

Effect of Activated Carbon on the Biodegradability of Direct Azo Dyes in a Sequential Batch Reactor under Anaerobic/aerobic Environments

¹Rosa María Melgoza–Alemán, ²Fernanda Morales-Guzmán

¹Faculty of Chemical Sciences and Engineering/Center of Research on Engineering and Applied Sciences, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001. Col. Chamilpa C.P. 62209. Cuernavaca, Morelos, México.

²Graduate studies on Engineering and Applied Sciences, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001. Col. Chamilpa C.P. 62209, Cuernavaca, Morelos, México.

Abstract: The effect of the addition of granular activated carbon (GAC) in the treatment of Direct Red azo dye 23 (DR23 C.I. 29160) by means of an anaerobic/aerobic bioprocess integrated in a single sequential batch reactor (SBR) was evaluated. Two reactors with suspended biomass were used: one added with GAC (R_1) and another without GAC (R_2), as control reactor, both operated alternating non-aeration and aeration phases to set anaerobic and aerobic conditions respectively. The efficiency of the process was evaluated by means of the reduction dye in the anaerobic phase. The by-products reduced were identified as total aromatic amines (TAAs). After of the anaerobic phase the reactors were aerated for the oxidation of by-product reduced until their degradation in the aerobic phase. The elimination of dye was made through microorganisms and not as a result of adsorption in the GAC as was determinate in the experiments of adsorption. The dye concentrations used went from 25 to 100 mg L⁻¹. In R_1 reactor the overall degradation efficiency of the dye was 90% while in R_2 reactor was 63%. The elimination of by-products as TAA was 100% in R_1 and 60% in R_2 .

Key words: anaerobic/aerobic process, DR23 azo dye, total aromatic amines, granular activated carbon, Redox mediator

INTRODUCTION

The textile processes generate large volumes of wastewaters that contain great variety of recalcitrant compounds mainly azo dyes that are characterized by a double linkage between two nitrogen atoms ($R_1-N=N-R_2$). The azo dyes since the environmental point of view are synthetic organic compounds difficult to degrade due to their high stability to the environmental conditions (Kirk and Othmer, 1993). Azo dyes represent the largest class of dyes applied in textile industry constituting 60-70% of all dyestuffs produced (Carliell *et al.*, 1995). Color in the effluent is one of the most important indicators of water pollution and the discharge of effluents highly colored are aesthetically displeasing and can damage the receiving water body by impeding penetration of light (Khehra *et al.*, 2006). Moreover, some azo dyes as well as their breakdown products are cytotoxic, carcinogenic and mutagenic compounds (Pinheiro *et al.*, 2004). Among the azo dyes family, the direct dyes are relatively large molecules with high affinity to the cellulose fibers, through Van der Waals forces. Most has one or more azo bonds or ftalocianine-, stilbene or oxazine-type compounds. Direct dyes are the second larger class of dyes with almost 1600 dyes, but only about 30% are currently produced (van der Zee, *et al.*, 2003). The Direct Red azo dye 23 (DR23 C.I. 29160) (C.I., 1992) was selected for study because it is not quickly biodegraded and is one of the most used dyes in the textile industry. It is used to dye cotton, linen and rayon fibers, it is stable to light, easily absorbed in the water and its degree of fixation in the fiber goes from 70 to 95% (O'Neill *et al.*, 1999).

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, the decolorization of azo dye by microorganism occurs by reductive cleavage of azo bond under anaerobic conditions (Tan *et al.*, 1999, 2001; Kalyuzhnyl and Sklyar, 2000; Harmer and Bishop, 1992; Jiang and Bishop, 1994; Gottlieb

Corresponding Author: Rosa María Melgoza–Alemán, Faculty of Chemical Sciences and Engineering/Center of Research on Engineering and Applied Sciences, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001. Col. Chamilpa C.P. 62209. Cuernavaca, Morelos, México.
E-mail: rmelgoza@uaem.mx

et al., 2003). This step leads the decolorization of dye but it generates by-products as aromatic amines that are not degraded under anaerobic conditions and tend to accumulate to toxic levels. However 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.*, 2000; O'Neill *et al.*, 1999; Melgoza *et al.*, 2004). This can be a method for the complete removal of azo dyes of the wastewaters and their by-products. In the reduction of azo dyes, the reaction rate can be improved by using redox mediator compounds of quinone type or enzymatic cofactors as flavin-adenin *dinucleotid* (FAD) that accelerates reaction rate by the transport of equivalent reducers between the electrodonor and electroacceptor compounds (Keck *et al.*, 1997). In works carried out by van der Zee *et al.*, (2003), they concluded that the use of a continuous dose of anthraquinone at catalytic concentrations highly increased the reduction efficiencies of azo dyes. They recommended that the redox mediator is immobilized, for example, in granular activated carbon (GAC) because it shows several active groups in its surface, including quinone structures.

The objective of this research was to evaluate the effect of activated carbon on the biodegradability of azo dye DR23 and evaluate the roll of the adsorption in the elimination of azo dye, to determine which system shows better removal efficiencies, and reduction rates. The production of total aromatic amines (TAAs) in the anaerobic phase and their degradation in the aerobic phase of the process were also evaluated.

MATERIALS AND METHODS

2.1. Dye and Granular Activated Carbon:

Direct Red azo dye 23 was obtained from Sigma-Aldrich and used without further purification (Fig.1). The granular activated carbon (Filtrisorb 200) used in the experiment has the following characteristics: effective size 0.8–1.0 mm, surface area of 1000 m^2/g and apparent density of 0.43 g/ml . All chemical compounds used were reagent grade.

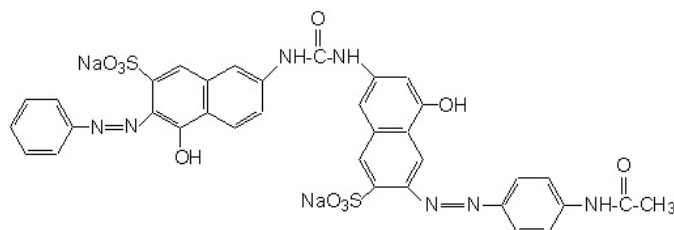


Fig. 1: Chemical structure of direct red azo dye 23 (DR23 C.I. 29160)

2.2. Experimental Determination of Adsorption Isotherm of DR23:

The DR23 adsorption in GAC was determined by the standard method D 3860-89 (ASTM, 1990). Different doses of activated carbon (adsorbent) were placed in contact with a solution of 100 mg L^{-1} of DR23 (adsorbate) for 24 hours. The concentration of adsorbate was determined after equilibrium by the equation 1. The equilibrium concentration was determined by spectrophotometry at a maximum wavelength (λ_{max}) of 501 nm.

$$q_e = (C_0 - C_e) V/m \quad (1)$$

Where q_e is the concentration of adsorbate after equilibrium, mg g^{-1} ; C_0 is the initial concentration of adsorbate, mg L^{-1} ; C_e is the final equilibrium concentration of adsorbate after adsorption, mg L^{-1} ; m is the mass of adsorbent, g; V is the Volume, L.

Experimental data were fitted to models mathematical Freundlich (2) and Langmuir (3) (Metcalf & Eddy, 2003) .

Freundlich

$$(q_e) = K_f C_e^{1/n} \quad (2)$$

Where q_e y C_e are explained above, K_f and $1/n$ are constants of Freundlich equation. K_f is the Freundlich adsorption capacity factor, $(\text{mg.g}^{-1}) (\text{L.mg}^{-1})^{1/n}$ and $1/n$ is the Freundlich intensity parameter.

Langmuir

$$q_e = q_{\max} \frac{bC_e}{1 + bC_e} \quad (3)$$

Where q_e is adsorption capacity (mg g^{-1}), C_e is the equilibrium concentration (mg L^{-1}); q_{\max} is maximum adsorption capacity (mg g^{-1}) and b the parameter equation (L mg^{-1}).

2.3. Characteristics of Substrate, Biomass and Operation Conditions:

Reactors were inoculated with a mix of aerobic activated sludge from two treatment plants, one of municipal wastewater and the other of industrial wastewater, in a ratio of 50 / 50. The initial concentration of biomass in each reactor was $4,200 \text{ mg L}^{-1}$. Synthetic wastewater was prepared with 25 mg L^{-1} of DR23 and 15 mg L^{-1} of CH_3COOH as co-substrate, used as source of carbon and electrons to complete the reduction reactions, in molar ratio 1:8 (DR23: CH_3COOH) and nutritious mineral medium with the following composition (expressed in mg L^{-1}). $65.25 \text{ K}_2\text{HPO}_4$, $100.2 \text{ Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$, $25.5 \text{ KH}_2\text{PO}_4$, $7.5 \text{ NH}_4\text{Cl}$, $22.5 \text{ MgSO}_4 \cdot 7\text{H}_2\text{O}$, $27.5 \text{ CaCl}_2 \cdot 2\text{H}_2\text{O}$, $0.25 \text{ FeCl}_3 \cdot 6\text{H}_2\text{O}$, $0.06 \text{ H}_3\text{BO}_3$, $0.04 \text{ MnSO}_4 \cdot \text{H}_2\text{O}$, $0.04 \text{ ZnSO}_4 \cdot 7\text{H}_2\text{O}$, $0.03 (\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ and 0.1 EDTA . For the acclimatization of biomass to DR23 and to changes from anaerobic/aerobic environments in both reactors, the strategy of constant efficiencies was used. This strategy consisted in allowing the adaptation of the biomass for the time needed to reach 80% reduction of DR23 as minimum in the anaerobic phase and after during the aerobic phase to reach 80% of elimination of TAAs (Melgoza *et al.*, 2000).

2.4 Experimental System:

Two cylindrical reactors of 34 cm high and 12 cm diameter were used, with a total volume of 2 L, operated as sequential batch reactors (SBR) as shown in Fig. 2. The R_1 reactor was operated with 200 g of GAC in a ratio of 30% of the volume. The reactor R_2 was operated with suspended biomass as a blank reactor. Reactors were controlled by means of three peristaltic pumps of variable rate (Master Flex, Cole-Parmer, Model 72200-62) and an aeration pump (Model Elite 802) connected to a programmable timer (Chrontronic Model XT) for the monitoring of the load, recirculation, discharge and aeration respectively. During the aerobic phase, the air was spread from the bottom of reactor through a porous diffuser. The temperature of the reactor was controlled at $30 \pm 1^\circ\text{C}$, by means of a water re-circulating-heating system (Poly Science Model 210). pH and oxide-reduction potential (ORP) electrodes were installed in the reactor

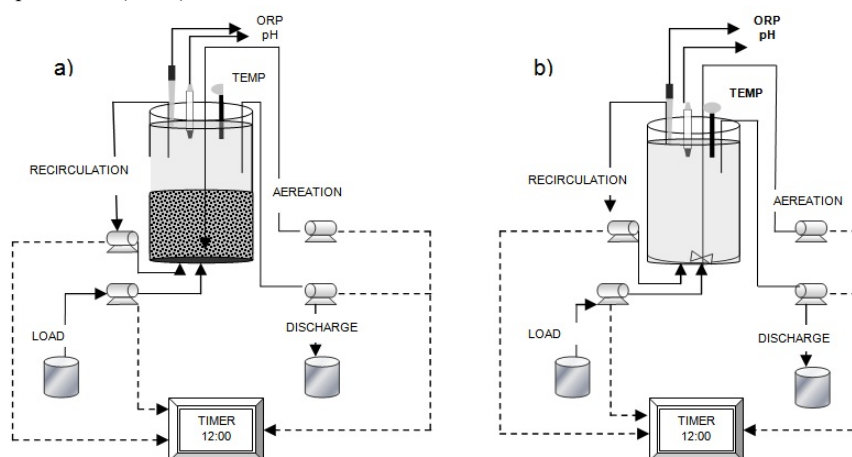


Fig. 2: Experimental System of SBR's for azo dye DR23 treatment

- a) Reactor with suspended biomass plus GAC (R_1)
- b) Reactor with suspended biomass without GAC (R_2)

2.5. Analytical Methods:

pH and ORP parameters were determined using a potentiometer (Model Thermo Orion 720A+). Total alkalinity as CaCO_3 was determined by volumetry; oxygen dissolved was determined by the electrometric method (APHA, 2005). The determination of dye DR23 was carried out at the wavelength of 501 nm in a spectrophotometer Perkin Elmer UV-VIS (Lambda 25); the TAAs were determined at 440 nm, according to the spectrophotometric method of p-dimethylamino-benzaldehyde (Oren *et al.*, 1991).

RESULTS AND DISCUSSION

3.1. Adsorption of DR23 in GAC:

The determination of the adsorption capacity of DR23 in GAC was carried out to assure that the elimination of dye was made by a biodegradation process and not by adsorption. The experimental data were analyzed according to the linear form of the Freundlich isotherm (equation 4) and Langmuir isotherm (equation 5) and are shown in the Fig. 3 (a) and (b)

$$\text{Log } q_e = 1/n \text{ log } C_e + \text{log } K \quad (4)$$

$$C_e/q_e = 1/b q_{\text{max}} + C_e/q_{\text{max}} \quad (5)$$

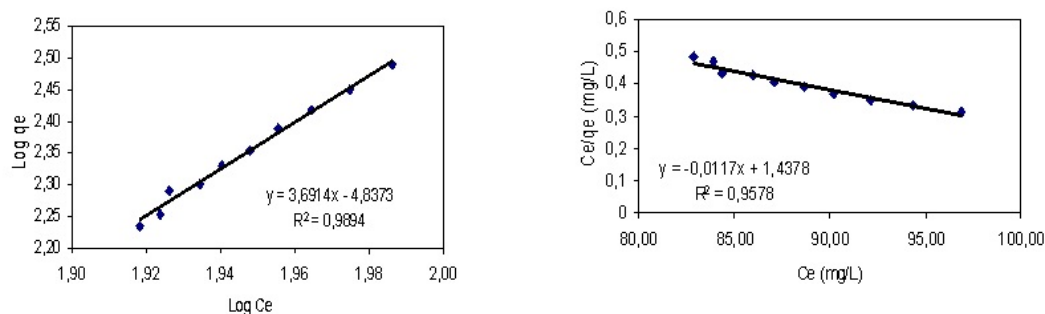


Fig. 3: RD23 adsorption in CAG. (a) Linear form of Freundlich equation. Freundlich equation: $x/m = K_f C_e^{1/n}$ $1/n = 1,454E-5 C_e^{1,86}$
(b) Linear form of Langmuir equation

Adsorption data obeyed both Freundlich and Langmuir models, exhibiting heterogeneous surface conditions and monolayer adsorption (Lee *et al.*, 1999). Model Freundlich is best fits to the experimental data, according the correlation coefficient shown for the linear equation Freundlich, $r^2 = 0.9894$. The values determined for the experimental constants were: $K_f = 1.454E-5 \text{ mg g}^{-1}$ suggests an adsorption capacity non beneficial and an intensity factor $n = 1.86$. It has been shown by McKay *et al.* (1982) that an n value between 2 and 10 indicates beneficial adsorption, so the results showed an adsorption capacity of GAC very low, only $0.08 \pm .002 \text{ mg dye per g of GAC}$. The adsorption capacity obtained in this experiment is in agreement with the results reported in the literature that indicates the direct dyes are easily dissolved in water and are hardly adsorbed in adsorbents as activated carbon (Slokar and Majcen, 1997; Cheremisinoff and Morresi, 1978). The results of adsorption indicated that only 0.08% of RD23 azo dye was adsorbed in GAC.

3.2. Acclimatization of Biomass:

The anaerobic/aerobic process integrated in a reactor has as purpose to acclimate the biomass to changes in anaerobic environment (redox potential values -250 mv minimum and absence of oxygen) to aerobic environment (redox potential values positive and 2 mg L^{-1} oxygen) in order to induce bacterial population with facultative features that support environmental change.

Reactors were inoculated with activated sludge not adapted to DR23 degradation. The acclimatization of biomass was made through the operation strategy of constants elimination efficiencies allowing the adaptation of biomass to changes of anaerobic and aerobic environments and to the degradation of dye in 80% as minimum. The biomass underwent a period of acclimatization including a phase of bacterial selection using acetate as co-substrate to provide electrons for DR23 reduction and as a source of carbon and energy for the growth and maintenance of the bacterial population. The initial feeding in both reactors was 25 mg L^{-1} of DR23. The acclimatization in R_1 was reached at day 44, with reduction efficiency of 80%. In R_2 after day 82 the reduction efficiency average was 42%. The 80% established in the operation strategy was not obtained. It suggest that the dye reduction was not reached was because the system did not have the equivalent reducers (H^+) necessary to perform electron transfer from the co-substrate to the azo dye while in R_1 the role of GAC was to enhance the reduction of dye due to GAC catalysis as was substantiated by van der Zee *et al.*, (2003).

3.3. Performance of Reactors:

Both reactors were operated for 82 days with a concentration of 25 mgL⁻¹. Fig. 4 shows the performance of the reactors. After in R₁ the concentration of dye was increased to 50 mg L⁻¹ and to 100 mg L⁻¹ because the reactor was acclimated and support increased dye. In R₂ the dye removal efficiency decreased to about 42% due to increased of dye. During anaerobic phase in R₁ reduction efficiencies were of 84 and 90% and the reduction rate of DR23 increased from 2.74 to 5.14 mg L⁻¹ h⁻¹ and was possible the recovery of by-products measure as TAAs in a 8% of the stoichiometry based on dye reduction. Subsequently in the aerobic phase of the process the TAAs were eliminated to 100% by oxidation.

The activated carbon contains quinone groups in its surface that act as redox mediator (Boehm, 1994), allowing the transfer of electrons between the donor (co-substrate) and the acceptor (dye). In the anaerobic phase this effect was observed since the reduction rate of dye increased twice as much than in R₂ where only co-substrate was added. This effect was also observed by van der Zee *et al.*, (2003) who researched the relevance of the activated carbon as redox mediator suggest that microorganism in anaerobic phase transfer electrons from substrate oxidation to electron accepting groups on activated carbon. The limiting stage of the process was the anaerobic reduction phase if an optimal reduction of DR23 is not made, the biotransformation to TAAs is not reached. After in the aerobic, phase the degradation of TAAs was reached, both phases complementing the total elimination of DR23.

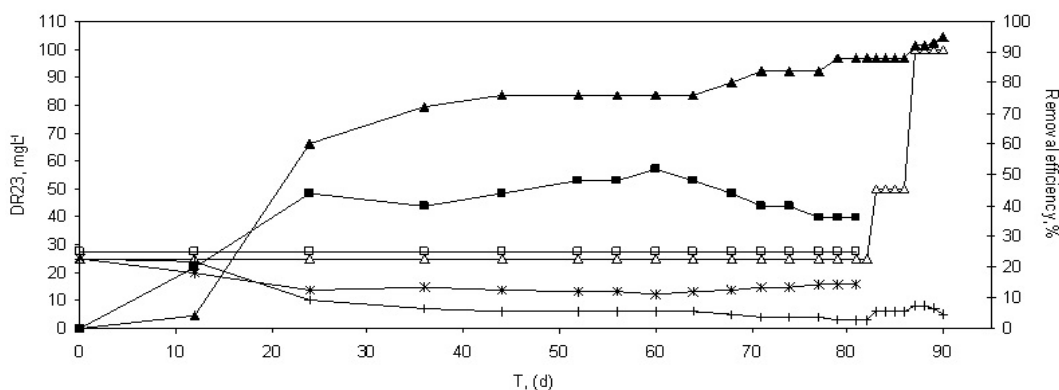


Fig. 4: Performance of reactors during the DR23 treatment

(Δ) R₁: DR23 start cycle, (+) R1: DR23 end cycle, (\blacktriangle) R1: Removal efficiency
(\square) R₂: DR23 start cycle, (\times) R₂: DR23 end cycle, (\blacksquare) R₂: Removal efficiency

The anaerobic/aerobic process integrated in a single sequential batch reactor offers the advantage that the purge of the system is not required due to the population dynamics that keeps the equilibrium of the bacterial consortium in the biofilm formed, causing a low production of sludge. This behavior was also observed in works carried out by Sirianuntapiboon *et al.*, (2007) in the treatment of textile wastewater in a sequential batch reactor; Buitrón *et al.*, (2006), van Haandel and Marais (1999), and von Sperling *et al.*, (2001) in anaerobic/aerobic processes for municipal water treatment.

Concerning control parameters, average ORP in R₁ was -298 mV in the anaerobic phase and +114 mV in the aerobic phase; the dissolved oxygen remained at 5.6 mg L⁻¹ in average. These results assured reduction and oxidation conditions in the system that are essential in this type of reactors that integrate anaerobic and aerobic environments (Kudlich *et al.*, 1997; Rau *et al.*, 2002).

3.4. Reaction Kinetic:

Reduction kinetic of DR23 was carried out in the anaerobic phase. The reduction rate maximal of DR23 (q_r) in R₁ was 5.14 mg L⁻¹ h⁻¹. In this work the addition of GAC as redox mediator in R₁ favored the reduction phase of the dye, increasing the reduction rate 12 times plus that R₂. Removal of the dye studied corresponds to a kinetic model first order. Dos Santos *et al.* (2004) used anthraquinone-2,6-disulfonate, anthraquinone-2-sulfonate and Riboflavine as redox mediators to evaluate their effect over the reduction rate of the dyes Reactive Red 2, acid Orange 7 and mordant Yellow 10 in laboratory tests and observed that using redox mediators the reduction rate increased 8 times. Sirianuntapiboon and Sansak (2008) treated textile wastewater that contained DR23 by means of a GAC-SBR system. The concentration they evaluated was 40 mg L⁻¹ and obtained removal efficiencies of 94-97% in a HRT of 180 h, this time was 2.5 times more elevated than the HRT obtained in this work.

4. Conclusions:

The treatment of azo dye DR23 in anaerobic/aerobic bioprocess integrated in a single sequential batch reactor (SBR) and granular activated carbon was more efficient for the elimination of DR23 and aromatic amines generated from its reduction. The activated carbon acted as redox mediator to enhanced azo dye reduction favoring the reduction rate of the dye 12 times faster than without GAC. The maximum reduction rate was 5.14 mg L⁻¹ h⁻¹. The dye removal was made by microorganisms and not by adsorption in the activated carbon. The adsorption capacity of DR23 in the activated carbon was low 0.08 mg g⁻¹. The cycle time duration was optimized from 288 h to 72 h. The overall average elimination efficiencies of DR23 were of 90%. In the anaerobic phase, the recovery of total aromatic amines was 8% these were eliminated 100% in the aerobic phase. To contrast the effectiveness of the treatment proposed in this work, further studies are required in batch systems at a larger scale.

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