Anaerobic treatment of phenol in a two-stage anaerobic reactor

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Abstract

The inhibitory effects of phenol are problematic for the anaerobic treatment of wastewater. The purpose of this study is to demonstrate that a two-stage anaerobic digester (TSAD) can degrade phenol, reducing its toxic effects in the first acidogenic reactor (R1) before going into a methanogenic reactor (R2). The system consisted of two reactors in semi continuous operation. R1 was a Continuous Stirred Tank Reactor at pH 5.5± 0.5; R2 was a packet reactor at pH 8.4± 0.05. Both were operated at a hydraulic retention time (HRT) of 10 days and 35 ^{0}C and fed with a nutritional supplement at organic loading rate (OLR) of 1.8 grams of COD per litre of reactor per day (L_R^{-1} Day^{-1}) until steady state conditions. Then one gram of phenol was fed daily over a period of 15 days. The performance of the system was monitored and analysed in terms of degradation of phenol and dissolved chemical oxygen demand (DCOD); concentration of organic acids (OA) and suspended organic carbon (SOC); biogas production and pH evolution. The removal of phenol and DCOD peaked at 99.7% and 70% respectively. The biogas production in the methanogenic reactor reached 0.8195 L_{biogas} L_R^{-1} Day^{-1}. These experiments demonstrate that, given the right conditions, a TSAD can degrade phenol without considerable inhibition.
Keywords: Two-stage anaerobic digestion, phenol degradation, mesophilic, acidogenesis, methanogenesis, cofermentation, inhibition.

1 Introduction

Aromatic compounds are very abundant in the environment [1]. Anaerobic digestion can be affected by the presence of these compounds, which are highly refractory and prejudicial to methanogenic reactions [2-7]. The anaerobic


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degradation of phenol has been reviewed in the literature [4; 8; 9]. Two-stage anaerobic digestion (TSAD) has been developed mainly to reduce toxicity of pollutants in the acidogenic reactor before going into the methanogenic reactor [10]. Dilution, ozonation, UV-hydrogen peroxide, enzymatic treatment and different reactor designs have been proposed to improve the biodegradation of wastewaters containing phenol [11]. Anaerobic degradation of phenol has been reported in batch [3; 5; 12; 13] and modified batch [8] as well as in different reactor designs like a gas-liquid-solid fluidised-bed [14], UASB [15-17] and expanded bed reactor [18]. Two-stage anaerobic digestion studies treating wastewaters containing non-identified phenols or polyphenols have been reported [17]. Similar co-fermentations were carried out using flavonoids (rutin and hesperidin) mixed with brewery wastewater in a two-stage system [19] and glucose and phenol in a single-stage reactor [20] but there is no information concerning the application of the two-stage anaerobic technology treating phenol. Considering the great amount of wastes containing phenol and its environmental toxic effects, the application of the TSAD system could provide a good alternative for degrading phenol by anaerobic waste treatment.

2 Materials and methods

The two reactors consisted of glass quick fit vessels 186 mm diameter and 290 mm height, with ports for sampling and feeding. Gas sampling was made by piercing a subba seal in the gas headspace. The active volumes were 4 L in both cases. R1 was filled with a RS model packing media (Flocor, UK) for bacterial attachment. Both reactors were magnetically stirred and submerged in water baths controlled at 35 ^{0}C. A graduated cylinder was coupled per reactor for collecting the biogas, fig. 1. The top of the cylinder was inverted and immersed in a barrier solution as detailed in DIN38414 (1985).

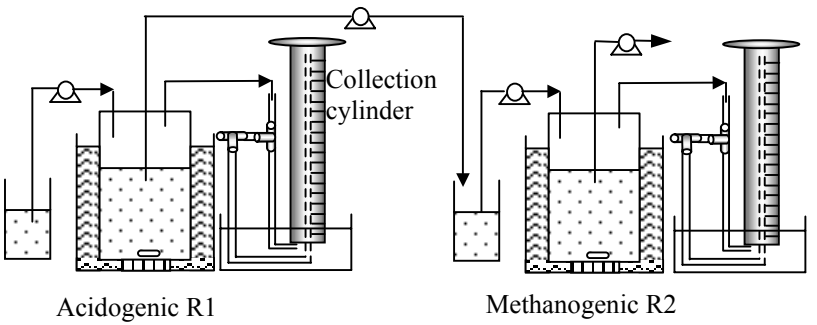

Figure 1: Schematic diagram of the two-stage anaerobic digestion system.

The degradation medium was a nutritional protein supplement, designed for human consumption (Boots, Nottingham, UK). Aqueous medium solutions were prepared at concentration of 250 g/L. Phenol was supplied by Fluka. A 2.5 g

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phenol/L solution was prepared by diluting phenol in medium solution. Test cuvettes for TOC, COD, OA and Phenol determination came from Dr. Bruno Lange, Co. All other chemicals used were from Merck. The reactors were inoculated with sludge (61% V/V) from an established anaerobic digester treating yeast wastewater. Acidogenic and methanogenic separation was developed by pH control over one month. The system was working at steady state conditions (35 ^{0}C, 10 days of HRT and 1.83 g COD $L_R^{-1}d^{-1}$) for six months before phenol experiments started. Then a mixed solution of medium and phenol was fed (0.2 g COD of phenol $L_R^{-1}d^{-1}$). The experiment was carried out semi continuously for 15 days. Biomass concentration was measured by suspended organic carbon (SOC) using the high-temperature combustion method; dissolved chemical oxygen demand (DCOD) degradation was analysed with the dichromate method, organic acids (OA) was determined with the esterification method and phenol concentration was determined with the 4-aminoantipyrine method (Dr. Bruno Lange, Düsseldorf, Germany). 0.45 μm pore diameter filters were used to separate the dissolved and suspended fraction. Biogas production was measured by using graduated collection cylinders. pH was determined using a portable temperature compensated pH meter. The inoculum was not previously acclimated to phenol. Liquid samples were taken and stored daily according to APHA 5220 for COD, 5310 for TOC, 5530 for phenols and 5560 for OA. A buffer solution 7.5 NaOH/10 $NaHCO_3$ was used to control pH at 5.5 ±0.5 in R1 and 8.4 ±0.05 in R2.

3 Results and discussions

Although the addition of phenol promoted little disturbance on pH in both reactors, acidity in R1 seemed to be unstable, fig. 2. In this reactor the amount of buffer required to maintain the pH at 5.5 reduced while phenol concentration increased. These results could be due to the interaction of phenol and carboxylic acids. Phenols are weaker acids (Ka in the order of 10^{-10}) than the carboxylic acids (Ka in the boundaries of 10^{-5}) produced by the fast growing acidogenic bacteria. Gas production in R2 was disturbed but recovered in one week. Gas production in R1 was reduced by half but recovered in four days and remained stable, fig. 3. These results imply that phenol is not converted to gas. Phenol accumulated in R1 (0 to 1452 mg/L) and showed high degradation rate in R2 (99%), fig. 4. These results suggest that phenol is not biodegradable under acidogenic conditions, which is supported by a previous report showing that polyphenols in olive oil mill effluents are not degraded under acidogenic conditions [2]. Phenol is too reduced to be able to give products, which are at the same energy level, without the addition of any suitable electron acceptor. The polarity of phenol (LogP = 1.482) is a cause of its low dissociation at pH < 7. Acidogenic bacteria able to degrade phenol under anaerobic condition have not been reported so far in the literature [21] and potential metabolic pathways are well known . These results imply that compounds [22-27]. The small amount of degradation of phenol observed in R1 was due to residual methanogenic activity.

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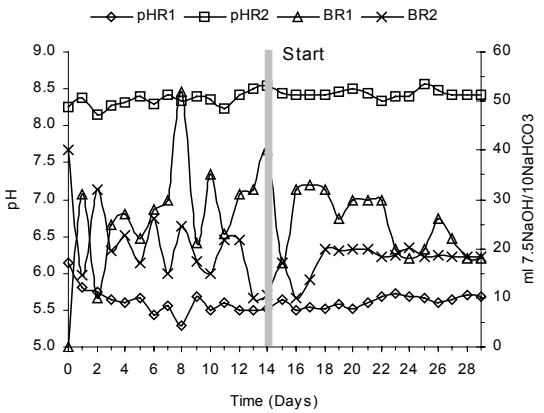

Figure 2: Monitoring and control of pH. Variables: pHR1 and pHR2, values of pH in R1 and R2; BR1 and BR2, volume of buffer solution added in R1 and R2.

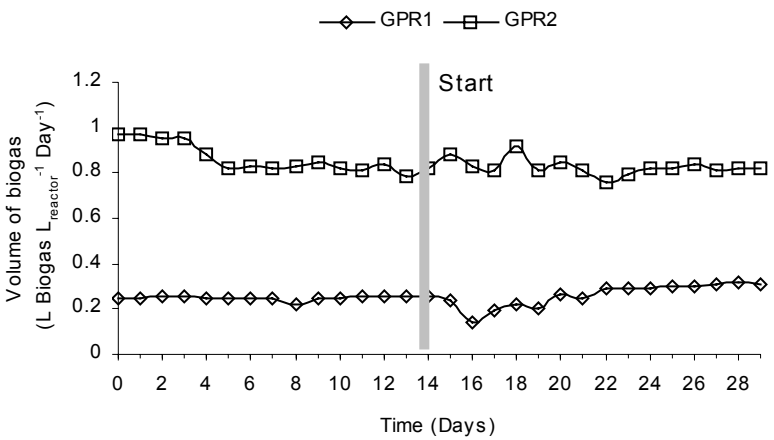

Figure 3: Biogas production. Both reactors experienced disturbances owing to the presence of phenol but they recovered rapidly. Variables: GPR1 and GPR2, volume of gas produced in R1 and R2.

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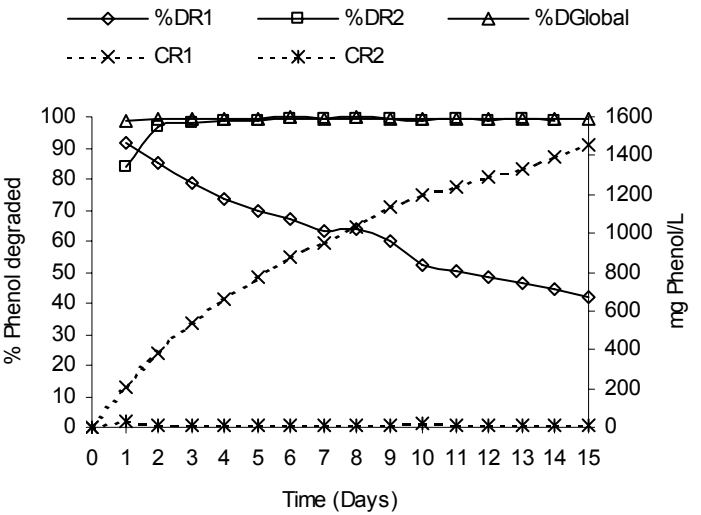

Figure 4: Percentage degradation and concentration of phenol. Variables: %DR1, %DR2, and % DGlobal, percentage of phenol degradation in each reactor and in the global system; CR1 and CR2, phenol concentration in the outlet of each reactor.

DCOD degradation in R1 was not affected by the presence of phenol. However, R2 showed a drop (80 to 65%), which caused a drop in the overall DCOD degradation, fig. 5. The average DCOD concentration in the outlet was 15500 mg/L for R1 and 6000 mg/L for R2. Note that the methanogenic reactor contributed more to DCOD degradation. The disturbance on day 12 was due to temperature fluctuation. This sensitive response to changes in temperature has been observed in a previous report [16].

An unstable condition of organic acid production was observed throughout the experimental period, fig. 6. The operation of R2 was stable as the organic acid concentration in the outlet was below 500 mg acetic acid/L [28]. Phenol was converted by the anaerobes to biogas in alkaline conditions, this methanogenic conversion of phenol to CO_2 and CH_4 has been demonstrated [29] and characterized [3] in batch cultures. The presence of phenol in R2 had no effect on organic acid degradation. These results show that 95% of the organic acids were converted to methane and other products. The concentration of phenol in R2 was less than the value reported in the literature for 50% inhibition of acetate methanogenesis (1250 mg/L) [5; 13].

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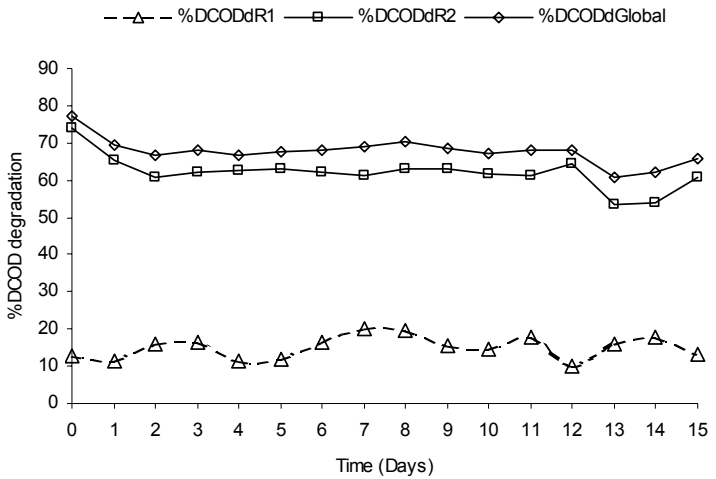

Figure 5: Percentage of dissolved chemical oxygen demand. Variables: %DCODdR1, %DCODdR2 and %DCODdGlobal, percentages of DCOD degradation in each reactor and in the global system.

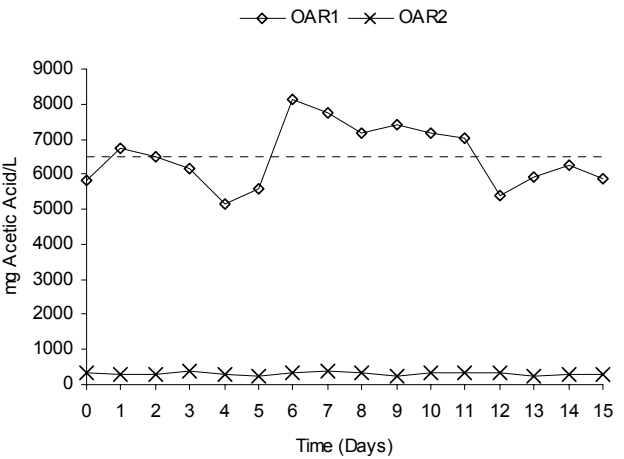

Figure 6: Organic acid concentration. Variable: OAR1 and OAR2, concentration of organic acids in R1 and R2 reported as acetic.

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The global biomass concentration in both reactors remained stable in the presence of phenol, fig.7 but then slightly reduced probably due to turn over due to the HRT.

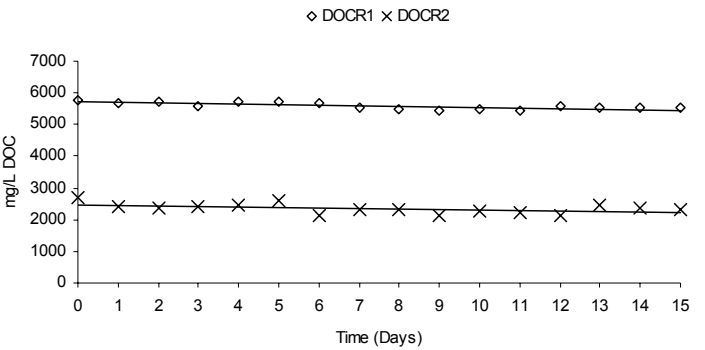

Figure 7: Evolution of Dissolved organic carbon. Variables: DOCR1 and DOCR2, dissolved organic carbon in the outlet of R1 and R2.

4 Conclusions

In this work, the anaerobic biodegradation of phenol under mesophilic condition in a two-stage anaerobic digester and its effects on COD degradation, biomass concentration; organic acid production and conversion, was studied.

The two stage anaerobic reactor in this experiments degraded 99% of fed phenol. Operating at 10 days of HRT, 35 ^{0}C and 0.2 g COD of phenol $L_R^{-1}d^{-1}$. Phenol is not degradable under acidogenic conditions by acidogenic bacteria. Methanogenesis was not affected by the increase in phenol concentration in the acidogenic feed. 95% of fed organic acids were transformed to CH_4 and CO_2. The DCOD degradation of cosubstrate was not affected by phenol in the acidogenic reactor but in the methanogenic reactor was reduced from 75% to 65%. For the conditions of the experiment, the biomass in both reactors was not affected by the presence of phenol.

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