Energy consumption in the mineralization of the azo dye direct red 23 in a sequencing batch reactor

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Abstract

The main objective of this work was to study the energy consumption in the start–up of an anaerobic/aerobic sequencing batch pilot reactor (SBR) for the mineralization of the azo dye C.I. Direct Red 23 (DR23). The reactor was packed with granular activated carbon as carrier medium of the biomass. A mixture 50/50 of activated sludge from two treatment plants was used like inoculums. It was used synthetic wastewater with 25 mg/L DR23 as substrate, 15 mg/L acetic acid as co-substrate and medium mineral nutrient. For the acclimatization of the biomass to the DR23 and to the changes of environmental anaerobic/aerobic, the reactor used the strategy of fixed efficiencies. The thermodynamic evaluation was made for start-up of SBR. The reactor was operated 253 cycles (160 days of operation). The acclimatization was reached in the cycle 27 (43 days of operation) with an initial concentration of 25 mg/L of DR23 The reaction time was reduced from 72 h to 24 h. The concentrations of azo DR23 were increasing of 25 to 200 mg/L with a global removal efficiency of 95 %. The reactor pilot of expanded bed SBR anaerobic/aerobic was evaluated for the treatment of the DR23 azo dye. Finally, the total energy balance of the start – up process during the first 27 cycles was of 544 MJ added to the SBR.

Keywords: Energy evaluation, sequencing batch reactor (SBR), azo dye RD23, anaerobic/aerobic process, textile effluent

1. Introduction

In Mexico the elimination of colour from textile wastewater is necessary for industrial reuse purposes. 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 underground water 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). The azo dyes present in textile effluents, is not toxic for themselves, but the formed products of their biotransformation anaerobic as they are it the amines aromatic, they were toxics and they are identified as carcinogenic and mutagenic compound (Cheng *et al.*, 1997; Pinheiro et al., 2004). In the case of the DR23, it is used in the dyed of cotton fibbers, linen and rayon; it is stable to the light and it is absorbed easily in the water, its fixation grade in the fibber is from 70 to 95% (O'Neill et al., 1999). In the figure 1 the structure of the DR23 is shown.

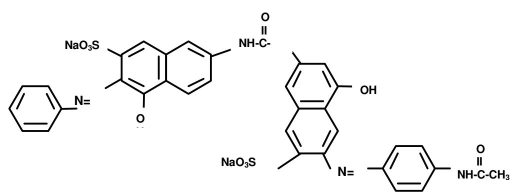


Figure 1. Structures chemistry of the azo dye DR23

The azo dyes present in textile effluents, are not toxic for themselves, but the formed byproducts of their anaerobic biotransformation are aromatic amines. They are toxics and are identified as carcinogenic and mutagenic compounds (Pinheiro *et al.,* 2004). An alternative for the treatment of these effluents is the application of biological processes conventionally combining ambient anaerobic and aerobic integrated in a single reactor. In these systems, in the reductive phase the aromatic amines are generated as byproducts of the anaerobic reduction of the azo dye due to biotransformation. These byproducts are not generally biodegraded in this stage but in an oxidative phase during aerobic conditions they are mineralized to NO_3, N_2, CO_2 y H_2O and in this way their carcinogenic and mutagenic character is eliminated (Tan *et al.*, 1999; O'Neill *et al.*, 1999; Melgoza *et al.*, 2004). This can be a method for the complete removal of azo dyes of the wastewaters. However, they present two limitations: the long retention time that frequently is applied in the anaerobic phase and the lack of knowledge on the fate of the aromatic amines in the aerobic phase for the biological and chemical transformations that will continue having the remainders of toxic aromatic amines in final effluents. Therefore it is important to assure the grade of mineralization of the aromatic amines (Van der Zee *et al.*, 2005).

2. Methodology

Experimental system

It was installed a sequencing batch reactor (SBR) with expanded bed at pilot level, that consisted of a cylinder of acrylic with double wall and collapsible cover, of 58 cm of height and 14 cm of internal diameter, with an useful volume of 9 L. SBR was packed with granular activated carbon. Three pumps peristaltic of variable speed (Master Flex Cole Parmer Model 72200-62, 77601-10) and an aeration pump (Model Elite 802) were connected to a programmable clock (Timer Chrontol), with the purpose of controlling the load, recirculation, aeration and the discharges. During the aerobic phase the air was diffused from the bottom of the reactor through a porous diffuser, allowing that the bubbles of air passed through the packing material. The temperature was controlled to 30 ±1 °C, by means of a recirculation and heating of the water system (Poly Science Model 210). Electrodes of pH, potential redox ORP), nitrates, ammonium nitrogen and dissolved oxygen were installed to the reactor.

Biomass

The reactor was packed with granular activated carbon and inoculated with a mixture in relationship 50/50 of sludge activated of municipal and industrial origin from two treatment plants both located in Jiutepec, Morelos, México. The concentration of sludge activated its 2,090 and 4,850 mg of SSV/L respectively. Synthetic wastewater with was prepared 25 mg/L DR23 as substrate, 15 mg/L of acetic acid (co-substrate) as source of carbon and of electrons to supplement the reduction reactions in the anaerobic phase and a mixture of mineral nutrient medium for the growth of the microorganisms.

Analytic methods

The obtained parameters were pH, ORP (redox potential), temperature, total alkalinity as $CaCO_3$, CO_2, dissolved oxygen, SST (total suspended solids), SSV (volatile suspended solids), SS (solid sedimentables), sulfurs, sulfates and nitrogen as $N\text{-}NH_4$ and $N\text{-}NO_3$, they were carried out for standardized methods according to APHA. (APHA, 1992). The determination of the DR23 was carried out in a spectrophotometer UV-VIS Agilen 8453E Spectroscopy System, to a wavelength of 501 nm. The total amines were determined by the method of the p-dimethyl aminebenzaldehyde (Oren *et al*., 1991) measures to a wavelength of 440 nm. The DR23 and the aromatic amines were also quantified by HPLC and by UV-VIS spectrum analysis

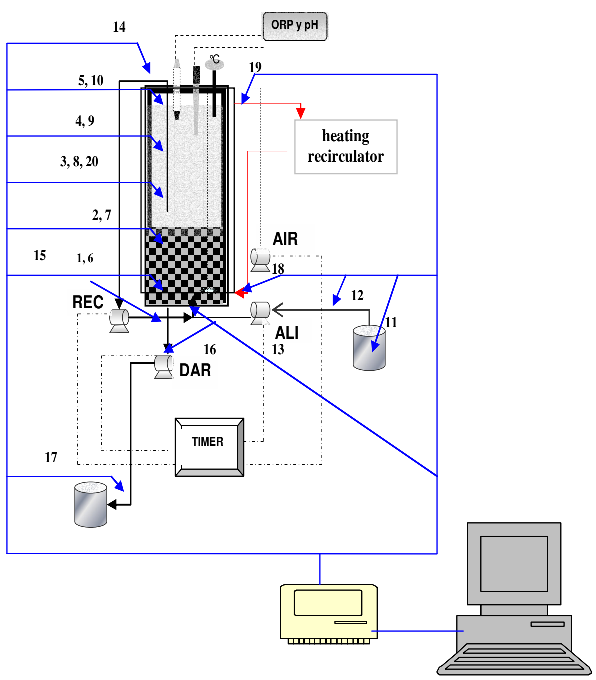
Operation strategy

For the acclimatization of the biomass to the azo DR23 and to the changes of anaerobic/aerobic environmental, the reactor used the strategy of fixed efficiencies, that consisted in to allow to the biomass the necessary time to reach 80% removal efficiency of azo DR23 in the anaerobic phase and 80% of mineralization of amines during the aerobic phase (Melgoza *et al*., 2000). When the biomass was acclimatized to the azo DR23, was evaluated the performance of the reactor and the concentration of the dye was increased of 25 to 200 mg/L of azo DR23 in the influent.

Thermal analysis

In order to make the evaluation of the energy consumption in the star-up of the SBR were installed 20 sensors in the experimental system as it is shown in the Figure 2. The sensors were connected to an adquisitor of data Agilent HP34970 with a personal computer. Measures of temperature were taken with the software HP-VEE 6.2 with programming directed to objects (Object Oriented Design OOD), with a calibration of sensors reported in a previous work (Romero *et al*., 2006). Each one of the sensors was associated to the thermal balances to determine the thermodynamic behavior of the SBR in the star-up and operation. The used energy balance contemplated a constant of heat capacity (Cp) with the value of 4.18 kJ/s°C and the characteristic flow of each bomb, multiplied by the difference of temperatures in each reading. Finally, it was evaluated the time that operated each bomb to obtain the quantity of energy consumed in each cycle. The determination of the lit time of the resistance that maintains the controlled temperature of the SBR the time of elevation of the registered temperatures was evaluated, obtaining as a result statistical the percentage of time in that it was lit the resistance.

The calculation of the energy that it used away based on the determination of the energy that entered to the system so that they could be carried out the anaerobic and aerobic phases in each cycle, it was not considered useful the energy that left the system since didn't contribute energy to the bombs and the heater-recirculator of water.



1,6 Bottom reactor (inside and outside)
2, 7 To 10 cm bottom reactor (inside and outside)
3,8, 20 To 20 cm bottom reactor (inside and outside)
4, 9 To 30 cm bottom reactor (inside and outside)
5, 10 To 50 cm bottom reactor (inside and outside)
11 Feed tank
12 Feed tank outlet
13 Reactor inlet
14 Water of recirculation outlet
15 Recirculation water inlet
16 Water unloaded
17 Unloading point
18 Water to jacket inlet
19 Water of the jacket outlet

Figure 2. Diagram of the SBR anaerobic/aerobic for the treatment of the DR23.

3. Results and discussion

Performance of the SBR anaerobic/aerobic

In the integrated biological processes the operation strategy is a very important factor because the acclimatization of the bacterial population to the dye and anaerobic/aerobic environmental induces the microorganisms to develop its metabolic activities in presence or oxygen absence. The reactor operated during 158 days (253 cycles). The concentration of DR23 fed in the influent was increased as it was adapted to each operation condition. The acclimatization of the SBR was achieved during the cycle 27 after 43 days of operation. The concentration initial was of 25 mg DR23/L, as it is observed in figure 3. The global removal of DR23 was stabilized to 85%. After the acclimatization, the concentration of DR23 was increased of 25 to 200 mg/L. The global removal efficiency of DR23 was from 91 to 97%, and the removal efficiency of color measured in units PtCo went from 92 to 98%. In works carried out by Tan *et al.,* (1999, 2001), in a reactor of expanded bed of sludge for the treatment of the dye mordent yellow 10 (MY10/L), for a concentration from 59 to 65 mg/L using ethanol as co-substrate, the removal efficiency of the MY10 was 100%.

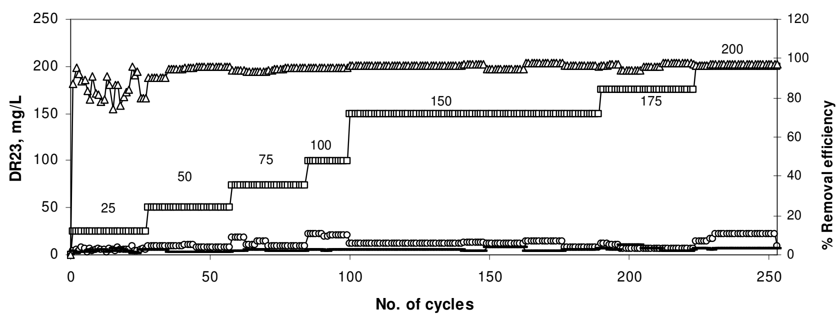


Figure 3. Performance of the SBR in the treatment of DR23. (■) Cycle start (●) Anaerobic phase end (-) Aerobic phase end (Δ) %Removal efficiency

A summary of the operation of the SBR is presented during the 253 cycles is shown in the table 1. The biggest efficiency in removal of DR23 was reached during the anaerobic phase what suggests that this acted like a phase of it roughdresses while the aerobic phase acted as polish of the wastewater, the above-mentioned suggests that the treatment of azo dyes in a single tank allows that the aerobic phase serves as polish of the anaerobic effluent, that in most of the cases it doesn't eliminate the present compounds, but rather it transforms them in even more toxic metabolites that those of the influent.

Table 1. Performance of the SBR in the treatment of the DR23

Operation	Cycles	Time of reaction anaerobic/aerobic	Si	So	S_{ANA}	S_{AER}	Anaerobic removal efficiency	Aerobic removal efficiency	Global removal efficiency
days		h	mg/L	mg/L	mg/L	mg/L	%	%	%
43	1-27	48/24	24	19	5	4	79	20	83
18	28-57	8/4	50	47	9	3	82	67	94
14	58-84	8/4	75	73	12	4	84	67	95
8	85-99	8/4	100	96	21	5	79	76	95
45	100-189	8/4	150	148	11	5	93	55	97
17	190-223	8/4	175	173	7	6	96	14	97
15	224-253	8/4	200	197	20	6	90	70	97

The maximum biotransformation of the DR23 to amines was 3% and the mineralization of these was 80%. In works carried out by FitzGerald and Bishop (1995), in the treatment of the dye orange acid 10 (AO10) using an anaerobic reactor of fluidized bed for a concentration of 10 mg/L, the recovery of the amines was <1%, Likewise, in carried out works by Sarsour *et al*. (2001), in an anaerobic-aerobic coupled system for a concentration of 5000 mg/L of reactive red 198 (RR198), using starch as co-substrate, the amines recovery were from 2 to 3%. In this work, the time of reaction was optimized to 12 h (8 h anaerobic phase, 4 h aerobic phase). In general terms the redox potential during the experimental cycles was -299 mV in anaerobic phase and +105 mV in the aerobic phase. The reactor operated under reduction conditions in the anaerobic phase and oxidation conditions in the aerobic phase. These conditions are indispensable in this type of reactors that integrate anaerobic and aerobic environments.

During the experiment was not detected production of biogas only the presence of CO_2. The average total alkalinity was from 350 to 450 mg $CaCO_3$/L which was enough buffer capacity to neutralize the volatile fatty acids during the process to avoid the inhibition of the reactor for acidification. The average pH was 7.0 in the anaerobic phase and 8.0 in the aerobic phase

Energy consumption in the start–up of SBR

A cycle of operation of the SBR start-up with the activation of the feed pump (ALI) which stayed on during 7 min to temperature ambient. After of the load of the reactor the pump was switch off. The anaerobic phase and the recirculation of the residual water began by means of pump (REC) during 19.88 h. In the anaerobic phase energy was required to maintain the system to 30 ºC (heating recirculator). Once concluded the anaerobic phase the pump (REC) was switch off and the aeration pump was activated (AIR) for one period of 3.88 h (23.76 h of global operation). After the pump (AIR) was switch off and the pump discharge (DAR) was on during 7 minutes. The energy consumed was based on the calculation of the energy that entered for the phases anaerobic and aerobic in each cycle, did not consider the energy useful that loged-off since it did not contribute energy to the pumps and to the water heater-recirculation.

The energy consumption at the beginning of the cycle was of 15,54 kJ by load of the reactor, after were consumed 10,74 MJ by the anaerobic process. The aeration shown a relative low consumption of 48.88 kJ and finally was the unload was made with an identical consumption to that of the load of 15.54 kJ.

During the anaerobic and aerobic processes the temperature of the SBR was controlled to 30.0 °C by means of a recirculator-heater of water with a nominal power of 750 W operating for a cycle of 24 h. It is necessary to mention that the recirculator-heater of water was switch on and it switch off automatically by the controller of temperature shown periods of 14.37 % (on the average) of the time switch on and the rest of the time stayed out, therefore the energy consumption for each cycle of 24 h was of 9.32 MJ for 6 L of wastewater.

The analysis of the variation of the temperature indicated that it was contributed to the jacket of the system indeed, a total amount of 1,8 MJ in the process of 24 h, with a pumping of 0,05 kg/s of water for heating, reason why the rest of the energy dissipated in heat form to the environment. The profile of temperature in a cycle of operation of the SBR is shown in Figure 4.

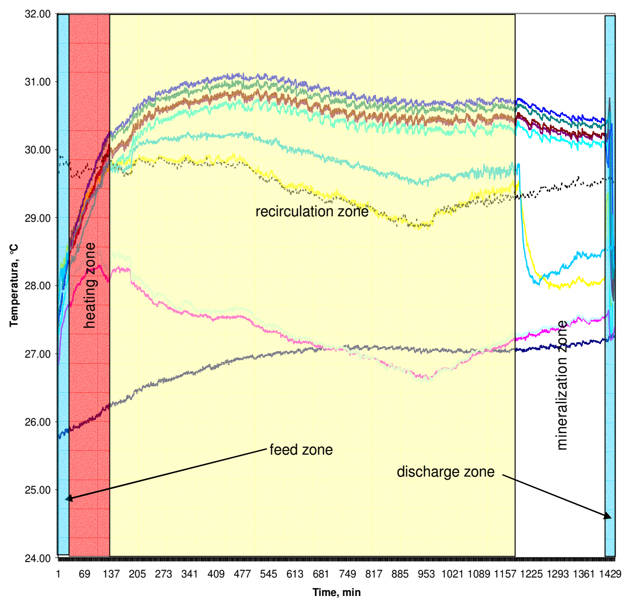


Figure 4. Temperature profiles for once cycle into the start up

4. Conclusions

It was carried out the mineralization and the energy consumption of the DR23 in a sequencing batch reactor of expanded bed, at pilot level, integrating anaerobic/aerobic environmental, alternating reductive and oxidative phases. In the reductive phase the biotransformation of the DR23 was reached and in the oxidative phases the mineralization of the amines to CO_2, H_2O and NO_3 was also investigated.

The acclimatization period was of 43 days (27cycles) with a concentration of 25 mg DR23/L with a constant temperature of 30 °C (+ / - 1).. The concentrations studied were from 25 to 200 mg DR23/L. The reaction times were diminished from 72 h (48 h phase anaerobia, 24 h aerobic phase) to 12 h (8 h anaerobic phase, 4 h aerobic phase). The global removal efficiencies of DR23 were from 91 to 97%, the biotransformation of amines was of 3% and the mineralization of these was of 80%.

The total of energy consumed in this process was of 544 MJ, for a volume of 6 L. The analysis of the variation of the temperature indicated that it was contributed indeed to the jacket of the system, a total amount of 1,8 MJ in the process of 24 h, with a pumping of 0,05 kg/s of water for heating, reason why the rest of the energy dissipated in heat form to the environmental.

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