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Thermal modification of activated carbon surface chemistry improves its capacity as redox mediator for azo dye reduction

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ABSTRACT

The surface chemistry of a commercial AC (AC_0) was selectively modified, without changing significantly its textural properties, by chemical oxidation with HNO_3 (AC_{HNO_3}) and O_2 (AC_{O_2}), and thermal treatments under H_2 (AC_{H_2}) or N_2 (AC_{N_2}) flow. The effect of modified AC on anaerobic chemical dye reduction was assayed with sulphide at different pH values 5, 7 and 9. Four dyes were tested: Acid Orange 7, Reactive Red 2, Mordant Yellow 10 and Direct Blue 71. Batch experiments with low amounts of AC (0.1 g L^{-1}) demonstrated an increase of the first-order reduction rate constants, up to 9-fold, as compared with assays without AC. Optimum rates were obtained at pH 5 except for MY10, higher at pH 7. In general, rates increased with increasing the pH of point zero charge (pH_{pzc}), following the trend $AC_{HNO_3} < AC_{O_2} < AC_0 < AC_{N_2} < AC_{H_2}$. The highest reduction rate was obtained for MY10 with AC_{H_2} at pH 7, which corresponded to the double, as compared with non-modified AC. In a biological system using granular biomass, AC_{H_2} also duplicated and increase 4.5-fold the decolourisation rates of MY10 and RR2, respectively. In this last experiment, reaction rate was independent of AC concentration in the tested range 0.1–0.6 g L^{-1}.

1. Introduction

Azo groups are the most common chromophore in acid, direct and dispersive dyes and are also frequently used as components in reactive dyes. Their industrial applications include the use as textiles dyes, leather, colouring agents in food and in pharmaceuticals, cosmetics and paper. Their environmental impact either as pollutants or carcinogens is of major concern [1]. As very small amounts of synthetic dyes in water (10–15 mg L^{-1}) are highly visible, they also have an undesirable aesthetic impact. Dye removal from wastewater with traditional physicochemical processes, such as coagulation, adsorption and oxidation with ozone is expensive, can generate large volumes of sludge and usually require the addition of environmental hazardous chemical additives [2]. Azo dyes are generally persistent under aerobic conditions because oxygen is a more efficient electron acceptor, therefore having more preference for electrons than azo dyes [3]. Under anaerobic conditions most azo dyes are reduced, although the rate of the reaction may be rather low, especially for dyes with high polarity or complicated structure, such as some sulphonated reactive azo dyes. This poses a serious problem for the application of high-rate anaerobic bioreactors for the treatment of dying wastewater, because long hydraulic retention time is necessary to reach a satisfactory extent of dye reduction. Enzyme cofactors like FAD are known as effective redox mediators for azo dye reduction [4]. Moreover, addition of compounds, usually exemplified by soluble quinone compounds, has also been proved to significantly accelerate the rate of azo dye reduction by favouring electron transfer from primary electron donor (co-substrate) to terminal electron acceptor (azo dye). Among them, anthraquinonedisulphonate (AQDS) and anthraquinone-2-sulphonate (AQS), as model quinonoid compounds, have received the greatest attention [5,6]. Using these redox mediators, higher reductive efficiency can be achieved in anaerobic bioreactors, operated at hydraulic retention time realistic for wastewater treatment practice [6,7,9]. However, the main problem limiting their application in anaerobic bioreactors is that continuous dosing implies continuous expenses of mediator as well as continuous discharge of this kind of biologically recalcitrant compound. Activated carbon (AC) has been shown as a feasible redox mediator [10,11]. An important advantage in comparison with soluble redox mediators is that it can be retained within the sludge bed. Furthermore, its amphoteric character enables to manifest reactivity for many organic and inorganic pollutants. Adsorption on AC has also been proved to be efficient in removing colour and organic matter from highly

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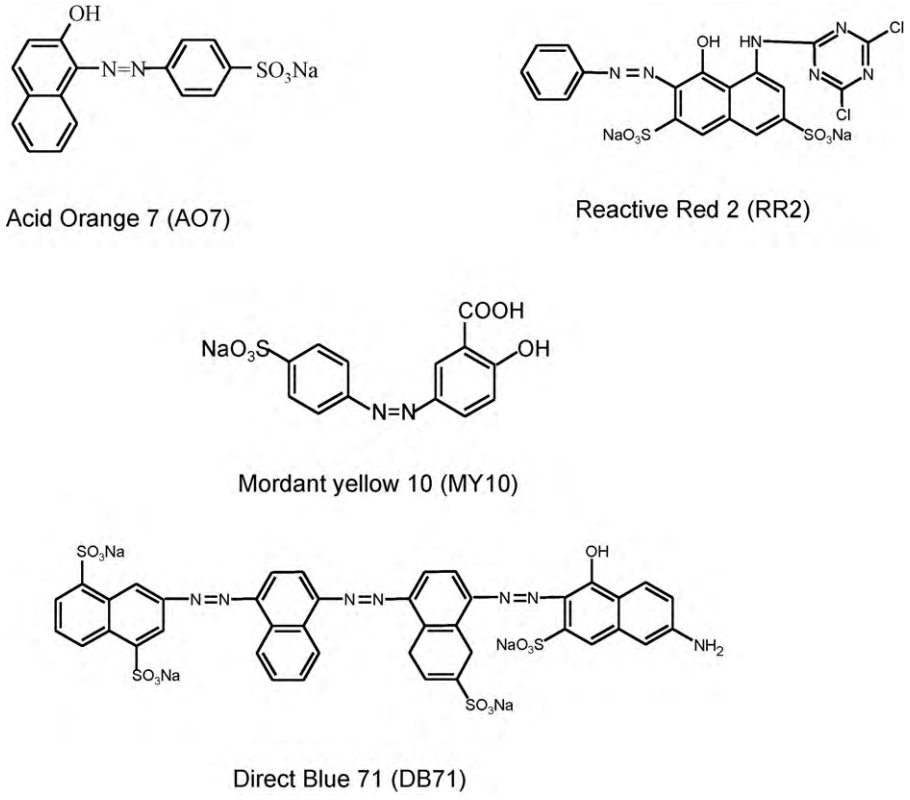

Fig. 1. Molecular structure of the azo dyes.

coloured effluents [12–16]. Some publications outline the use of AC as a catalyst in chemical reactions: oxidative dehydrogenation of ethylbenzene [16], NO and N_2O reduction [18,19], reduction of 2,4,6-trinitrotoluene [20] and decomposition of methane [21]. Other advantage of AC is that it can be modified physically and chemically, in order to optimise its performance. The effect of AC chemical surface on dye adsorption was previously studied [12,22,23], and very recently Mezohegyi et al. [24] found that decolourisation rates, in upflow stirred packed-bed reactors, were significantly influenced by the textural properties of AC and moderately affected by its surface chemistry. However, these authors performed experiments in reactors with working volumes of 2 mL and 500 g AC L^{-1}, which is too far from potential applicability.

In the present work, the redox mediating capacity of AC samples with different chemical superficial groups was explored in batch assays for the reduction of four azo dyes (acid, direct, mordant and reactive), at different pH values. Since sulphate is a common pollutant present in textile wastewater being biologically reduced to sulphide, during anaerobic treatment and sulphide has been reported to be an azo dye reducing agent [25,26], sulphide was initially elected as chemical reducing agent. This choice was also based on its suitability to limit the system variability. AC samples were obtained by chemical/thermal treatments of a commercial AC. Biological assays were performed in the best conditions obtained by the chemical dye reduction studies. Activated carbon was mixed with anaerobic granular sludge at final concentrations in the range of 0.1–0.6 g L^{-1}.

2. Experimental

2.1. Dyes

Reactive Red 2 (RR2, dye content 40%), Acid Orange 7 (AO7, dye content 85%), Mordant Yellow 10 (MY10, dye content 85%) and Direct Blue 71 (DB71, dye content 50%), were selected as azo dye model compounds. The chemical structures of the dyes are illustrated in Fig. 1. Dyes were purchased from Sigma and used without additional purification. Stock solutions of 14 mM were prepared in deionised water. RR2 was hydrolysed under alkaline conditions (pH 12 adjusted with 1 M NaOH) by boiling the solution for 1 h; after that period, solution was cooled down, pH was settled to 7 with 1 M HCl and final volume adjusted with deionised water.

2.2. Preparation of activated carbon samples

A Norit ROX 0.8 activated carbon (pellets of 0.8 mm diameter and 5 mm length) was used as supplied by Norit as a starting material (sample AC_0). In order to prepare AC with different chemical composition on the surface, maintaining the original textural properties as much as possible, different treatments were performed according to those previously described by Pereira et al. [12], as following: (i) chemical oxidation of AC_0 with 6 M of HNO_3 at boiling temperature for 3 h (sample AC_{HNO_3}) and (ii) starting from AC_{HNO_3}, 1 h of thermal treatment under N_2 flow at 900 °C (sample AC_{N_2}) or H_2 flow at 700 °C (sample AC_{H_2}). Gas oxidation of AC_0 with 5% O_2 at 425 °C for 6 h was made in order to prepare the sample AC_{O_2}; in this case, some burning of the sample occurred (12.5%) which will result in alteration of the textural properties [26].

2.3. Textural characterisation of activated carbons

The textural characterisation of the materials was based on N_2 adsorption isotherms, determined at 77 K with a Coulter Omnisorp 100 CX apparatus. The BET surface area (S_{BET}) was calculated using the BET equation. The micropore volume (W_{micro}) and mesopore surface area (S_{meso}) were calculated by the *t*-method, using the standard isotherms for carbon materials proposed by Rodriguez-Reinoso et al. [28]. The adsorption data were also analysed with the

Dubinin equation. In all cases, a type IV deviation was noted [29]. Two microporous structures were taken into account, and the corresponding volumes, W_{01} (smaller pores) and W_{02} (larger pores), were calculated [29]. The Stoeckli equation [30] was used to estimate the average micropore width of the smaller pores (L_1), using a value of 0.34 for the affinity coefficient of nitrogen.

2.4. Surface chemistry characterisation of activated carbons

Activated carbon samples have amphoteric behaviour and in general the more acidic samples are the less basic ones. Acidity and basicity are related with the chemical groups at the AC surface; the surface chemistry of AC samples was characterised by the estimation of material acidity and basicity, the pH of point zero charge (pH_{pzc}) and CO/CO_2 release by temperature-programmed desorption (TPD) as described by Figueiredo et al. [27,31]. Briefly:

(i) The CO_2 spectrum was decomposed into three contributions, corresponding to carboxylic acids (low temperatures), carboxylic anhydrides (intermediate temperatures) and lactones (high temperatures).
(ii) The carboxylic anhydrides decompose by releasing one CO and one CO_2 molecule. Thus, a peak of the same shape and equal magnitude to that found on the CO_2 spectrum was included in CO spectrum. This peak was pre-defined from the deconvolution of the CO_2 spectrum.
(iii) In addition to the carboxylic anhydrides, the CO spectrum includes contributions from phenols (intermediate temperatures) and carbonyl/quinones (high temperatures).

The pH_{pzc} is a critical value for determining quantitatively the net charge (positive or negative) carried on the AC surface as a function of the solution pH. Its determination was carried out as follows: 50 cm^3 of 0.01 M NaCl solution was placed in a closed Erlenmeyer flask. The pH was adjusted to a value between 2 and 12 with the solutions 0.1 M HCl or 0.1 M NaOH. Then, 0.15 g of each AC sample was added and the final pH measured after 48 h under agitation at room temperature. The pH_{pzc} is the point where the curve pH_{final} vs. $pH_{initial}$ crosses the line $pH_{initial} = pH_{final}$.

2.5. Chemical dye reduction

Batch experiments were conducted in order to evaluate the capacity of the synthesised AC samples as a redox mediator on the reduction of different azo dyes by sulphide. Buffered solutions at different pH values, 20 mM of sodium acetate for pH 5.0 and 60 mM sodium bicarbonate for pH 7.0 and 8.7, were prepared. AC pellets were crushed to obtain particles with different size. A preliminary screening showed that the size of AC particles significantly affects their role as a redox mediator for dye reduction by sulphide. An increase of the rate of decolourisation was obtained with decreasing the AC size. Therefore, all the experiments were conducted with AC particles with a diameter less than 0.315 mm. The flasks, containing different samples of activated carbon (0.1 g L^{-1}) and buffer, were sealed with butyl rubber stoppers and flushed for 5 min with oxygen-free N_2 gas for pH 5.0 and 8.7 and with N_2:CO_2 (80:20%) for pH 7.0. After flushing, sulphide was added with a syringe from a partially neutralised stock solution (0.1 M Na_2S) to obtain an initial total sulphide concentration of 1 mM for azo and 2 mM for trisazo dyes. According to the stoichiometry of dye reduction by sulphide, 2 moles of sulphide are required per mole of azo dye when sulphide is oxidised to elemental sulphur [10]. Controls without sulphide were incorporated to correct for dye adsorption, as well as to verify the stability of the dyes. The vials were pre-incubated (over night) in a 37 °C rotary shaker at 135 rpm. After that time, 0.3 mM of dye was added with a syringe (1 mL) to the reaction solution, from a concentrated stock (14 mM). All the experiments were prepared in triplicate. First-order reduction rate constants were calculated in OriginPro 6.1 software, applying the equation $C_t = C_o + C_i e^{-kt}$, where C_t is the concentration at time t; C_o, the offset; C_i, the concentration at time initial time; k, the first-order rate constant (d^{-1}) and t is the accumulated time of the experiment.

2.6. Biological dye reduction

Biological assays using anaerobic granular biomass (1 g VSS L^{-1}) were performed in batch. The best conditions from the chemical dye reduction were reproduced: sodium bicarbonate solution at pH 7 containing 0.3 mM of MY10 and 0.1 g L^{-1} of AC_{H_2}. As controls, assays without AC and with AC_0 were also run. Co-substrates are required as an electron source for the reduction; different carbon sources were tested (2 g L^{-1}): glucose, lactose, and volatile fatty acids (VFAs): acetic, propionic and butyric acid, 1:10:10. As macronutrients, 2.8 g L^{-1} NH_4Cl, 2.5 g L^{-1} KH_2PO_4, 1 g L^{-1} $MgSO_4{\cdot}7H_2O$ and 0.057 g L^{-1} CaCl, were added. All the assays were performed in triplicate. The effect of AC concentration was evaluated by testing increasing amounts of untreated (AC_0) and treated AC (AC_{H_2}) ranging from 0.1 g L^{-1} to 0.6 g L^{-1}.

2.7. Analytical techniques

Colour decrease was monitored spectrophotometricaly 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 AC and diluted, with the same buffer as of the reaction, due to the high absorbance of the dye, even at low concentrations. The visible spectra (300–900 nm) were recorded and dye concentration calculated at λ_{max}. Molar extinction coefficients were calculated for each dye at λ_{max}: $\varepsilon_{480\,nm} = 9600\ M^{-1}\ cm^{-1}$ for AO7; $\varepsilon_{540\,nm} = 28{,}637\ M^{-1}\ cm^{-1}$ for RR2; $\varepsilon_{350\,nm} = 15{,}519\ M^{-1}\ cm^{-1}$ for MY10 and $\varepsilon_{590\,nm} = 76{,}716\ M^{-1}\ cm^{-1}$ for DB71. No changes were observed in the visible spectra with the pH of the solution.

3. Results and discussion

3.1. Textural characterisation

A set of modified AC samples were prepared by different methods in order to obtain materials with different surface chemical groups (acidic and basic) but maintaining their textural properties. The results of textural characterisation resulting from the N_2 equilibrium adsorption isotherms at 77 K are presented in Table 1. No

Table 1
Textural characterisation of the activated carbon samples.

Sample	S_{BET} ($m^2\ g^{-1}$) (±10)	W_{micro} ($cm^3\ g^{-1}$) (±0.005)	S_{meso} ($m^2\ g^{-1}$) (±5)	W_{01} ($cm^3\ g^{-1}$) (±0.005)	W_{02} ($cm^3\ g^{-1}$) (±0.005)	L_1 (nm) (±0.1)
AC_0	1032	0.382	138	0.350	0.038	1.0
AC_{HNO_3}	893	0.346	102	0.309	0.032	1.0
AC_{O_2}	1281	0.497	149	0.450	0.045	1.2
AC_{N_2}	947	0.359	90.5	0.340	0.023	1.1
AC_{H_2}	987	0.377	129	0.334	0.039	1.1

Table 2
Chemical characterisation of the activated carbon samples.

Sample	CO[a] (μmol g^{-1}) (±20)	CO_2[a] (μmol g^{-1}) (±20)	Basicity (mequiv. HCl g^{-1}) (±0.005)	Acidity (mequiv. NaOH g^{-1}) (±0.005)	pH_{pzc} (±0.2)
AC_0	814	243	0.457	0.370	8.4
AC_{HNO_3}	2402	1103	−0.065	1.720	2.7
AC_{O_2}	4105	239	n.d.	n.d.	4.5
AC_{N_2}	890	120	0.547	0.432	9.2
AC_{H_2}	590	59	0.640	0.086	10.8

n.d., not determined.
[a] Amounts release in TPD experiments.

major changes were observed in the textural properties of AC for the liquid phase oxidations and thermal treatments, as expected. However, a slight decrease occurred in the surface area and pore volume for the oxidation with HNO_3. These changes may result from the collapse of some of the pore walls caused from the drastic conditions of the treatment. On the other hand, sample prepared by O_2 oxidation presents an increase of the micropore volume and average micropore width. This effect is directly related with the burn-off (BO) degree [26]. Consequently, an additional contribution of the textural properties of AC on its behaviour as a catalyst on dye reduction may be expected for the last material. For the other AC samples, the behaviour may be attributed mainly to differences on the chemical surface properties produced by different treatments (see below).

3.2. Surface chemistry characterisation

Table 2 summarises the results obtained from the chemical characterisation of AC samples used in this study. Surface oxygen groups on carbon materials decompose upon heating, releasing CO and/or CO_2 at different temperatures. According to this, it is possible to identify and estimate the amount of oxygenated groups on a given carbon by TPD experiments. Table 3 shows the amount of each type of oxygen-containing surface groups estimated from the deconvolution of the TPD spectra (Fig. 2) following the method previously proposed [26,30]. The highest amount of carboxylic groups was generated by the oxidation with HNO_3, which presents a value almost 7 times higher than those generated with other treatments. Although to a lesser degree, this sample also presents the highest amount of anhydrides and lactones groups. These acidic groups are responsible for the high acidity and the lower pH_{pzc} value obtained. In fact, the basicity and acidity of the samples are related with the chemical groups at the surface, thus complementing the results obtained from TPD experiments. Higher CO_2 release was obtained for more acidic samples, AC_{HNO_3} (pH_{pzc} of 2.7) and AC_{O_2} (pH_{pzc} of 4.5) which indicates that liquid and gas oxidation produce samples with a higher amount of surface oxygen-containing groups. The gas oxidation treatment (AC_{O_2}) was the most effective to introduce phenols and carbonyl/quinone groups, being almost the double when compared with the nitric acid treatment. Thermal treatments at high temperature produce materials with low amount of oxygen-containing groups and high basicity, resulting mainly from the ketonic groups remaining on the surface, from the low amount of acidic groups, and from the delocalised π-electrons of the carbon

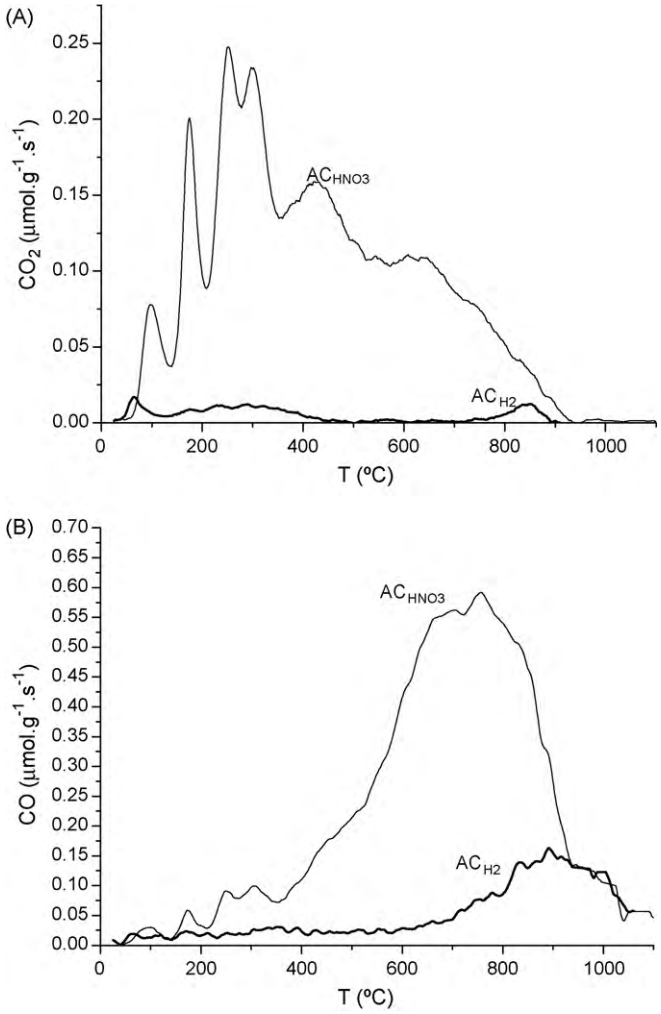

Fig. 2. TPD spectra before and after different treatments: (A) CO_2 evolution and (B) CO evolution. Examples for AC_{HNO_3} and AC_{H_2}.

basal planes. These electrons are responsible for the high basicity of the thermal treated samples. The acidic oxygen-surface groups have a withdrawal character fixing those π-electrons [32]. Comparing the two thermal treatments, with H_2 more basic materials

Table 3
Oxygen-containing surface groups estimated from the TPD spectra deconvolution (±10%).

Sample	Carboxylic acids (μmol g^{-1})	Anhydrides (μmol g^{-1})	Lactones (μmol g^{-1})	Phenols (μmol g^{-1})	Carbonyl/quinones (μmol g^{-1})
AC_0	110	79	54	428	307
AC_{HNO_3}	723	222	158	948	1232
AC_{O_2}	0	90	149	1321	2694
AC_{N_2}	67	15	38	307	568
AC_{H_2}	48	0	11	249	341

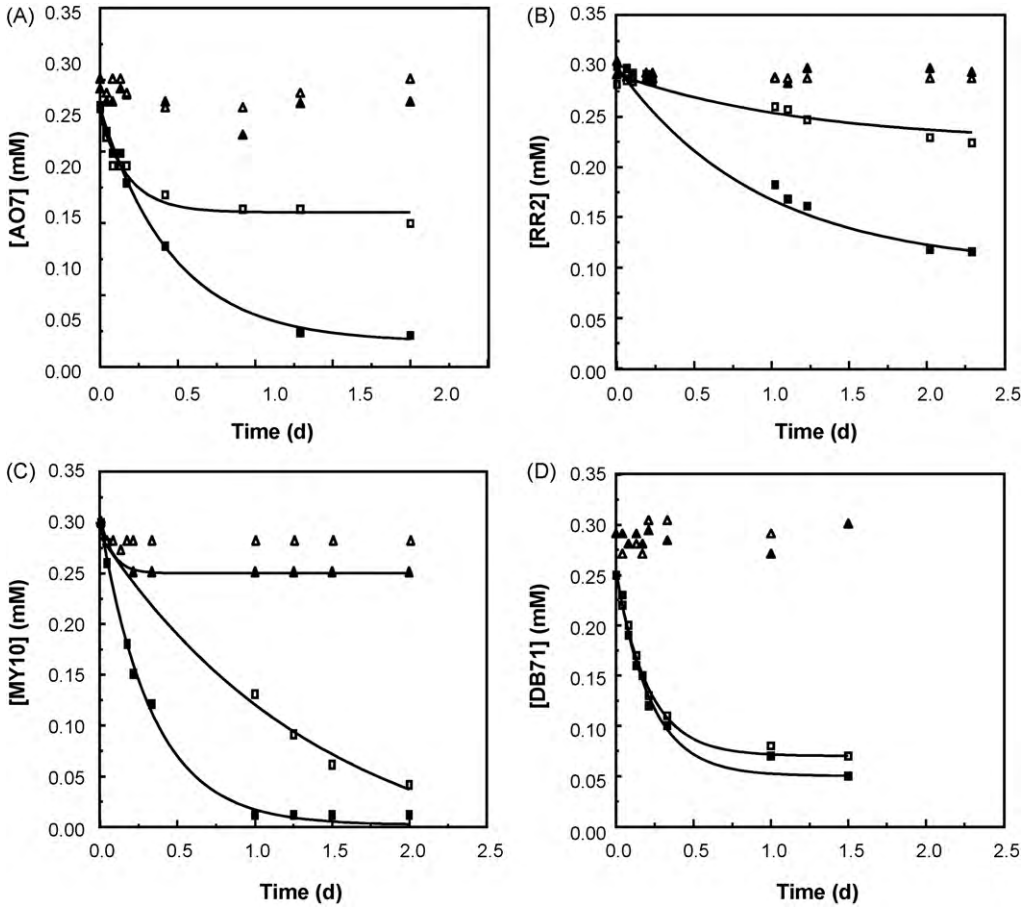

Fig. 3. Chemical azo dye decolourisation at pH 5, for the assays with dye alone (△), dye and AC_0 (▲), dye and Na_2S (□) and dye, Na_2S and AC_0 (■). (A) AO7; (B) RR2; (C) MY10; and (D) DB71.

are generated (pH_{pzc} of 10.8), since a stabilization of the reactive sites by C–H bonds occurs [12,32] and also an enhanced effect of the π-electron system. N_2 treatments leave unsaturated carbon atoms that are very reactive for subsequent oxygen adsorption, forming again some of the removed groups upon ambient air exposure. The pH_{pzc} of this sample is 9.2.

3.3. Azo dye reduction

Chemical azo dye reduction using sulphide was conducted under anaerobic conditions at pH values of 5.0, 7.0 and 8.7, both in presence and absence of AC_0 (Table 4). Different classes of dyes, acid (AO7), reactive (RR2), mordant (MY10) and direct (DB71), were tested. Decolourisation was followed spectrophotometricaly and a decrease in the intensity of the maximum absorption band was observed for all the dyes, indicating the cleavage of the aromatic azo groups (data not shown), generally related to the formation of lower molecular weight aromatic amines that may be more susceptive to degradation under biological aerobic conditions. The spectra of DB71 shifted from 590 to 550 nm and the solution changed from blue to light violet colour. All the reactions followed a first-order kinetic model (Fig. 3, example for pH 5) and the apparent rate constants and degrees of colour removal were calculated from the initial slope of the concentration vs. time data (Table 4). Undoubtedly, the pH of dye solution played an important role in the dye reduction. In the assays without AC, only DB71 was reduced at the three tested pH, but the rate was circa 3-fold higher at pH 5 ($4.4 \pm 0.6\ d^{-1}$). The mordant dye was decolourised only at pH 5 and 7, 1.1 ± 0.1 and $1.4 \pm 0.1\ d^{-1}$, respectively. AO7 and RR2 were the most resistant to the reduction by sulphide; very low rates were

Table 4
First-order rates (d^{-1}) of dye reduction by sulphide, calculated from the reaction at pH 5, 7 and 8.7, in the absence and presence of different AC samples.

Dye	pH	No AC	AC_{HNO_3}	AC_{O_2}	AC_0	AC_{N_2}	AC_{H_2}
AO7	5.0	0	2.2 ± 0.1	2.4 ± 0.2	2.6 ± 0.6	3.0 ± 0.3	3.4 ± 0.3
	7.0	0.2 ± 0.1	0.7 ± 0.1	0.6 ± 0.1	0.5 ± 0.1	0.8 ± 0.1	1.2 ± 0.1
	8.7	0	0.1 ± 0.1	0.2 ± 0.1	0.3 ± 0.1	1.1 ± 0.2	1.4 ± 0.2
RR2	5.0	0.9 ± 0.1	1.3 ± 0.1	1.2 ± 0.1	1.2 ± 0.1	1.3 ± 0.1	1.2 ± 0.1
	7.0	0	0.9 ± 0.1	1.1 ± 0.1	1.2 ± 0.1	1.2 ± 0.1	1.3 ± 0.1
	8.7	0	0.7 ± 0.1	0.9 ± 0.1	0.2 ± 0.1	0.9 ± 0.1	1.0 ± 0.1
MY10	5.0	1.1 ± 0.1	1.9 ± 0.3	3.8 ± 0.2	2.9 ± 0.2	4.3 ± 0.6	4.2 ± 0.4
	7.0	1.4 ± 0.1	2.8 ± 0.2	6.2 ± 1.1	5.9 ± 0.1	7.4 ± 0.7	12.1 ± 1.3
	8.7	0	2.3 ± 0.3	2.5 ± 0.7	0.9 ± 0.1	2.9 ± 0.1	4.0 ± 0.8
DB71	5.0	4.4 ± 0.6	4.9 ± 0.2	4.6 ± 0.1	4.9 ± 0.2	5.1 ± 0.2	5.6 ± 0.3
	7.0	1.7 ± 0.3	1.6 ± 0.2	1.6 ± 0.1	2.8 ± 0.4	2.9 ± 0.6	3.0 ± 0.1
	8.7	1.4 ± 0.1	3.3 ± 0.1	3.6 ± 0.1	3.2 ± 0.3	3.7 ± 0.2	4.8 ± 0.3

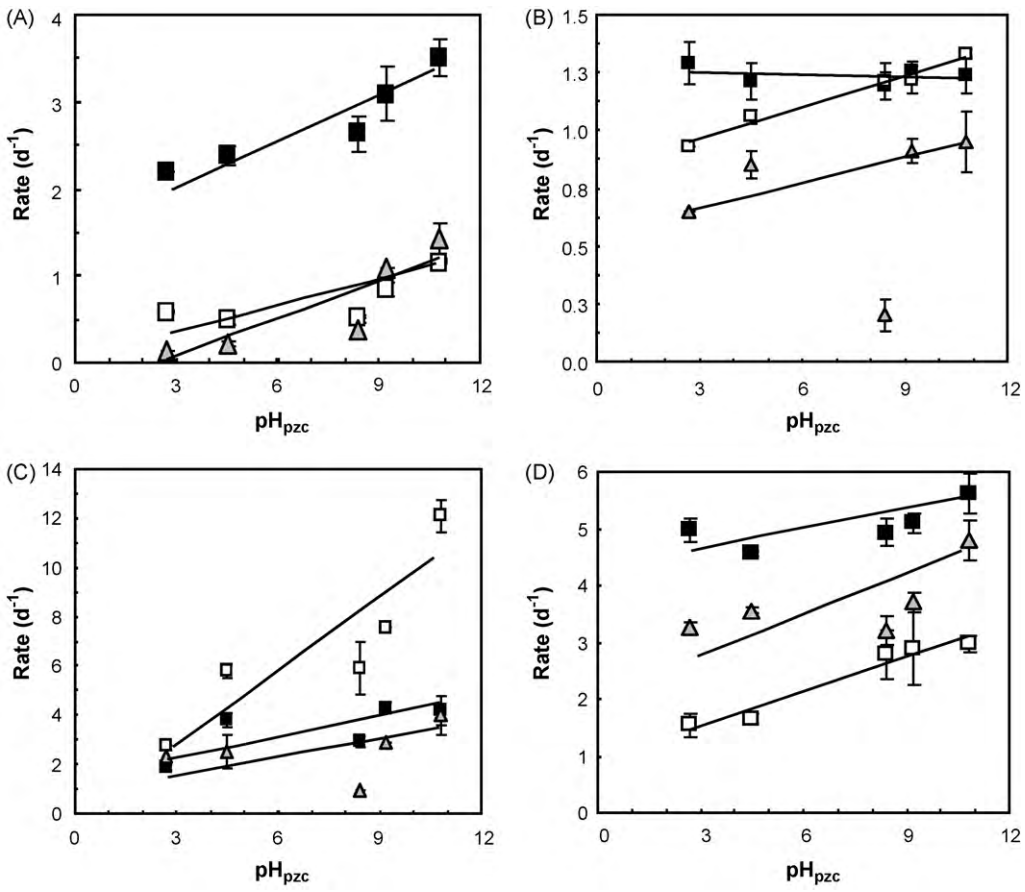

Fig. 4. First-order constant rates of dye reduction, calculated at different pH values, in function of the pH_{pzc} of the modified activated carbons. (■) pH 5; (□) pH 7 and (▲) pH 8.7. (A) AO7; (B) RR2; (C) MY10 and (D) DB71.

obtained: $0.2 \pm 0.1\ d^{-1}$ at pH 7, for AO7 and $0.9 \pm 0.1\ d^{-1}$ at pH 5, for RR2. The presence of AC in the reaction solution leads to an improvement of the reduction rates up to 5-fold for AO7, 4-fold for MY10 and 3-fold for DB71. Moreover, the presence of AC turned the decolourisation of all dyes possible at the three pH tested, with better results under acidic conditions, except for MY10, which was faster decolourised at pH 7 (Table 4). Contrary to the other dyes, for which worse values were calculated under alkaline conditions, no bigger differences were obtained for DB71 in the presence of AC_0 at pH 7 ($2.8 \pm 0.4\ d^{-1}$) and 8.7 ($3.2 \pm 0.3\ d^{-1}$). Activated carbon samples have amphoteric character and, as a result, their surfaces might be positively or negatively charged depending on the pH of the solution. Carbon surface becomes positively charged at pH < pH_{pzc} and negatively at pH > pH_{pzc}. Because the four tested dyes are anionic, adsorption and the transfer of electrons is more favourable when the carbon surface is positively charged. Negatively charged surface sites on the activated carbon might cause the electrostatic repulsion of the anionic dyes. Therefore, the worst performance at pH 8.7 is expected considering the pH_{pzc} of AC_0 of 8.4. Similarly, considering the pH_{pzc} of all the samples, higher rates at pH 5 than 7 and 8.7 would be expected with samples AC_{HNO_3} and AC_{O_2}, but not the bigger differences obtained with AC_{N_2} and AC_{H_2}; however, decolourisation varies also with other parameters such as the molecular structure, pK_a and potential redox of the dye, and those have also a dependence on the solution pH. Under optimum conditions, MY10 was almost completely decolourised; the degrees of decolourisation for the other dyes were lower, 80% for DB71 and 60% for AO7 and RR2. Colour removal due to adsorption on activated carbon occurs only for the smaller dyes and at low extent: ~25% for AO7 and 15% for MY10. Bigger molecules are more difficult to adsorb due to diffusion limitations. These data suggest that the major role of AC was to enhance the chemical reduction of dye, rather than dye adsorption; the low adsorption degrees are also explained by the little concentration of the catalyst in the solution and the high solubility of the used dyes. AC is the first electron acceptor, being chemically reduced by sulphide and secondly, the electrons from the reduced AC are transferred to the azo dye, the terminal electron acceptor. In previous experiments, chemical reduction of AO7 could also be accelerated by low amounts of AC [10]; with 0.5 mM of sulphide, AO7 removal of 80% was obtained within 5 days in the presence of AC and only 40% within 2 weeks in the absence. The amount of AC used was the same as in this study, resulting in similar AO7 adsorption, 22%. In experiments with higher AC concentration, the same reduction results were obtained, but the degree of adsorption increased. In the same study, it was demonstrated that the reduction of RR2 in a lab-scale bioreactor was largely enhanced by AC [10].

3.4. Effect of AC surface chemical groups on azo dye reduction

Activated carbon treatments are known to produce significant changes in carbon surface chemistry and these, in turn, can have dramatic effects on the behaviour as adsorbent [12,14,15] and as catalyst [17–21]. We investigated the influence of AC surface chemical groups on its behaviour as a redox mediator for dye reduction by sulphide. As pointed before, dye reduction is also dependent on the pH of the solution; thus the reaction was carried out at different pH values, in batch assays. The first-order rates are given in Table 4. A dependence of dye reduction on the type of AC can be observed, with higher rates for the reaction solutions containing

the most basic activated carbons (AC_{N_2} and AC_{H_2}). These AC are characterised by a high content of electron rich sites on their basal planes (electrons π) and by a low concentration of electron withdrawing groups. The electrons π are the responsible for the better performance as redox mediator, due to the high attainability by the dye. Mezohegyi et al. [24] have also postulated that delocalised π electrons seemed to play a role in the catalytic reduction in the absence of surface oxygen.

Fig. 4 represents the dye reduction rates as a function of the pH_{pzc} of AC. In general, rates increased with increasing the pH_{pzc}, following the trend $AC_{HNO_3} < AC_{O_2} < AC_0 < AC_{N_2} < AC_{H_2}$. This behaviour was less pronounced for RR2 reduction, with similar rates at all the conditions. Other deviations are the values for RR2 and MY10 reductions with AC_0 at pH 8.7, lower than the calculated with AC_{HNO_3} and AC_{O_2}. According to the previous sequence, MY10 reduction at pH 5 and 7 with AC_{O_2} is also higher than the expected; those results may be a consequence of the textural properties alteration due to the burn-off when treating this AC sample. The higher content of quinone groups present in AC_{HNO_3} and AC_{O_2} compared to AC_{N_2}, AC_{H_2} and the original AC would have promoted a higher decolourisation rates for the azo dyes studied considering that quinone groups have been proposed as the main electron-transferring groups in AC [10]. Nevertheless, the larger amount of oxygen-containing groups prevailing on the surface of AC_{HNO_3} and AC_{O_2}, compared to the other AC samples, also promotes a higher repulsion between the azo dyes and the surface of the these AC, which seems to be the main factor affecting the overall kinetics of the decolourisation process. As with AC_0, the adsorption obtained with modified AC samples was also low (maximal of 30% for AO7 and 18% for MY10 with AC_{H_2}). The low adsorption obtained is expected due to the small AC concentration used, therefore the total dye removal in the chemical assays is mostly due to their reduction. It is worth to mention that high AC concentration limits the process application, due to excessive costs. In their experiments, Mezohegyi et al. [24] have used 5000 times higher AC concentration than in our work. The effect of pH was also evident on the rates of dye reduction. Except for MY10, which was better degraded at neutral pH, higher rates were obtained at pH 5 with all type of activated carbons. Reactive dye reduction was less influenced by the type of AC and pH, since similar rates were obtained at all the conditions ($\sim 1\,d^{-1}$), apart from the strange low value with AC_0 at pH 8.7 ($0.2\,d^{-1}$). Comparing the four studied dyes, at the optimal conditions, better decolourisation was achieved in order of: MY10 > DB71 > AO7 > RR2. In fact, MY10 was completely reduced within 1 day, at a rate of $12 \pm 1.3\,d^{-1}$ with AC_{H_2}, being 2-fold, 4-fold and 9-fold higher than the obtained for the dyes DB71, AO7 and RR2, respectively. Its reduction was the largest improved by the presence of AC, with an increase of 9-fold as compared with the assay without AC. Decolourisation rates are also related with the electron density around the azo bond. Electro withdrawing groups such as –OH and $–NH_2$ decrease the electron density around the azo bond and facilitate its reduction. A similar effect in a simple reduction of the azo bond is observed for dyes carrying groups such as $–SO_3Na$ and –COOH [1]. NH group, on the other hand, are known to demote it [33]. MY10 and DB71 are richer in those first groups and RR2 have the secondary amine on is structure. Triazyl groups, also present in RR2, were found to give low dye reduction rates [25,26], explained by the reducing equivalents required for the reductive dechlorination, which may compete with the azo chromophore. Redox mediators are not only involved in the transfer of reducing equivalents, but also in minimizing the steric hindrance of the dye molecule [6].

3.5. Biological MY10 reduction

One of the limitations of biological dye decolourisation is the low rate of the process, which can be overcome by the use of redox mediators. The possibility of using AC as mediator in a biological system was investigated by conducting batch experiments with granular biomass. Different substrates were tested in the biological MY10 reduction, in the absence and presence of AC, and 4-fold higher rates were obtained with VFAs (data not shown). Our findings are in agreement with previous studies that investigated the role of various electron donors on the reduction of dyes, concluding that the rates vary with the type of substrate by stimulating specific microorganisms in a mixed culture [5,8,9]. Fig. 5A and B shows the results of biological MY10 reduction, with VFAs as substrate, in the absence and presence of unmodified (AC_0) and modified (AC_{H_2}) activated carbon. Contrarily to the obtained chemically, MY10 reduction rates in the absence and presence of AC_0 were the same, $10.2 \pm 1.4\,d^{-1}$ (Fig. 5B; Table 5). However, with the thermal treated AC (AC_{H_2}) the decolourisation rate duplicated ($19.4 \pm 0.2\,d^{-1}$). This result shows that, as observed in the chemical assays, AC surface chemistry plays a role in the biological dye decolourisation and that thermal modification of AC improves its capacity as redox mediator. Additionally, different AC amounts

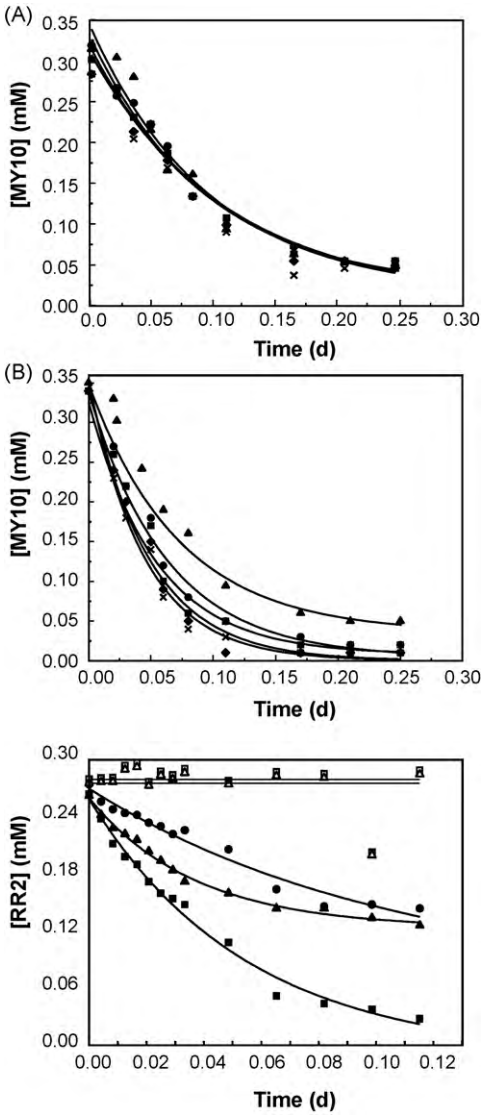

Fig. 5. Biological MY10 and RR2 dye reduction at pH 7 with VFAs as substrate. (A and B) MY10 decolourisation with increasing AC concentrations (AC_0 and AC_{H_2}, respectively): (▲) without AC; (●) $0.1\,g\,L^{-1}$; (■) $0.2\,g\,L^{-1}$; (♦) $0.4\,g\,L^{-1}$; (×) $0.6\,g\,L^{-1}$. (C) RR2 decolourisation with $0.1\,g\,L^{-1}$ of AC_0 (▲) and AC_{H_2} (■). Control without AC (●) and without biomass (Δ) AC_0 and (□) AC_{H_2}.

Table 5
First-order rates (d^{-1}) and degree of biological MY10 reduction in the presence of increasing unmodified (AC_0) and modified (AC_{H_2}) activated carbon concentrations.

AC sample	[AC] ($g\,L^{-1}$)	Rate (d^{-1})	Decolourisation (%)
No AC	0	10.2 ± 1.7	87 ± 1
AC_0	0.1	10.2 ± 1.4	86 ± 1
	0.2	9.9 ± 0.5	85 ± 1
	0.4	9.8 ± 2.2	83 ± 2
	0.6	11.3 ± 1.2	78 ± 1
AC_{H_2}	0.1	19.4 ± 0.2	87 ± 1
	0.2	18.7 ± 1.3	90 ± 1
	0.4	23.6 ± 3.8	88 ± 0
	0.6	19.6 ± 1.5	89 ± 1

were tested and it was found that increasing concentrations from 0.1 $g\,L^{-1}$ to 0.6 $g\,L^{-1}$ lead to an increase of the dye adsorption (from 10% to 65% not shown) but the reduction rates were similar with untreated and treated AC (Fig. 5A and B; Table 5). This finding is of great importance once activated carbon is costly and therefore the use of low amounts is an advantage for biological processes application.

Furthermore, as a redox mediator, AC is cycled from its oxidised and reduced states and thus should be very effect at low concentrations. Biological reduction of RR2 with untreated AC_0 and thermally treated AC_{H_2} was also studied. With this dye, previously found as a more recalcitrant one, untreated AC could increase 3-fold the rate of decolourisation (Fig. 5C). Once more, thermal treated AC reveals to be more effective, increasing 4.5-fold the dye reduction rate.

4. Conclusions

The results obtained in the present work demonstrate the catalytic effect, on azo dyes reduction rates, of activated carbon with different surface chemistry, obtained by chemical or thermal treatments. Dye reduction rates increased up to 9-fold using an AC concentration of 0.1 $g\,L^{-1}$, as compared with an assay not amended with AC. Amongst the four dyes tested, MY10, AO7, RR2 and DB71, better results were obtained at pH 5, except for MY10, with higher rates determined at pH 7. AC performance as a catalyst was, in this case, improved by surface modification, applying thermal treatments. In order to be an effective redox mediator for anionic dyes, the carbon should have a high pH_{pzc}. This means that at pH lower than pH_{pzc}, the carbon will be positively charged, favouring electrostatic attraction between the carbon and the anionic dyes tested. Reduction rates increased with the activated carbon basicity as following: $AC_{HNO_3} < AC_{O_2} < AC_0 < AC_{N_2} < AC_{H_2}$. Dye reduction rates in the presence of AC also varied among the different dyes. Higher rates were obtained in order of: MY10 > DB71 > AO7 > RR2. Dye reduction by sulphide in the absence of AC was very limited, since only DB71 was reduced at the three pH tested and MY10 at pH 5 and 7. AO7 and RR2 were more resistant to chemical reduction. We have also demonstrated that surface modified AC_{H_2} could duplicate and increased 4.5-fold the rates of MY10 and RR2 decolourisation, respectively, in a biological assay which was independent of the AC concentration in the tested range of 0.1–0.6 $g\,L^{-1}$. As AC can be retained in a reactor for prolonged time, it is an attractive alternative to soluble redox mediators in a biological reactor system. The low amount of AC used in this work and the positive results demonstrated for chemical and biological catalysis constitutes a significant breakthrough in the field of redox-mediated processes which will certainly open new perspectives for wastewater treatment processes of several xenobiotics.

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References

[1] H. Chen, Recent advances in azo dye degrading enzyme research, Curr. Protein Pept. Sci. 7 (2006) 101–111.
[2] T. Robinson, G. McMullan, R. Marchant, P. Nigam, Remediation of dyes in textile effluent on current treatment technologies with a proposed alternative, Bioresour. Technol. 77 (2001) 247–255.
[3] A. Stolz, Basic and applied aspects in the microbial degradation of azo dyes, Appl. Microbiol. Biotechnol. 56 (2001) 69–80.
[4] R. Russ, J. Rau, A. Stolz, The function of cytoplasmatic flavin reductases in the reduction of azo dyes by bacteria, Appl. Environ. Microbiol. 66 (2000) 1429–1434.
[5] A.B. dos Santos, F.J. Cervantes, R.E. Yaya-Beas, J.B. van Lier, Effect of redox mediator, AQDS, on the decolourisation of a reactive azo dye containing triazine group in a thermophilic anaerobic EGSB reactor, Enzyme Microb. Technol. 33 (2003) 942–951.
[6] A.B. dos Santos, I.A.E. Bisschops, F.J. Cervantes, J.B. van Lier, Effect of different redox mediators during thermophilic azo dye reduction by anaerobic granular sludge and comparative study between mesophilic (30 °C) and thermophilic (55 °C) treatments for decolourisation of textile wastewaters, Chemosphere 55 (2004) 1149–1157.
[7] F.J. Cervantes, F.P. Van der Zee, G. Lettinga, J.A. Field, Enhanced decolourisation of acid orange 7 in a continuous UASB reactor with quinines as redox mediators, Water. Sci. Technol. 44 (2001) 123–128.
[8] F.P. Van der Zee, R.H.M. Bouwman, D.P.B.T.B. Strik, G. Lettinga, J.A. Field, Application of redox mediators to accelerate the transformation of reactive azo dyes in anaerobic bioreactors, Biotechnol. Bioeng. 75 (2001) 691–701.
[9] F.P. Van der Zee, F.J. Cervantes, Impact and application of electron shuttles on the redox (bio)transformation of contaminants: a review, Biotechnol. Adv. 27 (2009) 256–277.
[10] F.P. Van der Zee, I.A. Bisschops, G. Lettinga, J.A. Field, Activated carbon as an electron acceptor and redox mediator during the anaerobic biotransformation of azo dyes, Environ. Sci. Technol. 37 (2003) 402–408.
[11] G. Mezohegyi, A. Kolodkin, U.I. Castro, C. Bengoa, F. Stuber, J. Font, A. Fabregat, Effective anaerobic decolorization of azo dye acid orange 7 in continuous upflow packed-bed reactor using biological activated carbon system, Ind. Eng. Chem. Res. 46 (2007) 6788–6792.
[12] M.F.R. Pereira, S.F. Soares, J.J.M. Órfão, J.L. Figueiredo, A desorption of dyes on activated carbons: influence of surface chemical groups, Carbon 41 (2003) 811–821.
[13] P.K. Malik, Dye removal from wastewater using activated carbon developed from sawdust: adsorption equilibrium and kinetics, J. Hazard. Mater. B 113 (2004) 81–88.
[14] P.C.C. Faria, J.J.M. Orfão, M.F.R. Pereira, Mineralisation of coloured aqueous solutions by ozonation in the presence of activated carbon, Water Res. 39 (2005) 1461–1470.
[15] P.C.C. Faria, J.J.M. Orfão, J.L. Figueiredo, M.F.R. Pereira, Adsorption of aromatic compounds from the biodegradation of azo dyes on activated carbon, Appl. Surf. Sci. 254 (2008) 3497–3503.
[16] Y.S. Al-Degs, M.I. El-Barghouthi, A.H. El-Sheikh, G.M. Walker, Effect of solution pH, ionic strength, and temperature on adsorption behaviour of reactive dyes on activated carbon, Dyes Pigments 77 (2008) 16–23.
[17] M.F.R Pereira, J.J.M. Orfão, J.L. Figueiredo, Oxidative dehydrogenation of ethylbenzene on activated carbon catalysts. I. Influence of surface chemical groups, Appl. Catal. A: Gen. 184 (1999) 153–160.
[18] J. Muñiz, G. Marbán, A.B. Fuertes, Low temperature selective catalytic reduction of NO over modified activated carbon fibres, Appl. Catal. B: Environ. 27 (2000) 27–36.
[19] Z.H. Zhu, L.R. Radovic, G.Q. Lu, Effects of acid treatments of carbon on NO and NO reduction 2 by carbon-supported copper catalysts, Carbon 38 (2000) 451–464.
[20] M.A. Moteleb, M.T. Suidan, J. Kim, J.L. Davel, N.R. Adrian, Anaerobic degradation of 2,4,6-trinitrotoluene in granular activated carbon fluidized bed and batch reactors, Water Sci. Technol. 43 (2001) 67–75.
[21] R. Moliner, I. Suelves, M.J. Lazaro, O. Moreno, Thermocatalytic decomposition of methane over activated carbons: influence of textural properties and surface chemistry, Int. J. Hydrogen Energy 30 (2005) 293–300.
[22] Y. Al-Degs, M.A.M. Khraisheh, S.J. Allen, M.N. Ahmad, Effect of carbon surface chemistry on the removal of reactive dyes from textile effluent, Water. Res. 34 (2000) 927–935.
[23] D.C.W. Tsang, J. Hu, M.Y. Liu, W. Zhang, K.C.K. Lai, I.M.C. Lo, Activated carbon produced from waste wood pallets: adsorption of three classes of dyes, Water Air Soil Pollut. 184 (2007) 141–155.
[24] G. Mezohegyi, F. Gonçalves, J.J.M. Órfão, A. Fabregat, A. Fortuny, J. Font, C. Bengoa, F. Stuber, Tailored activated carbons as catalysts in biodegradation of textile azo dyes, Appl. Catal. B: Environ. 94 (2010) 179–185.
[25] F.P. Van der Zee, G. Lettinga, J.A. Field, Azo dye decolourisation by anaerobic granular sludge, Chemosphere 44 (2001) 1169–1176.
[26] F.J. Cervantes, J.E. Enríquez, E. Galindo-Petatán, H. Arvayo, E. Razo-Flores, J.A. Field, Biogenic sulphide plays a major role on the riboflavin-mediated

decolourisation of azo dyes under sulphate-reducing conditions, Chemosphere 68 (2007) 1082–1089.
[27] J.L. Figueiredo, M.F.R. Pereira, M.M.A. Freitas, J.J.M. Orfão, Modification of the surface chemistry of activated carbons, Carbon 37 (1999) 1379–1389.
[28] F. Rodriguez-Reinoso, J.M. Martin-Martinez, C. Prado-Burguete, B. McEnaney, A standard adsorption isotherm for the characterization of activated carbons, J. Phys. Chem. 91 (1987) 515–516.
[29] A. Linares-Solano, in: J.L. Figueiredo, J.A. Moulijn (Eds.), Carbon and Coal Gasification, Martinus Nijhoff Publishers, Dordrecht, The Netherlands, 1986, pp. 137–178.
[30] H.F. Stoeckli, L. Ballerini, S. De Bernardini, On the evolution of micropore widths and areas in the course of activation, Carbon 27 (1989) 501–502.
[31] J.L. Figueiredo, M.F.R. Pereira, M.M.A. Freitas, J.J.M. Orfão, Characterization of active sites on carbon catalysts, Ind. Eng. Chem. Res. 46 (2007) 4110–4115.
[32] J.A. Menéndez, J. Phillips, B. Xia, L.R. Radovic, On the modification and characterization of chemical surface properties of activated carbon: in the search of carbons with stable basic properties, Langmuir 12 (1996) 4404–4410.
[33] Z. Shen, W. Wang, J. Jia, J. Ye, X. Feng, A. Peng, Degradation of dye solution by an activated carbon fibre electrode electrolysis system, J. Hazard. Mater. B 84 (2001) 107–116.