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Full Length Research Paper

Degradation of di-, tri-, tetra-, and pentachlorophenol mixtures in an aerobic biofilter

Luis G. Torres[1]*, Miguel Hernández[2], Yolanda Pica[2], Verónica Albiter[3] and Erick R. Bandala[4]

[1]Unidad Profesional Interdisciplinaria en Biotecnologia, Instituto Politecnico Nacional, Av. Acueducto s.n. Colonia Barrio la Laguna Ticoman, Mexico 07340 D.F. México.
[2]Instituto Mexicano de Tecnología del Agua, Paseo Cuahunahuac 8532, Jiutepec, Morelos, Mexico.
[3]Intituto de Biotecnologia, Universidad Nacional Autonoma de Mexico, Apartado Postal 510-3, Cuernavaca, Morelos. 62271, Mexico.
[4]Departamento de Ingeniería Civil y Ambiental, Universidad de Las Americas-Puebla. Sta. Catarina Martir, Cholula 72820 Puebla, Mexico.

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Chlorophenols are highly toxic xenobiotic compounds, normally found in the effluents of many industries. Due to the high toxicity of these compounds, it is difficult to treat effluent streams containing high concentrations of chlorophenols. The aim of this work is to demonstrate the capabilities of an aerobic submerged filter previously characterized in the degradation of phenol and chlorophenols in the treatment of highly toxic di-, tri-, tetra- and penta- chlorophenols mixtures (200 - 800 mgL^{-1} as total phenols concentration). It is shown that the system is capable of treating up to 600 mgL^{-1} of total chlorophenols with excellent reduction values, and biodegradation rates (BDRs) between 87 - 97%, and 34 - 157 mgL^{-1} day^{-1}, respectively (total organic carbon, TOC degradations up to 80%). In the case of the 800 mgL^{-1}, a strong inhibition due to the high toxicity of the mixture was observed. The system reduced the influent toxicity (EC50 or toxic units) by 48 - 76%, even when the initial toxicities of the mixtures were in the range of 40 - 358 toxic units (classified as very toxic). The kinetics of the phenol and TOC degradation were characterized through a first order kinetic expression. The values of TPh_o, TOC_o, k_1 and k_2 are reported for the biodegradation of the total phenols and for the TOC, respectively. A system with powerful capabilities in the treatment of industrial streams, contaminated aquifers or accidentally contaminated municipal wastewaters containing high quantities of chlorophenols, is described.

Key words: Aerobic biodegradation, chloropheols, industrial efluents, phenols, submerged filter.

INTRODUCTION

Chlorophenols are highly toxic xenobiotic compounds, normally found in the effluents of industries such as pulp and paper, oil and petrochemical, synthetic plastics, pesticides, timber products, and others. Phenol and chlorinated phenols are one of the major components of industrial wastewater and it is toxic to the receiving environment. Mexico has an important oil and petro-chemical industry. It has been calculated that approximately, 10,000 barrels of crude oil refinement yield almost 100 kg of phenols (Nemerow 1987), which is alarming. Pentachlorophenol is the highest chlorine-ted phenol and is widely used as an excellent wood preservative (Bryant et al., 1991), very frequently used in combination of 2,4,6-trichloro-phenol or other polychlorinated phenols. Due to the high toxicity of these products, only a few biological treatments are suitable for the treatment of streams containing high concentrations of these compounds.

Different systems have been proposed in order to eliminate phenol and chlorophenols from water streams. Physical-chemical and biological approximation have

*Corresponding author. E-mail: LTorresB@iingen.unam.mx or LTorresB@ipn.mx.

been employed in those studies. Ku et al. (2006) reported the ozonation of 2-chlorophenol in a packed contactor (physical-chemical), while Li and Loh (2007) worked with the transformation of 4-chlorophenol and phenol in hybrid-hollow-fiber membrane bioreactors, using the bacteria *Pseudomonas putida* (physical-chemical/ biological combination). On the other hand, Chen et al. (2005) studied the biodegradability of 2,4-dichlorophenol in an upflow anaerobic sludge bed biorector (biological). In the same line of research, Eker and Kargi (2007) reported the treatment of wastewater containing 2,4,6-trichlorophenol using a hybrid-loop bio-reactor system (biological).

One of the systems reported because of its high efficiencies and removal capacities is the submerged aerobic filter, inoculated with one or more specific microorganisms (Bettman and Rehm, 1985; Zache and Rehm, 1989; Seignez et al., 1993; Khlebnikov and Péringer, 1996; Fava et al., 1996; Torres et al., 1997; Kim et al., 2002).

The aim of the series of experiments here reported was to assess the capabilities of an aerobic submerged filter previously characterized in the degradation of phenol and chlorophenols (Torres et al., 1997a), in the treatment of highly toxic di-, tri-, tetra- and pentachlorophenol mixtures (200 - 800 mgL^{-1} as total phenols concentrations). Total and specific phenols, as well as TOC removal efficiencies and biodegradation rates were compared for the different assessments, as well as the capability of the system in reducing the influent toxicity (EC_{50} or toxic units).

MATERIALS AND METHODS

A 0.054 L glass column, very similar to the one used in a previous study (Torres et al., 1999), was employed in this investigation. The column was packed with *tezontle,* a red basaltic scoria (mesh 12, 13 and 14 at equal proportions) very abundant in Central Mexico. This material is commonly used with decorating purposes in yards and walls. It has also been used as a filtering material because of its high porosity and strength. The column was inoculated with a 24 h yeast peptone glucose (YPG) pure culture of *Pseudomonas fluorescens*. The aerobic bacteria was isolated from sediment and characterized by means of a set of biochemical tests. Specifically the API20e kit (Biomeraux, France) was employed to determine genera and species. Some preliminary test showed that this *P. fluorescens* strain is able to degrade phenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2,3,4,6-tetrachlorophenol, pentachlorophenol, 2,4-dichloro-phenoxy acetic acid, phenyl acetic acid and chlorinated pesticides (Torres et al., 1998c; Bandala et al., 2006; Santacruz et al., 2005). Bacteria were grown in YPG medium (in gL^{-1}: yeast extract, 10; casein peptone, 10; glucose, 10). Mixtures of 2,4-dichlorophenol (2,4-DCPh), 2, 4, 6- trichlorophenol (2,4,6-TCPh), 2,3,4,6-tetra-chlorophenol (2,3,4,6-TeCPh), and pentachlorophenol (PCPh) at equal proportions and total phenol concentrations of 200, 400, 600 and 800 mgL^{-1}, were prepared in Dapaah medium (Dapaah and Hill, 1992) (in gL^{-1}: monobasic potassium phosphate, 0.84; dibasic potassium phosphate, 0.75; ammonium sulfate, 0.488; sodium chloride, 0.06; calcium chloride, 0.06; magnesium sulfate, 0.06 and ferric chloride, 0.006). The mixtures proportions were decided arbitrarily, since it was decided to test low (200), medium (400), high (600) and extra-high (800 mgL^{-1}) total concentrations. In all the cases the chlorophenols propor-tions were the same. Temperature was kept at 28°C. Total phenols were measured during the biodegradation run by the 4-aminoantipirine method (APHA, AWWA; WPCF, 1989). The plate-total count (CFU $g_{support}^{-1}$) was developed as follows. Total counts were carried out as reported in Torres et al. (2005), but using YPG medium. The specific phenols (2, 4-DCPh; 2,4,6-TCPh; 2,3,4,6-TeCPh and PCPh) were analyzed at the beginning and the end of every biodegradation run (when total chloro-phenols removal reached approximately 95%) by means of a GC/Mass system, as described in Torres et al. (1997b). Total organic carbon (TOC) was measured at the beginning and the end of the experimental runs in a Beckman 915B (USA) equip-ment. Toxicity (as EC50 in mgL^{-1}, or Toxic units, TU) was mea-sured using a Microtox equipment (Beckman Instruments, USA).

RESULTS AND DISCUSSION

Biodegradation of the mixtures assessment

The chlorophenol concentrations for the experiments with 200, 400, 600 and 800 mgL^{-1} are shown in Figure 1, in which the very different phenols *vs*. time profiles for each total phenol concentration are displayed. As mentioned in the materials and methods section, the biodegradation reactions were stopped when the chlorophenols concentration were degraded at up to 95%. For the 200, 400 and 600 mgL^{-1} experiments, the time was about 123, 64 and 89 h, respectively, though most of the phenols disappeared in the first 15 - 20 h. The case of the 800 mgL^{-1} experiment was quite different. The experiment was stopped at 281 h, but the removal value did not reach more than 50%. Some problems with the 4-aminoantipirine method were detected (different colors from those expected were observed). It was decided to finish the test and analyze the samples by means of the gas chromatography/mass spectrometer system. In Figure 1, solid lines represent the results predicted by equation (1)

$$TPh = TPh_o \exp(-k_1 t) \quad (1)$$

Where TPh_o is a model parameter for the initial phenol concentration (mgL^{-1}), k_1 is a kinetic constant ($hours^{-1}$), and t is the process time (h).

These general results are summarized on Table 1. The final total phenol (TPh) concentrations are those found by GC/MS. As shown, these results are similar to those presented on Figure 1. At the end of the 200 mgL^{-1} experiment, 26.23 mgL^{-1} of TPh remained (86.88% removal), giving a global biofilter biodegradation rate (BDR) of only 33.9 $mgL^{-1}day^{-1}$. In the 400 mgL^{-1} experiment, only 10.8 mgL^{-1} of TPh was left (97.29% removal), giving a better BDR of 145.9 mgL^{-1} day^{-1}. The third experiment showed the best results, because only 17.84 of the initial 600 mgL^{-1} were detected at the end of the process (97.02% removal), giving a 156 $mgL^{-1}day^{-1}$

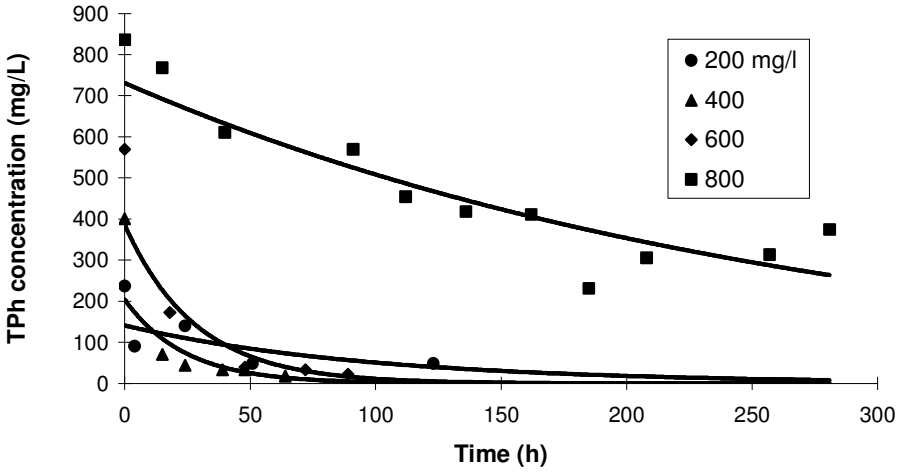

Figure 1. TPh concentration *versus* degradation time.

Table 1. Biodegradation of the chlorophenol mixtures in the packed column.

Initial conc. (mgL^{-1})	Final conc. (mgL^{-1})	Degraded (%)	Process time (h)	BDR (mgL^{-1} day^{-1})	Initial (FCU $g_{support}^{-1}$)	Final (FCU $g_{support}^{-1}$)
200	26.23	86.88	123	33.90	$1x10^4$	$1x10^2$
400	10.80	97.29	64	145.94	$1x10^4$	$7x10^4$
600	17.84	97.02	89	156.98	$1.3x10^7$	$1x10^4$
800	699.51	12.56	281	8.58	$7x10^4$	$2x10^4$

Table 2. Resuts of the experiments with 200 mgL^{-1} of TPH. Degradation of every specific CPh.

Compound	Initial conc. (mgL^{-1})	Final conc (mgL^{-1})	Degraded (%)	BDR (mgL^{-1} day^{-1})
2,4-DCPh	50	0.078	99.80	9.74
2,4,6-TCPh	50	4.084	91.83	8.95
2,3,4,6-TeCPh	50	10.901	78.19	7.62
PCPh	50	11.174	77.65	7.57
TPh	200	26.237	86.88	33.9

BDR. The highest concentrated test failed, since 699 of the initial 800 mgL^{-1} of TPh remained at the end of the process (12.56% removal), resulting in the worse biofilter BDR (8.58 mgL^{-1} day^{-1}).

The initial and final CFU $g_{support}^{-1}$ for every experiment run is also shown at Table 1. It is worth noting that the differrent compound load in the stream affected positively or negatively, the immobilized biomass, but the average was around 1.6×10^6 FCU $g_{support}^{-1}$. The first experimental runs started with a TPh concentration of 400 mgL^{-1}. During the test, the average biomass was lightly increased. The second test (600 mgL^{-1}) started with 10^7 and finished with 10^4 FCU $g_{support}^{-1}$, which means a drastic decrease in biomass load due to the toxicity of the chlorophenols mixture. In the third experimental run (800 mgL^{-1}) a new decrement was observed in the biomass load. The ending test was carried out with a TPh concentration of 200 mgL^{-1}. In this test, a two-order decrement was observed probably related to a lack in C-source available for the immobilized bacteria.

In Tables 2, 3, 4 and 5, the specific phenols removals and filter BDRs are compared. In the case of the 200 mgL^{-1} experiment, removals from 77.65 to 99.8% were reached, giving BDRs of 7.57 - 9.74 mgL^{-1} day^{-1}. The global values for removal and BDRs of the TPh were 86.88% and 33.9 mgL^{-1} day^{-1}, respectively. The test, which started with 400 mgL^{-1} of TPh, reached a better removal values for the specific chlorophenols (94.55 - 99.99%) and biofilter BDRs (34.49 - 37.27 mgL^{-1} day^{-1}).

Table 3. Results when working with 400 mgL^{-1} of TPh. Degradation of every specific CPh.

Compound	Initial conc. (mgL^{-1})	Final conc. (mgL^{-1})	Degraded (%)	BDR (mgL^{-1} day^{-1})
2,4-DCPh	100	0.0073	99.99	34.49
2,4,6-TCPh	100	0.596	99.40	37.27
2,3,4,6-TeCPh	100	4.755	95.24	35.71
PCPh	100	5.455	94.55	35.45
TPh	400	10.803	97.29	145.94

Table 4. Removal found in the 600 mgL^{-1} of TPh experiments. Degradation of every specific CPh.

Compound	Initial conc. (mgL^{-1})	Final conc. (mgL^{-1})	Degraded (%)	BDR (mgL^{-1} day^{-1})
2,4-DCPh	150	0.0678	99.95	40.43
2,4,6-TCPh	150	1.207	99.19	40.12
2,3,4,6-TeCPh	150	7.79	94.80	38.34
PCPh	150	8.78	94.14	38.08
TPh	600	17.84	97.02	156.98

Table 5. Failed experiments with 800 mgL^{-1} of TPh. Degradation of every specific CPh.

Compound	Initial conc. (mgL^{-1})	Final conc. (mgL^{-1})	Degraded (%)	BDR (mgL^{-1} day^{-1})
2,4-DCPh	200	145.72	27.13	4.63
2,4,6-TCPh	200	180.33	9.83	1.67
2,3,4,6-TeCPh	200	173.46	13.26	2.26
PCPh	200	200.0	00.00	0.0
TPh	800	699.51	12.56	8.58

The global removal and BDRs were, respectively, 97.29% and 145.94 mgL^{-1} day^{-1}.

The experiment with 600 mgL^{-1} of initial TPh was, undoubtedly, the best of the series assessed. The specific phenols removals were in the range of 94.14 - 99.95% with BDRs of 38.08 - 40.43 mgL^{-1} day^{-1}. The global removal and biofilter BDRs were 97.02%, and 156.98 mgL^{-1} day^{-1}, respectively. Definitely, the test with 800 mgL^{-1} of TPh failed. The specific phenol removals were as low as 0.0 - 27.13%, with the consequent lower filter BDRs: 0.0 - 4.63 mgL^{-1} day^{-1}. These figures give a total removal of 12.56% and BDR of 8.58 mgL^{-1} day^{-1}.

It must be stressed that the system was capable of treating 200 - 600 mgL^{-1} of TPh with excellent removals and BDRs between 86.88 - 97.02% and 33.9 - 156.9 mgL^{-1} day^{-1}, respectively. In the case of the 800 mgL^{-1}, a strong inhibition due to the high toxicity of the mixture was observed. It is important to recall the results for the experiments with single chlorophenols were obtained in a packed column quite similar to this (Torres et al., 1999). The system was able to treat 100 - 1,000 mgL^{-1} of phenol, 50 - 600 mgL^{-1} of 2-chlorophenol or 2, 4-DCPh, 50 - 700 mgL^{-1} of TCPh and 50 - 300 mgL^{-1} of PCPh. Even though the, 2, 3, 4, 6-TeCPh was not tested before, it was very well degraded by the system (78.2 - 95.2% for the 200 - 600 mgL^{-1} experiments).

The specific phenol biofilter BDRs were quite low compared to those previously reported (Torres et al., 1999). For example, the 9.74 - 40.43 mgL^{-1} day^{-1} 2, 4-DCPh biofilter BDR is low compared with the 45 - 656 mgL^{-1} day^{-1} BDRs reported for 50 - 200 mgL^{-1} of 2,4-DCPh. In the case of the 2,4,6-TCPh the differences are larger: 52 -770 mgL^{-1} day^{-1} for 50 - 200 mgL^{-1} of the single compound, compared to the 8.9 - 38.3 mgL^{-1} day^{-1} determined herein. Finally, the values for PCPh are 7.6 - 38 and 16.6 - 203.6 mgL^{-1} day^{-1}, reported herein and in the previous work, respectively. In fact, BDRs for the single compounds as high as 1,779, 1,669, 2,193 and 203 mgL^{-1} day^{-1} (for 2-CPh; 2,4-DCPh; 2,4,6-TCPh and PCPh, respectively).

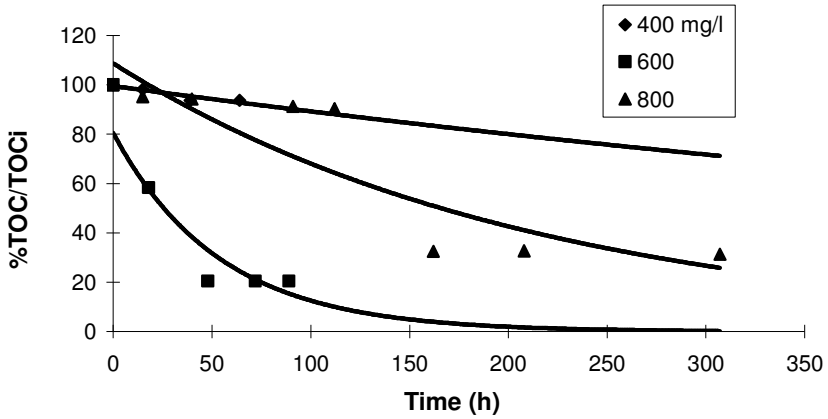

Figure 2. Percentage of TOC/TOC_i *versus* process time.

Some other studies have been reported regarding the rates of biodegradation for aerobic biofilters and related systems. For example, Bettman and Rehm (1985) immobilized *P. putida* in polyacridamide-hidracide. This biocatalyst was used in a 0.9 L airlift reactor for the treatment of mixtures containing phenol (1,000 - 5,000 mgL^{-1}), 4-chlorophenol (25 - 65 mgL^{-1}) and cresol (30 mgL^{-1}). They found removals in the range of 75 - 100% with BDRs as high as 3,120 - 7,200 $mgL^{-1}day^{-1}$.

Khlevnikov and Péringer (1996) immobilized *Commamonas testosteroni* in a plastic static mixer for the treatment (in a 8 L packed column) of p-toluensulphonic acid in concentrations of around 1,140 mgL^{-1}. They concluded that it is possible to treat these streams with efficiencies as high as 90 - 100% with column BDRs of 2,400 - 4,800 $mgL^{-1}day^{-1}$.

Fava et al. (1996) experimented with a bacterial coculture immobilized in silica beads, frosted glass beads, and polyurethane foam cubes. The total internal volume of the packed column employed was 0.57 L. The substrates degraded for the system were 2,5-dichlorobiphenyl, 2,3´-dichlorobiphenyl, 2,4´-dichlorobiphenyl, 3,3´-dichlorobiphenyl and 4,4´-dichlorobiphenyl at concentrations of 75 mgL^{-1}. They reported that the system was able to biodegrade any of the substrates, measuring dechlorinations from 30 to 90% in 100 - 150 h periods.

Finally, Seignez et al. (1993) employed an immobilized mixed bacterial culture for the treatment (in a 1.2 L fixed bed column) of anthraquinone-2-sulfonate SAS (1,200 mgL^{-1}) and phenol (4,800 mgL^{-1}) streams. They showed that it is possible to obtain removal efficiencies of about 99%, with biodegradation rates of 4,080 $mgL^{-1}day^{-1}$ of SAS, and 6,720 $mgL^{-1}day^{-1}$ of phenol.

In general, all these studies have been carried out with compounds less toxic than those used in the present research (phenol, 4-chlorophenol, p-tolensulphonic acid, and SAS). Only in the case of the polychlorinated biphenyls, toxicities may be higher than those reported for the chlorophenols. Besides, it is important to underline that the chlorophenol mixtures showed toxicities higher than the sum of the individual compounds. Another relevant benefit of the system characterized herein, is the inoculation time. Seignez et al. (1993) reported 25 days of continuous operation for reaching the maximal flow rate with the heterogeneous microbial population, since they used municipal treatment plant consortia as inoculum. At the other hand, Fava et al. (1996), mentioned that the cell suspension was recycled during 5 days as inoculation procedure. In this work, the cell suspension was recycled during 12 - 24 h before the biodegradation assessments. Yet, it is possible to start biodegradation runs with simple compounds or mix-tures, at high concentrations, while in other research, the systems need to be acclimated starting with very low concentrations of the toxic compounds and increase little by little.

TOC degradation and kinetic characterization

Figure 2, shows the TOC development during the biodegradation process. It is presented as the percentage of the TOC $TOC_{initial}^{-1}$ *vs.* process time. The solid lines represent the equation

$$TOC\ TOC_{initial}^{-1} = TOC_o \exp(-k_2 t),$$

where TOC $TOC_{initial}^{-1}$ is the ratio between the TOC at any process time and the beginning of the process (%), TOC_o is the initial TOC concentration parameter, k_2 is the kinetic parameter (h^{-1}), and t is the process time (h). As shown, in the experiments with 600 and 800 mgL^{-1} of TPh, the TOC $TOC_{initial}^{-1}$ value reached 68 - 79%, while in the 400 mgL^{-1} test, the ratio was of only 2% removal. Most of the TOC disappeared in 50 and 160 h for the 600 and 800 mgL^{-1} tests.

In Table 6, the values of the kinetic constants for the chlorophenols and TOC degradation are displayed. As shown, for the case of the chlorophenols, the TPh_o

Table 6. Kinetic constants for the chlorophenols mixtures´ biodegradation.

Mixture conc. (mgL^{-1})	Phenols (expressed as mgL^{-1})				TOC (expressed as % of the initial TOC)		
	TPh_o	k_1	r		TOC_o	k_2	r
200	140.96	0.0102	0.7512		-	-	-
400	203.87	0.0419	0.9046		96.75	0.0001	0.1191
600	385.75	0.0353	0.9575		80.53	0.0106	0.9163
800	730.8	0.0036	0.8578		108.71	0.0047	0.8818

Table 7. Toxicity results.

Mixture or compound (mgL^{-1})	Initial toxicity TU (EC50, mgL^{-1})	Final toxicity TU (EC50, mgL^{-1})	Toxicity removal (%)
Mixture, 400	40.81(2.45)	21.09 (4.73)	48.32
Mixture, 600	52.39 (1.90)	12.25 (8.15)	76.61
Mixture, 800	358.0 (0.28)	278.24 (0.36)	22.28
Phenol, 100	3.85 (25.98)	-	-

values are not close to the real initial concentrations. At the other hand, the k_1 values are quite variable, and no clear relationship between them and the initial TPh concentration is observed. We observed a tendency to have relatively high and very similar k_1 coefficients for the experiments with 400 and 600 mgL^{-1} initial TPh concentrations. For the experiments with 200 mgL^{-1} initial TPH, this value was about four times less, possibly due to an inadequate carbon concentration to sustain the bacterial population. This treatment also had a relatively poor correlation coefficient (r = 0.7512) and may not truly represent first order rate kinetics. Likewise, the k_1 coefficient for the experiment with 800 mgL^{-1} initial TPh is much lower and roughly ten times less than the experiments with 400 and 600 mgL^{-1} initial TPh, probably due to toxicity.

The r values were quite good for most of the fittings, maybe except for the 200 mgL^{-1} test, as stated earlier. For the TOC biodegradation, TOC_o values are close to 100%, which is the expected value for the first TOC $TOC_{initial}^{-1}$ ratio. The k_2 values were also diverse and higher for the 600 mgL^{-1} test. No clear relationship between k_2 and TOC_o was found. Finally, the r values were good enough for the 600 and 800 mgL^{-1} tests, but not for the 400 mgL^{-1} one. Unfortunately, chloride release was not measured.

Eckenfelder (1991) reported hydrogen peroxide oxidation of some chlorophenols using stoichiometric dosages of H_2O_2. Among other experiences, he found for 2-chlorophenol (625 mgL^{-1}) 75 and 48% reductions of COD and TOC, respectively. For 2, 4-DCPh (815 mgL^{-1}), values of 69 and 50% as COD and TOC removals were found. Finally, for 2, 4, 6-TCPh (800 mgL^{-1}), maximum removals of 47 and 44% of COD and TOC were reported. These values are a reference point in the evaluation of the system oxidative capabilities, even when the total concentrations are not the same, and in the case of this work the phenols are mixed and not treated separately, as in Eckenfelder´s work.

Toxicity reduction

The tests developed with the Microtox system in order to estimate the initial toxicity of the 400, 600 and 800 mgL^{-1} TPh mixtures, as well as the final value, are shown in Table 7. The initial toxicity values, as EC_{50} (in mgL^{-1}), were 2.45, 1.9, and 0.28 for the different mixture concentration values, as high as 40.8, 52.4, and 358 toxicity units. A toxicity unit is defined as $TU = 100/EC_{50}$ (in mgL^{-1}) for an easier understanding of the changes in toxicity during the process. The higher the value of TU, the higher the toxicity of the sample. As comparison, the reference value for a 100 mgL^{-1} phenol solution is shown (with an EC_{50} and TU value of 3.85 mgL^{-1} and 25.98, respectively).

From these values it is evident that all the mixtures are quite toxic (a TU value higher than 4 is considered as very toxic). The relationship between TU and TPh concentration is not linear, but rather quadratic ($TU = 0.0037\ TPh - 3.6175\ TPh^2 + 899.74$, r = 1). The toxicity of the 800 mgL^{-1} mixture is almost 10 times that of the 400 mgL^{-1} one.

The toxicity was reduced as a consequence of the TPh degradation, but not in the same proportion. The final toxicities of the mixtures are 21, 12.25, and 278.24 as TU for the 400, 600, and 800 mgL^{-1} tests. This means a toxicity removal of about 48.3, 76.6, and 22.3%, respectively. The quantity of TU reduced is 19.7, 40.1, and 79.8 for each case (the higher the TPh

concentration, the higher the number of TU removed). If the process time is considered, the resulting TU removals per time unity (an arbitrary removal index) are quite similar: 7.4, 10.8, and 6.8 TU day^{-1}.

With these facts in mind, it is possible to establish that the toxicity removal is a function of time. Unfortunately, at this stage, data of toxicity *versus* degradation time are lacking and no further conclusions could be drawn. It is important to remember that the EC_{50} values for 2, 4-DCPh; 2, 4, 6-TCPh and PCPh have been reported (Blum and Speece, 1991) as 2.0, 1.9, and 0.735 mgL^{-1}, respectively, which means that the mixtures contain 50, 75, and 100 times the EC_{50} for the 2, 4-DCPh only (400 mgL^{-1} test), 52, 79, and 105 times the EC_{50} value for the 2, 4, 6-TCPh only (600 mgL^{-1} test) and 136, 204, and 272 times the EC_{50} value for the PCPh only (800 mgL^{-1} test). Of course, the single compounds in the mixtures make a synergistic effect not previously quantified.

CONCLUSIONS

This aerobic submerged filter posses interesting potential applications for the treatment of highly toxic chlorophenols mixtures up to 600 mgL^{-1} of total chlorophenols with excellent removal values and biodegradation rates between 87 -97%, and 34 - 157 mgL^{-1} day^{-1}, respectively. In the case of the 800 mgL^{-1} experiment, a strong inhibition due to the high toxicity of the mixture (358 TU) was observed; almost 10 fold the toxicity of the 400 mgL^{-1} mixture. Total organic carbon degradations up to 80% were reached for the 600 mgL^{-1} mixture, but of 2 and 69% for the 400 and 800 mgL^{-1} mixtures, respectively.

The system reduced the influent toxicity in 48 - 76%, even though the initial toxicities of the mixtures were in the range of 40 - 358 toxic units, classified as very toxic. A quadratic relationship between TPh and TU removal was found, but if time is taken into account, the most significant relationship is that existing between TU removal and time.

The kinetics of the TPh and TOC degradation were characterized through a first order kinetic expression. The raw data were fairly represented with the equations $TPh = TPh_o \exp(-k_1 t)$ and $TOC\ TOC_{initial}^{-1} = TOC_o \exp(-k_2 t)$, respectively. The values of TPh_o, TOC_o, k_1 and k_2 are reported for the biodegradation of the total phenols and for the TOC, respectively.

The system could be a powerful tool in the treatment of industrial streams, contaminated aquifers or accidenttally contaminated municipal wastewaters containing high quantities of di- tri, tetra, and pentachlorophenol.

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