Pernambuco, signs and symptoms of acute neurotoxicity and sub-acute hepatotoxicity were detected in patients of a hemodialysis clinic. All 126 patients developed those symptoms, and 60 died (Pouria et al., 1998).

The toxins dissolved in water are not removed by conventional water treatment. In 1988, the World Health Organization (WHO) issued a consumption guideline of 1 µg of LR-microcystin $L^{-1}.day^{-1}$ in treated drinking water. This limit in treated drinking water has been globally accepted. Brazil included this limit in legislation in 2004 (Almeida et al., 2006). In this scenario, several techniques have been developed to remove cyanobacterial cells and to degrade cyanotoxins. Oxidation with potassium permanganate removes microcystin and eliminates its toxicity. This process, however, depends on dose and contact time. In the presence of live cyanobacterial cells, the removal of soluble toxins is low. No consensus has been reached about whether potassium permanganate causes cyanobacterial lysis (Lam et al., 1995; Rositano et al., 1998; Hrudey et al., 1999). Activated coal adsorption has been shown to be effective in removing cyanotoxins (Falconer et al., 1989; Donati et al., 1994; Drikas et al., 2001). However, decontamination takes place by pollutant adsorption, and the pollutant is transferred from the liquid to the solid matter; that means that there is only transference of the pollutant phases, but no destruction (Ziolli and Jardim, 1998). Mondardo et al. (2006) tested ozonisation and chlorination to remove cyanobacteria. Ozonisation proved to be an excellent option for the pretreatment of water with high concentrations of micro-algae and cyanobacteria. It uses a direct filtration technique to make water potable and produces filtered water that matches the potability standards established by Norm 518 issued by the Brazilian Ministry of Health (Brasil, 2011). Mazur-Marzec et al. (2006) tested nodular degradation of cyanotoxin exposed to UVA or UVB radiation for 48 hours. They found that UVB was more effective and produced a greater removal rate (73.3%). Bourne et al. (2006) studied the degradation of microcystin-LR when exposed to a biofilm produced by the bacteria generated in a water body using a sand filter. Two days were necessary to remove 90% of all microcystin. Mesquita et al. (2006) tested the removal of microcystin-LR using a biologically-active activated coal

system, and removal was 100% in the first 10 days. After the 8th day, the amount of cyanotoxins in the effluent increased. After the 50th day and for one month, microcystin removal was detected again.

The removal efficiency of cyanotoxin degradation using chlorine depends on chlorine dose, contact time, and pH (Campinas et al, 2002). A more general problem of water chlorination lies in the production of trihalomethane. Chloroform is the compound that raises greater concern because it is believed to be carcinogenic and to have adverse effects on reproduction and development (Baird, 2002).

Advanced oxidation processes (AOP) have been widely used for the degradation of organic compounds (Xavier, 2006). They are based on the generation of hydroxyl radicals (OH), which have a high oxidation power and may promote the degradation of several pollutant compounds in a few minutes (Freire et al., 2000). A large variety of toxic organic compounds may be degraded using AOP; in most cases, degradation leads to full mineralization and generates H_2O and CO_2. Some classes of compounds that may be degraded are alkanes, chloroaliphatic compounds, alcohols, carboxylic acids, phenols, chlorophenols, herbicides, surfactants and dyes (Nogueira and Jardim, 1998).

Shephard et al. (1998) studied the effect of photocatalytic degradation of microcystin using UV radiation and TiO_2. Microcystin concentration fell to 11% in about 15 minutes. It took 4 minutes for microcystin to reach levels below the test detection limit when a 1 g/l concentration of TiO_2 was used.

Photoelectrooxidation (PEO) is an AOP that uses only two reagents: photons and electrons. PEO is the combination of two other AOPs: electrolysis and heterogeneous photocatalysis (Pelegrini et al., 2001). This study evaluated the use of PEO in the degradation of cyanotoxins from *Microcystis aeruginosa*.

2. Material and Methods

2.1. Cyanobacterial culture

The cyanobacterial sample in this study consisted of *Microcystis aeruginosa* (strain NPLJ-4) isolated from the Jacarepaguá lagoon, in the state of Rio de Janeiro, Brazil, and supplied by the Laboratory of Ecophysiology and Toxicology of Cyanobacteria, Carlos Chagas Filho Institute of Biophysics, Federal University of Rio de Janeiro, and cultivated in ASM-1 growth medium (Gorham et al., 1964) in the Institute of Hydraulic Research of the Universidade Federal do Rio Grande do Sul (IPH-UFRGS). This toxic strain (NPLJ-4) was batch-cultured in 250 mL Erlenmeyer

flasks in an incubator at 25° C with a 14:10 h light dark cycle and light intensity of 2000 lux. When it reached a phase of exponential cell growth of 10^7, the culture was frozen and thawed three times to promote cell lysis. The solution used in the degradation experiments was prepared by mixing 100 mL of concentrate NPLJ-4 crude extract with 1200 mL of water.

2.2. The experiments

The system used in the tests, developed by Rodrigues et. al. (2008) was composed of an electrochemical cell (Figure 1). Reactor volume was 1.4 L. Titanium-coated titanium and ruthenium oxide (Ti-70%TiO_2/30%RuO_2) electrodes were used, and the glass bulb of a 250 W mercury-vapor lamp was replaced with a quartz tube to allow the passage of UV radiation; a source was used to apply the electric field. The solution under study was placed in the reactor. A thermostatic bath was used to keep the temperature at 25° C. In the reactor, the electrodes were placed concentrically around the lamp, with the cathode outside and the anode inside because of the photoactivity of the electrode material.

The performance of the oxidative processes involved was evaluated separately:

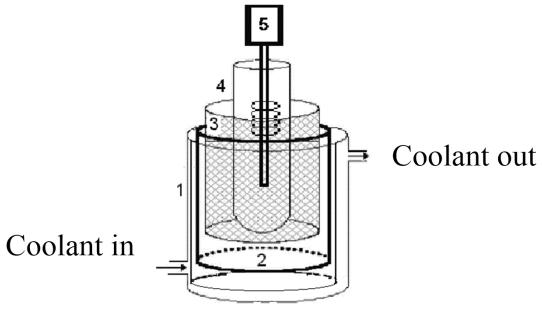

Figure 1. Reactor configuration: (1) glass jacket reservoir; (2) and (3) titanium-coated TiO_2/RuO_2 cathode and anode; (4) quartz tube; (5) mercury-vapor lamp.

- Photocatalysis (PC) - UV irradiation on the surface of the anode, without applying an electric current.
- Electrolysis (EL) - electric current, without UV radiation.
- Photoelectrooxidation (PEO) - electric current, combined with UV irradiation of the anode.

2.3. Cyanotoxin analysis

This study used a commercial enzyme-linked immunosorbent assay (ELISA Beacon®) kit to measure microcystin concentration before and after the degradation trials. ELISA is an analytic biochemistry assay that uses a solid-phase enzyme immunoassay (EIA) to detect the presence of a substance, usually an antigen, in a liquid sample or wet sample. The test uses antibodies and color change to identify a substance.

3. Results

Table 1 describes experimental conditions and results of toxin degradation. Results of trials I-PEO, II-PEO and III-PEO, with 99% removal rates using currents of 4.0, 2.0 and 1.0 mA/cm^2, indicated that excellent degradation rates are achieved for all current densities used. Even when low current densities were used (1.0 mA/cm^2), cyanotoxin concentrations after treatment was 0.3 $\mu g.L^{-1}$, a value below the limits established in international legislation. For solutions with a low electrical conductivity, supporting electrodes should be used to reduce system resistance. In this study, sodium chloride was chosen as the supporting electrolyte, because it forms oxidant compounds, in addition to reducing system resistance still during oxidations, which contributes to toxin degradation. However, the comparison of PEO III and IV results revealed that, even in the absence of sodium chloride, cyanotoxin concentration is below the accepted limit after treatment.

However, when current was not added (PC experiments) and UV radiation was not used (EL experiments), there was a great reduction of the removal rate, from

Table 1. Experimental conditions and results of toxin degradation.

Trials	Photoelectrooxidation Trials				Electrolysis Trial	Photocatalysis Trial
	I-PEO	II-PEO	III-PEO	IV-PEO	EL	PC
Parameters						
Time [min]	10	10	10	10	10	10
Current density [mA/cm^2]	4.0	2.0	1.0	1.0	1.0	**No**
NaCl [4 g/L]	Yes	Yes	Yes	No	No	No
UV radiation	Yes	Yes	Yes	Yes	No	No
Initial microcystin [μgL^{-1}]	6.91	6.91	6.91	6.91	6.91	6.91
Final microcystin [μgL^{-1}]	< 0.3*	< 0.3*	< 0.3*	< 0.3*	3.49	3.12
Removal rate [%]	**99%**	**99%**	**99%**	**99%**	**49%**	**41%**

*ELISA Beacon® detection limit.

99% to 41% and 49%. In these experiments, cyanotoxin concentration after treatment had values above legal limits. These results suggest that, in PEO experiments, there was an interaction between UV radiation and electrical current, which cause a greater toxin degradation due to a synergistic effect on microcystin degradation.

4. Conclusions

This study found that the photoelectrooxidation system under test was effective for the degradation of cyanotoxins. Electrical current and UV radiation were directly associated with toxin degradation. The analysis of the application of UV radiation revealed an improvement in the performance of the microcystin degradation process, and confirmed the synergistic effect of combined oxidative processes. Results confirmed that the use of a supporting electrolyte was not necessary for degradation. Photoelectrooxidation, as investigated in this study, seems to be a promising process for the treatment of public supply waters.

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