Journal of Applied Sciences

ISSN 1812-5654

science alert

ANSInet
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Journal of Applied Sciences 7 (12): 1652-1655, 2007
ISSN 1812-5654

Removal of 3-monochlorophenol in Anaerobic Baffled Reactor

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Abstract: Monochlorophenols, particularly 3-monochlorophenol (3-MCP) are resistant to biodegradation than many poly- chlorinated compound. The presence of chlorophenols in water has become a significant pollution problem. The biodegradation of 3-monochlorophenol was investigated by Anaerobic Baffled Reactor (ABR). A mixture of 3-MCP and glucose as synthetic wastewater was treated in a laboratory scale. The ABR reactor volume was 9 L and wastewater with different concentration of 3-MCP and hydraulic retention time of 2 days, was treated. The parameters that determined include COD, volatile suspended solids (VSS) and 3-MCP concentration. The initial sludge for reactor feeding was isolated from full scale ABR that was operated in an industrial complex. When the concentration of 3-MCP was 10 mg L^{-1} and less, 3-MCP was able to be metabolized to mineral end products and the COD removal was about 90% and more. With increasing of 3-MCP concentration from 10 to 30 mg L^{-1}, the degradation of 3-MCP and COD removal were decreased significantly ($p<0.001$). The variations of VSS in different concentration of 3-MCP was significant ($p<0.001$). Increasing of COD to 2000 mg L^{-1}, improved the reactor performance and reduced the toxicity of 3-MCP. In the toxicity evaluation of 3-MCP on ABR biomass, the ratio of glucose/3-MCP is more important parameter than 3-MCP concentration.

Key words: Wastewater 3-monochlorophenol biodegradation ABR

INTRODUCTION

Chlorophenols are common water contaminants, released into environment as a result of wood preserving, wood treating, pulp and paper bleaching, pesticide manufacturing and leaching to groundwater from contaminated soil (Farrokhi *et al*., 2003). Effluents containing chlorinated phenols are particularly problematic due to their recalcitrance in environment and their high solubility in fat and bioaccumulation within the tissues of organisms (Farrokhi *et al*., 2004). 3-monochlorophenol (3-MCP) is one of the most toxic chlorophenols which is very difficult to biodegradation (Bae *et al*., 2003). 3-MCP has been designated as a priority pollutant and is a probable human carcinogen (AWWA, 1990). Monochlorophenols, particularly 3-monochlorophenol are resistant to biodegradation than many poly- chlorinated compound (WHO, 1987). The presence of chlorophenols in water has become a significant pollution problem.

Several researches have indicated that biodegradation of highly chlorinated compounds by aerobic bacteria is hindered (Yao *et al*., 2006). It is well recognized that anaerobic biological processes are able to dehalogenate and degrade more highly chlorinated phenols (Droste *et al*., 1998). Anaerobic degradation is conversion without an external electron acceptor of complex organic to the most oxidized (CO_2) and most reduced (CH_4) form of carbon (Batstone *et al*., 2006).

Far less is known about the biodegradation especially anaerobic degradation of organohalides (Milliken *et al*., 2004). Anaerobic biodegradation of chlorophenols occurs by reductive dechlorination. In this process, chlorines are replaced with hydrogen, while degrading microorganisms use chlorinated chlorophenols as terminal electron acceptors in an anaerobic respiration. Therefore reductive dechlorination is partially or completely inhibited by the presence of other electron acceptors such as sulfate, nitrate, O_2 and CO_2 (Geofeng *et al*., 2004).

Degradation of chloroaromatic compound was observed most often in methanogenic environment and in enrichment amended with bromoethane sulfonic acid. Degradation observed least often in enrichment with added nitrate and sulfate (Barbara *et al*., 1989). Inhibition of anaerobic degradation due to elevated chlorophenols concentrations in many processes such as UASB and AF, have been demonstrated (Hendriksen and Ahring, 1991; Pringer and Bhattacharya, 1999).

Mc Carty and co-workers removed the rotating discs from Rotating Biological Contactor (RBC) and developed the Anaerobic Baffled Reactor (ABR) (Weiland and Rozzi, 1991).

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In the ABR process, baffles are used to direct the flow of wastewater in an upflow mode through a series sludge blanket reactors (Barber and Stuckey, 1999). there are many advantages associated with the anaerobic baffled reactor, such as: simple design, no moving parts, no mechanical mixing, low sludge generation, high solids retention time, no special gas or sludge separation required operation, protection from toxic material and high stability to organic shocks (William and David, 1999). Many researches have been done with the ABR process focused on organic loading, temperatures effect and number of compartment, but toxic effect of chlorophenols on ABR process no reported (Willaim and David, 1999).

In this study the degradation of 3-MCP and its toxicity on ABR biomass in laboratory scale was investigated. The main objectives of this study were 1-determination of ABR reactor removal efficiency for 3-monochlorophenol in deferent level of 3-MCP and COD, 2-examination of toxic effects of 3-MCP to ABR performance.

MATERIALS AND METHODS

Experimental apparatus and methods: This study was conducted in school of health of Guiala University of Medical Sciences, 2005-2006.

ABR reactor with 9 liter volume and three compartment (each of compartment volume = 3L) containing anaerobic sludge was employed. The reactor was made of glass. The reactor temperature controlled at 25°C. At the beginning of experiment, according to previous similar studies (Droste *et al*., 1998; Barber and stucky, 1999) Hydraulic Retention Time (HRT) of 2 day were selected but the HRT could be change by changing of influent flow rat. Synthetic wastewater was made with distilled/deionized water and pH adjusted to 7. In the Synthetic wastewater, concentration of 3-MCP was predeterminated to (5, 10, 20 and 30 mg L^{-1}) and equal amount of glucose as carbon source was added an a COD basis (COD = 1000 and 2000 mg L^{-1}). Requirement nutrients were added to it. Synthetic wastewater was fed into the reactor by dosing pump. The initial sludge for reactor starting was isolated from full scale ABR that was operated in an industrial complex.

Mass balance of 3-MCP and COD were performed in around the reactor therefore the sampling done from effluent of third compartment. Samples were immediately filtered (0.45 μm membrane filter) into glass tube with teflon caps and stored at 4°C until analysis.

In VSS analysis sampling was performed from three, compartment and the average VSS was reported.

The frequency of analysis varied from 1 to 2 times per week, except for VSS that was measured at the end of experiment.

Analytical methods: All chemicals were purchased from MERCK and ALDRICH Company. All chemicals were of analytical grade and were used without further purification.

The concentration of 3-MCP was determined, using a gas chromatograph (Philips UP 4410) with FID and packed column 1% sp. 1240. Temperature program was 80°C at injection and immediate 8°C min^{-1} to 150°C. The sample was acidified by H_2SO_4 and extracted with methylen chloride.

Definitively, COD removal is indicator of toxicity. For assessment of 3-monochlorophenol toxicity on ABR biomass COD was analyzed in effluent according to method 5220-C in standard methods (APHA, AWWA, WEF, 1995).

Biomass was estimated by measurement of Volatile Suspended Solids (VSS) according to method 2940E in standard methods (APHA AWWA WEF, 1995).

RESULTS AND DISCUSSION

The ABR biomass collected from full scale ABR operated in an industrial complex and fed to lab scale ABR and VSS adjusted to 5 g L^{-1}. The synthetic wastewater (glucose + 3-MCP) with different concentration of 3-MCP and COD equal 1000 mg L^{-1} was treated in two day hydraulic retention time.

When the concentration of 3-MCP is 10 mg $L^{-1}$and below the degradation of 3-MCP is more than 90% but with increasing of 3-MCP concentration to 20 mg L^{-1} and more, the reduction decrease to less than 50%. It is observed that ABR biomass was able to degrade significant amount of 3-MCP in low concentration (Fig. 1). It is observed that adaptation of biomass with 3-MCP after 2 months was not occurred and increasing of 3-MCP, reduced the activity and ability of biomass to degradation of 3-MCP, this is same as UASB reactor (Draste *et al*., 1998). In the low concentration of 3-MCP degradation rate of 3-MCP reaches to steady state after 10 day, steady state for COD removal occurred at the same time (Fig. 2). In activated sludge from treatment plants previously exposed to phenols, the degradation of 3-MCP in 6 h was 100% for 1 mg L^{-1}, 40% for 10 mg L^{-1} and none for 100 mg L^{-1} (Baried *et al*., 1974), therefore it is indicated that anaerobic processes have more abilities for 3-MCP degradation than aerobic ones.

It is observed that COD removal efficiency decreased from 90% to less than 50% when the concentration of 3-MCP increase to 20 mg L^{-1} and more. In the concentration of 3-MCP equal 20 mg L^{-1} and more the reactor performance never reaches to steady state (Fig. 2). These results indicate that 3-MCP have toxic effect on ABR biomass in the concentration of 20 mg L^{-1} and more, in this condition of operation (HRT = 2 days and COD =

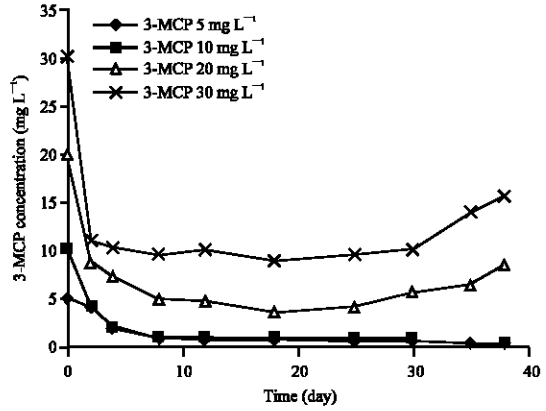

Fig. 1: Degradation of 3-MCP in ABR reactor in different concentration of 3-MCP

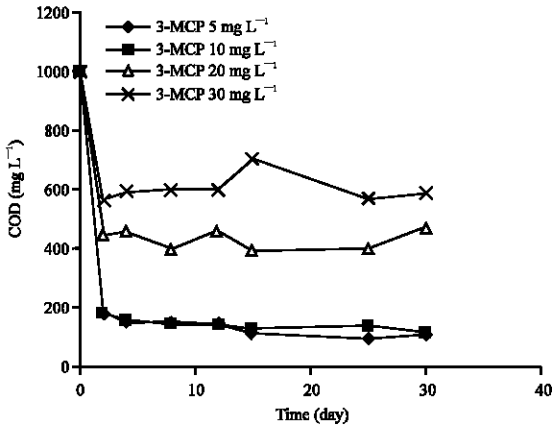

Fig. 2: Reduction of glucose (COD) in ABR reactor in different concentration of 3-MCP

1000 mg L^{-1}). Previously this is reported that in biodegradation of polychlorinated phenols 3- and 4-monochlorophenol are persistent degradation products (Mohn and Kennedy, 1992).

The loss of about 70% of VSS as indicator of biomass, via 3-MCP increasing from 10 to 30 mg L^{-1}, confirms the toxicity of 3-MCP on ABR biomass (Table 1). In VSS analysis sampling was performed at the end of experiment from three, compartment and the average VSS was reported. In the all conditions the minimum VSS was measured in first compartment (10-20%). This fact is due to down and up movement of flow and VSS within the reactor rise and settle to flow characteristics and gas production.

The initial biomass adjusted to 5 g VSS L^{-1} and the VSS measured at the end of the experiment period. For the prevention of biomass increasing in reactor and better evaluation of toxicity effect, organic loading adjusted to

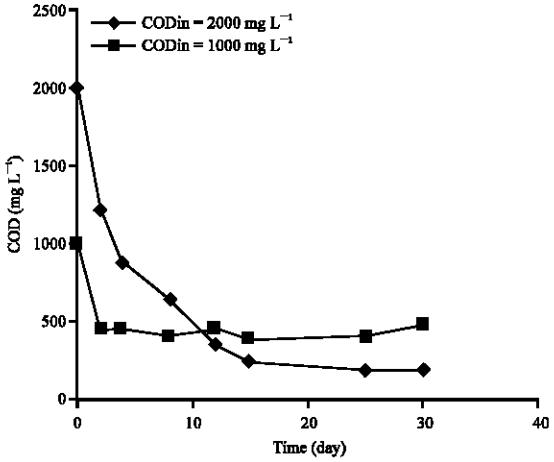

Fig. 3: Effect of COD increasing on enhancement of ABR reactor efficiency (3-MCP = 20 mg L^{-1})

Table 1: Effect of 3-MCP concentration on VSS in ABR reactor (at the end of experiment)

VSS (mg L^{-1})	3-MCP Con. (mg L^{-1})
5497	5
5632	10
2732	20
1264	30

0.2 g COD g VSS^{-1}. It is expected that in this rate of organic loading the rate of washout of biomass is equal to its production. In low concentration of 3-MCP (<10 mg L^{-1}) the VSS only increased from 5000 to 5632 mg L^{-1}, it is indicated that this process has low yield coefficient and the minimum sludge production occurred.

The main factor causing the drop in VSS may be toxic effect of 3-MCP on biomass and prevention of growth of mixed population.

Drop of VSS can be main factor cause decreasing of COD removal efficiency in low COD/3-MCP ratio, <100.

When COD increased to 2000 mg L^{-1} in 3-MCP concentration of 20 mg L^{-1}, COD removal was improved and reaches to about 90% (Fig. 3) and the concentration of 3-MCP at the last 3 days of experiment was less than 0.5 mg L^{-1} (removal efficiency > 97%).

It is indicated that increasing of biodegradable matter concentration (glucose) decrease toxic effect of 3-MCP on biomass and toxicity of 3-MCP in COD/MCP ratio equal 100 or more is Negligible. With increasing of COD the VSS build up and reaches to 3873 mg L^{-1} at the end of experiment. It is concluded that biomass yield improved and toxicity effect reduced. The VSS increasing can be an important factor for the improvement of removal of COD and 3-MCP. Difference between biomass yield in two different conditions (COD = 1000 mg L^{-1} and COD = 2000 mg L^{-1}), may be due to different organic loading and

initial biomass density, that cause different F/M ratio (Food/Microorganism) that is very important parameter as organic loading in biological processes design and performance. When COD adjusted to 2000 mg L^{-1} and VSS was equal 1264 mg L^{-1} the organic loading will be 1.58 g COD g VSS^{-1}, while previous organic loading at the beginning of experiment was 0.2 g COD g VSS^{-1} and normally, if there is no toxic effects, in high rate system (high F/M ratio) the specific growth rate and specific substrate utilization rate will be high. Under this condition the process yield is maximized. These results suggested that the degradation of 3-MCP may be a co-metabolic process where glucose serves as the primary substrate and the degradation of glucose provide electron donors for dehalogenation and degradation of 3-MCP.

CONCLUSIONS

From this study, it was concluded that 3, monochlorophenol can be metabolized in ABR process. High level of 3-MCP affects both the degradation of glucose and biomass density in ABR process. Increasing of glucose improved stability of process against toxicity of high level of 3-MCP. This is indicated that ABR process can be used for degradation of high level 3-MCP, when the concentration of biodegradable compound is high or, in the other word when there is strong wastewater from BOD point of view.

ACKNOWLEDGMENTS

The authors thank Mr. A soleymanian for his kind help in the analyzing of 3-MCP in wastewater laboratory of Department of Environmental Health, Medical Faculty, Tarbiat Modarres University, Tehran.

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