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Alternative Treatment of Recalcitrant Organic Contaminants by a Combination of Biosorption, Biological Oxidation and Advanced Oxidation Technologies

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1. Introduction

Industrial activity produces increasing amounts of effluent. Dyes and surfactants are typical examples of such pollutants, and both are present in various industries such as textiles, which are widely distributed in South-American, Indo-Asian and African countries. These industries are an important source of resources in the 3rd World Countries and also a source of pollution. Many compounds present in them are recalcitrant and therefore persistent in the environment, causing deleterious effects on the ecosystem (Padmavathy et al. 2003; Stolz et al. 2001). These compounds are usually found in very low concentrations and large volumes of effluent, characteristics that make very difficult its treatment by conventional means. Conventional techniques for removal of recalcitrant pollutants from wastewaters are based on the use of activated carbon, ionic exchange resins, chemical precipitation or membrane filtration. However, these technologies are usually not very convenient due to the large volumes to be treated and the low concentration of pollutants, excessive use of chemicals, accumulation of concentrated sludge and disposal problems, high cost of operation and maintenance of plant, sensitivity to other components of the liquid effluent (Balaji and Matsunaga 2002, Chen and Lin 2001). Traditional and alternative biological processes have received increasing interest owing to their cost, effectiveness, ability to produce less sludge and environmental benignity (Chen et al 2003; Volesky 2007) but some organic industrial and agricultural pollutants are recalcitrant to biological treatments . Several common compounds such as dyes, surfactants and pesticides, among others, are biorecalcitrant and can produce microbial death or other problems in water treatment plants. The biological treatment of liquid effluents containing this type of pollutants involves a previous separation step, or the isolation and use of specialized strains that can resist and degrade these toxic contaminants (Padmavathy et al. 2003).

In the case of effluents with these features, it is possible to use different combinations of processes to ensure proper treatment. Adsorption on low-cost substances, mainly biomass (biosorption), and combinations of special biological treatments (resistant strains in biofilm bioreactors) (Curutchet et al. 2001, Palmer and Sternberg 1999) with advanced oxidation technologies (such as photocatalysis, photo-Fenton, etc.) can be selected among the most versatile and economical treatments. Biosorption does not require expensive facilities. Advanced oxidation technologies partly mineralize the pollutants, using solar light as a source of energy and medium price oxidants, reducing the amount of contaminated sludges.

Biosorption is a process that utilizes various natural materials of biological origin, including bacteria, fungi, yeast, algae, etc. (Volesky 2007; Vijayaraghavan and Yun 2008). These biosorbents have heavy metal and organics sequestering properties, and can decrease the soluble concentration of these contaminants.

The use of biosorbents is an ideal alternative method for treating high volumes of wastewater with low concentrations of heavy metals (Volesky 2007) or persistent organic compounds (Wang et al. 2007, Patel & Suresh 2008). Compared with conventional treatment methods, biosorption has the following advantages (Volesky 2007): high efficiency and selectivity for absorbing contaminants in low concentrations, energy-saving, broad operational range of pH and temperature and, in some cases, easy recycling of the biosorbent.

However, biosorption generates huge quantities of sludge that should be treated or disposed to avoid secondary pollution (Stolz 2001). Most of the works in the literature study only the process of adsorption and do not mention the fate of the adsorbent loaded with contaminants and converted into a hazardous waste.

Knowledge of the mechanisms of degradation of the adsorbed contaminants (particularly in the case of dyes adsorbed on biomass, or biomass associated with matrixes found in natural environments such as clays and sediments) is very important to understand the processes involved in its fate in natural environments and to develop remediation alternatives for polluted water. In the case of organic contaminants, the adsorption enables fast and efficient decontamination of water (natural or residual), and the possibility of further degradation in solid phase allows to regenerate the adsorbent for further use or its decontamination to avoid expensive disposal processes.

Composting is known to stabilize biosolids (Tandy et al., 2009), transforming compounds to a high fraction of humic and fulvic acids and carbon dioxide. Therefore, composting biosolids is a good alternative for biowaste disposal (Ho et al 2010).

Adsorption of contaminants on metal oxides with photocatalytic activity is another way to remove pollutants by a fast adsorption followed by slow degradation under solar or UVA illumination. There are several metal oxides with high adsorptive capacity and photocatalytic activity. Most metal oxides display the property to catalyze the oxidation of organic (and inorganic) compounds under illumination with light with appropriate wavelength (energy higher than the metal oxide band-gap) (Litter 1999, Candal et al. 2004). The activation of a photocatalytic oxide involves the promotion of an electron from the valence band to the conduction band. Both species migrate to the surface of the catalyst where can recombine or react with adsorbed species like organics or water. The reaction of a hole with water produces highly oxidant $OH^{\bullet}$ radicals, which also react with organic or inorganic species adsorbed and/or dissolved in water. TiO_2 is one of the most well known

photocatalyst, and it can be used in water treatment in areas with high solar light illumination and in several commercial products. TiO_2 displays photocatalytic activity under UVA illumination. Iron oxide and oxohydroxide also present photocatalytic activity and their band gap lies in the visible region, which is appropriate for the use of solar light. Unfortunately its oxidant ability is lower, it is easy photo-corroded and have low chemical resistance (Lackoffand et al; 2002) However, it was recently reported the degradation of pesticides and dyes mediated by different iron oxides (Vittoria Pinna et al., 2007; Chien-Tsung et al, 2007; C. Pulgarin et al, Langmuir, 1995, Gilbert et al, 2007). Besides, colloidal iron oxides are present in natural waters displaying an important adsorption capacity which, combine with its photocatalytic activity, may play an important role in the final fate of contaminants in water.

On the other hand, adsorption of contaminants on biomass (for example, bacteria) and/or oxides with photocatalytic activity are processes that occur in natural environments when a polluted effluent reach a course of water.

This article describes fundamental and applied experiments that may contribute to the development of alternative processes for wastewater treatment and to a better understanding of the mechanisms involved in the fate and transformation of dyes and surfactants in natural environments such as streams.

2. Research methods

2.1 Culture media and microbiological methods

Appropriate culture media were used to isolate bacteria from consortia in reactors and from the José León Suarez channel an affluent to the Reconquista river in the neighborhood of Buenos Aires. The isolation medium had the following composition: 5.0 g L^{-1} glucose, 3.0 g L^{-1} peptone, 0.5 g L^{-1} $(NH_4)_2SO_4$, 0.5 g L^{-1} K_2HPO_4, 0.1 g L^{-1} $MgSO_4$, 0.010 g L^{-1} $CaCl_2$, 1.7% agar. The same medium without agar was used as liquid medium for growing the bacteria in the reactors. 100 mg L^{-1} of BKC was added as selective pressure in order to obtain apropiate consortia.

The culture medium used to feed the reactors (reactor medium) during the experiments had a different composition to avoid the formation of micelles, which interfere in the determination of BKC by HPLC (see below). The composition of such media was: 5.0 g L^{-1} glucose, 2.0 g L^{-1} $(NH_4)_2SO_4$, 5.0 g L^{-1} K_2HPO_4, 0.1 g L^{-1} $MgSO_4$, 0.01 g L^{-1} $CaCl_2$. In some experiments, the glucose concentration of the media was changed.

Biomass was measured by dry weight, turbidimetry, and plate counting, as indicated in each experiment.

2.2 Isolation of microorganisms

Native strains were isolated from contaminated streams with noticeable presence of dyes and tensioactives and a strong autodepurative capacity. These streams are affluents of Reconquista River, one of the most polluted rivers near Buenos Aires City (Argentina).

Other microbial consortia coming from conventional wastewater treatment plants were subjected to selective pressure (high concentrations of colorants or surfactants) in a packed bed bioreactor to select resistant organisms. The reactor was operated for six months, and cultivable microorganisms in the supernatant were isolated in solid media. The different strains obtained were characterized by biochemical analysis. The characterization of the

genera was made by the API 20-E and 20 NE biochemical tests (Biomeriaux), catalase, oxidase and Gram test.
The isolation was carry out in agar plates with PCA medium. Strains isolated from the JLS channel were denominated StA, StB StC StD. Strains isolated from bioreactors were denominated SbA, SbB, SbC, SbD SbE.

2.3 Biosorption experiments

2.3.1 Biosorption dynamics and equilibria

Biosorption experiments were performed in batch systems with a constant amount of biomass of different individual and in consortium isolates and different concentrations of crystal violet (dye) or benzalkonium chloride (BKC) (surfactant). Experiments were conducted to determine the dynamics of the process and the equilibrium (isothermal) conditions for different model compounds. At different incubation times, the biomass was separated by centrifugation (5000 g) and the remaining dye or surfactant concentration was determined in supernatant. Crystal violet was measured by visible spectrophotometry at 590 nm and BKC was determined by HPLC (Ding et al, 2004).
The data were fitted by the Langmuir isotherm. Experiments with living biomass (active uptake) and died biomass (passive adsorption) were performed. For crystal violet, the effect of pH on the adsorption was studied.

2.4 Treatment of the liquid (effluent) and solid (sludges) obtained by adsorption of dyes. Liquid batch and solid phase dye degradation

2.4.1 Bacterial growth in liquid medium in the presence of dye

To study the effect of crystal violet on the growth of the isolated strains, an experiment of growth kinetics was carry out in agitated flasks. The same base culture medium was used with the addition of different dye concentrations. Optical density (OD) at 410 nm and dye concentration for spectrophotometry at 590 nm after centrifugation were measured. All the strains isolated from the JLS channel grew to the concentration of 0.023 at the same speed as the control without dye.

2.4.2 Solid phase dye degradation

Solid phase degradation experiments were carried out in plastic vessels of 50 ml using StB and StC strains. Biomass and sediment-adsorbed biomass were generated in agitated flasks with and without 1% w/v of previously desiccated sediment. Cultures in stationary phase with 2 g L^{-1} biomass were incubated with a know amount of dye. After equilibrium was reached, biomass was separated by centrifugation at 5000 g and the dye concentration in the supernatant determined by spectrophotometry. The dye-charged biomass was washed and mix with 3 g of desiccated aquatic plants (*Salvinia sp*.) isolated of the same environment than bacterial strains and cultivated in a greenhouse in dechlorinated tap water. This mixture was placed in the containers and composted for different times. Remaining dye in the mixtures was measured by extraction of the dye with 10 g L^{-1} Sodium dodecyl sulphonate (SDS) and spectrophotometric quantification.

2.5 Batch and continuous BKC biodegradation coupled with TiO_2-photocatalysis

Experiments were performed in agitated vessels and in a continuous packed bed reactor (CPBR). Both types of reactors were inoculated with bacteria obtained from a conventional

wastewater treatment plant from which several subcultures with 150 mg L^{-1} BKC as selective pressure were made. The CPBR was operated in continuous mode at 50 mL h^{-1} feeding rate. The reactor was formed by two cylindrical vessels 60 cm long and 5 cm internal diameter, with a packed bed of glass chips (-5 +3.5 mesh). One of the reactors was fed from the bottom with the liquid media. The outlet of this reactor was the feeding media of the second reactor, which was fed from the upper part. The first cylinder was oxygenated by bubbling air from the bottom, in the opposite direction to the feeding liquid. The second cylinder was not oxygenated, but the liquid was always in contact with air as it moved towards the outlet, placed in the bottom part of the cylinder. In regular experiments, the reactor was fed with the liquid medium described above (2500 mg L^{-1} Chemical Oxygen Demand (COD), mainly glucose) and the corresponding amount of BKC. Samples of the liquid were taken at the inlet, at the outlet and at a point between the two cylinders.

The aqueous effluent obtained after microbiological treatment was submitted to photocatalytic treatment. The photocatalytic BKC oxidation was performed in a 0.6 L recirculating batch system consisting of an annular glass reactor (415-mm length, 32-mm internal diameter), a peristaltic pump (APEMA BS6, 50 W), and a thermostatted (298 K) reservoir. The TiO_2 suspension (1 g L^{-1}) containing BKC was recirculated at 1 L min^{-1} from the reservoir through the photoreactor. The total volume of the circulating mixture was 450 mL, of which 100 mL were inside the photoreactor. Air was bubbled in the reservoir at 0.2 L min^{-1} all throughout the irradiation time. The illumination source was a black light tubular UV lamp (Philips TLD/08, 15 W, 350 nm < λ < 410 nm, maximum emission at 366 nm) installed inside the annular reactor. A photon flux of 7.4 μeinstein s^{-1} L^{-1} was determined by actinometry with ferrioxalate, assuming a 366 nm monochromatic light.

TiO_2 (Aeroxide® TiO_2 P25) was incorporated to the effluent in order to obtain a 1.0 g L^{-1} suspension. The system was ultrasonicated for 1 minute and recirculated in the reactor for 30 minutes to reach the adsorption equilibrium (as determined in preliminary experiments). Periodically, samples were taken from the suspension and filtered through a 0.2 μm cellulose acetate membrane before analysis or for biological treatment.

Alternatively, aqueous solutions containing only BKC (200-50 mg L^{-1}) were treated by photocatalysis during different periods in the reactor described before. The obtained solutions were mixed with a carbon rich media and submitted to biological treatment

3. Results

3.1 Isolation and characterization of cultivable bacteria strains

Five strains (StA, StB, StC, StD and StE) were isolated from samples of water from the José León Suarez (JLS) channel, a tributary of Reconquista river. This river, considered the second most contaminated river of Argentina, receives an important load of pollutants of domestic and industrial origin. The track of the basin in which the channel is located practically combines all the elements typical of a hyper-degraded area: informal occupation of the plain of flooding, high population density, extreme poverty, clandestine industrial and sewage discharges and presence of the biggest sanitary fill of the metropolitan region.

Strains were selected by morphological differences of the colonies in agar plates with PCA medium. Biochemical tests were carried out for metabolic characterization. StB strain shows correspondence within *Enterobacter cloacae.* StC Strain was identified as belonging to the *Pseudomonas* genus. The other three strains were Gram negative rod, catalase + and oxidase. Biochemical characterization did not allow genera identification of these bacteria.

Presence of *Escherichia coli* and other fecal Enterobacteria was detected by isolation in DEV and EMB (Merck) media, showing fecal contamination of the stream.
Another six strains were isolated from bioreactors working in our laboratory by several months with selective pressure (BKC 100 mg L^{-1}). Twenty days were needed to form a biofilm of BKC-resistant bacteria on the glass support. After 30 days, the film had homogeneously covered all the support inside the column, as shown in Figure 1. Six strains could be isolated from the biofilm (strains SbA to SbF).

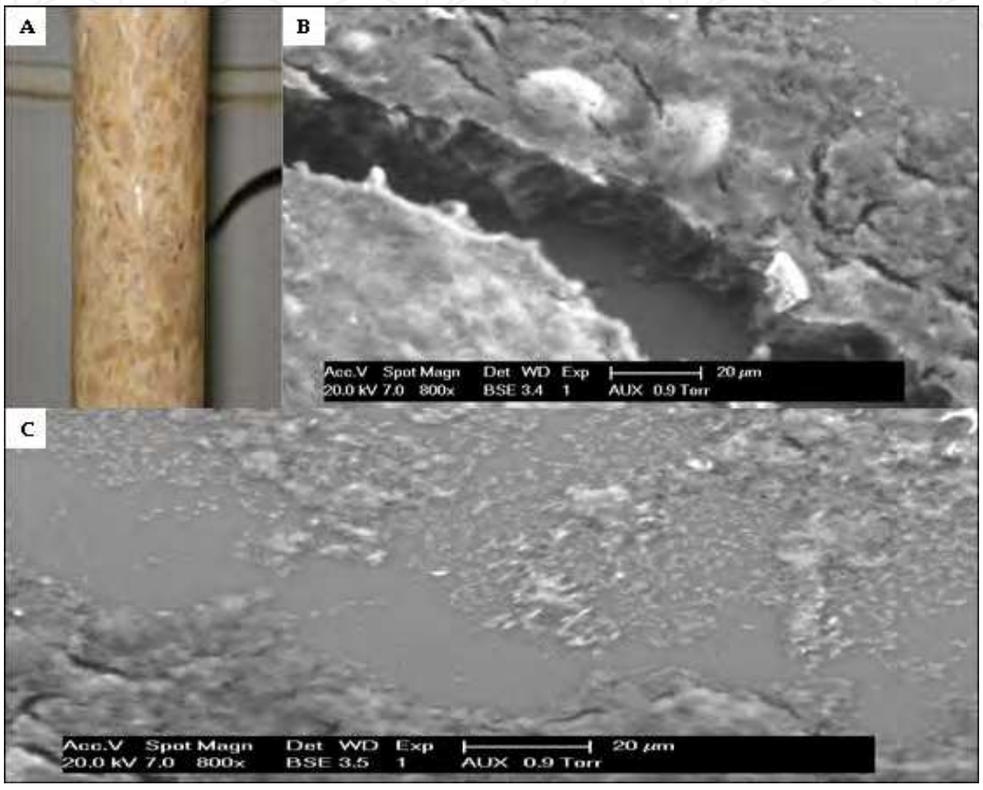


Fig. 1. *Biofilm in packed bed reactor.* A) Biofilm in the support. B) Scanning electronic microscopy of the biofilm, where the thickness of biofilm is shown. C) Scanning electronic microscopy of the biofilm after 30 days from inoculation of reactor.

Biochemical tests allowed the identification of two BKC-resistant bacterial genera (*Pseudomonas sp.* and *Saccarococcus sp.)*. This agrees with literature reports of degradation of quaternary ammonium compounds (QACs) by microorganisms present in activated sludges, where the majority of microorganisms able to utilize QACs as the carbon and energy source (QACs degraders) were classified as *Pseudomonas sp.*, *Xanthomonas sp.* and *Aeromonas sp.* (Zhang 2011, Ismail 2010).

3.2 Biosorption experiments
3.2.1 Crystal violet experiments
3.2.1.1 Adsorption dynamics

Figure 2 shows crystal violet concentration in solution vs. time. For the 5 strains (StA to StE), one hour was necessary to reach the equilibrium.

Experiments in the presence of an energy source (glucose) show the same pattern. This suggests a strong and fast physicochemical adsorption and no significant contribution of active uptake mechanisms (at least in the time range studied).

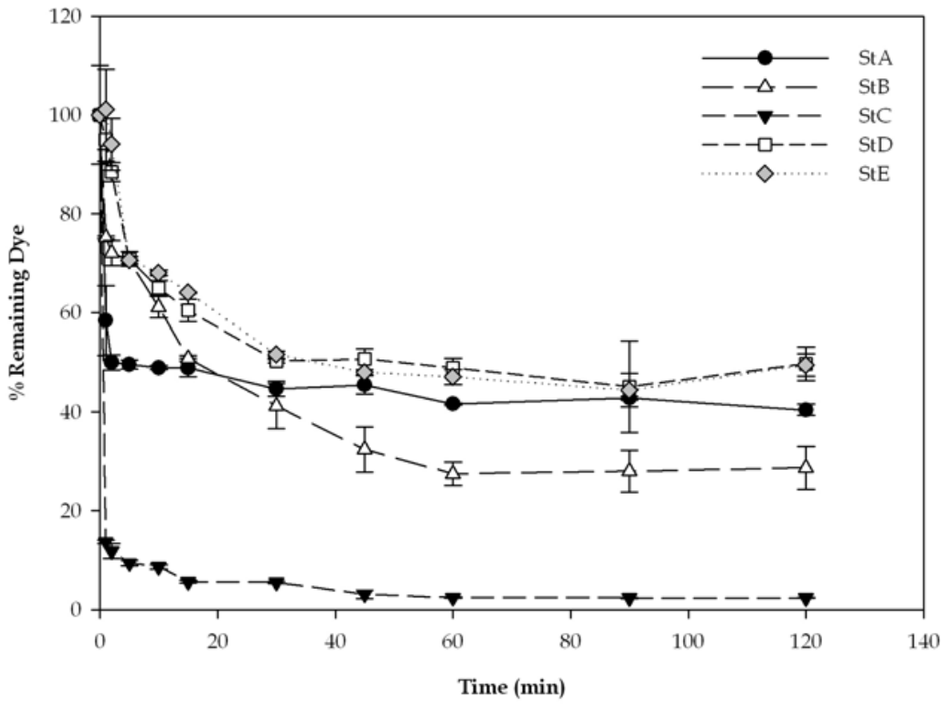


Fig. 2. Percentage of dye remaining in solution vs. time.

Sorption kinetics was fitted with an equation corresponding to a pseudo-second order model (Equation 1).

$$\frac{t}{q} = \frac{1}{k_2 q_{eq}^2} + \frac{1}{q_{eq}} t$$

Equation 1. Pseudo-second order model of biosorption dynamics.

where t is the time, q_{eq} is the specific adsorption reached at equilibrium and k_2 is the second-order rate constant.
Values of k_2 and correlation coefficients are shown in Table 1.

	R^2	k_2 (g s^{-1} mg^{-1})
A	0.9988	0.020
B	0.9943	0.006
C	0.9999	0.084
D	0.9955	0.009
E	0.9895	0.006

Table 1. Dynamic constants and correlation coefficients for the pseudo-second order model of biosorption dynamics.

The pseudo-second order model is based in chemisorption. A monolayer of adsorbate is formed on the sorbent surface by ionic interaction. The dynamic equilibrium is reached when all the bonding sites are saturated (Ho et al. 1999). Based on the previous model, the results obtained in this work indicate that the adsorption of crystal violet on the bacteria is due to electrostatic interaction between the dye and the wall of the cells.

3.2.1.2 Adsorption of crystal violet by the isolated strains. Effect of pH

Figure 3 shows the variations of specific adsorption (Q_{eq}) with the initial pH of the solution for 50 mg L^{-1} initial concentration of the dye. It is seen that Q_{eq} does not change significantly in a wide range of pH (from 5 to 8). From pH 3 to 5-6, Q_{eq} rises drastically. pH values below 3 or above 8 lead to changes in color or solubility of the dye, and were not studied.
The results agree with a typical behavior for biosorption of cationic species. Changes in the protonation of the active sorption groups in biomass (carboxyl, hydroxyl, amino, etc.) lead to a minor specific adsorption (Volesky 2007).
The maximum Q_{eq} value was reached in the typical range of pH found in natural waters and most of the industrial effluents containing dyes (Chen 2003, Akar 2010).

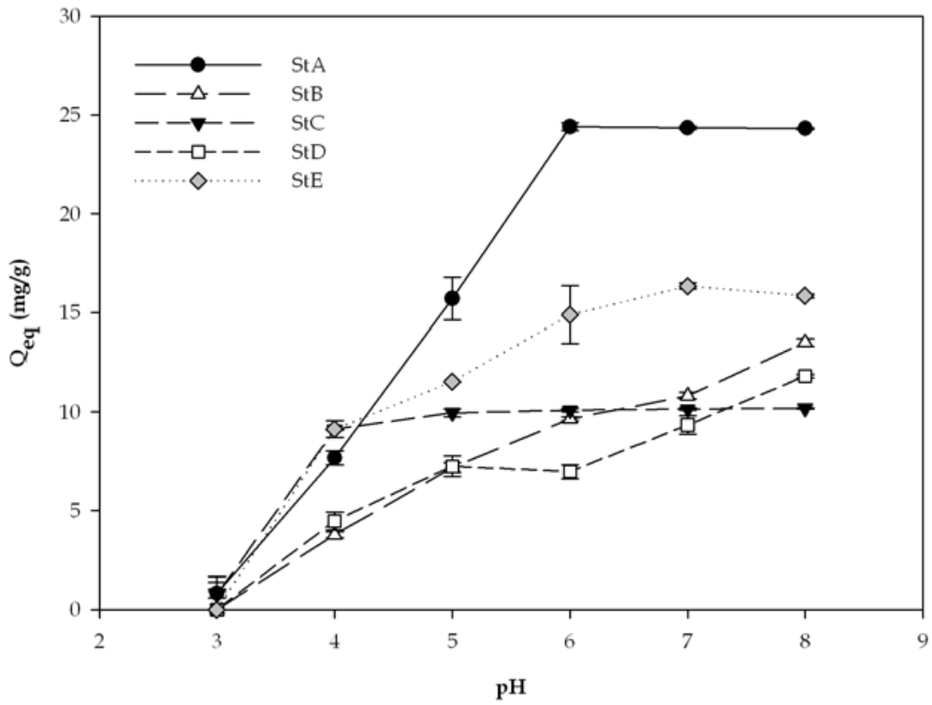


Fig. 3. Specific biosorption vs. pH for crystal violet adsorbed in strains isolated from the JLS channel.

3.2.1.3 Crystal violet adsorption isotherms

Figure 4 shows the adsorption isotherms for strains StA to StE. As shown in Figure 2, the strains show Q_{eq} between 100 and 300 mg L^{-1} and different profiles.
Linearization of the isotherms of Figure 4 was attempted by a Langmuir model. This was made only to get a phenomenological description of the plots and for calculation of specific adsorption Q^0. The respective extracted adsorption parameters are presented in Table 2. Strain B shows a sigmoidal shape and was fitted with a Hill model.

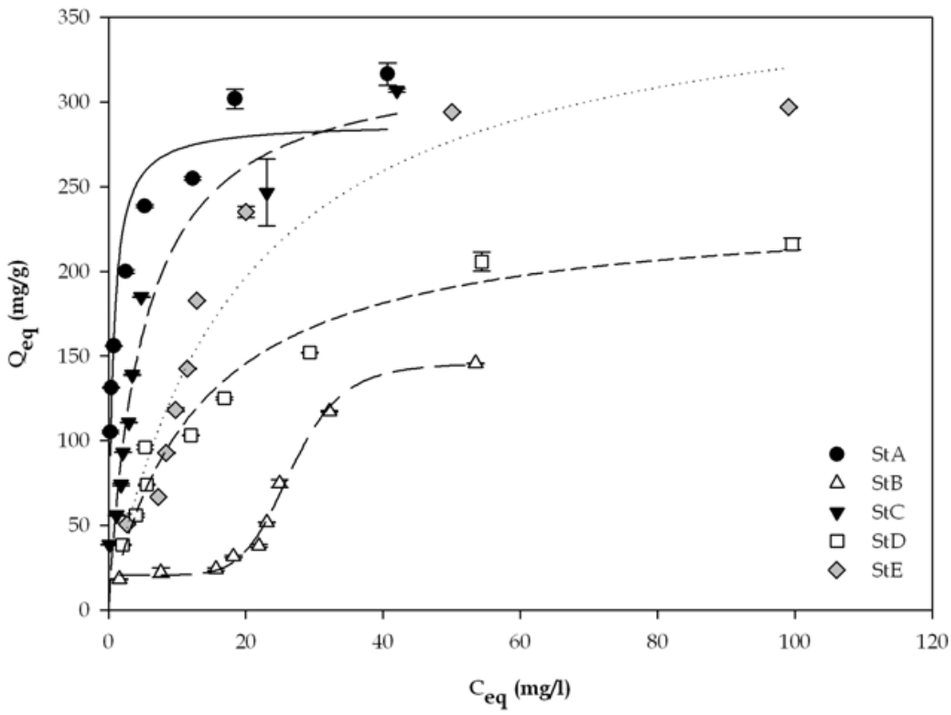


Fig. 4. Adsorption isotherms of crystal violet on the five isolated strains. The initial crystal violet concentration was in the 10-200 mg L^{-1} range.

	R^2	Q^0 (mg g^{-1})	K_L (mg L^{-1})
A	0.9027	288 ± 15	0.59 ± 0,15
B	0.9927	125 ± 6	26.7 ± 0,6
C	0.9573	328 ± 22	5.1 ± 0,9
D	0.9564	240 ± 15	13 ± 2
E	0.9215	381 ± 40	19 ± 5

Table 2. Constants and correlation coefficients for the Langmuir and Hill biosorption models.

The strains isolated in the JLS channel show higher Q_{max} values than those reported in the literature for cationic dyes adsorbed on other strains (Chu and Chen 2002, Fu and Virarahavan 2000). These high adsorption capacities (close to 30% in mass) suggest the importance the biosorption processes in the natural attenuation of the contaminants discharged to the stream.

3.2.2 BKC experiments

Kinetic studies indicated that BKC adsorption on the biomass in the studied range is very fast. After 20 min, the saturation equilibrium was reached in all cases. Due to these results, adsorption isotherms were evaluated after 30 min incubation. Figure 5 shows the isotherms obtained by adsorption of BKC on the six isolated strains (strains SbA to SbF).

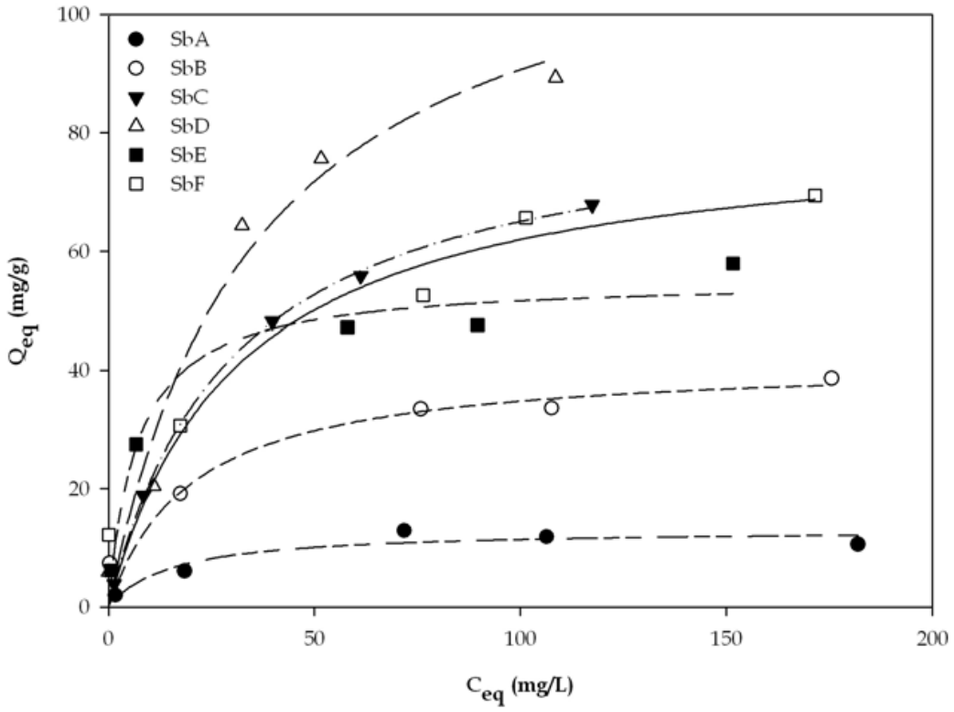


Fig. 5. Adsorption isotherms of BKC on the six isolated strains. The initial BKC concentration was in the 7-209 mg L^{-1} range.

In a similar way as in the crystal violet adsorption experiments, linearization of the isotherms of Figure 5 was attempted by a Langmuir model (only for phenomenological description of the plots and for calculation of $\mathbf{Q^0}$). The respective extracted adsorption parameters are presented in Table 3.

	R^2	Q^0 (mg g^{-1})	K_L (mg L^{-1})
A	0,977	11	9,3
B	0,987	37	7,9
C	0,999	85	31
D	0,875	104	21
E	0,985	56	10
F	0,971	71	14

Table 3. Adsorption parameters obtained from the linearization of the adsorption isotherms applying the Langmuir model.

With the data obtained from the adsorption isotherms extracted for each strain, it can be estimated that the BKC sorption capacity on this consortium is in the range 11-110 mg BKC per gram of dry biomass. In further experiments with the consortium, an average value of 50 mg BKC g^{-1} biomass was taken, in agreement with previous data found for BKC adsorption on activated sludges.

3.3 Treatment of sludges from adsorption processes. Adsorption-composting coupled experiments with crystal violet

3.3.1 Solid phase dye degradation

Figure 6 shows the percentage of degradation of adsorbed dye on biomass (strains StB and StC) and biomass-sediment.

StB and StC show 40 and 30% of dye degradation in only 12 days. In the systems with biomass associated to sediment, the degradation rate is delayed. This behavior may be due to the distribution of adsorbed dye between the biomass and the abiotic surfaces (clays, humic substances, etc.). In systems with biomass and sediments, the highest proportion of sediment could favor adsorption on the abiotic component. Under these conditions, the population of microorganisms that catalyze the degradation of this fraction of the dye would be less than the present when the dye is directly adsorbed on biomass.

Although experiments with higher incubation times are needed to understand the precise involved mechanisms, the degradation rates observed in the case of C and B strains are high enough to show that this degradation process in solid phase has a high potential for the treatment of wastes produced in the remediation of contaminated sludge and produced by biosorption of dyes.

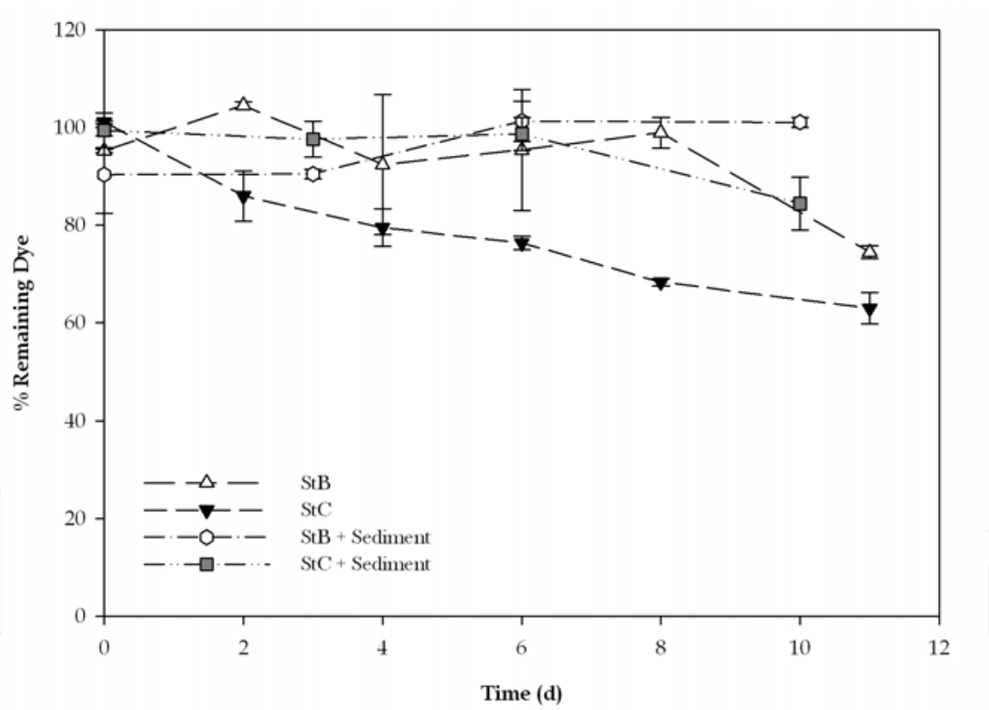


Fig. 6. percentage of remaining dye vs. time for composting experiments.

3.4 Biological-photocatalytic coupled treatment of surfactants

Biodegradation experiments were conducted in shaken flasks and a packed bed reactor with a consortium of microorganisms adapted to grow as a biofilm in the presence of BKC. Operational variables were studied to optimize the process, mainly the presence and concentration of organic matter other than the studied recalcitrant contaminants, such as is usually found in real effluents.

The photocatalytic degradation of benzyl alkyl ammonium was studied by Hidaka et al. (2002) and in our laboratories. Degradation of these compounds by oxidative photocatalysis is possible, but mineralization is slow. However, photocatalysis is an interesting alternative to reduce the BKC concentration entering biological plants, to avoid the biomass death provoked by the presence of relatively high BKC concentrations. In this case, the role of the oxidized byproducts on the performance of the biological reactor should be investigated. Also, the presence of an extra source of carbon should be considered in order to feed the growing biomass. Some studies in batch and supported reactors were performed in this work.
Alternatively, when a relatively low BKC concentration is present in the effluent, biological treatment followed by photocatalysis may be useful to completely remove BKC from the treated water. In this case, the effect of organic matter (other than BKC) on the photocatalytic reactor should be tested.

3.4.1 Batch experiments

In the photocatalytic experiments, BKC concentration was rapidly reduced from 100 to 5 mg L^{-1} after 150 min irradiation (97% total degradation). However, TOC was reduced only 21% (from 213 mg L^{-1} to 168 mg L^{-1}) in the same period, indicating a low mineralization degree with several byproducts generated during the treatment. BKC decay followed an excellent pseudo-first order kinetics ($R^2 = 1$), with $k = 5 \times 10^{-4}$ s^{-1}.
When the pure and the photocatalyzed BKC solutions (with added nutrients but no another carbon source) were inoculated and incubated, few changes in BKC concentration were observed, but the suspended biomass decreased during the first 50 h incubation time, until a minimum value was reached. The viable bacterial population determined by plate counting also decreased dramatically during the whole incubation period (not shown). These results indicate that the cells died as a consequence of the pollutant and/or the low level of biodegradable organic matter (carbon and electron source), unable to sustain the microorganisms.
When the experiments were repeated with the incorporation of a carbon source (glucose in the reactor medium), the results changed notably. BKC concentration decreased approximately 22% for pure BKC at the end of experiment (230 h). The patterns in BKC concentration and bacterial growth (data not shown) suggest that BKC is adsorbed by the growing biomass. The average sorption capacity of the biomass in system with pure BKC (30 mg BKC L^{-1}) calculated from data of isotherms is enough to produce the observed reduction in BKC concentration by biosorption. When BKC and its oxidation byproducts are present, BKC concentration also decreased, although the amount eliminated in 230 hours was 75% of the initial amount. Unlike the previous case, the profile of the curves (data not shown) suggests a different mechanism for BKC elimination, e.g., a combination of biosorption and biodegradation.

3.4.2 Biodegradation of pure and photocatalyzed BKC solutions in a packed bed reactor operated in continuous mode (CPBR)

3.4.2.1 Medium optimization in CPBR experiments

The batch experiments demonstrated that the presence of an energy and carbon source other than BKC is necessary to maintain the biomass alive and available for adsorption and biodegradation of BKC. The optimum concentration of this carbon source was found to be around 2500 mg L^{-1} COD (data not shown).

3.4.2.2 Coupled CPBR-photocatalytic treatment

3.4.2.2.1 Experiments with 100 mg L-1 BKC

The biological system was fed with a solution containing culture plus 102 mg BKC L^{-1}, and the experiment was run during 110 h. Samples were taken during 5 days and analyzed for COD and BKC. Figure 7 shows BKC and COD concentration at inlet and outlet at different times of the CPBR operation. The total BKC elimination rate was calculated. BKC concentration in the R1 outlet was near 50% of the R1 inlet concentration. The BKC elimination rate remained almost constant, about 6.5 mg L^{-1} h^{-1}, which means that in this reactor about 30% of the incoming BKC was biodegraded. There is a slight tendency of the rate to decrease at longer times, possibly because of deterioration of the biofilm. In R2, total BKC elimination rate decreased with the operation time, due to the decrease of the biodegradation rate, which may be a consequence of the low concentration of the carbon source entering R2 and leads to the degradation of biomass. Both reactors reduce BKC concentration to below 40 mg L^{-1}.

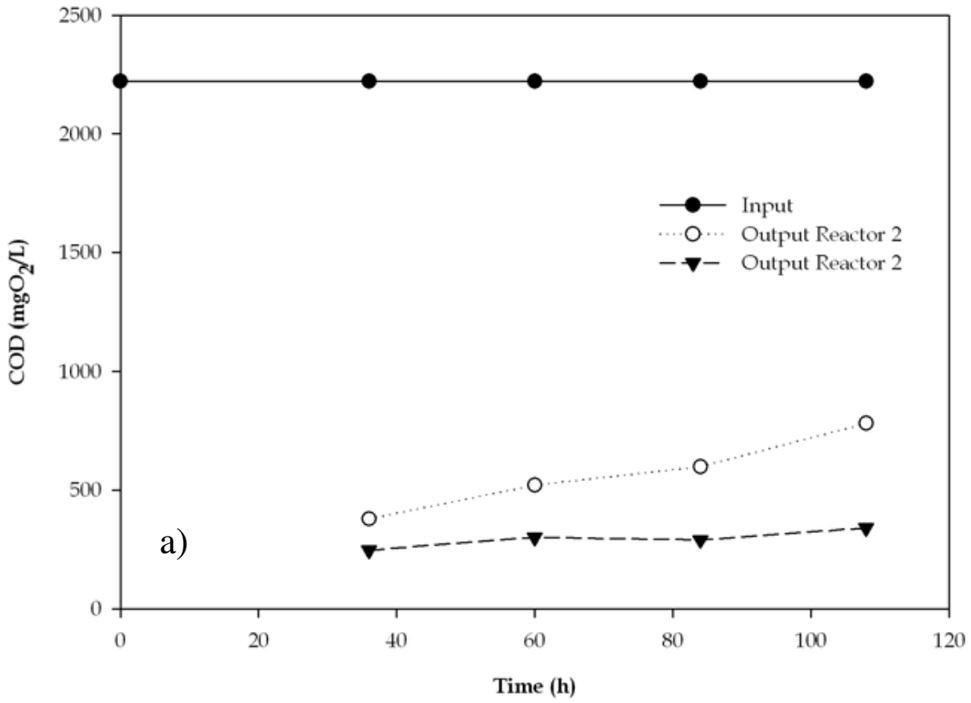
Figure 7a shows a substantial reduction in COD. COD consumption rate in R1 was in the range 263-206 mg $L^{-1}h^{-1}$, and in R2 19-63 mg L^{-1} h^{-1}. The lower COD consumption rate in R2 would be explained in terms of the Monod model (Zhang 2011) due to the low COD concentration (carbon and energy source) at R2 inlet. Continuous operation of R1 leads to diminish slightly the efficiency of the reactor, but R2 was able to assimilate all the COD. The COD degradation rate agrees again with the Monod model. The decrease of COD degradation rate in R1 led to an increase of COD concentration in R2 inlet, which led to an increase of COD degradation rate in this reactor.

A 500 mL sample of the R2 outlet was collected after the first 36 h of biological treatment ([BKC] = 38 mg L^{-1}), and submitted to a photocatalytic treatment. The BKC concentration decreased to 27.6 mg L^{-1} (28%) after TiO_2 incorporation and, after 2 h of HP treatment, more than 99% BKC was eliminated. Again an excellent pseudo-first order decay (not shown, $R^2 = 0.94$, $k = 6 \times 10^{-4}$ s^{-1}) was obtained. These results demonstrate the feasibility of using photocatalysis as a post-biological treatment to eliminate the recalcitrant pollutant. As observed, the biological treatment reduced the organic charge present in solution from 2222 to 246 mg L^{-1} , concentrations that do not hinder the activity of the photocatalyst (at least with the nutrients used in this work); further photocatalytic treatment eliminates the remaining toxic contaminant.

3.4.2.2.2 Experiments at 180 mg L-1 BKC

A new set of experiments were run by feeding the CPBR with a solution containing 2500 mg COD L^{-1} and 180 mg BKC L^{-1}. COD decreased notably at the outlet of both R1 and R2. BKC concentration also decreased at the beginning of the experiment, but after 2 days of continuous working, the concentration rose dramatically (not shown). These results would indicate that the biofilm collapses after 2 days and that BKC is released to the environment. R2 adsorbs part of the BKC but, after 5 days, the concentration in the solution rose until values close to the inlet concentration.

These results indicate that effluents containing up to 100 mg L^{-1} of BKC and biodegradable organic matter can be purified by a biological reactor followed by photocatalytic treatment. The bioreactor eliminates most of the organics and the photocatalytic treatment eliminates the remaining BKC. In contrast, higher BKC concentrations (about 180 mg L^{-1}) degrade the biofilm and avoid this type of coupling.



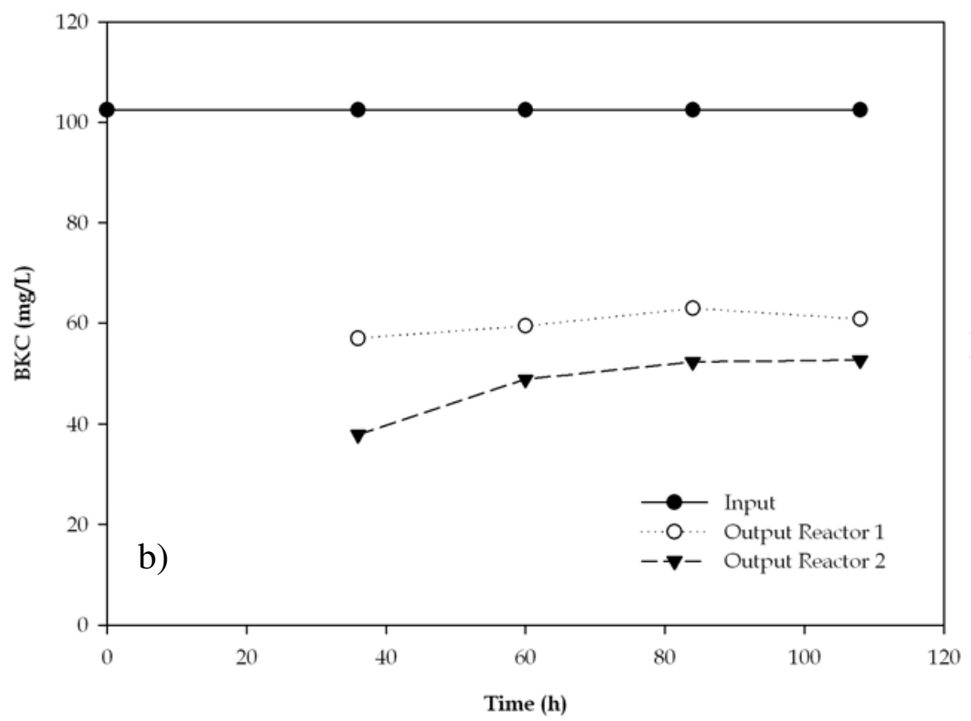


Fig. 7. Biological BKC treatment before the photocatalytic treatment: a) COD vs. time; b) BKC concentration vs. time

3.4.2.3 Coupled photocatalytic-CPBR treatment

A BKC sample previously treated by HP with an initial concentration of 81 mg L^{-1} was diluted with culture medium, leading to a final solution with 48 mg BKC L^{-1} and 2050 mg COD L^{-1}, and this solution was submitted to the biological treatment. Results are shown in Figure 8.

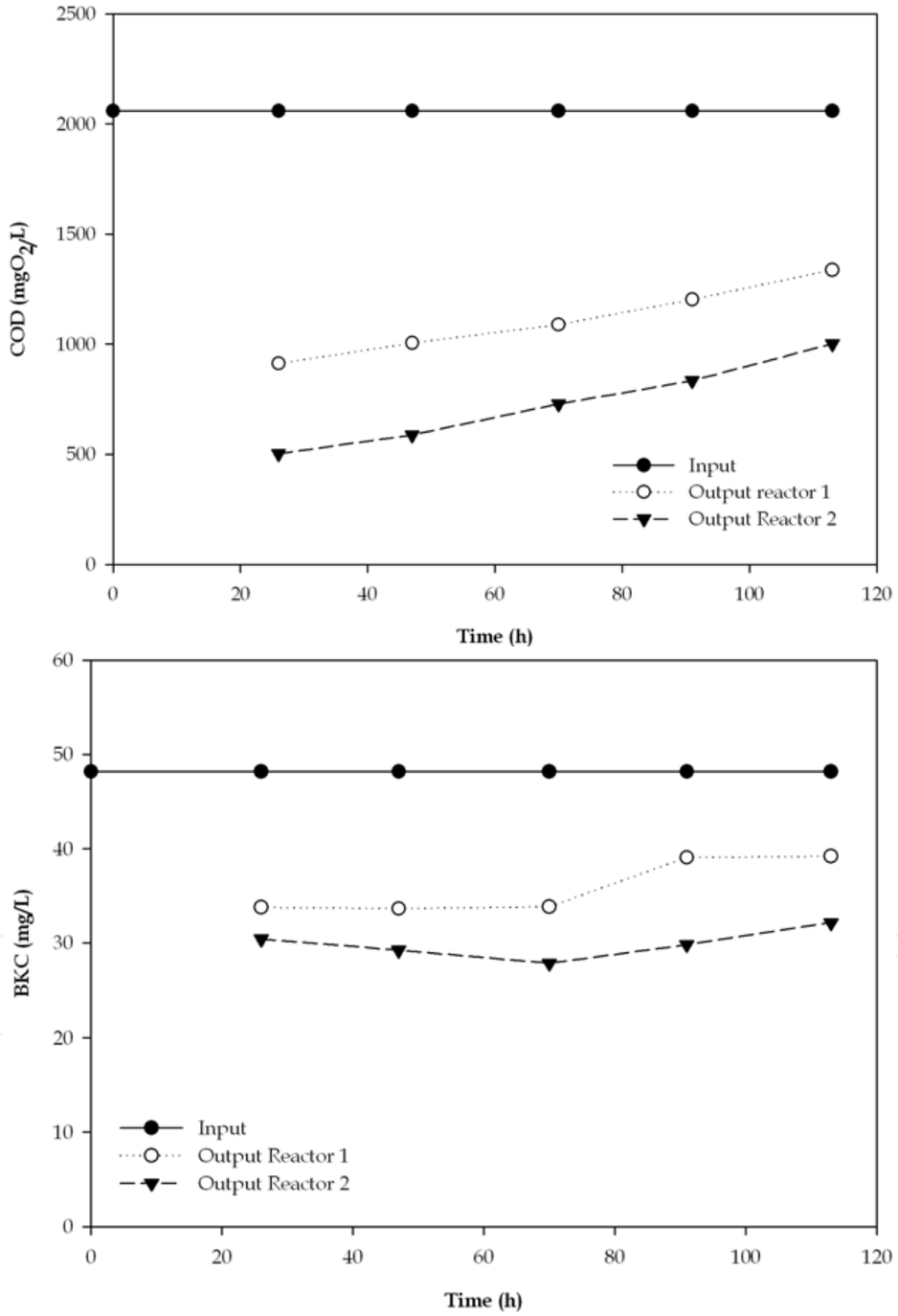


Fig. 8. *Biological treatment after photocatalysis:* A) DQO vs. time; B) BKC concentration vs. time.

The BKC removal rate in R1 was constant around 2 mg L^{-1} h^{-1} during the first 70 h; then it decreased to 1.3 mg L^{-1} h^{-1}, probably by degradation of the biofilm. These values are also considerably lower than 6.5 mg L^{-1} h^{-1}, value found in the previous biological-photocatalytic experiment; this, as observed also for COD removal, strongly suggests that incomplete degradation products are more toxic to the biofilm than pure BKC. In R2, the total removal rate increased BKC from 0.48 to 1.0 mg L^{-1} h^{-1}, resulting lower than the rate in the previous experiment. The COD degradation rate in R1 decreased 37% throughout the experiment. Compared to the previous experiment in which the initial rate was 263 mg L^{-1} h^{-1} and its decrease in time was 23%, it can be assumed that (below 100 mg L^{-1} BKC) the presence of partially degraded products produced during photocatalysis have a partial inhibitory effect on biomass, stronger than that of BKC. R2 shows a relatively constant COD degradation rate (60-48 mg L^{-1} h^{-1}), similar to that obtained in R2 in the previous experiment and lower than the one shown by R1. This fact is consistent with the Monod model, according to the input substrate concentrations (R1 output). In R2, the concentration of inhibitory compounds (BKC and intermediates) is lower than those in R1, and the biofilm activity did not decrease over time.

4. Conclusions

The results of this study show that coupling processes based on different technologies such as adsorption, biodegradation and photocatalysis are potentially useful in both, the understanding of the dynamics and fate of pollutants in superficial waters such as streams and rivers and for develop alternatives for effluent treatment.

The adsorption of dyes on biomass of native bacterial strains is a very fast process that occurs in a wide range of pH with very high specific adsorption (near 30 % of the dry weight). In natural waters, biomass is commonly growing as biofilms on sediment surfaces. This fact could lead to the immobilization of the contaminant. The dye-charged biomass alone or associated with sediments shows dye degradation capacity in composting processes.

With respect to potential effluent treatment processes, the isolated native strains show interesting capacities: StA strain shows very high affinity for crystal violet and could be used to treat large volumes of diluted effluents, and StE strain shows very high specific adsorption, and could be used to treat smaller volumes of concentrated effluents.

From the technological point of view, adsorption-based processes could be used to reach a very fast separation of the contaminants from large volumes of water. Later use of advanced oxidation technologies could be used to the final polish of the effluent, while composting of the contaminated biomass appears to be an excellent alternative to the treatment of the formed sludge, avoiding secondary contamination or high disposal costs.

With regard to the treatment of BKC, the process can be improved if the samples are submitted to a coupled treatment of a photocatalytic treatment combined with a biological system. For this purpose, different configurations of coupled photocatalytic-biological reactors can be adopted, depending mainly on the BKC concentration and the total organic load.

For BKC concentrations up to 100 mg L^{-1}, the CPBR-HP treatment configuration shows some advantages. In the biological reactor, 50% BKC is degraded and this drastically reduces the COD of the effluent. The subsequent photochemical treatment leads to total BKC removal without losing efficiency by oxidizing other readily degradable compounds present in the matrix.

In the case of BKC concentrations below 100 mg L^{-1}, the HP pretreatment does not work properly, because the toxicity of the photodegradation byproducts on the biofilm is higher than that of pure BKC.
In the case of higher BKC concentrations (180 mg L^{-1}), the bacterial biofilm is not able to be sustained over the time; therefore, it is necessary to perform a previous HP pretreatment to reduce BKC concentration.
In spite that the biomass activity decreases with time, the deleterious effect of BKC and byproducts on biofilm activity is less important compared with that of an effluent containing a very high charge of BKC and directly submitted to the biological treatment. As shown, if BKC concentration is too high (for example 180 mg L^{-1} or more), the biomass is strongly affected and BKC is released to solution. However, if the highly concentrated BKC solution is first photocatalytically treated, the biosystem can support the effluent containing the remaining BKC and its oxidation byproducts.

5. Acknowledgements

This work was performed as part of Agencia Nacional de Promoción Científica y Tecnológica PICT-512, PAE 22257, CONICET PIP 11220090100079, and Universidad de San Martín, UNSAM SA08/011.

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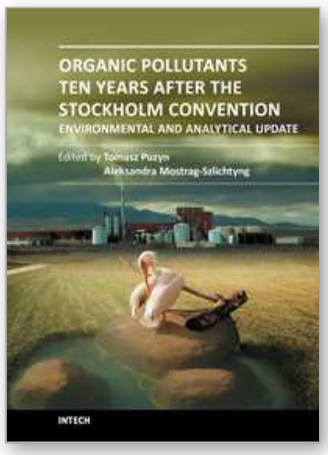
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Organic Pollutants Ten Years After the Stockholm Convention - Environmental and Analytical Update

Edited by Dr. Tomasz Puzyn

ISBN 978-953-307-917-2
Hard cover, 472 pages
Publisher InTech
Published online 24, February, 2012
Published in print edition February, 2012

Ten years after coming into force of the Stockholm Convention on Persistent Organic Pollutants (POPs), a wide range of organic chemicals (industrial formulations, plant protection products, pharmaceuticals and personal care products, etc.) still poses the highest priority environmental hazard. The broadening of knowledge of organic pollutants (OPs) environmental fate and effects, as well as the decontamination techniques, is accompanied by an increase in significance of certain pollution sources (e.g. sewage sludge and dredged sediments application, textile industry), associated with a potential generation of new dangers for humans and natural ecosystems. The present book addresses these aspects, especially in the light of Organic Pollutants risk assessment as well as the practical application of novel analytical methods and techniques for removing OPs from the environment. Providing analytical and environmental update, this contribution can be particularly valuable for engineers and environmental scientists.

How to reference

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Roberto Candal, Marta Litter, Lucas Guz, Elsa López Loveira, Alejandro Senn and Gustavo Curutchet (2012). Alternative Treatment of Recalcitrant Organic Contaminants by a Combination of Biosorption, Biological Oxidation and Advanced Oxidation Technologies, Organic Pollutants Ten Years After the Stockholm Convention - Environmental and Analytical Update, Dr. Tomasz Puzyn (Ed.), ISBN: 978-953-307-917-2, InTech, Available from: http://www.intechopen.com/books/organic-pollutants-ten-years-after-the-stockholm-convention-environmental-and-analytical-update/alternative-treatment-of-recalcitrant-organic-contaminants-by-a-combination-of-biosorption-biologica

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