

Anaerobic/aerobic treatment of colorants present in textile effluents

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Abstract The operation of an anaerobic/aerobic process used to degrade the colorants present in textile wastewater is presented. The objective is to produce water that can be reused. Two particular cases were studied: the degradation of a synthetic wastewater containing the colorant disperse blue 79 (DB79) as a model compound and a real textile effluent containing reactive azo dyes. The biodegradation was achieved using a single tank operated as sequencing batch reactor. It was observed that the DB79 was biotransformed to amines in the anaerobic stage decolorizing the wastewater. The amines formed were subsequently mineralized in the aerobic phase. An increase of toxicity was observed in the anaerobic stage due to the amines formation, but the wastewater was detoxified after the aerobic treatment. Removal efficiencies of DB79 around 92% were observed after the treatment. Around 96% of the initial color of the real wastewater was effectively removed. It was observed that the biomass pre-acclimatized to the degradation of DB79 was more effective for the color removal than a freshly inoculum used.

Keywords Anaerobic/aerobic process; azo dyes; disperse blue 79; reuse; SBR; textile effluent

Introduction

In Mexico there exists interest in the elimination of color from textile wastewater in order to reuse the water in the process. The textile industry consumes approximately two thirds of the total production of dyes. During textile processing, inefficiencies in dyeing result in large amounts of the dyestuff being directly lost to the wastewater, which ultimately finds its way into the environment. The amount of dye lost is dependent on the class of dye application used, varying from 2% loss when using basic dyes to a 50% loss when reactive azo dyes are used (McMullan *et al.*, 2001). These residual of dyes are unloaded in residual waters of the systems of treatment or to the environment in form of dispersion or true solution in industrial effluents causing a severe contamination of rivers and groundwater in the areas with high concentration of textile industries (Chudgar, 1985; Stolz, 2001). Azo dyes are xenobiotics compounds characterized by the presence of one or more azo groups ($-N=N-$). They are considered a very important group of synthetic colorants. Of the annual world-wide production of dyes more than 50% are azo dyes, and around 2000 of them are used in the textile, leather, plastics, paper, cosmetics and foods industries (Stolz, 2001).

Dispersed blue 79 (DB79) is one of the colorants with more application in the textile industry (Figure 1). It is used in the dyeing of polyester, nylon, diacetate and triacetate of cellulose as well as in acrylic fibers. The reductive cleavage of the azo linkage of the DB79 resulting in the formation of the amine 2-bromine-4,6-dinitroaniline (BDNA), which is toxic and mutagenic, and of the amine NN-disubstituted 1,4-diaminobencene.

Azo dyes are organic compounds difficult to biodegrade due to their high stability to the light and the microbial attack. They are resistant to the aerobic biodegradation in conventional plants of treatment (Pagga and Brown 1986; Shaul *et al.*, 1991) and under anaerobic

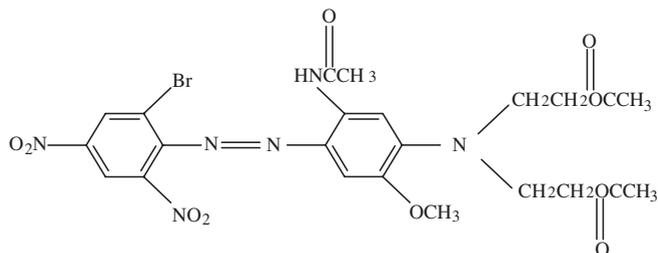


Figure 1 Structure of the azo dye disperse blue 79

conditions it has been observed the generation of reduced colorless compounds. In the initial stage of the anaerobic degradation of azo dyes a reductive cleavage of the linkage azo takes place, originating aromatic amines considered as potentially toxic, mutagenic and carcinogen products. Some of these amines have been reported as recalcitrant to the anaerobic bacteria (Zaoyan *et al.*, 1992; Weber and Adams, 1995) with exception of few aromatic amines substituted with hydroxyl and carboxyl groups which were degraded under methanogenic conditions (Razo-Flores *et al.*, 1996). Nevertheless, the aromatic amines are readily degraded aerobically (Brown and Laboureur, 1983; Loidl *et al.*, 1990).

The combination of the anaerobic reductive cleavage of the azo dyes with the aerobic treatment to degrade the generated amines can be an effective treatment to obtain the mineralization of azo dyes. Cruz and Buitrón (2001), studied a system constituted of two tanks. An anaerobic biofilter coupled to an aerobic one was utilized to study the degradation of disperse blue 79, obtaining efficiencies of biotransformation of 95% in 72 h in the anaerobic biofilter. In the aerobic biofilter the degradation was 65% for the amines produced in 24 h, finding that the effluent of anaerobic biofilter inhibited the activity of the biomass of aerobic biofilter.

The aim of the present work was to investigate in a laboratory pilot reactor the degradation of a synthetic wastewater containing the colorant DB79 as a model compound and a real textile effluent containing reactive azo dyes in order to obtain water for reuse in the process industry.

Methodology

Wastewater containing DB79

A pilot reactor with capacity of 7 L was used. Oxygen, pH and O.R.P. (Oxide-reduction potential) electrodes were connected to the reactor. The reactor control was through a programmable timer to which were connected 3 peristaltic pumps (Master Flex, Cole-Parmer) for recirculation control, load, unloading. In the aerobic phase the air was spread from the bottom of the reactor through a porous diffuser. Aeration was controlled through a solenoid valve also commanded by the timer. The reactor was provided with a system of heating with recirculation (Poly Science Model 210) to maintain the temperature of the reactor in an interval from 25 to 28°C and an intermittent agitation system (180 r.p.m.) with the purpose of favoring the mass transference. The reactor operated as a sequencing batch reactor (SBR) with an exchange volume of 75%. Activated sludge from a municipal wastewater treatment plant was used as inoculum. Biomass concentration inside the reactor was 1,100 mg VSS/L. Mean cellular retention time was maintained in 30 d. The biomass was acclimated with the azo dye DB79. The synthetic wastewater was constituted by azo dye DB79, nutrients and propionate or ethanol, used as co-substrate in a molar proportion in relation to the azo dye of 1:50 (DB79:propionate). A commercial preparation of the dye containing 50% of the dye and 50% of a dispersing agent was used. At the beginning, the reactor was

fed with 25 mg DB79/L, after the concentration was increased with increments of 25 mg/L until 100 mg DB79/L.

Start-up and operation of the reactor

To acclimatize the biomass to the anaerobic/aerobic conditions a strategy of fixed efficiencies was used. In this, the biomass was acclimatized to the toxic the necessary time to reach a removal efficiency of 70% of DB79 in the stage anaerobic and a removal efficiency of 90% of the aromatics amine during the aerobic stage (Melgoza *et al.*, 2000). The reactor operated with variable reaction periods until the acclimatization of the biomass to the changes of anaerobic/aerobic environmental was achieved. A strict monitoring of the adsorption of the azo dye onto the biomass was accomplished in order to assure that the degradation took place by the microorganisms and not by abiotic conditions. For this extractions with methanol of the azo dye sorbed on the biomass were conducted. Azo dye concentrations were increased whenever constant efficiencies of removal were obtained during 3 consecutive cycles.

Industrial effluent

The effluent was obtained from a textile industry that uses mainly reactive azo dyes with a very high solubility in water. The batch used for experiments had a total COD of 997 mg/L, 769 Pt-Co color units, 250 mg SO₄⁻²/L, and a conductivity of 5,210 µmhos/s. The experiments were conducted in a SBR packed with a porous volcanic stone (puzzolane) of 2.7 cm of mean diameter. The working volume was 5.0 liters, and was operated at a constant temperature of 35°C. In order to promote the mass transfer the liquid in the reactor was recycled. The reactor was inoculated with flocculent and granular sludge in a relation of (1:1) and operated for almost two years with wastewater containing the azo dye disperse blue 79. The color evolution was followed according the next procedure: the sample was ultracentrifuge at 14,000 rpm during 30 min, and residual color in the supernatant was determined by measuring the absorbance at the maximal wavelength of absorption of the water (540 nm) with a UV-Visible Spectrophotometer, Beckman, DU 650. In addition, color was measured using the Pt-Co units. The amine formation was determined according to Oren *et al.* (1991).

Analytical techniques

The reactor was monitored by determination of pH, O.R.P., total alkalinity, TSS (Total suspended solids), VSS (Volatile suspended solid), COD (Chemical oxygen demand centrifuged), COT (Total organic carbon), N-NO₃, N-NO₂, N-NH₄. All the parameters were measured following APHA (1992). DB79 concentration was measured in the methanol phase at 568 nm and 547 nm in water phase. Total amines were determined by the method of p-dimetilaminebenzaldehyde (Oren *et al.*, 1991). The amine BDNA was identified by HPLC, with a Hewlett Packard (Series 1100) chromatograph equipped with a UV-VIS detector and a reverse phase column C-18 Spherisorb ODS2 was used. The eluent was an isocratic mixture 60:39:1 of acetonitrile, water and phosphate buffer, at a flow rate of 1 ml/min, the reaction time was 3.4 minutes and detection wavelength was 344 nm. Injection volume to autosampler was 30 µL and the temperature was maintained at 40°C. Analyses of toxicity were done by the method of Microtox.

Results and discussion

Anaerobic/aerobic treatment of DB79

The reactor was operated during 120 days. The acclimatization of the reactor was reached in cycle 10, after 45 days of operation and when the global removal of DB79 was stabilized

in 72%. During the anaerobic phase (ORP of -321 mV) no significant biogas production was observed. Samples taken from the headspace of the reactor indicated the presence of carbon dioxide. No methane was detected. It was observed a biotransformation of DB79 to aromatic amines in the reductive phase of 60% in average, but the amount of amines recovery was only 25%. During the aerobic phase the mineralization of amines was of 90%.

Figure 2 depicts an example of the chromatograms obtained for the initial wastewater and after the anaerobic and aerobic phases of the process. Two intermediate products were generated in the reductive phase, corresponding to the amines 2-bromo-4,6 dinitroaniline (BDNA) and the N,N- disubstituted 1,4-diaminobencene (NNDB). After the aerobic stage the initial product and intermediates were degraded by the microorganisms. Identity of NNDB was confirmed by infra-red analyses that indicated the presence of the ester groups, aromatic amine, metoxi aromatic and amide characteristic of amine NNDB.

The operation of the reactor was divided in two stages depending on the cosubstrate utilized. For the first stage (days 44 to 70 and 10 to 19), propionic acid was used as co-substrate and for the second one (days 73 to 110 and cycles 20 to 32) ethanol was used. When propionic acid was used, influent concentrations of DB79 varied from 25 to 50 mg DB79/L and global removal efficiencies of the azo dyes varied from 72 to 86%. The maximal removal rate was 8.8 mg DB79/g VSS-d. The biotransformation of DB79 to aromatic amines was of 61% and the mineralization of total amines average was of 96% with a maximal rate of removal of 2.1 mg amines/g VSS-h.

In the second stage of operation, using ethanol as co-substrate, the concentrations of DB79 varied from 30 to 100 mg/L. The biotransformation in the reductive phase was in average of 60% with a maximum value of 95% and a degradation rate of 9.5 of mg DB79/g VSS-d. The mineralization of amines was of 95%, with a maximal rate of 0.22 mg total amines/L-h. The global removal of DB79 was of the 72 to 95%.

Figure 3 shows as the rate of specific degradation of the DB79. From the concentration of 45 mg DB79/L, the rate of specific degradation was constant with a value of 11.5 mg DB79/g VSS-d, indicating that in this interval of concentration inhibition did not appear.

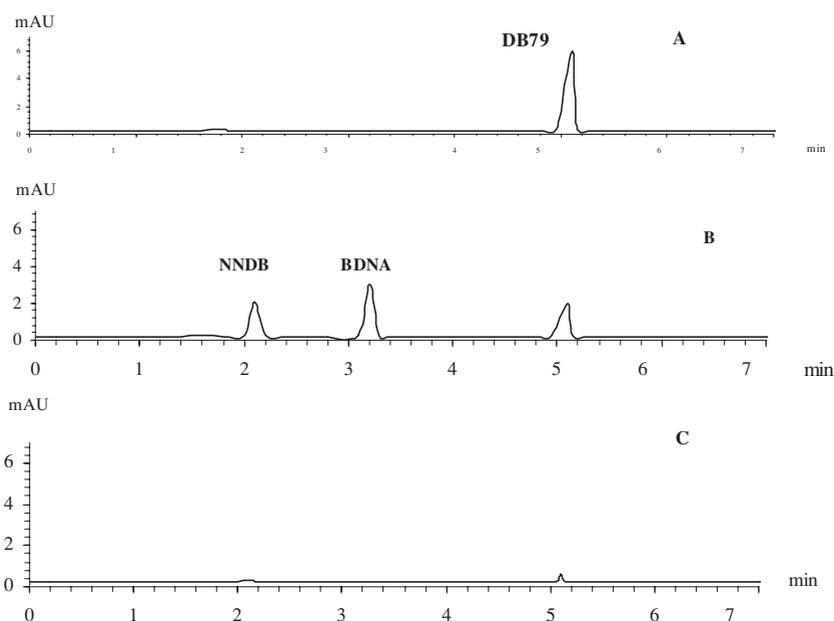


Figure 2 Chromatograms of the influent and effluent of the anaerobic and aerobic phases of process during cycle 13. a) Influent, b) Effluent after anaerobic phase, c) Effluent after aerobic phase

The maximal specific degradation rate was of 15 mg DB79/g VSS-d. Maximal rate of decolorization (reduction) in the reactor was of 17 mg DB79/L-d for the concentration of 75 mg DB79/L, being in the same order of magnitude of the values determined by Cruz and Buitrón (2000), for DB79 treated in an anaerobic biofilter, using as co-substrate sodium acetate. These authors reported a maximal rate of decolorization of 33 mg DB79/L-d. Rajaguru *et al.* (2000), obtained similar rates of elimination for sulfonated azo dyes: 61 mg/L-d for acid orange 10 (at a concentration of 100 mg/L) and of 51 mg/L-d for the black amide 10B (110 mg/L). It is important to indicate that the characteristics of low solubility and complexity of substitutes in DB79 originate minor rates of degradation than the sulfonated azo dyes, making its biotransformation more difficult.

The kinetic of reduction of the DB79 was followed (Figure 4). When a concentration of 75 mg DB79/L was used, a first order constant of $5 \times 10^{-3} \text{ min}^{-1}$ was calculated. The formation of the BDNA is a slow process. Weber and the Adams (1995) reported a two-phase reaction in the degradation of the DB79 with a fast phase of azo dye elimination and a slow phase of biotransformation, with a constant rate of reduction of $2.6 \times 10^{-3} \text{ min}^{-1}$.

Toxicity analysis

The synthetic wastewater influent (75 mg DB79/L) did not show toxicity, but after the anaerobic phase the toxicity of the residual water was of 14.4 Toxicity units, which indicates a highly toxicity according to the Mexican Official Norm NMX-AA-112-1995-SCFI. The toxicity increase was due to the biotransformation products of the DB79, i.e., the BDNA and NNDB amines. During the aerobic phase the amines were mineralized and the toxicity was eliminated. This indicates the ability of the system to really eliminate toxicity of the effluent.

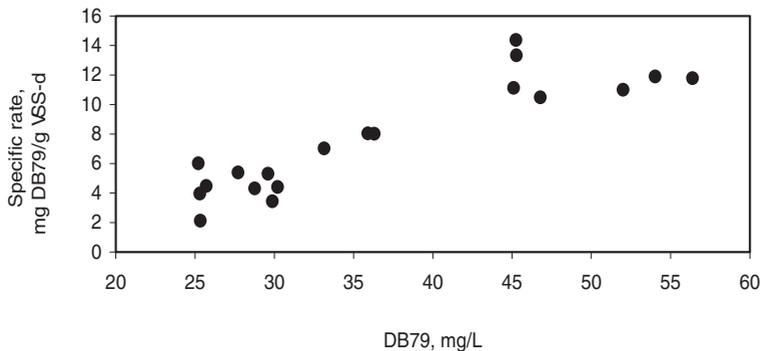


Figure 3 Specific rate of degradation of DB79 based on the initial concentration

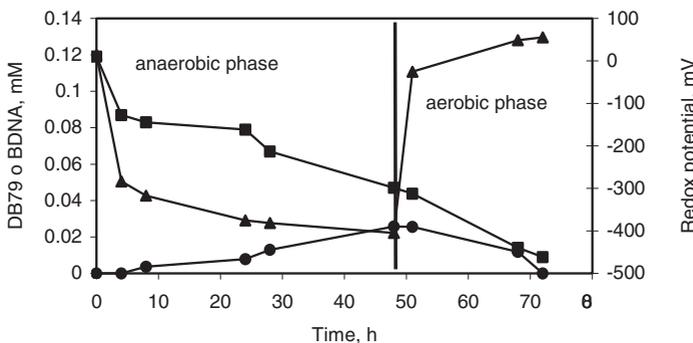


Figure 4 Kinetic of reduction of DB79 and formation and mineralization of BDNA in the anaerobic/aerobic SBR reactor during the cycle 29 of operation. (■) DB79; (●) BDNA; (▲) Oxidation-reduction potential

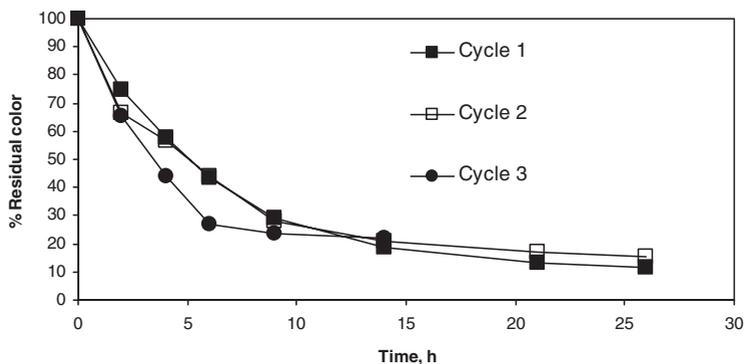


Figure 5 Residual color evolution as a function of time for three anaerobic sequencing batch biofilter cycles. Note the effect of acclimatization to reactive dyes on the slope increase of the cycle 3 compared to cycle 1

Textile effluent

For all the conditions studied, a removal of color was observed in the textile effluent. No inhibition due to toxic effects of the effluent was noted. Decolorization times were 45, 56 and 68 h for the initial concentrations of 1/3, 2/3 and direct wastewater, respectively. For these times, color removal efficiency varied from 95 to 98%.

As no inhibition was observed when the textile effluent was used without dilution, the biofilter was fed with the wastewater directly. Figure 5 shows the results obtained in three cycles of the discontinuous reactor. This indicates that the attached biomass was acclimated by the azo compound previously utilized. It was necessary around 21 h to obtain 80% of color removal. In this case, the sorption phenomenon was not observed. The decolorization began immediately probably because of the higher activity of the microorganisms.

The biofilter effluent had a pH of 7.6, and color of 335 Pt-Co units. Total amines varied between 14 and 41 mg/l, indicating that the anaerobic decolorization proceeds through the cleavage of the azo bond. COD removal was around 53% and no significant methane production was observed. The spectral analysis of the anaerobic reactor effluent showed the disappearance of the peak due to the azo dyes. In addition, the analysis revealed the presence of a new pick, probably due to the amines formation. In order to accomplish with the standards in respect to toxicity (amines) and organic matter, an aerobic stage was implemented degrading the amines and reducing the toxicity.

After the aerobic treatment the effluent was decolorized (70% of color removal) and the toxicity was reduced. This indicates that the water can be reuse in the dyeing bath.

Conclusions

The discontinuous anaerobic/aerobic reactor was an appropriate system for the biodegradation of azo dyes in residual waters. It was possible to implement in one tank the anaerobic phase, where the azo dyes are reduced to corresponding aromatic amines, and an aerobic phase where the amines are mineralized. The discontinuous process anaerobic/aerobic sequencing was very efficient in the removal of DB79. The efficiency of global removal of DB79 in reactor SBR was of 92%. In the anaerobic stage the biotransformation efficiencies were of 65%. Mineralization of amines produced by the cleavage of azo was of 96%. Maximal concentration of DB79 that treated was of 100 mg/L and the reaction time necessary to obtain removal efficiencies arrives of 90% was of three days (two days of anaerobic phase and a day of aerobic phase).

The process was also efficient for the treatment of a real textile effluent. Biomass effectively removed color from a textile effluent containing reactive azo dyes. Non toxic

effects were observed when the effluent was used without dilution. A faster decolorization was observed with the biomass acclimated since only 21 h were required to eliminate 80% of the initial color. In the aerobic stage the amines formed and the residual organic matter were successfully eliminated. The quality of the water of the treated effluent was suitable for reuse purposes in the textile plant.

Acknowledgement

Rosa María Melgoza thanks FCQI – PROMEP – UAEM for the award of a scholarship. Arturo Cruz thanks CONACYT for the award of a scholarship. This study was supported by a grant of the DGAPA (IN106002) and by Consejo Nacional de Ciencia y Tecnología, México (40248).

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