Effective Anaerobic Decolorization of Azo Dye Acid Orange 7 in Continuous Upflow Packed-Bed Reactor Using Biological Activated Carbon System

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The anaerobic reduction of azo dye Acid Orange 7 (AO7) was investigated in a continuous upflow packed-bed reactor (UPBR) containing biological activated carbon (BAC). Preliminary batch experiments using graphite proved the catalytic effect of using a solid electron mediator in the reactor. Before the start of continuous experiments, AO7 adsorption studies were done to control adsorption effects on initial decolorization rates. In a continuous UPBR-BAC system, high azo dye conversion rates were achieved during very short space times (τ) up to 99% in 2.0 min. In order to know which are the crucial and most influencing properties of BAC in AO7 reduction, other materials—graphite and alumina—with different properties were also tested in UPBRs. The results show that both electron-mediating capability and specific surface area of activated carbon contribute to higher reduction rates. Compared to other continuous and biological processes treating azo dyes, UPBR-BAC seems to be a very effective and promising system for anaerobic azo dye degradation.

Introduction

Azo dyes are chemical substances commonly used in the textile, pharmaceutical, and food industries and characterized by the N═N bond. Their production is more than 1 million tons per year in the world, and during dying processes, about 40% of this huge amount of azo dyes ends up in wastewaters. In addition, about 40−65 L of textile effluent is generated per kg of cloth produced.[1] There is no adequate process to treat these wastewaters at high concentrations and at soft conditions on the industrial scale for the time being, and the release of these compounds into the environment presents serious problems of pollution related to both aesthetic reasons and their toxicity.

Several methods have been found to treat azo dye wastewaters.[2] Removal techniques for dyes include coagulation, advanced oxidation processes, membrane processes, and adsorption. These physical and chemical treatments are effective for color removal but use more energy and chemicals than biological processes[3] and, in addition, some of them produce large amounts of secondary waste solids or streams that require further treatment or disposal.[4] Among all of the existing techniques, the most economic and environmentally friendly are biological treatments. Because of the fact that azo dyes are artificial compounds and especially designed to be resistant in the natural environment, their biological degradation has serious obstacles. Investigations of the biodegradability of water-soluble azo dyes by an activated sludge process have indicated that, in most cases, these dyes could not be degraded under aerobic conditions. On the other hand, azo reduction can be relatively easily achieved under anaerobic conditions.[5] Moreover, most of the products created by the breaking of the N═N bond could be successfully degraded under aerobic conditions. These suggest a sequential anaerobic−aerobic process as the reasonable scheme of treating wastewaters containing azo dyes.[6] The bottleneck of this process is the anaerobic reduction, so by having an efficient first step in azo dye degradation, the more complete sequential treatment can be carried out.

The only, but serious, disadvantage of the anaerobic biological techniques is the need for long hydraulic residence times. Several studies indicate that reduction of many azo dyes is a relatively slow process.[7−13] However, by using an appropriate catalyst during the reduction, anaerobic biodegradation could be speeded up, resulting in much higher efficiency. In different experimental systems, redox mediators, like quinones and flavine-based compounds, have been demonstrated to accelerate azo dye reduction.[14−18] These electron mediators shuttle reducing equivalents from an electron-donating cosubstrate to the azo linkage. Although the effective redox mediator dosage levels are low, continuous dosing implies continuous expenses. Therefore, it is desirable to immobilize the redox mediator in the bioreactor. For this purpose, activated carbon (AC) was considered (Figure 1) since it is known to contain surface quinonic structures.[19] Despite these facts, only a very few studies have been done using activated carbon as a catalyst for azo dye biodegradation.[19−21]

Considering the amount of azo dye wastewaters mainly originated from the textile industry, it is clear that continuous systems have to be designed for treating these effluents. The main objective of this study was to investigate the anaerobic decolorization of azo dye Acid Orange 7 (Figure 2) using a continuous upflow packed-bed reactor (UPBR) filled with biological activated carbon (BAC). This system was compared with UPBRs using different support materials such as graphite or alumina to evaluate the significant role of activated carbon in the anaerobic degradation of Acid Orange 7 (AO7).

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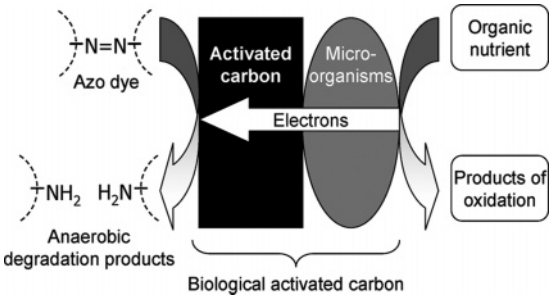

Figure 1. Role of activated carbon in anaerobic azo dye degradation.

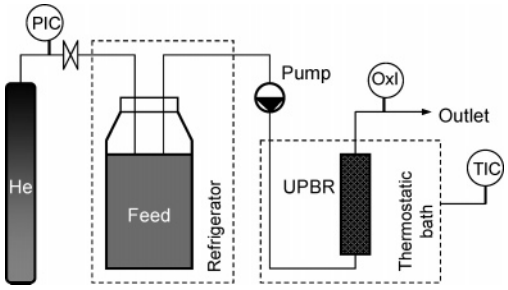

Figure 3. Continuous and anaerobic upflow packed-bed reactor setup.

Materials and Methods

Chemicals. Azo dye Orange II (C.I. Acid Orange 7) Sodium Salt (dye content 99%, Sigma, ref O8126) was selected as a model compound since, on the one hand, this azo dye is representative of a large class of azo dyes used commercially and, on the other hand, quantitative determination of one of its anaerobic degradation products, sulfanilic acid, is relatively easy. Sulfanilic acid (SA) was supplied by Sigma (min. 99%, ref S5263). Sodium acetate (99%, Aldrich, ref 11019-1) was used as the carbon source for sludge and also as the source of reductive equivalents for azo dye reduction. Acetic acid (99.8%, Aldrich, ref 10908-8) was used for batch experiments as the continuous carbon source and also as a pH controller. Alumina (Norton S.A., ref 6275) with a granule size of 25−50 mesh (0.3−0.7 mm), graphite flakes (Aldrich, particles of 75+ mesh, ref 33246-1), and activated carbon (Merck, granules of 2.5 mm, ref 1.02518.1000) were used as support materials for biodegradation. Activated carbon was crushed, and granules of 25−50 mesh size were separated, washed with distilled water, dried at 104 °C for 15 h, and stored under normal conditions until use. Carborundum granules (Carlo Erba Reagents, ref 434766) were used as inert diluent for the activated carbon catalyst. The basal media contained the following compounds (mg L^{-1}): $MnSO_4 \cdot H_2O$ (0.155), $CuSO_4 \cdot 5H_2O$ (0.285), $ZnSO_4 \cdot 7H_2O$ (0.46), $CoCl_2 \cdot 6H_2O$ (0.26), $(NH_4)_6Mo_7O_{24}$ (0.285), $MgSO_4 \cdot 7H_2O$ (15.2), $CaCl_2$ (13.48), $FeCl_3 \cdot 6H_2O$ (29.06), NH_4Cl (190.9), KH_2PO_4 (8.5), $Na_2HPO_4 \cdot 2H_2O$ (33.4), and K_2HPO_4 (21.75).

Batch Experiment. For batch experiments, a stirred-tank reactor was used with a useful volume of 1.2 L maintained at a constant temperature of 35 °C. The mixed culture of anaerobic sludge was obtained by partial digestion of aerobic sludge under anaerobic conditions. The reactor was agitated by a magnetic stirrer only for 20 s/experiment—to avoid destruction of biofilm on the catalyst surface—immediately after changing 300 mL of decolorized dye solution for a fresh one. Acetic acid (4.0% v/v) was continuously fed not just to keep the acetate level nearly constant in the batch but also to help keep the pH level between 6.7 and 7.2. Anaerobic conditions were maintained by continuous bubbling of helium into the reactor. The redox potential was continuously monitored.

The batch contained 20 g of graphite as an electron-conducting catalyst. In fact, the reason for using graphite instead of activated carbon was that graphite has no adsorption properties; thus, dye degradation in the batch reactor could be clearly followed. In the case of AC, which can easily adsorb a higher amount of azo dyes, it is more difficult to examine adsorption and catalytic effects separately since adsorption is not constant and depends both on azo dye concentration in the liquid phase and on contact time.

The objective of the batch experiment was to compare Acid Orange 7 anaerobic degradation in traditional and discontinuous biological systems—operating with high contact times—with a batch containing a solid electron mediator.

Continuous Experiments. Figure 3 shows schematically our continuous system. The upflow packed-bed reactor has a diameter of 15 mm with a useful volume of 9 mL. It is filled with the mixture of 10 g of carborundum granules—its inert property was previously tested, and carborundum did not show any positive effect on decolorization rates—and 1 g of activated carbon with the size of 25−50 mesh. To prevent washing out of AC, two filters were placed into the top and bottom of the reactor. The UPBR was working at a constant temperature of 35 °C. The entering feed was 100 mg L^{-1} Acid Orange 7 solution containing 200 mg L^{-1} of sodium acetate as substrate and the basal media with microelements. The flow rate of the feed was varied between 25 and 70 mL h^{-1}. The pH of the outlet solution varied between 6.8 and 7.2. The anaerobic condition in the feeding bottle (5 L) was maintained by both cooling of the solution (at 5 °C) and bubbling of helium. The redox potential was continuously monitored and remained below −500 mV (referred to Ag^+/AgCl electrode).

To prepare the biological system, anaerobic sludge was filtered by a filter with a pore size of 20−25 μm to only have single cells and spores. This filtrate was pumped through the activated carbon for a week. During this period, the biofilm was immobilized on the AC surface, resulting in the so-called biological activated carbon. Then the biofilm was adapted to AO7 by continuous flowing of the dye solution containing both the basal media and the carbon source through the reactor. To maintain the same culture of sludge, every new reactor was set by using the outlet of an already operated reactor as the inlet to the new one.

In order to know what are the crucial and most influencing properties of the BAC system in AO7 reduction, different materials—graphite and alumina—with different conducting and surface properties were also tested in UPBRs. These reactors were set up in the same way as the one with AC.

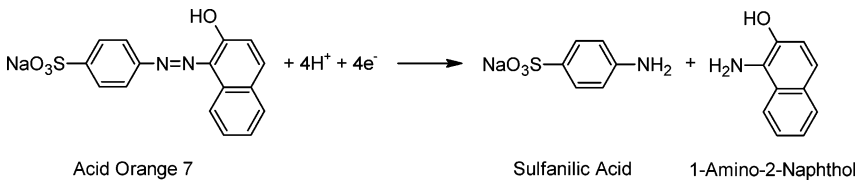

Figure 2. Anaerobic degradation of Acid Orange 7.

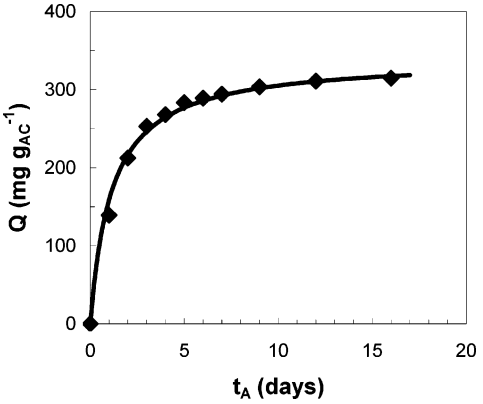

Figure 4. Acid Orange 7 adsorption on activated carbon predicted by a second-order kinetic model (line).

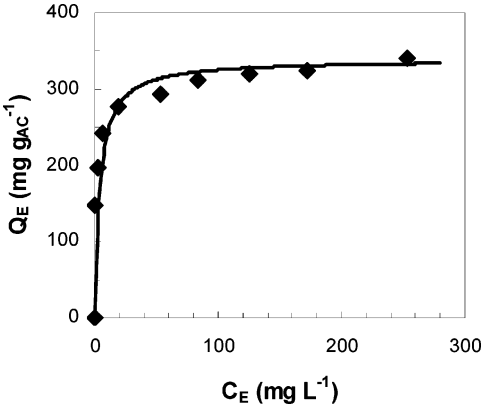

Figure 5. Acid Orange 7 equilibrium adsorption on activated carbon predicted by Langmuir isotherm (line).

Adsorption Experiments. Before starting experiments in UPBRs, all reactors with activated carbon, graphite, and alumina were saturated with azo dye to avoid the influence of initial dye adsorption during the initial period of operation. To know exactly the sorption capacities of these materials and the time of saturation needed, adsorption experiments were done. Nine bottles, each of them containing 100 mg of activated carbon, were filled with 100 mL of AO7 solution in different initial concentrations between 150 and 600 mg L^{-1}. Adsorption was allowed to run for 16 days, and then samples were taken. For alumina, graphite, and AC, dye adsorption was also examined as a function of time. Bottles containing 100 mg of either alumina or graphite or AC and 100 mL of AO7 solution with an initial concentration of 400 mg L^{-1} were left for 16 days, and during that period, samples were taken 10 times. All solutions were slowly stirred for 30 s each day. The pH of the solutions was always adjusted to be between 7.0 and 7.5.

Analytical Methods. Acid Orange 7, sulfanilic acid, and acetate were measured by high-performance liquid chromatography (HPLC) on a C_{18} Hypersil ODS column in a gradient of methanol−water mobile phase with a flow rate of 1 mL min^{-1}. AO7 was determined on 487 nm (at a retention time (RT) = 17.55 min), sulfanilic acid was determined on 252 nm (RT = 2.18 min) and acetate was determined on 210 nm (RT = 3.68 min). 1-Amino-2-naphthol (1A2N), the other product generated during the anaerobic degradation of AO7, was not determined because of its partial precipitation.

Results and Discussion

Adsorption Kinetics. In the cases of alumina and graphite, Acid Orange 7 adsorption was found to be almost zero. On the contrary, activated carbon showed a strong adsorption capacity for AO7. Azo dye adsorption as a function of time is shown in Figure 4. Adsorption fits very well to a second-order kinetic model[22] (eq 1),

$$Q = \frac{KQ_E^2 t_A}{1 + KQ_E t_A} \quad (1)$$

where Q (mg g_{AC}^{-1}) represents the AO7 concentration in the solid phase, Q_E (mg g_{AC}^{-1}) is the corresponding value at equilibrium, t_A (days) is the contact time, and K (g_{AC} mg^{-1} day^{-1}) is the adsorption rate constant. Values of Q can be obtained from eq 2,

$$Q = \frac{(C_{0A} - C_A)V}{m_{AC}} \quad (2)$$

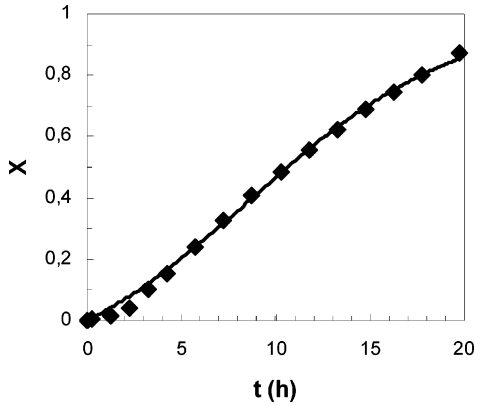

Figure 6. Acid Orange 7 conversion in batch reactor using graphite as solid electron-mediator catalyst. Line shows the fitting to second-order autocatalytic model.

where C_A (mg L^{-1}) is the AO7 concentration in the solution, C_{0A} (mg L^{-1}) is the initial dye concentration, V (L) is the volume of solution, and m_{AC} (g) is the mass of activated carbon. After linearization of eq 1, Q_E and K values were found to be 340 mg g_{AC}^{-1} and 2.59 × 10^{-3} g_{AC} mg^{-1} day^{-1}, respectively.

Equilibrium Adsorption Isotherm. The sorption process is well-described by the Langmuir isotherm (Figure 5). According to the model (eq 3),

$$Q_E = \frac{QK_L C_E}{1 + K_L C_E} \quad (3)$$

where the variables Q_E (mg g_{AC}^{-1}) and C_E (mg L^{-1}) are the azo dye equilibrium concentrations in the solid and liquid phases, respectively, Q_L (mg g_{AC}^{-1}) is the maximum adsorbance capacity according to the Langmuir model, and K_L (L mg^{-1}) is the Langmuir constant; a maximum adsorption of 339 mg g_{AC}^{-1} with a K_L value of 0.242 L mg^{-1} was found by using the linearized form of eq 3. Before the start of continuous experiments, more than 6 times this amount of dye was pumped through the reactors to ensure avoidance of initial adsorption effects on outlet dye concentration.

Batch Experiment. Initial concentrations of Acid Orange 7, sulfanilic acid, and acetate in the batch reactor were 48, 41.5, and 110 mg L^{-1}, respectively. The pH of the solution at the start was 6.8 and at the end was 6.7. Figure 6 shows AO7 conversion vs time. When using graphite in the batch, after 20 h, azo dye degradation was about 88%. In our previous study, operating with the same initial parameters but having no catalyst in the reactor, no decolorization was observed during the first 24 h (data not shown). This means that using graphite together

Table 1. Anaerobic Degradation of Acid Orange 7: Selected Results of Studies Reported in the Literature

reactor type[a]	main influent characteristics[b]	$C_{IN\ DYE}$ (mg L^{-1})	time (h)[c]	color removal or removal rate constant[d]	ref no.
semicont.	simulated textile wastewater	100	240	82−100%	1
SBR	COD = 2.66−5.32 g L^{-1} day^{-1}	50−100	21.5	30−80%	3
batch	COD = 0.30−3.00 g L^{-1}	100	>10	>75%	7
batch	glucose = 1.80−2.60 g L^{-1}	25−320	48−120	100%	10
UASB	glucose = 2.00 g L^{-1}	100−200	10−80	92−98%	11
UASB	COD = 5.3 g L^{-1} day^{-1} AQDS = 0−30 μM	100	6	>85%	14
batch	glucose = 1.8−2.6 g L^{-1}	100−300		0.72−1.11 day^{-1}	23
batch	sulfide = 0.6−0.7 mM 1A2N = 0.0−1.0 mM	80−100		0.09−1.2 day^{-1}	24

[a] Reactor types: UASB, upflow anaerobic sludge blanket; SBR, sequencing batch reactor. [b] Abbreviations: COD, chemical oxygen demand; AQDS, anthraquinone-2,6-sulfonic acid; 1A2N, 1-amino-2-naphthol. [c] Time corresponds either to contact time (batch) or to hydraulic residence time (continuous-type reactors). [d] Removal rate constant refers to first-order kinetics.

with anaerobic sludge results in a significant increase of color removal. Moreover, in different traditional and discontinuous biological systems—using different initial dye concentrations—high Acid Orange 7 conversion (>90%) has generally required longer contact times (Table 1). Although it is difficult to compare decolorization efficiencies of these systems to ours since wastewater characteristics could be rather different, considering the required contact times, it also implies that using a solid electron mediator in the bioreactor can speed up AO7 degradation.

In earlier studies, it was found that 1-amino-2-naphthol (1A2N) is a redox mediator that plays a significant role in the transport of electrons to the dye, thus giving to the whole process an autocatalytic nature.[23,24] For this, a second-order kinetic model—supposing autocatalysis—was proposed by Van der Zee et al.[24] in which X varies as a function of time according to eq 4,

$$X = \frac{1 - (k_2 c_0 + k_1)}{k_1 \exp(k_2 t c_0 + k_1 t) + k_2 c_0} \tag{4}$$

where X is the dye conversion, c_0 (mmol L^{-1}) is the initial azo dye concentration, t (h) is the elapsed time, and k_1 (h^{-1}) and k_2 (L $mmol^{-1}$ h^{-1}) are the first-order and second-order kinetic constants, respectively. As Figure 6 shows, the model fits very well the experimental points. Significant deviations from the model can only be observed in the period of the first 4 h of decolorization, which can be explained by having a certain concentration of 1A2N in the batch at initial conditions and, also, having higher redox potential values at the start because of the initial mixing of fresh and decolorized solution.

Continuous Experiments. In the case of continuous packed-bed reactors working with catalysts, it is better to examine conversion values as a function of space time rather than of hydraulic residence time, since the crucial factor in these reactions is the amount of catalyst rather than the reactor volume. Space time (τ, min) is defined by eq 5,

$$\tau = \frac{m_C}{F_V \rho} \tag{5}$$

where m_C (g) is the mass of catalyst in the reactor, F_v (mL min^{-1}) is the volumetric flow rate of azo dye solution, and ρ (g mL^{-1}) is the density of the solution.

AC is not just a redox mediator having the ability to conduct electrons; it also has important functional groups on its surface. To test the importance of all these properties in azo dye decolorization, graphite, which is an electron conductor having no specific surface properties, and alumina, having neither functional groups on its surface nor conductive properties, were also used in a UPBR to compare them with the BAC system. Results are shown in Figure 7. Using alumina in the anaerobic reactor did not result in high values of AO7 conversion, even at high space time. Only 33% of decolorization was achieved at a space time of 15.8 min, which cannot be considered as an effective treatment. A UPBR working with graphite showed much higher decolorization rates than that in the case of alumina. 77% of AO7 conversion was achieved at a τ of 9.7 min. The difference in efficiencies of these two systems suggests that the conductive property of the support material strongly affects azo dye decolorization.

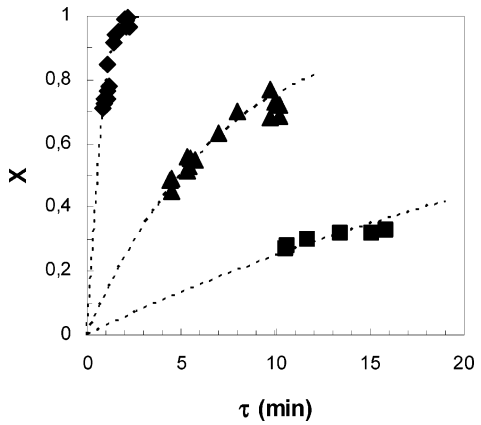

Figure 7. Acid Orange 7 conversion in continuous UPBR using different support materials: (◆) activated carbon, (▲) graphite, and (■) alumina.

On the other hand, Figure 7 also shows that the BAC system definitely gave higher azo dye conversions than the UPBR with graphite. This can be explained by the different structural and adsorption properties of these two materials. While graphite has a structure that consists of only aromatic rings with delocalized electrons—causing its electron-mediating property—and has no adsorption capability for AO7, the activated carbon structure contains both aromatic rings and surface functional groups. These specific quinonic groups are capable of transporting electrons by the way of keto−enol tautomerism that results in a more efficient reducing equivalent transfer compared with that of the delocalized electron system. In addition, in the case of AC, the strong adsorption capacity of AO7 and its high concentration on the carbon surface also help the electron transport from the electron donor acetate to the azo linkage.

In UPBR-BAC, almost complete decolorization was achieved at short space time. AO7 conversion was about 95% at 1.6 min, and 2.0 min of τ resulted in 99% of decolorization. These values of space time correspond to extremely short hydraulic residence times of about 4.4 and 5.4 min (with packed-bed porosity of 0.3), respectively. By comparing these with hydraulic residence times applied in other continuous biological systems using

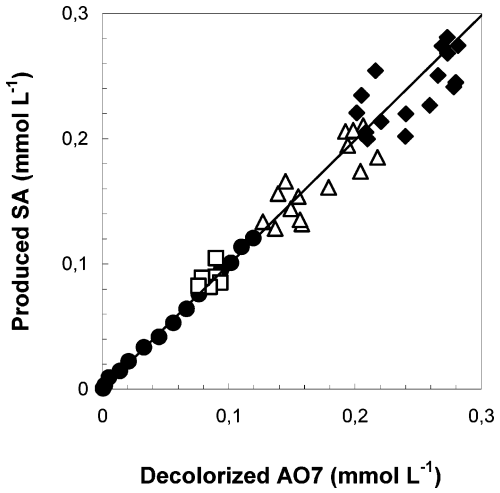

Figure 8. Ratio between destroyed Acid Orange 7 and produced sulfanilic acid in different reactor systems: (●) batch with graphite, (□) UPBR with alumina, (△) UPBR with graphite, and (◆) UPBR with BAC.

similar initial dye concentrations (Table 1), it seems that UPBR-BAC requires one of the shortest times needed to achieve almost complete decolorization of AO7.

AO7−SA Ratio. As was shown in Figure 2, during the anaerobic degradation of Acid Orange 7, sulfanilic acid (SA) and 1-amino-2-naphthol are produced. To confirm the proposed reaction and check if only the azo bond was broken in the dye molecule or whether there were subsequent reactions, SA concentration in the outlet was also determined. Figure 8 shows sulfanilic acid concentrations as a function of degraded AO7. It can be seen that the amount of produced SA is proportional to the amount of decolorized azo dye in the ratio of 1:1—independent of the reactor system—giving evidence that the proposed reaction takes place. In addition, sulfanilic acid adsorption on the support materials or its possible consumption by microorganisms as a carbon source can be neglected.

Conclusions

To the best of our knowledge, a continuous upflow packed-bed reactor with biological activated carbon was applied, for the first time, for anaerobic azo dye decolorization. High conversion rates of Acid Orange 7 were achieved at very short space times, corresponding to extremely short hydraulic residence times. Different support materials were also used to determine the crucial roles of BAC in azo dye reduction. The results show that both electron conductivity and specific carbon surface with functional groups contribute to higher reduction rates. Compared to other continuous and biological processes treating azo dyes, UPBR with BAC seems to be one of the most effective and promising systems for anaerobic azo dye degradation.

Acknowledgment

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Literature Cited

(1) Manu, B.; Chaudhari, S. Anaerobic decolorisation of simulated textile wastewater containing azo dyes. *Bioresour. Technol.* **2002**, *82*, 225.

(2) Forgacs, E.; Cserháti, T.; Oros, Gy. Removal of synthetic dyes from wastewaters: A review. *Environ. Int.* **2004**, *30*, 953.

(3) Ong, S.-A.; Toorisaka, E.; Hitara, M.; Hano, T. Treatment of azo dye Orange II in aerobic and anaerobic-SBR systems. *Process Biochem.* **2005**, *40*, 2907.

(4) Georgiou, D.; Hatiras, J.; Aivasidis, A. Microbial immobilization in a two-stage fixed-bed-reactor pilot plant for on-site anaerobic decolorization of textile wastewater. *Enzyme Microbiol. Technol.* **2005**, *37*, 597.

(5) Beydilli, M. I.; Pavlostathis, S. G.; Tincher, W. C. Biological decolorization of the azo dye Reactive Red 2 under various oxidation−reduction conditions. *Water Environ. Res.* **2000**, *72* (6), 698.

(6) Kalyuzhnyi, S.; Sklyar, V. Biomineralisation of azo dye and their breakdown products in anaerobic−aerobic hybrid and UASB reactors. *Water Sci. Technol.* **2000**, *41* (12), 23.

(7) Brás, R.; Ferra, M. I. A.; Pinheiro, H. M.; Gonçalves, I. C. Batch tests for assessing decolourisation of azo dyes by methanogenic and mixed cultures. *J. Biotechnol.* **2001**, *89*, 155.

(8) Kapdan, I. K.; Tekol, M.; Sengul, F. Decolorization of simulated textile wastewater in an anaerobic−aerobic sequential treatment system. *Process Biochem.* **2003**, *38*, 1031.

(9) Manu, B.; Chaudhari, S. Decolorization of indigo and azo dyes in semicontinuous reactors with long hydraulic retention time. *Process Biochem.* **2003**, *38*, 1213.

(10) Méndez-Paz, D.; Omil, F.; Lema, J. M. Anaerobic treatment of azo dye Acid Orange 7 under batch conditions. *Enzyme Microbiol. Technol.* **2005**, *36*, 264.

(11) Méndez-Paz, D.; Omil, F.; Lema, J. M. Anaerobic treatment of azo dye Acid Orange 7 under fed-batch and continuous conditions. *Water Res.* **2005**, *39*, 771.

(12) Rajaguru, P.; Kalaiselvi, K.; Palanivel, M.; Subburam, V. Biodegradation of azo dyes in a sequential anaerobic−aerobic system. *Appl. Microbiol. Biotechnol.* **2000**, *54*, 268.

(13) Sponza, D. T.; Işik, M. Decolorization and azo dye degradation by anaerobic/aerobic sequential process. *Enzyme Microbiol. Technol.* **2002**, *31*, 102.

(14) Cervantes, F. J.; Van der Zee, F. P.; Lettinga, G.; Field, J. A. Enhanced decolourisation of Acid Orange 7 in a continuous UASB reactor with quinones as redox mediators. *Water Sci. Technol.* **2001**, *44* (4), 123.

(15) Dos Santos, A. B.; Traverse, J.; Cervantes, F. J.; Van Lier, J. B. Enhancing the electron transfer capacity and subsequent color removal in bioreactors by applying thermophilic anaerobic treatment and redox mediators. *Biotechnol. Bioeng.* **2005**, *89* (1), 42.

(16) Field, J. A.; Brady, J. Riboflavin as a redox mediator accelerating the reduction of the azo dye Mordant Yellow 10 by anaerobic granular sludge. *Water Sci. Technol.* **2003**, *48* (6), 187.

(17) Rau, J.; Knackmuss, H.-J.; Stolz, A. Effects of different quinoid redox mediators on the anaerobic reduction of azo dyes by bacteria. *Environ. Sci. Technol.* **2002**, *36*, 1497.

(18) Van der Zee, F. P.; Bouwman, R. H. M.; Strik, D. P. B. T. B.; Lettinga, G.; Field, J. A. Application of redox mediators to accelerate the transformation of reactive azo dyes in anaerobic bioreactors. *Biotechnol. Bioeng.* **2001**, *75* (6), 691.

(19) Van der Zee, F. P.; Bisschops, I. A. E.; Lettinga, G.; Field, J. A. Activated carbon as an electron acceptor and redox mediator during the anaerobic biotransformation of azo dyes. *Environ. Sci. Technol.* **2003**, *37*, 402.

(20) Pasukphun, N.; Vinitnantharat, S. Degradation of organic substances and reactive dye in an immobilized-cell sequencing batch reactor operation on simulated textile wastewater. *J. Environ. Sci. Health* **2003**, *A38* (10), 2019.

(21) Walker, G. M.; Weatherley, L. R. Biological activated carbon treatment of industrial wastewater in stirred tank reactors. *Chem. Eng. J.* **1999**, *75*, 201.

(22) Órfão, J. J. M.; Silva, A. I. M.; Pereira, J. C. V.; Barata, S. A.; Fonseca, I. M.; Faria, P. C. C.; Pereira, M. F. R. Adsorption of a reactive dye on chemically modified activated carbons—Influence of pH. *J. Colloid Interface Sci.* **2006**, *296*, 480.

(23) Méndez-Paz, D.; Omil, F.; Lema, J. M. Modeling of the Acid Orange 7 anaerobic biodegradation. *Water Sci. Technol.* **2003**, *48* (6), 133.

(24) Van der Zee, F. P.; Lettinga, G.; Field, J. A. The role of (auto)-catalysis in the mechanism of an anaerobic azo reduction. *Water Sci. Technol.* **2000**, *42* (5−6), 301.

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