

SIMULTANEOS DEGRADATION OF PHENOLIC COMPOUNDS UNDER METHANOGENIC CONDITIONS

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ABSTRACT

Phenolic compounds are important constituents of petrochemical wastewaters arising from transformation processes. Phenolic compounds may account for 2-50 g/L in effluents like the spent caustic liquors. Phenol together with substituted alkylphenols are the main constituents. Information about anaerobic treatment of a mixture of these compounds is scarce. In this work, the objective was to evaluate the effect of *o*-cresol, *m*-cresol on phenol and *p*-cresol biodegradation in a continuous system under methanogenic conditions. A continuous experiments were conducted in two 160 ml up-ward anaerobic sludge bead reactors at organic load of 3 kg chemical oxygen demand (COD)/m³-d of a phenolic compounds mixture (R1: phenol/*p*-cresol/*o*-cresol and R2: phenol/*p*-cresol/*m*-cresol). The inoculum was anaerobic granular sludge adapted to phenol and *p*-cresol degradation. R1 and R2 were operated for more than 300 days. In R1, 80% of *o*-cresol was mineralized after 40 days of adaptation period, whereas in R2 *m*-cresol was degraded at 60% but with an undesired effect on the phenol biodegradation. At a phenol/*m*-cresol ratio 1:1, the *m*-cresol removal increased to 100%. At the end of the operation in R2 the *o*-cresol was introduced to the mixture. Any negative effect was observed when this compound was present, the removal efficiencies for phenol/*p*-cresol and *m*-cresol reached were 100%. Only 60% of *o*-cresol was removed during this period. Relevant result was the fact that a mixture of three components was successfully treated in a UASB reactor under methanogenic conditions.

INTRODUCTION

Oil industry is one of the most important industries around the world with the production of 52.71 MBPD of oil last year (17). The oil transformation to different products demands the use of natural resources like water. The use of water in this industry reached 252 million m³ per year with the consumption of 0.7 and 10.95 m³ of water per Ton of product (17).

Nowadays, the refineries and petrochemical plants are facing stricter controls on liquid effluents discharge that can cause water pollution. The effluents coming from these industries are a complex mixture of organic and inorganic compounds, as the spent caustic liquors. These effluent contain up to 13%-w of sodium hydroxide (pH 12-14), neutralized acids as formic, acetate and benzoic, sulfur compounds, carbonates and phenolic compounds. The phenolic compounds in the spent caustic liquors are in the range of 2-50 g/L, where 75% is phenol and 10% are *alkyl*-substituted compounds like cresols, xylenols and ethylphenols (13; 2). The conventional treatment systems are chemical regeneration (oxidation, neutralization), disposition or they can be sold as treating agents in paper plants, mining industry or intermediate chemicals recovering plants. The use of biological treatments either aerobic or anaerobic has been considered. Anaerobic treatment compared with the aerobic treatment presents diverse advantages like: low sludge production, low energy consumption and methane generation. The phenol and *p*-cresol biodegradation has been widely studied since the 80' s under anaerobic conditions (5, 4, 10, 15). However, the majority of the studies applying anaerobic technology have been carried out using single compounds as a model substances present in the industrial wastewaters. But the information about the biodegradability of phenolics in mixtures is scarce.

In this work, continuous experiments with adapted anaerobic granular sludge were conducted in order to determine the effect of specific *alkyl*-phenols (*m*- and *o*-cresol) towards the phenol and *p*-cresol degradation. Phenol and cresylic isomers were used as the only carbon and energy source.

MATERIALS AND METHODS

Inoculum and basal medium

The methanogenic granular sludges used in this study were obtained from laboratory UASB reactors treating phenol and *p*-cresol during more than 100 days. The specific biodegradation rate for phenol and *p*-cresol were 156.29 and 75.07 mg COD/g volatile suspended solids (VSS)-d, respectively. The basal medium was prepared according to Donlon *et al.*, (7) with the modification of bicarbonate content of 2.5 g/L and 10 mg/L of yeast extract.

UASB reactors

The continuous experiments were performed in two separate glass UASB reactors (0.145 m of length and 0.039 m of internal diameter) with liquid volumes of 160 mL placed in a temperature controlled room at 30°C. Both reactors were inoculated with 12.8 g VSS/L of granular sludge. The reactors were started-up with a mixture of phenol and *p*-cresol. The inlet phenolics concentration for UASB 1 (R1) and UASB (2) it is shown in Table 1. The reactors received a sub-toxic concentration of mixed phenols at the influent and were the only carbon and energy source used. The reactors were operated at a hydraulic retention time (HRT) of 12 h along the experiments. The methane production was measured by liquid displacement using a 4% (w/v) NaOH solution to scrub out the carbon dioxide from the biogas. The performance of the reactors was monitored by measuring the pH, COD, and the concentration of the phenolic compounds in the effluent.

Analytical methods

Phenolic compounds were analyzed by Gas chromatography (Hewlett Packard) using an AT-1000 column (50 m x 0.25 mm x 0.40 μ m) with a split flow of 0.8 mL/min (50:1), the oven and detector temperature were 180-200°C (2°C/min) and 275°C, respectively. The pH was determined immediately after sampling with an Accumet 915 pH-meter (Fisher Scientific) and a Corning electrode. All other analytical determinations were performed as described in APHA (1). Phenol, *p*-cresol (J.T. Baker) *o*-cresol and *m*-cresol (Merck) and all the other chemicals were of the highest purity available.

RESULTS

Presence of *o*-cresol in the mixture

The reactor R1 was started up with a mixture of phenol and *p*-cresol at a ratio of 2:1 at organic loading rate (OLR) of 3 kg COD/m³-d (data not showed). Both phenolic compounds were completely eliminated from the effluent until day 134. The COD removal during this period was almost 100%. On day 135, *o*-cresol was introduced to the mixture at a OLR of 0.45 kg COD/m³-d (132 mg/L), in order to study the effect of this compound of difficult biodegradation towards the phenol and *p*-cresol degradation (Figure 1A). The phenol and *p*-cresol concentrations were 550 mg/L (2 kg COD/m³-d) and 132 mg/L (0.45 kg COD/m³-d), respectively. The results obtained during the first 40 days demonstrated any negative effect to the biodegradation of the phenolic compounds. The phenol and *p*-cresol were completely eliminated due to the absence of these compounds in the effluent. At the same time it was observed (Figure 1B) that *o*-cresol was not completely eliminated from the effluent. During the firsts 40 days, the removal efficiency obtained was not favorable, only 60% of this compound was mineralized. However, on day 175 the removal efficiency increased up to 85% for this compound. The RI was maintained in steady state during more than 100 days when the removal efficiencies for the phenolics did not present any change. During this period the COD removal was between 80-85%. On day 275, the concentration of the three phenolic compounds was increased at an OLR of 5 kg COD/ m³-d. During this phase the removal of phenolics fall down until removal levels of 20%. This results showed that OLR near 5

kg COD/m³-d at a phenolic ratio 1:1 was toxic to the system but not inhibitory because when the previous conditions were reestablished, the reactor recovered its capability to mineralize the phenol and cresols at the same level.

Presence of *m*-cresol in the mixture

The strategy followed for reactor R1 was similar for reactor R2. R2 was started up with a mixture of phenol and *p*-cresol at a ratio 2:1 at OLR of 3 kg COD/m³-d (data not shown). Both phenolic compounds were completely eliminated from the effluent until day 119. The COD removal during this period was almost 100%. On day 120, *m*-cresol was introduced to the mixture at a OLR of 0.45 kg COD/m³-d (132 mg/L), in order to study the effect of this cresylic isomer towards the phenol and *p*-cresol degradation (Figure 2A). The phenol and *p*-cresol concentration were 550 mg/L (2 kg COD/m³-d) and 132 mg/L (0.45 kg COD/m³-d), respectively. The *p*-cresol degradation was not affected at all, since the *m*-cresol was present in the mixture the removal efficiency for this isomer was higher than 85%. The results obtained for the phenol degradation presented a different behavior. The phenol removal obtained during a period of 40 days was above 80%. On day 180, the phenol degradation reached removal efficiencies of 90%. The phenol and *p*-cresol were completely eliminated due the absence of this compounds in the effluent after 60 days of adaptation period. At the same time, it was observed (Figure 2B) that *m*-cresol was not completely eliminated from the effluent, after 120 days, as was not possible to remove more than 40%. However, when the phenol concentration was reduced 50% in the influent, on day 260, the removal efficiency increased up to 95% for this compound. R2 was maintained in steady state during 40 days when the removal efficiencies for the phenolics did not present any change. During this period the COD removal was 95%. On day 300, *o*-cresol was added to the mixture. The concentration of each cresylic isomer was 88 mg/L (0.3 kg COD/m³-d). The biodegradation of phenol, *p*- and *m*-cresol was not affected as the mineralization of these phenolics remained stable. In the other hand, it was possible to remove only 60% of the *o*-cresol present in the mixture.

DISCUSSION

The biodegradability of phenolic compounds has been studied by many years, mainly the phenol and *p*-cresol since these compounds are metabolites of the aromatic compounds biodegradation. In a same way, these compounds are present in effluents of different industries mainly in the coal and oil industry. These studies have concluded that phenol and *p*-cresol are easily degraded and the consortium adaptation to this type of compounds favored decarboxylation and dehydroxylation reactions necessary for the elimination of the isomers and other aromatic compounds under anaerobic conditions (11). In continuous experiments there are some reports that demonstrated a 100% of phenol removal, at OLR of 7 kg COD/m³-d in an expanded bed reactor (20). Other system tested was the granular activated carbon packed reactor treating satisfactorily synthetic effluents which contained phenol at OLR between 1.03 and 2.58 kg COD/m³-d (14). Subsequent studies carried out in UASB reactors reported maximum OLR of 6 kg COD/m³-d and 7.2 kg COD/m³-d for phenol and *p*-cresol, respectively (8; 12). Fang *et al.* (9) using UASB reactors eliminated the 98% of a mixture of phenol and *p*-cresol at OLR of 2.6 kg COD/m³-d (1200/400

mg/L, respectively). The performance of these reactors was not the same when the OLR was increased to 4.2 kg COD/m³-d, in this stage only 75% of the total COD was removed from the effluent (9). The capability to eliminate cresylic isomers from the complex phenolic mixture under methanogenic conditions was first tested by Blum *et al.* (4). Their results showed that *o*-cresol, xylenols and 3-ethylphenol were the most recalcitrant compounds among 12 aromatic compounds present in a complex mixture at concentrations around 100 mg/L. During many years the *o*-cresol has been considered as a recalcitrant compound. In previous batch studies the *o*-cresol was only transformed to toluic acid (3). Recent results published by Charest *et al.* (6) demonstrated that phenol and *o*-cresol were mineralized (148 and 27 mg/L) in a fixed film anaerobic reactor, inoculated with an adapted consortium. But, *p*-cresol and *m*-cresol were not degraded. Tawfiki *et al.* (19) in a UASB reactor inoculated with granular sludge at a HRT of 3 days, reached 85% phenol (450 mg/L) removal, 90% *p*-cresol removal (135 mg/L) and 56% *o*-cresol removal from a mixture after more than 100 days, 60 days and 276 days of operation, respectively. According to the previous results, the mineralization of 112 mg/L of *o*-cresol after 50 days of adaptation period at HRT of 0.5 days obtained in this study has a great relevance. In the case of the results obtained for *m*-cresol it is clear that the ratio phenol/*m*-cresol determined their degradation in the mixture. This result suggests a possible interference or common pathway among these compounds. Some data showed that *m*-cresol degradation was inhibited by the presence of 4-hydroxybenzoate, the main intermediate of the phenol degradation (15). Same results were reported by Zhou and Fang (21) when they could eliminate only 20% of *m*-cresol from a mixture with phenol at a ratio 3:1 (900/320 mg/L). In general, these results suggests the variable capability of the microorganisms to degraded isomers and the difference in pathways that can be followed in the degradation under anaerobic conditions.

CONCLUSIONS

The anaerobic digestion represents a good alternative for the removal of aromatic compounds from industrial wastewaters or complex mixtures. Mixture of phenolics can be converted to methane at maximum OLR of 3 kg COD/m³-d. The phenol and *p*-cresol biodegradation was not affected by the presence of other isomers, but it is important to consider the phenol/cresols ratio to avoid toxic effects and, in the other hand to degrade the *m*-cresol. The most important result from this study was the high *o*-cresol removal efficiency (85%) obtained under methanogenic conditions, even when the mixture included *m*-, *p*-cresol and phenol.

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Table 1. Organic loading rate of phenolics for R1 and R2 at different periods.

	Period I		Period II		Period III		Period IV	
	R1	R2	R1	R2	R1	R2	R1	R2
Operation days	0-134	0-119	135-275	120-259	275-314	260-299	315-340	300-380
phenol (kg COD/m ³ -d)	2.12	2.42	2	2	2.6	1	2	1
<i>p</i> -cresol (kg COD/m ³ -d)	1.085	1.1	0.45	0.45	1.2	0.45	0.45	0.3
<i>m</i> -cresol (kg COD/m ³ -d)	-	-	-	0.45	-	0.45	-	0.3
<i>o</i> -cresol (kg COD/m ³ -d)	-	-	0.45	-	1.2	-	0.45	0.3

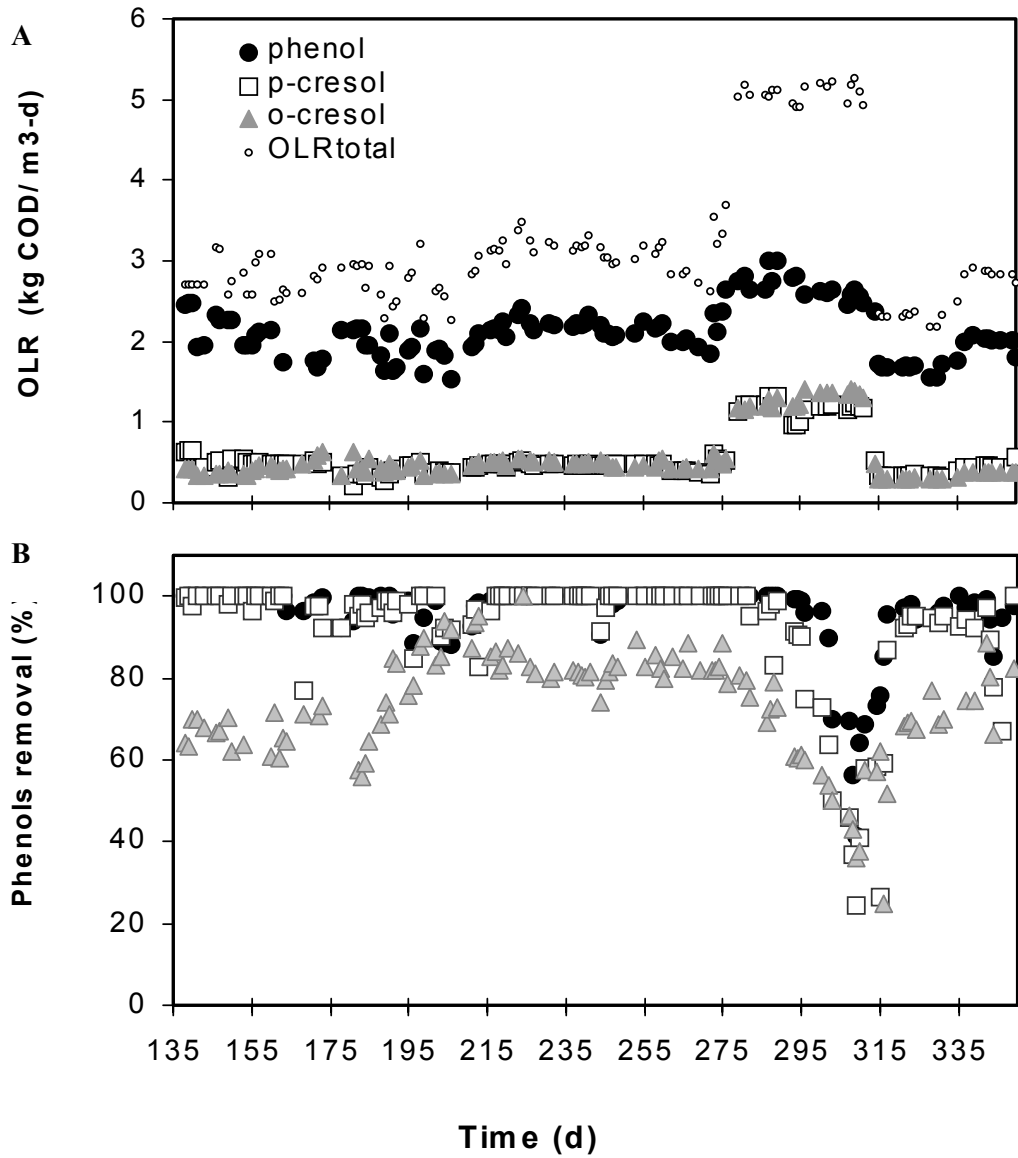


Figure 1. Organic load (A) and phenols removal (B) in the UASB reactor 1.

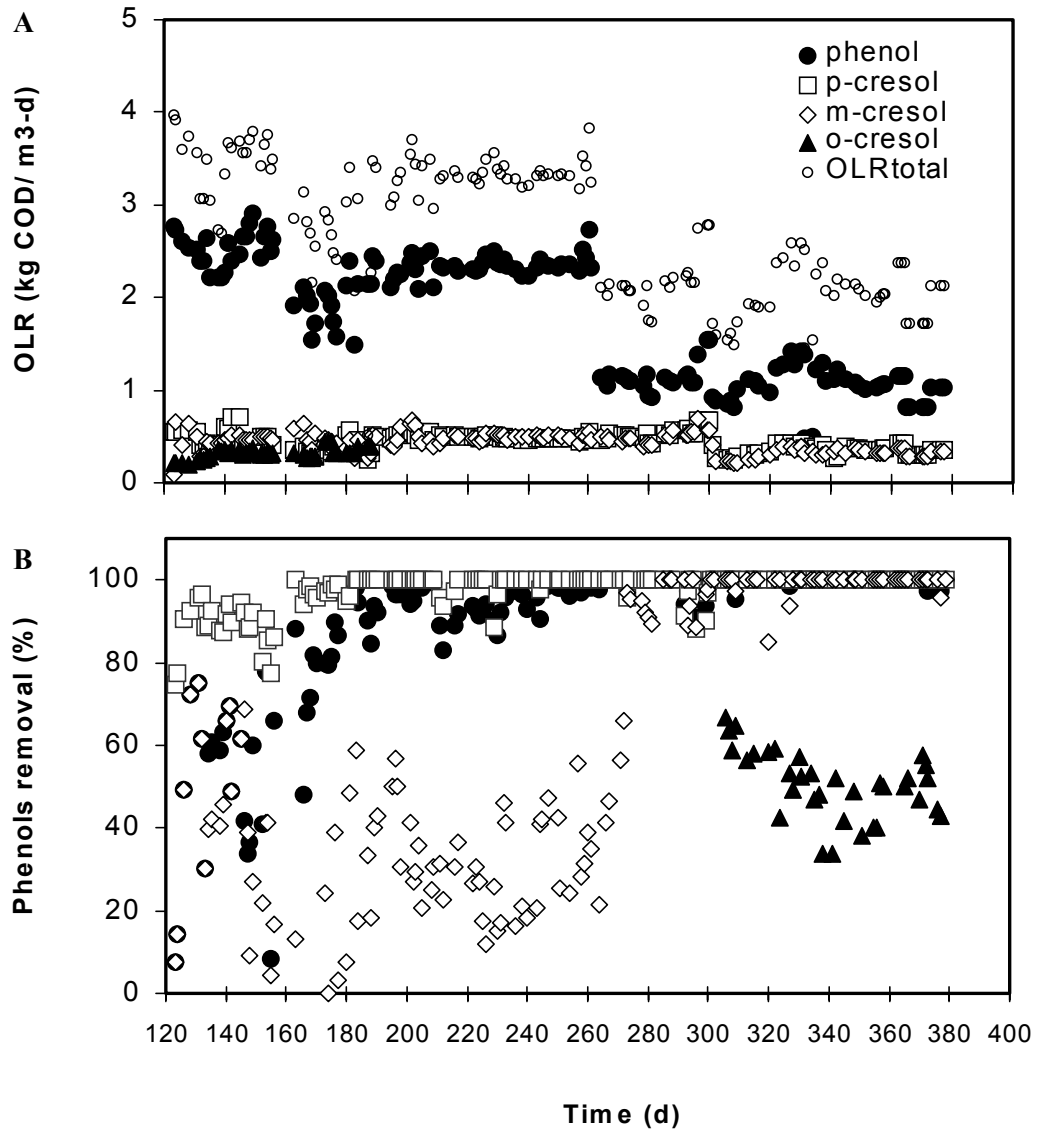


Figure 2. Organic load (A) and phenols removal (B) in the UASB reactor 2.