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EFFECT OF FERROMAGNETIC NANOPARTICLE ON DYES BIODEGRADATION

BY

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Abstract. In this study the biodecolourisation of two dyes, a xanthene dye, Erythrosine B (Ery B) and an azo dye, Reactive Red 51 (RR120), was investigated colourdecolourisation under batch anaerobic conditions by using non - acclimated anaerobic granular sludge. The effect of ferromagnetic nanoparticle (FN) (as adsorbent or mediator) on dyes removal was experienced.

Key words: anaerobic biodegradation, ferromagnetic nanoparticle, xanthenes dyes, azodyes

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1. Introduction

Dyes are widely used in the textile, paper, cosmetics, food and pharmaceutical industries. Synthetic dyes presented in wastewater institute serious environmental problems in the aquatic system when improperly disposed. Research in the dyeing wastewater bioremediation technologies has received high attention. Anaerobic techniques are an efficient alternative for colour removal from wastewater because the dyes themselves are generally resistant to oxidative biodegradation (Pavko, 2011). Mixed cultures (i.e. granular sludge) are capable of decolourizing dyed solutions. Several studies show that, in that types of processes, little biodegradation actually occurs and that the primary mechanism is adsorption to the microbial biomass (Robinson et al, 2001; Karapanagiati et al., 2001) which may pose an additional problem. Furthermore, in anaerobic systems, the rate of the reaction may be rather low, which may poses a serious problem for the application of high-rate anaerobic bioreactors for the treatment of dyeing wastewater, because long hydraulic retention time is necessary to reach a satisfactory extent of dye reduction. . Using redox mediators, usually exemplified by soluble quinones, higher reductive efficiency can be achieved (Van der Zee and Cervantes, 2009, Pereira et al., 2011). Recently, nanoparticles technology have received intense attention because their particular physical properties for utilisation in catalytic reactions (Creamer et al., 2008). Magnetic nanoparticles are particularly useful support materials for catalysts as they can combine the advantages of high dispersion through a liquid with ease of recovery (Laurent et al., 2008). Recent research is moving towards applications of nano- and micro-sized particles, such as zero valent iron, in azo dye bioremediation (Lin et al., 2008; Fan et al., 2009). Nanomaterials used as adsorbents are one of the best candidates for dye removal due to their large surface areas, especially those with magnetic properties by using magnetic nanoparticles or by magnetization of non-magnetic materials, introduced by addition of magnetic nanoparticles. The adsorption behaviour of carbon nanotubes-iron oxides magnetic composite has been investigated for the removal of cationic dyes (Gong et al., 2009) from water. In the present study, the effect of ferromagnetic nanoparticles (FN), both as adsorbent or mediator on dye bioremoval, was investigated under batch anaerobic conditions by using non - acclimated anaerobic granular sludge. Two dyes from different classes were tested, colourdecolourisation xanthene, Erythrosine B and an azo dye, Reactive Red 51., and the effect of.

2. Experimental

2.1. Materials

Dyes

The two dyes used in this study, the xanthenes Erythrosine B (Ery B, C.I. Acid Red 51, 45430) and the azo Reactive Red 120 (RR 120) were purchased from Sigma–Aldrich at the highest purity available, 95% and 50-70 % purity, respectively. The chemical structures of the dyes are illustrated in Figure 1. Stock solutions of 14 mM were prepared in deionised water, without any further purification, from which dilutions were done in order to obtain the desired concentration..

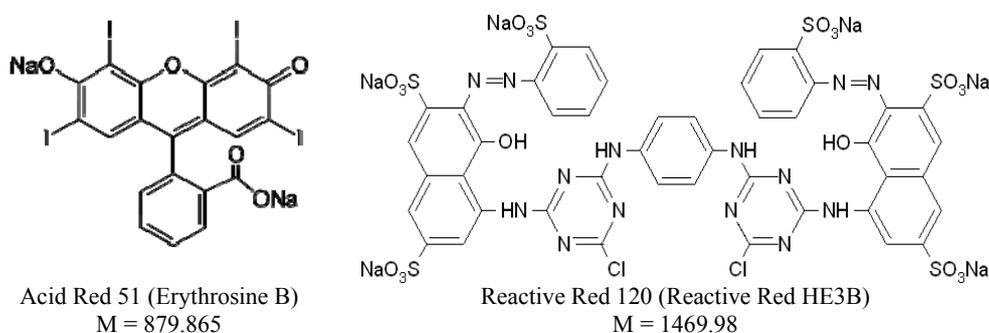


Fig. 1 – Chemical structures of the dyes tested

Granular anaerobic biomass

Non – acclimated anaerobic granular sludge was collected from wastewater treatment plant of “Central de Cervejas,” Vialonga, Portugal. The granular sludge was washed gently to reduce the inorganic mineral contents, prior to the experimental use. The volatile suspended solids content of the biomass was determined as 1.6 g L⁻¹.

Ferromagnetic nanoparticles preparation

Fe₃O₄ magnetic nanoparticles (FP) were synthesized according to the protocol described by Berger et al. (1999). The principle is to prepare the metal particles by co-precipitation by mixing Fe(II) and Fe(III) salts together in a basic solution (NH₃). Ferromagnetic particles size was obtained by Dynamic Light Scattering (DLS), 10 9 nm.

2.2. Methods

Biological dye reduction

For the anaerobic biological dye decolourisation, batch assays were performed in 120 mL serum bottles with butyl rubber stopper, containing 50 mL of medium and an overlying headspace composed of N₂ : CO₂ (80% : 20%). The medium containing the biomass, the substrate and macronutrients was buffered at a pH of 7 ± 0.2 with NaHCO₃ (2.5 g L⁻¹). The headspace of the serum bottles was flushed with the N₂ : CO₂ (80%: 20%) and pre-incubation of the sludge was done for 1 day at 37°C, in a rotary shaker at 120 rpm. As macronutrients, 2.8 g L⁻¹ NH₄Cl, 2.5 g L⁻¹ KH₂PO₄, 1 g L⁻¹ MgSO₄·7H₂O and 0.06 g L⁻¹ CaCl₂ were added. Volatile fatty acids (VFAs: acetic, propionic and butyric acid, 1:10:10) (2 g COD L⁻¹) were used as substrate, representing the electron source for the reduction.

After the pre-incubation period, the dyes were added with a syringe from the stock solution to a final desiderate concentration. The serum bottles were further incubated at 37°C in a rotary shaker at 120 rpm, during the entire decolourisation experiment.

The effect of ferromagnetic nanoparticules (0.1 g L⁻¹ and 1 g L⁻¹), prepared as described below, was tested. All the experiments were prepared in triplicate.

Analysis

Color decrease was monitored spectrophotometrically in a 96- well plate reader (ELISA BIO-TEK, Izasa). At select intervals, samples were withdrawn (300 μL), centrifuged at 1500 rpm for 10 min to remove the biomass and the FP and diluted, with the same buffer as of the reaction, to obtain less than 1 absorbance unit (AU), due to the high absorbance of the dyes, even at low concentrations. The visible spectra (300–900 nm) were recorded and dyes concentrations calculated at λ_{max}. Molar extinction coefficients were calculated for each dye at λ_{max}: ε_{524nm} = 67282 M⁻¹ cm⁻¹ for Erythrosine B; ε_{510nm} = 49.34 M⁻¹ cm⁻¹ for RR120.

Colour removal ratio was determined according to eq. 1:

$$R(\%) = \frac{A_0 - A_t}{A_0} * 100 \quad (1)$$

where: A₀, is the light absorbance for λ_{max} at the beginning of incubation and A_t, the light absorbance of dyes at λ_{max} at a selected time (t).

First-order reduction rate constants were calculated in OriginPro 6.1 software, applying the eq. 2:

$$C_t = C_o + C_i e^{-kt} \quad (2)$$

where: C_t is the concentration at time t; C_o, the offset; C_i, the concentration at initial time; k, the first-order rate constant (h⁻¹) and t is the accumulated time of the experiment.

3. Results and Discussions

3.1. Anaerobic dyes biodegradation

In order to test the capacity of anaerobic granular sludge for two different class of dyes biodegradation, the azo dye Reactive Red 120 and xanthene dye Erythrosine B were tested as model. The decolourisation followed a first-order rate and increase of the rate with increase of dye concentration was obtained reaching the maximum with 0.4 mM Ery B and 0.6 mM RR120, above which, inhibition occurred (Fig. 2). Comparing the maximal rates, the xanthene dye was decolourised at a ~ 6-fold higher rate, but higher degrees were obtained with the azo dye, 20 and 80 %, respectively.

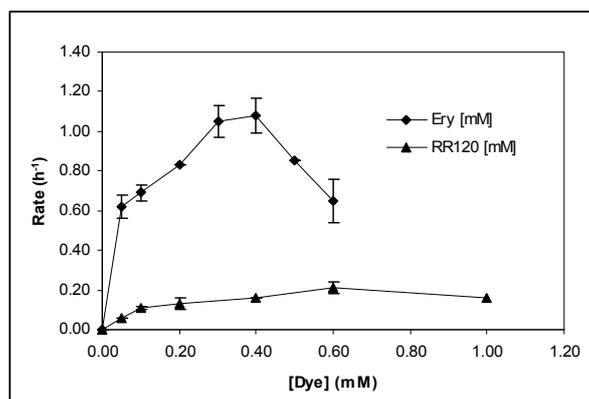


Fig. 2 – Kinetics of Ery B and RR120 decolourisation with anaerobic granular biomass

3.2. Ferromagnetic nanoparticle

Table 1 gives the percentages and first order rates of Erythrosine B and Reactive Red 120 biological decolourisation in the presence of ferromagnetic nanoparticles (FN).

For the xanthene Ery, using low concentration of FP lead to a ~ 2-fold rate increase, though the same level of colour removal. When the amount of FP was increased, lower decolourisation was obtained (almost half) and the rate decrease from 0.98 ± 1.10 to $0.73 \pm 0.37 \text{ h}^{-1}$. This result propose inhibition by the presence of high quantity of FP. Oppositely, in the case of the azo dye, RR120, the presence of FP at low concentration lead to a ~ 2-fold decrease of the decolourisation rate, despite the same level of decolourisation. When FP were present at higher amount, 1 g L^{-1} , both the degree and rate of dye removal were negatively affected, with a decrease from $75 \pm 1 \%$ and $0.21 \pm 0.03 \text{ h}^{-1}$ in

the absence, to $52 \pm 5 \%$ and $0.08 \pm 0.10 \text{ h}^{-1}$, in the presence of 1 g L^{-1} FP. Controls without biomass were also conducted in order to evaluate the effect of FN on colour removal by adsorption. Colour removal in these conditions was obtained only with 1 g L^{-1} of particles ($34 \pm 4 \%$, and 2% for Ery B and RR120, respectively).

As we can see in Fig. 3, the degree of dyes decolourisation is very similar in the assay with biomass and biomass with FN, but in the presence of ferromagnetic nanoparticle the percentage decreased with 30 - 50 %. The presence of 1 g L^{-1} of ferromagnetic nanoparticle inhibits the biomass activity. The results suggest that the FP have the capacity to increase the electron transfer to the dye, increasing the rate of reduction, but some inhibitory effect may also be presented, justifying the lower degrees.

Table 1
Effect of ferromagnetic nanoparticle on Erythrosine B and Reactive Red 120 biodegradation

Dye	Experimental conditions	Decolourisation (%)	Rate (h^{-1})
<i>Ery B</i> ($C_i=0.3 \text{ mM}$)	Biomass	36 ± 5	0.45 ± 0.3
	Biomass + (0.1 g L^{-1}) FP	31 ± 1	0.98 ± 1.10
	Biomass + (1 g L^{-1}) FP	13 ± 4	0.73 ± 0.37
<i>RR120</i> ($C_i=1 \text{ mM}$)	Biomass	75 ± 1	0.21 ± 0.03
	Biomass + (0.1 g L^{-1}) FP	79 ± 3	0.12 ± 0.6
	Biomass + (1 g L^{-1}) FP	52 ± 5	0.08 ± 0.1

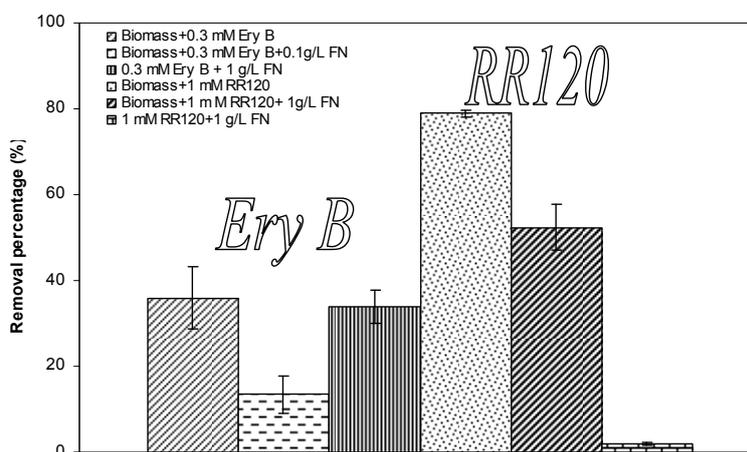


Fig. 3 – Percentages of Ery B and RR120 decolourisation with anaerobic granular biomass and in the presence of 1 g L^{-1} of FP

4. Conclusions

Despite the higher decolourisation rates obtained for the xanthenes dye, circa 6-fold higher, the anaerobic treatment was more effective on the removal of an azo dye, RR 120, 80 % as compared with the 20 % obtained for Ery. (~rates with xanthene Ery B). Substrate inhibition kinetics occurred for both dyes at dye concentrations of 0.4 mM Ery B and 0.6 mM for RR 120.

Biological decolourisation was affected by the presence of ferromagnetic nanoparticles. The use of lower amount of FP, 0.1 g L⁻¹, led only to an increase of the rate ~ 2-fold, though the little increase of decolourisation. The efficiency of Ery colour removal decreased to half with 1 g L⁻¹ FP, although the higher rate obtained (0.45 ± 0.3 and 0.73 ± 0.37 h⁻¹, respectively). Oppositely, for RR120 both the degree and rate decreased. (Adsorption onto FP was observed only at higher catalyst concentration and for the xanthenes dye. The results suggest biomass inhibition at high FP concentrations.

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