Degradation of phenol and p-cresol in reactors

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Abstract The effects of hydraulic retention time (HRT) and phenol concentration on the degradation of phenol and p-cresol in wastewater were investigated in two respective UASB (upflow anaerobic sludge blanket) reactors with effluent recirculation at 37 °C for over 440 days. After acclimation, nearly all the phenol and p-cresol at moderate concentrations could be degraded without carbohydrate as a co-substrate. Treating a wastewater containing 800 mg/l of phenol and 300 mg/l of p-cresol at HRT ranging 2-12 hours, the first reactor consistently removed 95% of phenol, 65% of p-cresol and 85% of COD at 8-12 hours of HRT; the efficiency, however, decreased at lower HRT. Treating wastewater containing a constant p-cresol concentration of 400 mg/l at 24 hours of HRT, the second reactor was able to remove 75-80% of COD when the phenol was 1200 and 1500 mg/l; the removal efficiency decreased as phenol concentration further increased. High levels of residual phenol and p-cresol in the effluent suppressed the activity of biogranules. The suppression of bioactivity was not permanent. Biomass was able to regain its activity fully after lowering the phenolic concentrations in the wastewater.

Keywords anaerobic; bioactivity; p-cresol; phenol; UASB; wastewater

Introduction

Phenols are raw materials used for making a variety of specific chemicals, such as synthetic resins for construction materials and adhesives, antioxidants, herbicides, photo-developing chemicals, etc. Phenolic pollutants are thus abundant in the wastewaters of these industries. In addition, they are also often found in wastewaters from coal gasification, coke-oven batteries, oil refinery and petrochemical plants (Patterson, 1975). Phenolic pollutants at high concentrations are toxic to microorganisms in biological wastewater treatment.

Aerobic degradation of phenolic compounds have been studied for many years (Buswell, 1975; Hill and Robinson, 1975). However, anaerobic degradation of these pollutants have only been studied more recently (Roberts and Fedorak, 1987; Haggblom, *et al*., 1990; Kennes, *et al*., 1997). Anaerobic treatment technologies have gained wide acceptance in the past decade for the treatment of high-strength industrial wastewater. Anaerobic treatment has a number of intrinsic advantages. Compared with the more conventional aerobic processes, anaerobic processes save the energy for aeration, produce substantially lower quantities of sludge and convert organic pollutants into a readily usable fuel, methane. Recent studies have shown that upflow anaerobic sludge blanket (UASB) process (Lettinga, *et al*., 1980; Fang and Chui, 1993) was effective for the degradation of simple aromatic pollutants, such as benzoate (Li *et al*., 1995) and phenol (Fang *et al*., 1996). Over 97% of phenol was removed with 12 hours of hydraulic retention time (HRT) for phenol concentration up to 1260 mg/l, corresponding to 3000 mg/l of chemical oxygen demand (COD) and a loading rate of 6 g COD/(l˙d), and 97-99% of benzoate was removed for loading rates up to 30.6 g COD/(l˙d). For the treatment of wastewater containing more complex phenols or mixture of phenolic pollutants, many suggested dosing activated carbon to anaerobic reactors as an adsorbent for the toxic phenolic pollutants as well as a carrier for bacterial growth (Wang *et al*., 1986; Nakhla *et al*., 1990). However, very little information is available on the feasibility of treating this kind of wastewater solely by biological means.

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This study was conducted to investigate the feasibility of treating wastewater containing concentrated phenol and p-cresol using the UASB process. The effects of phenolic concentrations and the maximum loading rates were examined. In addition to phenol, p-cresol was chosen because it is one of the most common phenolic pollutants, and is more recalcitrant to biodegradation and more toxic than simple phenol to anaerobes (Blum *et al*., 1986).

Materials and methods

Continuous treatment

Synthetic wastewaters were treated in two 2.8 l UASB reactors (Fang *et al*., 1996) at 37 ˚C. Both reactors were seeded with 1.0-l of flocculent sludge from the anaerobic sludge digester of a local wastewater treatment plant plus 0.5-l of partially granulated sucrose-fed sludge in a 65-l UASB reactor. Reactor A was used to study the effect of HRT, which was reduced stepwise from the initial 12 hours to as low as 2 hours. Reactor B was used, on the other hand, to study the effect on increased phenolic concentrations at a constant HRT of 24 hours. The synthetic wastewaters contained balanced nutrient, trace elements and buffer chemical (Fang *et al*., 1996), plus phenol and p-cresol as organic substrates. The concentration ratio between phenol and p-cresol was kept approximately 3:1 throughout the study. Sucrose was added to the wastewater as a co-substrate only during the start-up (days 1-134). The concentration of sucrose was gradually decreased from the initial concentration of 2000 mg/l while phenol and p-cresol concentrations increased correspondingly. At the end of the start-up, sucrose was completely absent from the wastewater, whereas the phenol/p-cresol concentrations were 600/200 mg/l for Reactor A and 680/250 mg/l for Reactor B. Starting on day 135, a fraction of the effluent was recirculated to the bottom of the reactors to dilute the phenolic concentrations of the incoming wastewater; the recycle flowrate equalled to that of the incoming wastewater.

During days 135-170, Reactor-A was operated at phenol/p-cresol concentrations of 600/200 mg/l. Starting on day 170, the phenol/p-cresol concentrations were raised to 800/300 mg/l and kept at those levels throughout the experiment, while the HRT was lowered stepwise from 12 hours to 2 hours, corresponding to an increase of loading rates from 5.8 to 33.8 g-COD/(l·d). On the other hand, Reactor B was conducted in two phases: Phase 1 (days 135-352) was conducted at increased phenol/p-cresol concentrations, until reaching 1430/500 mg/l on day 295. At these levels, the removal efficiency of phenol/p-cresol deteriorated rapidly, due to the toxicity of the increased phenolic concentrations. The phenol/p-cresol concentrations were thus lowered first to 1020/310 mg/l during days 305-326, and later to 630/210 mg/l during days 327-352. Phase 2 (days 353-444) was conducted to examine the effect of increased phenol concentration (from 1200 to 2500 mg/l) at a fixed concentration of p- cresol (400 mg/l).

Batch tests

Biogranule samples taken from Reactors-A and B on day 293 were tested for specific methanogenic activities (SMA) using the method developed by Owen *et al*. (1979). All SMA tests were conducted in duplicate at 37 ˚C using 157 ml serum vials containing 100 mg-VSS of biogranules and 100 ml of feed solution containing an individual substrate, plus nutrient and trace metals. Additional batch tests on the degradation of phenol (800 mg/l) and p-cresol (300 mg/l) were also conducted. During these tests, mixed-liquor was analyzed on regular time intervals for residual phenol and p-cresol, and probable metabolic intermediates, such as benzoate and volatile fatty acids (VFAs), and the biogas was analyzed for production rate and composition.

Analytical methods

The methane content in the biogas and the VFAs (from acetic to heptanoic acids) concentrations in the effluent were analyzed by two gas chromatographs (GC, Hewlett-Packard, Model 5890 Series II), as reported previously (Fang *et al.*, 1996). Sucrose was analyzed by a spectrophotometer at 625 nm wavelength (UV-160A, Shimadzu). The detectable levels were less than 1 mg/l for phenol, m-cresol, benzoate, VFA and sucrose. On the other hand, VSS and COD were measured according to the *Standard Methods* (APHA, 1985).

Results

Continuous experiments

Throughout the experiment, the effluent pH remained stable, ranging 7.5-8.1 in Reactor-A and 7.5-8.2 in Reactor B. Sludge in both reactors agglutinated during the start-up period to form 0.5-1.5 mm granules. These biogranules had superb settleability; thus, little sludge was washed out throughout the experiment. The VSS content in the effluent both reactors never exceeded 50 mg/l.

Start-up of the reactor. During start-up, biomass was allowed to acclimate to the increasing concentrations of phenol and p-cresol, and decreasing sucrose concentration. Sucrose was completely absent from the wastewater at the end of the start-up. Results showed that both reactors removed, without sucrose as co-substrate, nearly all the phenol; the removal of p-cresol increased, however, with HRT. By day 131, Reactor-A at 12 hours of HRT removed 99.2% of phenol and 44.6% of p-cresol, whereas Reactor-B, with double HRT, removed 97.9% of phenol and 98.2% of p-cresol. The degradation rates of phenol were 1968 mg/(l·d) in Reactor A and 978 mg/(l·d) in Reactor-B; the corresponding degradation rates of p-cresol were 323 and 328 mg/(l·d), respectively.

Effect of HRT. Figure 1 illustrates the following: (a) phenol and (b) p-cresol concentrations in both influent and effluent, and (c) COD removal efficiency. During days 170-327 when HRT was ranging 12-8 hours, Reactor A consistently removed 95% of phenol and 65% of p-cresol; the effluent on average contained 40 mg/l of phenol and 75 mg/l of p-cresol. The average COD removal efficiency was 85%, while the methane production rate increased from 1.5 l/(l·d) to 2.5 l/(l·d). During days 328-407, as HRT continued to decrease, the overall COD removal efficiency decreased. At 6 hours of HRT, the COD removal efficiency was decreased to 75% as the effluent contained 100 mg/l of residual phenol and 150 mg/l of residual p-cresol. At 4 hours of HRT, the corresponding efficiency and concentrations were 56%, 217 and 203 mg/l, respectively. However, as this level of HRT, methane production further increased to 3.0 l/(l·d) indicating that the residual phenol and p-cresol did not inhibit the activity of the biogranules. When the HRT was further lowered to 3 hours on day 408, both of methane production rate and COD removal efficiency were reduced drastically. They were further decreased when the HRT was lowered to 2 hours reaching 22% and 1.8 l/(l·d), respectively, when the experiment was terminated on day 467.

Effect of increased phenol and p-cresol concentrations. Figure 2 illustrates the performance of Reactor-B treating wastewater with increased concentrations of phenol and p-cresol at a constant HRT of 24 hours, including (a) phenol and (b) p-cresol concentrations in influent and effluent phenol, and (d) COD removal efficiency. In Phase 1 (days 135-352), phenol and p-cresol concentrations increased proportionally at a constant concentration ratio at 3:1. During days 135-294 when the COD loading rate was increased from 2.6 g/(l·d) to 4.3 g/(l·d), Reactor-B performed satisfactorily removing on average 93% of COD. The effluent contained on the average 35 mg/l of residual phenol and 47 mg/l of p-cresol.

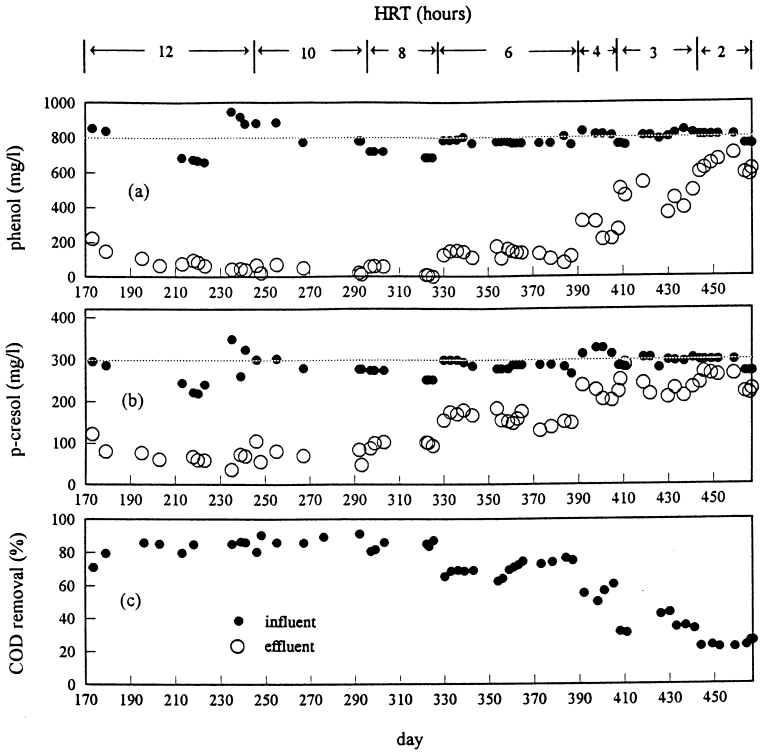

Figure 1 Performance of reactor-A treating wastewater containing constant concentrations of phenol and p- cresol at decreased HRT: (a) phenol and (b) p-cresol concentrations, and (c) COD removal efficiency

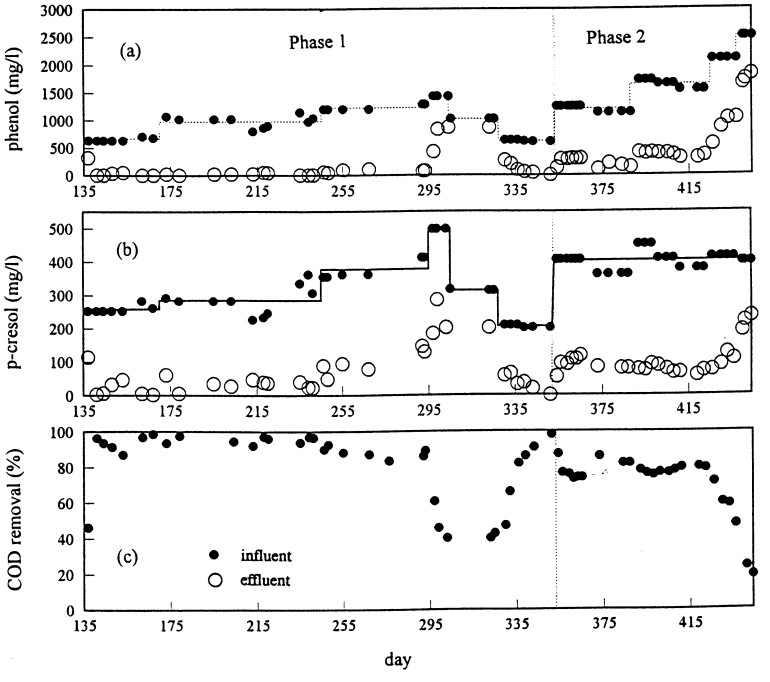

Figure 2 Performance of reactor-B treating wastewater with increased concentrations of phenol and p-cresol at 24 hours of HRT: (a) phenol and (b) p-cresol concentrations, and (c) COD removal efficiency

Reactor performance dropped, however, drastically as the loading further increased to 5.2 g/(l·d) on day 295. Figure 2 illustrates that, at this loading rate, the residual effluent phenol and p-cresol increased to 860 and 200 mg/l, respectively, and the COD removal efficiency was lowered to 40%, as the methane production rate reached 0.37 l/(l·d). To avoid permanent inhibition of sludge activities, the loading rate was soon lowered first to 4.2 g/(l·d) during days 305-326, and, after the reactor performance failed to recover, then to 2.2 g/(l·d) during days 327-352. At the latter loading rate, the reactor performance was slowly recovered. At the end, the reactor was able to remove 98% of COD as the effluent contained less than 1 mg/l of residual phenol and 1 mg/l of residual p-cresol. This indicates the inhibition of bioactivities by the concentrated phenol and p-cresol was not permanent. Biomass was able to regain its bioactivities fully when the phenolic concentrations were lowered.

During Phase 2 (days 353-444), p-cresol concentration in the wastewater was kept at the constant level of 400 mg/l while phenol concentration was stepwise increased from 1200 mg/l to 1500, 2000, and finally 2500 mg/l. Figure 2 illustrates that the reactor was able to remove 75-85% of COD when the phenol was 1200 and 1500 mg/l, corresponding to COD loading rates of 4.2 and 5.2 g/(l·d). As the phenol increased to 2000 mg/l and later to 2500 mg/l, i.e. 6.2 and 7.4 g COD/(l·d), the reactor performance dropped drastically.

Batch Experiments

Degradation of phenol and p-cresol in batch reactors. Biogranules were sampled from both Reactors A and B for separate batch tests on day 293, when Reactor-A was treating wastewater containing 800 mg/l of phenol, 300 mg/l of p-cresol at 7.0 g/(l·d) of COD loading rate and 10 hours of HRT, and the corresponding conditions for Reactor B were 1200 and 380 mg/l, 4.3 g/(l·d) and 24 hours. The feed solution in both batch reactors contained 800 mg/l of phenol and 300 mg/l of p-cresol. Figure 3 illustrates the decreases of phenol and p-cresol concentration in the mixed liquor and the cumulative production of methane in both batch reactors. Biogranules from Reactor A were slightly more reactive than those in Reactor B, as evidenced by the faster methane production (Figure 3c) and the shorter time

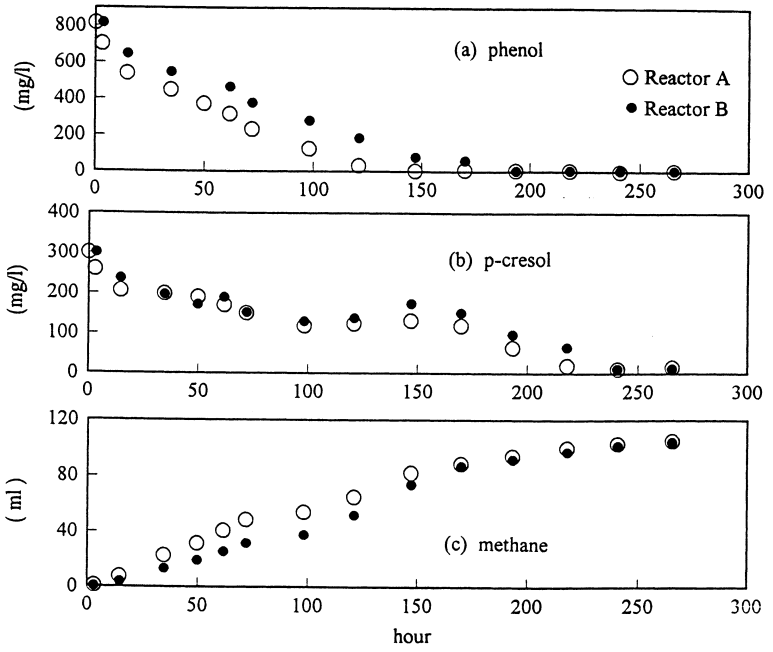

Figure 3 Degradation of phenol and p-cresol in batch reactors: (a) phenol and (b) p-cresol concentrations in mixed liquors, and (c) production of methane in biogas

Table 1 Bioactivity of the biogranules from both of reactors

substrate	concentration (mg/l)	COD (mg/l)	SMA (g-CH_4-COD/(g-VSS·d))	
			Reactor-A	Reactor-B
acetate	2300	2500	1.02	1.10
propionate	1630	2500	0.39	0.37
butyrate	1360	2500	0.89	0.90
benzoate	1260	2500	0.60	0.61
phenol	420	1000	0.30	0.25
p-cresol	159	400	0.08	0.07

to deplete phenol in the mixed liquor (150 vs 193 hours, as illustrated in Figure 3a). Figures 3a and 3b illustrate that both phenol and p-cresol degraded at a faster rate at the beginning of the batch test, because of the higher initial substrate concentration. Throughout the operation, all intermediate VFA were below the detectable levels, except benzoate which was detected at concentrations up to 70 mg/l,

SMA. Biogranules were sampled from both reactors for SMA tests on day 257, during which the reactors were operated under the same conditions as on day 293 when biogranules were sampled for batch degradation tests. The SMA tests were conducted using six individual substrates, including acetate, propionate, butyrate, benzoate, phenol and p-cresol. Concentrations of the four intermediate VFA in the feed solution had a COD-equivalent of 2500 mg/l, but those of phenol and p-cresol were kept at 1000 and 400 mg/l of COD equivalent because of their toxicity at high concentrations.

Table 1 summarizes the SMA results of the biogranules. Biogranules from both reactors had similar methanogenic activities using various substrates. The SMA of both biogranules using phenol and p-cresol as substrate were significantly lower than those using acetate, butyrate, and benzoate as substrates. Furthermore, there was little accumulation of these intermediate VFA in the effluent of the UASB reactors and in the mixed liquor of the batch reactors throughout the experiment. All of these observations seem to suggest that the initial conversion from phenol and p-cresol to benzoate was likely the rate-limiting step in the methanogenic degradation process. Furthermore, the SMA using p-cresol as substrate was in the range of 0.07–0.08 g methane-COD/(g-VSS·d), which was substantially lower than the 0.25–0.30 g methane COD/(g-VSS·d) of phenol, indicating the former was much more refractory to anaerobic degradation than the latter.

Discussion

COD removal efficiency and substrate removal rates

Figure 4 illustrates variations of (a) COD removal efficiency, and removal rates of (b) phenol and (c) p-cresol at various COD loading rates in both Reactors A and B. Figure 4a illustrates that COD removal efficiency decreased in each reactor with the increase of COD loading rate. However, the effect of loading rate was much more drastic in Reactor B with increasing phenol/p-cresol concentrations than in Reactor A which had constant phenol/p-cresol concentrations. Figure 4b illustrates that the phenol and p-cresol removal rates in Reactor A increased with loading rate until reaching respective maximum values of 3.6 and 0.7 g/(l·d) at 16.8 g COD/(l·d); they were then decreased slightly at higher loading rates. The maximum phenol removal rate in Reactor A was higher than the 2.4 g/(l·d) reported in a previous study (Fang, *et al.*, 1996), in which over 97% of phenol was removed at 12 hours of HRT for a wastewater containing phenol as sole substrate at concentration up to 1260

mg/l. On the other hand, the maximum phenol and p-cresol removal rates in Reactor B were only 1.32 and 0.37 g/(l·d), respectively, at the loading rate of 5.2 g COD/(l·d).

The differences between Reactors A and B in substrate removal and in the sensitivity towards loading rate were likely due to the toxicity of residual phenol/p-cresol concentrations in the effluent. The combined residual phenol/p-cresol concentration in Reactor B increased from 380 mg/l at 3.9 g-COD/(l·d) up to 1990 mg/l at 7.4 g COD/(l·d). Bioactivities of granules at the latter loading rate were severely inhibited as reflected by the SMA measurements. Biogranules in Reactor B were sampled on day 443 at the loading rate of 7.4 g COD/(l·d) for SMA analysis. Using phenol and p-cresol as individual substrates, the SMA values were 0.10 and 0.04 g- COD/(l·d), respectively, about 60% lower than those sampled on day 257 when the loading rate was 4.3 g COD/(l·d), as reported in Table 1.

Degradation without co-substrate

It has been known that degradation of refractory organic chemicals can be enhanced by the presence of more readily biodegradable substrates, such as carbohydrates and VFA. However, Figures 1 and 2 illustrate that, after sludge had been acclimated to the presence of phenolic pollutants during the start-up phase, both UASB reactors were able to degrade nearly all the phenol and p-cresol at moderate concentrations without sucrose as a co-substrate. Furthermore, results of batch tests show that degradation of p-cresol ceased during hours 100–175 when phenol became depleted, as illustrated in Figure 3b. This suggests that degradation of the more refractory p-cresol also requires phenol as a co-substrate. However, after hour 175 the residual p-cresol was able to be further degraded and became nearly depleted by hour 250, indicating the biomass after a period of acclimating to the phenol-free environment was able to degrade p-cresol without a co-substrate.

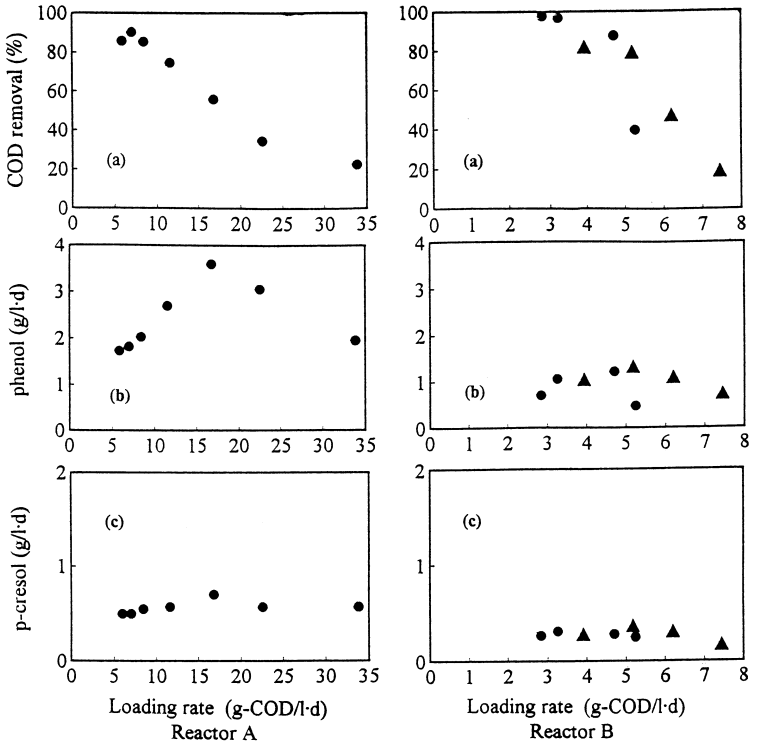

Figure 4 (a) COD removal efficiency, (b) phenol removal rate, and (c) p-cresol removal rate at various loadings

Conclusion

The following conclusions can be drawn based on results of this experimental study.

1. UASB reactor is effective for the removal of phenolic pollutants in wastewater at a combined concentration of over 1000 mg/l. About 90% of phenolic pollutants can be removed without any other co-substrate at 8–12 hours of HRT. The efficiencies depend on the HRT and phenolic concentration in wastewater.
2. Residual phenolic pollutants in the effluent could inhibit the bioactivity of the reactor at high concentrations; such an inhibitory effect can be significantly reduced by effluent recirculation.
3. Bioactivity inhibition by the phenolic residues is not permanent; it can be fully recovered after lowering the phenolic concentration in the wastewater.
4. Phenol was preferentially removed over p-cresol.

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References

Standard Methods for the Examination of Water and Wastewater. (1985). 17th ed. American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC, USA.

Blum D.I.J., Hergenroeder R., Parkin G.F. and Speece R.E. (1986). Anaerobic treatment of coal conversion wastewater constituents: biodegradability and toxicity. *J. Wat. Pollut. Control. Fed*. **58**(2), 122–131.

Buswell, J.A. (1975). Metabolism of phenol and cresols by *Bacillus stearothermophilus*. *J. Bacteriol*. **124**, 1077– 1083.

Fang H.H.P. and Chui H.K. (1993). Maximum COD loading capacity in UASB reactors at 37ºC. *J. Envir. Eng.*, **119**(1), 103–119.

Fang H.H.P., Chen T., Li Y.Y. and Chui H.K. (1996). Degradation of phenol in an upflow anaerobic sludge blanket reactors. *Wat. Res*. **30**, 1353–1360.

Haggblom, M.M., Rivera, M.D., Bossert, I.D., Rogers, J.E., Young, L.Y. (1990). Anaerobic biodegradation of para-cresol under three reducing conditions, *Microb. Ecol*. **20**, 141–150.

Hill, G.A., Robinson, C.W. (1975). Substrate inhibition kinetics: phenol degradation by *Pseudomonas putida*. *Biotechnol. Bioeng*. **17,** 1599–1615.

Kennes, C., Mendez, R., Lema, J.M. (1997). Methanogenic degradation of p-cresol in batch and in continuous UASB reactors. *Wat. Res*. **31**, 1549–1554.

Lettinga G., van Velsen A.F.M., Hobma S.M., de Zeeuw W. and Klapwijk A. (1980). Use of the Upflow Sludge Blanket (USB) reactor concept for biological wastewater treatment. *Biotechnol. Bioeng.*, **22**, 699–734.

Li Y.Y., Fang H.H.P., Chen T. and Chui H. K. (1995). UASB treatment of wastewater containing concentrated benzoate. *J. Environ. Eng*. **121**(10), 748–751.

Nakhla G.F., Suidan M.T. and Pfeffer J.T. (1990). Control of anaerobic GAC reactors treating inhibitory wastewaters. *J. Wat. Pollut. Control Fed.*, **62**(1), 65–72.

Owen W.F., Stuckey D.C., Healy J.B., Young L.Y. and McCarty P.L. (1979). Bioassay for monitoring biochemical methane potential and anaerobic toxicity. *Wat. Res*., **13**, 485–492.

Patterson J.W. (1975). *Wastewater Treatment Technology*. Ann Arbor Sci., Ann Arbor, Michigan.

Roberts, D.J., Fedorak, P.M. (1987). Comparison of the fates of the methyl carbons of m-cresol and p-cresol in methanogenic consortia. *Can. J. Microbiol*. **33**, 335–338.

Wang Y.T., Suidan M.T. and Rittman, B.E. (1986). Anaerobic treatment of phenol by an expanded-bed reactor. *J. Wat. Pollt. Control Fed*. **58**(3), 227–233.