

Potential method to improve the treatment efficiency of persistent contaminants in industrial wastewater

Michele R. Silva, Maria A.Z. Coelho, Magali C. Cammarota*

Departamento de Engenharia Bioquímica, Escola de Química, Universidade Federal do Rio de Janeiro, Centro de Tecnologia, Bl.E, Sl.203, 21949-900 Rio de Janeiro, Brazil

Received 11 September 2006; received in revised form 17 April 2007; accepted 29 April 2007
Available online 3 May 2007

Abstract

The objective of this work was to evaluate a potential method for improving the treatment efficiency of persistent contaminants in industrial wastewater. Adsorption with powdered activated carbon (PAC) was applied as pre-treatment and operational conditions as pH, temperature, carbon concentration and time were investigated in laboratory scale for different streams generated in a fine chemical industry. Chemical oxygen demand (COD) removal efficiencies of 63 and 50% were attained for two important industrial streams, Product C after acid treatment and precipitation and Influent, at pH 7, room temperature and with 5 and 15 g l⁻¹ of PAC, respectively. Biodegradation assays showed that PAC adsorption enhanced COD removal efficiency. PAC pre-treatment increased the COD removal of Product C after production stream from 15 to 80% and improved the biodegradability of the Influent stream by 50%.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Adsorption; Biodegradability; Fluorescent whitening agents; Powdered activated carbon; Persistence

1. Introduction

The fine chemical industry, in Rio de Janeiro, Brazil, produces 7700 t (year)⁻¹ of chemicals, of which the largest portions are for use as textile auxiliaries and optical brighteners (44% of the total). For each ton of product, 13 m³ of wastewater containing fluorescent whitening agents (FWAs) are generated.

FWAs absorb light in the UV range (290–400 nm) and emit visible blue light (400–480 nm). They are used in detergents to whiten fabrics and can be exploited for their analytical determination applications [1]. The most common FWAs are characterized by the presence of stilbene-based groups derived from stilbene (*trans*-1,2-biphenyl ethylene) bound to one or more azo or azoxy groups. In solution there is a dynamic equilibrium between the two isomeric forms of stilbene-based FWAs, the (*E*-) isomer (*trans*) and the (*Z*-) isomer (*cis*), the latter being the non-fluorescent isomer. Some FWAs are derived from 4,4'-bis-(2-sulphostyryl)-biphenyl (DSBP); for these, there are four possible isomeric forms because of the presence of two ethylene

bonds. FWAs (Fig. 1) with one ethylene bond are industrially produced by the oxidation of 4-nitrotoluol-2-sulphonic acid to 4,4'-dinitrostilbene-2,2'-disulphonic acid (DNS), which is then reduced to 4,4'-diaminostilbene-2,2'-disulphonic acid (DAS). Cyanurichloride reacts with the DAS amino groups and subsequent reactions with aniline, morpholine or diethanolamine result in the final products [2].

The chemical structures of these compounds do not have readily hydrolysable bonds. In addition, the presence of [HSO₃⁻] groups, added to increase water solubility, reduces the compounds' biodegradability, resulting in high persistence of the industrial effluent [1]. Such persistence is corroborated by the effluent's low biochemical oxygen demand/chemical oxygen demand ratio (BOD/COD), which is 0.37, on average. The effluent also has a high salt concentration (11 g l⁻¹), due to the industrial application of a saline precipitation process followed by nanofiltration with the aim of product recovery [3].

FWAs absorb ultraviolet (UV) light and undergo photodegradation [1], but are basically not biodegradable under aerobic and anaerobic conditions [4]. No biodegradation was found in biological oxygen demand tests, whereas limited biodegradation was observed in activated sludge after an adaptation period of 10–15 days [5]. The apparent affinity of FWAs to sewage

* Corresponding author. Tel.: +55 21 2562 7568; fax: +55 21 2562 7567.
E-mail address: christe@eq.ufrj.br (M.C. Cammarota).

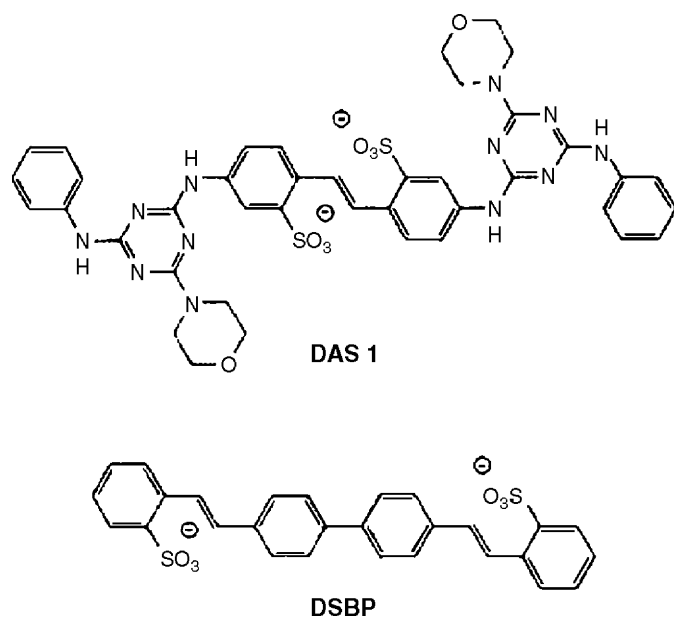


Fig. 1. Structures of two FWAs: DAS 1 (4,4'-bis-[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulfonate and DSBP (4,4'-bis-(2-sulfostyryl)-biphenyl).

sludge leads to partial removal of FWAs from wastewater during primary and secondary clarifications through biomass adsorption [4,6]. The non-retained fraction of FWAs reaches surface waters [6]. In surface waters, photodegradation takes place at the surface with half-lives of several hours in the top 15 mm layer under summer noon sunlight [1]. Below the photic zone, FWAs can be assumed to be persistent, since no biodegradation has been observed [7]. Predicted no-effect concentrations (PNEC) of $100 \mu\text{g l}^{-1}$ have been measured, however, toxic effects of FWAs have not yet been characterized in natural waters [4].

The chemical stability and persistence of FWAs avoid their degradation by conventional physicochemical and biological treatments. Thus, the industrial treatment system (coagulation/flocculation with aluminum sulphate followed by activated sludge) has faced difficulties in achieving the Brazilian discharge limit established for this effluent ($\text{COD} \leq 250 \text{ mg l}^{-1}$). However, the industry made significant progress between 2001 and 2003, including enhancement of the aeration system of the biological reactor, segregation of some toxic streams and leak prevention during production. Indeed the COD of the treated effluent was reduced from ≥ 2.5 to $\sim 1 \text{ g l}^{-1}$. However, further modifications will be required to reduce the COD to desired levels ($\leq 250 \text{ mg l}^{-1}$).

Most organic substances are removed by biodegradation in activated sludge processes, whereas toxic substances with less or no biodegradability must be removed by adsorption. The adsorption process with activated carbon may be applied to remove a great diversity of contaminating agents in liquid and gaseous streams [8–10]. It involves a non-specific process, widely used when the stream composition is unknown, and is reversible in that the activated carbon may be retrieved. However, the cost/benefit ratio is not attractive for processing material with a

low organic matter concentration or for those systems that use large amounts of carbon.

Carbon may be used in powder or granulated form. Most commonly, the granular activated carbon (GAC) form is employed in tubular reactors. Powdered activated carbon (PAC) is generally used in completely mixed and plug flow reactors. Both reactor types involve agitation to keep the carbon in suspension, which creates a perfect mixture and enhances contact between the adsorbate and adsorbent materials [8]. Ultimately the PAC must be separated from the solution using a clarifier, often with the aid of a coagulant.

In this study, the effect of adsorption treatment with activated carbon on the biodegradability of most persistent contaminants in the streams generated in the industry was examined.

2. Experimental

2.1. Collection and characterization of the streams studied

The streams studied were collected in several simple samplings (instantaneous) during the period from January 2002 to October 2003. Samples were refrigerated (4°C) and each characterization analysis was carried within 24 h after collection. Those streams previously determined to have the highest impact on the COD value along the characterization period were selected for this study.

For adsorption experiments, samples from the selected streams were collected and immediately used. The mixed liquor (effluent + sludge) was instantly collected in the period between March and April 2003, and tested immediately in biodegradation assays.

2.2. Adsorption experiments with activated carbon

The adsorption experiments were carried in 500 ml flasks with 200 ml of effluent being shaken at 200 rpm and kept at controlled temperature for 6 h. Each flask was sealed with a rubber cork and eventual losses through volatilization at the highest temperatures were corrected for by the addition of distilled water. Every experiment was run in duplicate to test the results' reproducibility. The results of the duplicates were consistent, indicating good data reproducibility. The organic matter reduction efficiency was evaluated through analyses of the soluble COD (after vacuum filtration through Whatman filter paper #4). Powdered carbon (Isofar p.a. carbon with granulometry such that 50–80% passes through a 325-mesh sieve) was regenerated by heating at 550°C for 30 min to drive off the organic contaminants [11].

Different pH values and temperatures were evaluated to verify the carbon adsorption potential on compounds present in the different streams under conditions similar to those in which the streams are generated as well as after mixture with other streams has occurred (Table 1). The time effect was evaluated with the optimal pH, temperature and carbon concentration conditions in experiments carried with the Products A and C after precipitation streams.

Table 1
Conditions evaluated in PAC adsorption assays

Parameter	Stream	Values	Assays conditions
PAC (g l ⁻¹)	Products A and B	0.25, 0.5, 1.5, 3, 6	Adjust pH to 7 with H ₂ SO ₄ or NaOH, room temperature (25 ± 1 °C)
	Product C after production	0.15, 0.5, 1.5, 3, 5, 15	
	Product C after precipitation	0.15, 0.5, 1.5, 3, 5, 15	
	Influent	0.5, 1, 2, 5, 10, 15	
pH	Products A and B	5, 6, 7, 8	Room temperature, 3 g l ⁻¹ PAC
	Product C after precipitation	3.8, 4.5, 5, 6, 7, 8	Room temperature, 5 g l ⁻¹ PAC
	Influent	6, 7, 8, 9	
T (°C)	Products A and B	25, 30, 35, 40	3 g l ⁻¹ PAC, pH 7
	Product C after precipitation	25, 40, 50, 60, 80, 90	5 g l ⁻¹ PAC, pH 7
	Influent	25, 30, 35, 40	
Time (h)	Products A and B	4, 6, 8, 24	30 °C, 6 g l ⁻¹ PAC, pH 8
	Product C after precipitation	4, 8, 24	80 °C, 5 g l ⁻¹ PAC, pH 7

The adsorption data were used to determine equilibrium isotherms for the streams studied. In all cases, the difference between the initial COD and the equilibrium concentration (COD after 6 h of reaction) was calculated to obtain the adsorptive capacity, using the following equation:

$$q = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where q is the amount of organic compounds adsorbed by PAC, quantified as COD (mg g⁻¹), C_0 the COD initial concentration (mg ml⁻¹), C_e the COD residual concentration (mg ml⁻¹), V the total volume of solute solution (ml) and W is the mass of the PAC used (g).

To quantify the adsorption capacity of PAC for COD removal from the streams, two-parameter isotherm models (Langmuir Eq. (2) and Freundlich Eq. (3)) were applied in linearized form.

$$\frac{1}{q} = \frac{1}{q_m} + \frac{1}{bq_m C_e} \quad (2)$$

$$\log(q) = \log(k) + \frac{1}{n} \log(C_e) \quad (3)$$

where q is the quantity of COD adsorbed per carbon weight unit (mg g⁻¹) at equilibrium, C_e the COD equilibrium concentration in solution (mg l⁻¹), b the Langmuir constant (l mg⁻¹) characterizing strength of organic compounds present in effluents (carbon bond), q_m adsorptive capacity (mg g⁻¹), k the Freundlich affinity parameter for a hetero-disperse system (l g⁻¹) and n is the adsorptive intensity related to the magnitude of the adsorption driving force and to the distribution of the energy sites on the adsorbent.

2.3. Biodegradation assays

The biodegradation of the contaminants in the industrial streams was evaluated by Zahn–Wellens methodology before and after treatment with activated carbon. This methodology is based upon internationally approved biodegradation assays that have been optimized [12]. It allows determining the toxicity degree of the samples on the activated sludge bacteria,

with the sludge of the effluent treatment plant serving as the inoculum.

The experiments were carried in 500 ml flasks with 200 ml of medium being shaken (140 rpm) at room temperature (25 ± 1 °C). The dissolved organic carbon concentration (DOC) corresponding to each stream tested at the beginning of the assay was of 200 mg l⁻¹. The inoculum was composed by the mixed liquor collected in the industrial wastewater treatment station (WTS) and was added to the medium to obtain an initial mass of 20–40 mg of total suspended solids (TSS).

The medium included a sample volume determined to achieve a DOC initial concentration of 200 mg l⁻¹ and 2 ml of nutrient solution with the following composition in g l⁻¹: NH₄Cl, 21; NaH₂PO₄·2H₂O, 78; K₂HPO₄, 87. The pH was adjusted to 7.0–7.5 (using HCl or NaOH), the sludge (inoculating agent) was added and the volume was brought to 200 ml by addition of distilled water. A 10 ml aliquot was removed for DOC analysis and 0.55 ml of co-substrate solution containing the following (in g l⁻¹) was added: K₂HPO₄, 35; CH₃COONa, 45; C₆H₄(COOH)(COOK), 30. An additional 10 ml aliquot was then removed for DOC analysis (initial DOC + co-substrate DOC). The flask was covered with gauze and incubated at room temperature while shaking at 140 rpm.

A sample free Reference flask was similarly prepared. DOC reduction through adsorption by means of the sludge or through volatilization was evaluated in Control and Stripping flasks, respectively. DOC sources (sample to be tested and the co-substrate solution) were not added to the Control flasks. The Stripping flasks contained only the sample and 1 g l⁻¹ of sodium azide; the pH was corrected, the volume was brought to 200 ml and a 10 ml aliquot was collected (neither the nutrient and co-substrate solutions nor the inoculating agent were added).

The experiments monitoring was performed through daily measures of pH (corrected whenever necessary to 7.0–7.5) and DOC. The DOC removal percentage was calculated as follows:

Reference flask:

$$\% = 1 - \left(\frac{\text{DOC}_{r=3} - \text{DOC}_{c=3}}{\text{DOC}_{r=0} - \text{DOC}_{c=0}} \right) \quad (4)$$

Test flask:

$$\% = 1 - \left(\frac{\text{DOC}_{t=3} - \text{DOC}_{r=3}}{\text{DOC}_{t=0} - \text{DOC}_{c=0}} \right) \quad (5)$$

Stripping flask:

$$\% = 1 - \left(\frac{\text{DOC}_{s=3}}{\text{DOC}_{s=0}} \right) \quad (6)$$

where DOC is the dissolved organic carbon concentration (mg l^{-1}) in the flask indicated by sub-indexes, r is the Reference flask, c is the Control flask, t is the Test flask, s is the Stripping flask, 0 corresponds to the initial day and 3 to the third day. For the removal determination in the Test flask, the value of $\text{DOC}_{t=0}$ corresponds to the flask before the addition of the co-substrate solution.

2.4. Analytical methods

A Shimadzu Total Organic Carbon analyzer (TOC 500) was used for DOC analysis after samples filtration through a Millipore membrane ($0.45 \mu\text{m}$). COD, salinity, TSS, VSS and BOD were analyzed according to standard methods [13].

3. Results and discussion

3.1. Characteristics of the streams generated in industry

The three main types of industrial products are the stilbene-type FWAs, such as DSBP (4,4'-bis-(2-sulfostyryl)-biphenyl) and textile chemicals. Effluents that originated from the production of stilbene-type compounds presented the highest contribution to the effluent's COD. Table 2 summarizes the characteristics of the main industrial streams between January 2002 and October 2003. The COD values obtained verified that the Products A and B streams contribute for the effluent's greatest organic load. The Product C stream also makes a substantial contribution to the Influent COD (final mixture of all inlet streams of the WTS), which has prompted the adoption of a pre-treatment process for this stream. Notably, acid treatment and precipitation has reduced the organic matter content of the Product C stream by nearly 50%.

The average BOD_5 , COD and salinity (expressed in terms of chloride concentration) values of the effluent before (Influent) and after physicochemical treatment, measured during the month of September 2003 are presented in Table 3. The value obtained for the BOD_5/COD ratio (0.37) shows the low

Table 3
Indicative parameters of effluents quality (September 2003)

Parameter	Influent	Coagulation/flocculation process effluent
BOD_5 ($\text{mg O}_2 \text{l}^{-1}$)	1,031	951
COD ($\text{mg O}_2 \text{l}^{-1}$)	2,778	2,259
BOD_5/COD	0.37	0.42
Salinity (mg Cl l^{-1})	11,799	10,700

biodegradability degree of the Influent. FWAs contained in effluents undergo photochemical degradation with half-lives of several hours under summer noon sunlight, but are basically not biodegradable under aerobic and anaerobic conditions [1,4]. One study reported that wastewaters from different production steps of the two FWA types have $\text{BOD}_{28}/\text{COD}$ values ranging from 0.04 to 0.44 after dilutions to working solutions of 1:2–1:10 [2].

After physicochemical treatment (coagulation/flocculation with aluminum sulphate and polyelectrolyte), the average COD, BOD_5 and salinity removal efficiencies were low at 19, 8 and 9%, respectively. Furthermore, the effluent biodegradability degree did not change appreciably with treatment (from 0.37 to 0.42), with the BOD_5/COD ratio increasing only 13.5%.

An important consideration in physicochemical process evaluation is the batch-operated system applied in industry production, such that batches differ with market demand. In other words, the treatment control is complicated by the fact that different compounds are produced each day. This effluent composition variability may influence the activated carbon adsorption process as well as other factors, such as pH and temperature. The physicochemical properties of the organic compounds intimately related with adsorption are altered by variation of these parameters.

3.2. Effects of pH, temperature, time and carbon concentration

COD removal, measured after agitation of the streams samples at 200 rpm, pH 7 and room temperature ($25 \pm 1^\circ\text{C}$) for 6 h, increased with carbon concentration (Fig. 2). This result was expected since an increase in carbon concentration increases the availability of active sites for adsorption. The results obtained for the Influent, Product C after production and Product C after precipitation streams show that the uptake of the organic compounds ($\text{mg COD g}^{-1} \text{PAC}$) decreases as the PAC mass increases (Fig. 3). These results are presumably due to the availability of specific surface area and active sites of the PAC [6].

Table 2
Characterization of the streams studied (January 2002–October 2003)

Stream	pH	T ($^\circ\text{C}$)	COD ($\text{mg O}_2 \text{l}^{-1}$)	Flux ($\text{m}^3 \text{batch}^{-1}$)
Influent	7.6	–	2500 ± 600	–
Final effluent	7.1	29–35	1300 ± 200	$310 \text{m}^3 \text{d}^{-1}$
Product C after production	9.8	80–90	3300 ± 700	22.95
Product C after acid precipitation	3.8	80–90	1600 ± 300	–
Product A	6.4	25–35	9900 ± 600	21
Product B	6.5	25–35	8400 ± 600	21

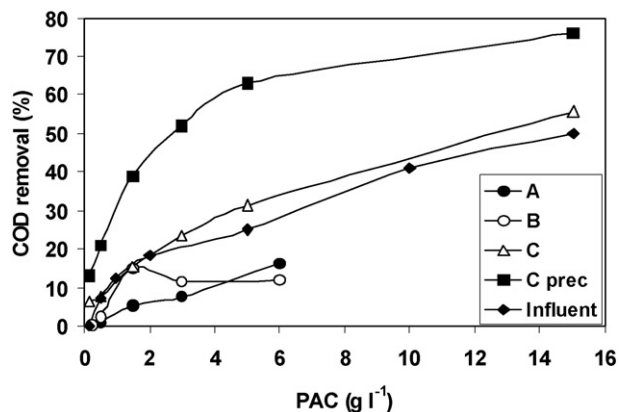


Fig. 2. COD removal efficiencies of the streams studied under different powdered activated carbon concentrations (PAC).

Employment of activated carbon to reduce COD levels would not be feasible for Products A and B streams, as their removal efficiencies were quite low (<20%). Although the initial COD concentrations of these two streams were much higher than other streams (Table 2), the removed low organic load would not be enough to attain the discharge limit. These results were similar to that reported in previous studies where the dissolved organic carbon removal increased with carbon concentration up to 6 g l⁻¹ [3].

The results obtained for the Product C stream (COD removal of 31 and 55% for carbon concentrations of 5 and 15 g l⁻¹, respectively) suggest that activated carbon pre-treatment may reduce organic load. In Germany 66 and 80% DOC removal efficiencies were obtained for a Product C stream with carbon concentrations of 5 and 15 g l⁻¹, respectively [3]. Activated carbon pre-treatment of Product C after acid treatment stream resulted in COD removal efficiencies of 63% with a carbon concentration of 5 g l⁻¹, at initial pH of 7.0 and room temperature. Acid treatment enhanced carbon-adsorbed COD removal; the COD removal in the Product C after production stream was 30% under similar conditions. For the Influent stream, COD analyses indicated that increased carbon concentration favored the organic matter removal. For the highest concentration tested (15 g l⁻¹), COD was removed at a value of 50%.

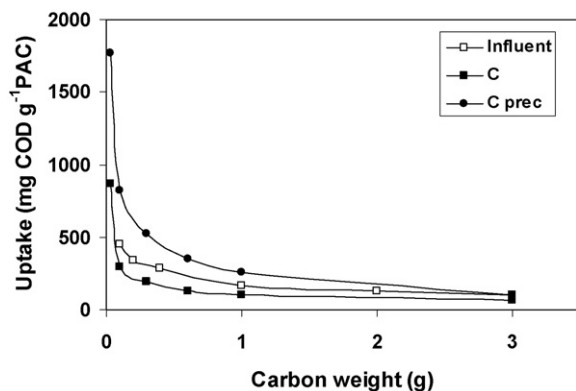


Fig. 3. Effect of PAC mass on adsorption of organic compounds present in the analysed streams.

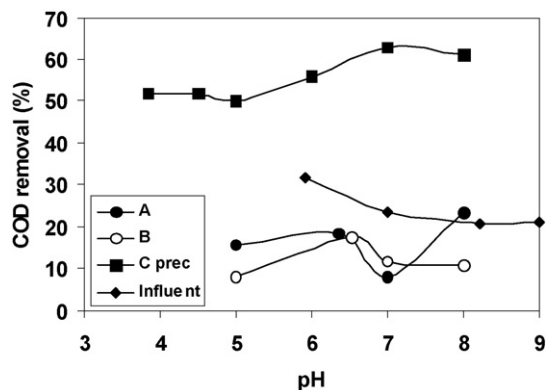


Fig. 4. COD removal efficiencies of the streams studied under different pH values.

The affinity of the distinct compounds within each stream to PAC cannot be predicted easily. Several types of physicochemical interactions between PAC and these different compounds are possible. Even small structural differences between these compounds result in substantial differences in affinity for the PAC.

Comparison of COD removal efficiencies through adsorption with powdered activated carbon (3 or 5 g l⁻¹ PAC at 200 rpm and 25 °C for 6 h) under different pH values (Fig. 4) reinforces the view that activated carbon treatment would not be feasible for Products A and B streams. For the Product C after precipitation stream however, pH values of 7 and 8 enabled better COD removal efficiencies, relative to the efficiencies obtained with the other pH values. Generally, pH did not influence significantly the adsorption process; the maximal difference between the lowest and the highest value of COD reduction obtained in the pH range tested was 10%.

For all streams evaluated, increased temperature favored COD reduction (data not shown). However, the increase obtained (only 10%) would not justify an adsorption stage at temperatures higher than those in which the streams are generated in industry. Better adsorption at higher temperatures may be attributed to the acceleration of some originally slow adsorption steps, to the creation of some new active sites on the adsorbent surface or to the enhanced mobility of compounds from the bulk solution to the adsorbent surface. Adsorption interaction in this case must involve some type of specific interaction at higher temperature, i.e., probable bond cleavage (endo-process) that results in smaller entities that can fit within small pores. Alternatively, such behavior may be ascribed to “activated” adsorption which accelerates diffusion into certain pores in the adsorbent [8].

Under optimal conditions for Product C after precipitation (5 g l⁻¹ PAC, 80 °C, pH 7) and Product A (6 g l⁻¹ PAC, 30 °C, pH 8) streams, COD removal obtained after a 24-h period was not significantly greater than those observed after a 4-h period (Fig. 5). These findings indicate that the 6 h reaction time adopted in the present experiments was sufficient to remove all adsorbable compounds present in the effluent.

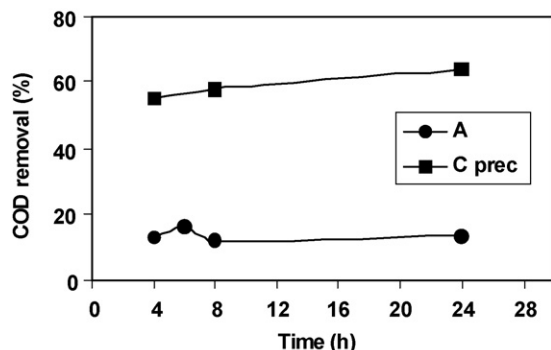


Fig. 5. COD removal efficiencies for the Product C after precipitation and Product A streams under different reaction times.

3.3. COD adsorption equilibrium isotherms

The experimental data were used to determine the constants of Langmuir and Freundlich adsorption isotherms equations. Freundlich and Langmuir adsorption plots of the Influent, Product C after production and Product C after precipitation streams with PAC are shown in Fig. 6. These models did not fit the experimental results obtained with other streams studied (Product A and B). The constants of the two models were calculated from the slopes and intercepts of Fig. 6 and listed in Table 4. The r^2 values indicate that the isotherms correlate well with the experimental data. However, in terms of equilibrium, the Langmuir model fit the experimental data better than the Freundlich model. In the models, the adsorption capacity of the Product C after precipitation stream was predicted to be much higher than those of the Product C before acid treatment and Influent, which is consistent with the experimental results shown in Fig. 2. The relative affinities, bq_m , of the organic compounds present in the streams, quantified as COD, to the PAC surface were determined to be higher for the Product C after precipitation stream than for the other streams. The Freundlich constant (k), which is considered to be an indicator of adsorption capacity, was also higher for the Product C after precipitation stream than for the other streams. $1/n$ is an empirical constant related to the magnitude of the adsorption driving force; the Product C after precipitation stream is associated with a higher $1/n$ value, and thus a higher tendency for organic compounds adsorption. The greater affinity for PAC of the Product C after precipitation stream than of the Influent and Product C before acid treatment streams can be attributed to the chemical structure of the compounds after acid treatment. The molecular struc-

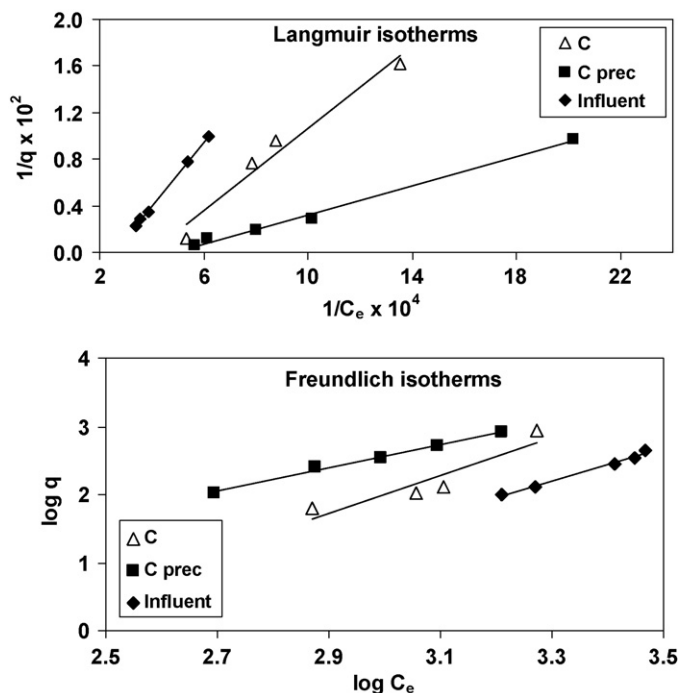


Fig. 6. Adsorption isotherms (Langmuir and Freundlich) of COD on adsorbent PAC.

ture of the compounds is a determining factor of the extent to which they will be adsorbed by activated carbon. Generally, adsorbability is enhanced by increased molecular size and aromaticity, and by decreased solubility, polarity and carbon chain branching. In addition, compounds that contain more sulphonic acid groups may have decreased PAC adsorbability [14].

GAC and PAC are the most common adsorbent materials because they provide an excellent adsorption capability for organic compounds. Indeed, with Product C after production, Product C after acid treatment and precipitation and Influent streams, COD removal efficiencies of 50–75% were obtained with 15 g l^{-1} of activated carbon. However, the use of activated carbon may be limited due to its high cost. Alternative carbon sources may potentially be developed from cheaper substitutes, such as fly ash, silica gel, wool wastes, blast furnace sludge and clay materials (bentonite, kaolinite, montmorillonite, etc.). These materials have already been demonstrated to remove color and organic matter [15]. Another alternative would be the treatment of the Influent stream with lower carbon concentrations,

Table 4
Comparison of Langmuir and Freundlich constants and correlation coefficients of COD adsorption with PAC

Stream	Langmuir				Freundlich		
	q_m (mg g^{-1})	b (l g^{-1})	bq_m (l g^{-1})	r^2	$k \times 10^2$ (l g^{-1})	$1/n$	r^2
Influent	141	0.26	0.04	0.999	0.2	2.42	0.988
Product C after production	143	0.40	0.06	0.963	0.05	2.78	0.869
Product C after precipitation	333	0.48	0.16	0.993	290	1.70	0.990

Langmuir model: $q/q_m = bC_e/(1 + bC_e)$; b : Langmuir constant (l g^{-1}); C_e : equilibrium concentration (mg l^{-1}); q_m : maximum quantity of COD adsorbed (mg g^{-1}); Freundlich model: $q = kC_e^{1/n}$; k : Freundlich constant (l g^{-1}); n : empirical coefficient.

as the use of 6 g l^{-1} of PAC produced $\cong 40\%$ COD removal. The best treatment conditions (physicochemical/biological) could only be determined by comparing pre- and post-carbon treatment biodegradability of the streams to observe persistence alterations.

3.4. Biodegradation assays

Adsorption treatment with activated carbon yielded better results with the Influent, Product C at production outlet and Product C after acid treatment and precipitation streams. Therefore, these streams were selected for biodegradation assays by the modified Zahn–Wellens test relative to their respective controls (samples not submitted to adsorption with PAC). The objective of this assay was to evaluate whether or not the adsorption treatment would reduce the persistence of the compounds present in the streams. The sample that received no adsorption treatment served as the Control, and the sample treated with PAC (10 g l^{-1} , room temperature and pH 7) was called the Test-sample.

As shown in Fig. 7, the PAC treatment reduced the persistence of the compounds in Product C after production and Influent streams; DOC removal after 3 days increased from 13 to 79% and from 48 to 86%, respectively, after adsorption treatment. This noteworthy result indicates that in addition to DOC removal through adsorption, the PAC treatment also reduced the persistence of the contaminants in these streams. Removal values higher than 5% in the stripping test indicated that organic matter loss through volatilization occurred in the experiment with the Product C after production stream. On the other hand, the stripping test determined that the volatilization loss was not significant ($<5\%$) from the Product C after precipitation and Influent samples, indicating that the removal percentage of the organic matter in these streams was due to biological activity. In addition, the observations of good sludge activity (DOC removal values of 80–90% in the Reference flask) with these streams validated the biodegradation assay.

For the experiments with the Product C after precipitation stream, the incubation time was extended to 6 days in order to observe DOC reductions in the Reference flasks close to 80%. After 6 days, the sample treated with activated carbon presented higher DOC removal relative to the sample that received no treatment. However, the difference was very small (42% versus 32%), indicating that this stream must have presented persistent compounds that were not removed by the carbon treatment.

The relatively low DOC removal values observed in the Reference flasks indicate that the activity of the sludge used (from the industry Wastewater Treatment Station) was not adequate. However, as the sludge exhibited similar activity in the Control experiments and with the activated carbon-treated samples, it was possible to compare the results.

The COD removal kinetics of the Influent stream after PAC adsorption (10 g l^{-1} , pH 7, room temperature) is shown in Fig. 8. The increment on the soluble COD value in the Test (average value for the testing sample) is a result of COD analysis before and after the addition of co-substrate to the reaction medium (Influent) at the beginning of the experiments. It was observed

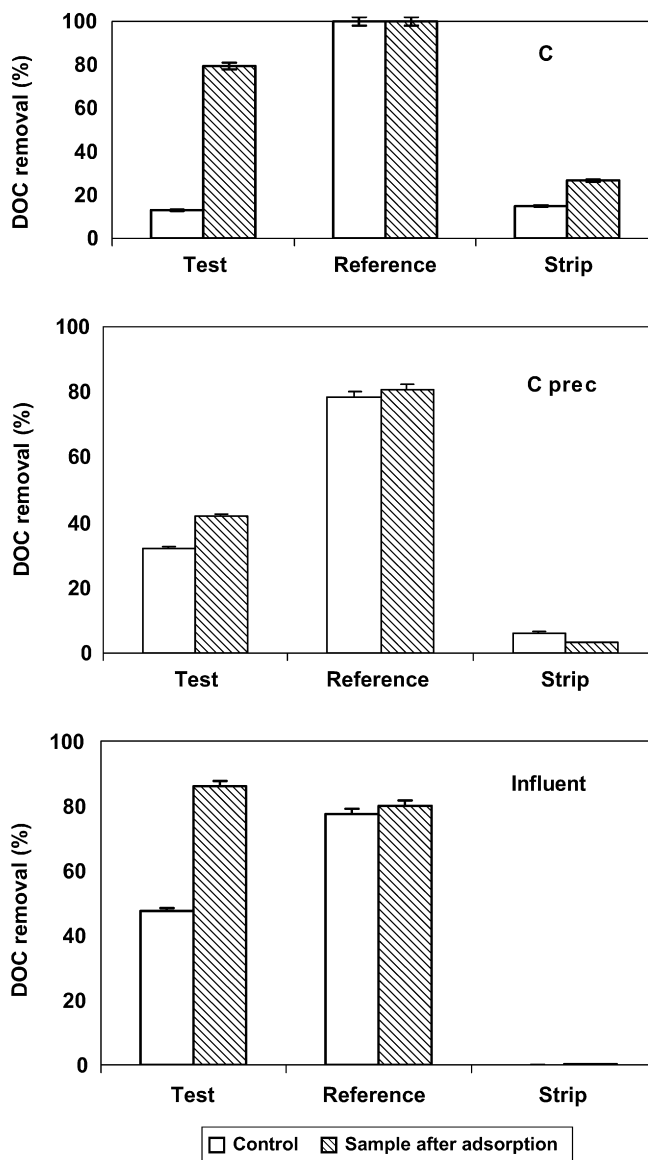


Fig. 7. DOC removal efficiencies in biodegradability tests with and without (control) adsorption pre-treatment.

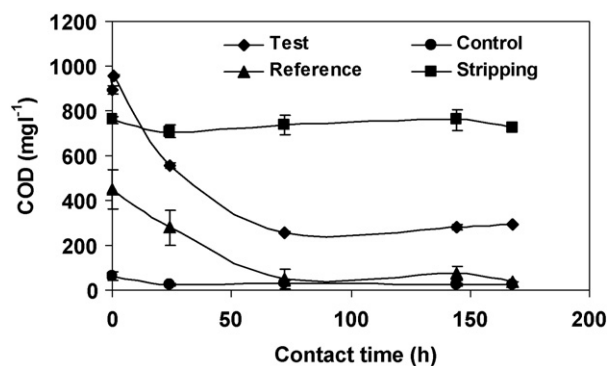


Fig. 8. COD removal kinetics in biodegradability test for the Influent stream treated with PAC.

that the COD values in the Experiment (average value for the testing sample) and Reference (average value for the testing reference) flasks decreased with time, indicating a progressive degradation of the organic matter. On the other hand, in the Stripping flask curve (average value for the flask that evaluates the loss of organic matter through volatilization) COD did not change, which indicates that the organic matter was reduced exclusively through microbiological action. The curve corresponding to the Control flask had a low value because the only contribution to COD in this flask was the cell material removed during filtration.

The organic matter loss related to a possible adsorption on the cell wall present in the system or on walls of the Erlenmeyer flask was also assessed. The sampling for this analysis was performed with the Influent stream 3 h after the beginning of the experiment, a period insufficient to verify the microbiological action but sufficient for observing physical adsorption. The COD removal values obtained for the Experiment, Control, Reference and Stripping flasks (4.5, 0.0, 0.0 and 4.3%, respectively) indicated that organic matter was not reduced through adsorption to the flask or cell wall.

It can be observed that the pre-treatment with PAC removed COD until values very similar to the discharge limit (around 260 mg l^{-1} after 72 h). In the actual treatment system employed in the industry (coagulation/flocculation and activated sludge operating with hydraulic retention time of 48 h), COD final values around 800 mg l^{-1} are obtained. However, to become PAC application economically viable, its concentration must be reduced. More studies are being lead with other types of PAC.

4. Conclusions

The employment of PAC was not suitable for the treatment of the Products A and B streams, which exhibited COD reductions below 20%. For the Product C after acid treatment and precipitation stream, however, the COD removal was 63% at pH 7, room temperature and 5 g l^{-1} of PAC.

For the Influent stream, 50% COD removal efficiencies were obtained with 15 g l^{-1} of PAC. Extreme pH or temperature values did not promote relevant alterations. Thus, the use of the conditions in which the stream was generated (e.g. pH 7 and room temperature) was justified. In addition, the adsorption time data indicated that 4 h was enough to adsorb all adsorbable compounds present in the streams studied. Indeed this period could even be reduced.

The biodegradation evaluation by the Zahn–Wellens method showed that the sludge present in the wastewater treatment station presented problems in relation to its activity. PAC treatment

reduced the persistence of the compounds present in Product C after production and Influent streams. The COD removal increased from 15 to 80% when the Product C after production stream was treated with PAC, while the Influent stream was found to be 50% more biodegradable after PAC pre-treatment.

Acknowledgements

This study was partially supported by Ciba Speciality Chemicals Ltda., Rio de Janeiro, Brazil. The authors are grateful to CNPq.

References

- [1] J.B. Kramer, S. Canonica, J. Hoigné, J. Kaschig, Degradation of fluorescent whitening agents in sunlit natural waters, *Environ. Sci. Technol.* 30 (1996) 2227–2234.
- [2] P. Hörsch, A. Speck, F.H. Frimmel, Combined advanced oxidation and biodegradation of industrial effluents from the production of stilbene-based fluorescent whitening agents, *Water Res.* 37 (2003) 2748–2756.
- [3] M. Heitzmann, Dissertation Fachhochschule Offenburg Studiengang Verfahren und Umwelttechnik, Sweden, 2001.
- [4] T. Poiger, J.A. Field, T.M. Field, H. Siegrist, W. Giger, Behavior of fluorescent whitening agents during sewage treatment, *Water Res.* 32 (1998) 1939–1947.
- [5] R. Zinkernagel, in: R. Anliker, G. Müller (Eds.), *Fluorescent Whitening Agents in the Environment*, Stuttgart, 1975.
- [6] C.J. Pearce, J.R. Lloyd, J.T. Guthrie, The removal of color from textile wastewater using whole bacterial cells: a review, *Dyes Pigm.* 58 (2003) 179–196.
- [7] J.-M.A. Stoll, W. Giger, Mass balance for detergent-derived fluorescent whitening agents in surface waters of Switzerland, *Water Res.* 32 (1998) 2041–2050.
- [8] A.A.M. Daifullah, B.S. Girgis, H.M.H. Gada, A study of the factors affecting the removal of humic acid by activated carbon prepared from biomass material, *Colloids Surf., A: Physicochem. Eng. Aspects* 235 (2004) 1–10.
- [9] R.L. Tseng, F.C. Wu, R.S. Juang, Liquid-phase adsorption of dyes and phenols using pinewood-based activated carbons, *Carbon* 41 (2003) 487–495.
- [10] T.C. Voice, *Activated Carbon Adsorption*, Freeman, Washington, DC, 1989.
- [11] M.A. Waer, V. Snoeyink, K.L. Mallon, Carbon regeneration dependence on time and temperature, *J. AWWA* 84 (1992) 82–91.
- [12] OECD, Guideline for Testing of Chemicals, Proposal for a New Guideline TG 302B, Inherent Biodegradability—Zahn–Wellens/EMPA Test, Organization for Economic Co-operation and Development, Paris, 1994.
- [13] A.E. Greenberg, J.J. Connors, D. Jenkins, *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, Washington, DC, 1992.
- [14] S. Papic, N. Koprivanac, A.L. Bozic, A. Metes, Removal of some reactive dyes from synthetic wastewater by combined Al(III) coagulation/carbon adsorption process, *Dyes Pigm.* 62 (2004) 291–298.
- [15] M.S. El-Geundi, Adsorbents for industrial pollution control, *Adsorpt. Sci. Technol.* 15 (1997) 777–787.