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# Biodegradation of mixture of phenol and formaldehyde in wastewater using a single-basin MSCR process

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ABSTRACT

A novel moving-bed sequential continuous-inflow reactor (MSCR) was developed and investigated for the degradation of high concentrations of phenol and formaldehyde. Results indicated the MSCR could simultaneously remove greater than 99% of the target compounds for concentrations up to 1300 mg $L^{-1}$ each (corresponding to the loading rate of 1.04 kg $m^{-3}$ $d^{-1}$), and around 96% of the chemical oxygen demand of ~4800 mg $L^{-1}$ with a 6-h cycle time. An increase of the inlet concentrations to 1500 mg $L^{-1}$ (loading rates of 1.2 kg $m^{-3}$ $d^{-1}$), however, caused a slight reduction in the removal efficiency. The MSCR handled hydraulic shock loads of up to three times the normal flow rate without adversely affecting the elimination performance of the contaminants. These unique features, combined with the efficient and compact nature of the process, thus recommend MSCR as a promising technique for the removal of mixture of toxic compounds in a single-basin bioreactor.



## 1. Introduction

Synthetic resins such as phenol-formaldehyde (PF) resins are chemical products used as adhesives in several applications such as wood processing (Tomitaa and Hse, 1998; Schmidt et al., 2006). During the production and application of these products some amount of the primary compounds, i.e., phenol and formaldehyde find their way into the plant effluent wastewater stream. Phenol and formaldehyde are included in the CERCLA priority list of hazardous substances (ATSDR, 2007), and are toxic materials for human and environmental health. Therefore, this wastewater must be efficiently treated before discharging to the environment, preferably using a technique capable of simultaneous removal of the mixture of contaminants.

A variety of physical, chemical and biological methods are available for eliminating toxic contaminants from wastewater. Biological processes are widely preferred due to their capability of eliminating a wide range of contaminants, flexibility and reliability, simplicity of operation and maintenance, cost-effectiveness, environmental benignity, degradation of contaminants to less toxic or harmful products rather than transferring them into another phase, potential for full-scale applications, etc. Several reports have been published on the biological removal of phenol (e.g., Busca et al., 2008; Moussavi et al., 2009a) and formaldehyde (e.g., Pedersen et al., 2007; Pereira and Zaiat, 2009), suggesting the bioprocess as a viable method for treating effluents containing such compounds. Nonetheless, literature on the biodegradation of the mixture of phenol and formaldehyde from wastewater is limited (Eiroa et al., 2005; Kochany and Lipczynska-Kochany, 2009), However, as noted above, when dealing with wastewater generated in PF resin synthesis plants, the simultaneous elimination phenol and formaldehyde, each at concentration up to several hundred mg $L^{-1}$, is required. That is, the selected process must simultaneously remove mixture of these toxic compounds, which remains a challenge from the point of view of a conventional process. This necessitated the development of a novel bioreactor and process to treat the wastewater as described.

Among the biological systems, sequencing batch reactor (SBR) is one the most applied processes for industrial wastewater treatment (Rao et al., 2005; Marañón et al., 2008). Despite its unique features (Mohan et al., 2005), one of the main deficiencies of SBR when treating toxic and inhibitory compounds is the batch feeding of the substrate, which affects its degradation (Metcalf and Eddy, 2003). In this regard, we have recently begun efforts to modify SBR to overcome its defects. In the first phase of our modification attempts, we found that adding a moving-bed to the SBR (MSBR) could improve the elimination capacity of the applied contaminant (Moussavi et al., 2009a). Nonetheless, due to the batch feeding mode, it still required multiple reactors to treat a continuous-inflow. Therefore, modifying the mode of feeding the MSBR from batch to continuous, thus achieving the moving-bed sequential continuous-inflow reactor (MSCR), seemed to be a promising approach to improve its performance in treating toxic and inhibitory compounds through a mitigation of the loading peak and shock (Sahinkaya and Dilek,

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2007), as well as in allowing continuous treatment of wastewater in a single-basin bioreactor. In fact, this modification allows exploitation of the unique advantages of the conventional SBR, intermittent-cycle extended-aeration activated sludge, MSBR and moving biofilm.

The purpose of the present study was therefore to investigate the performance of a novel MSCR for simultaneous degradation of a mixture of phenol and formaldehyde, and removal of chemical oxygen demand (COD) at different concentrations. The effects of cycle time and inlet concentrations on the simultaneous removal of phenol and formaldehyde in the MSCR were investigated. The effect of hydraulic shock loading rate on MSCR performance was also studied.

## 2. Materials and methods

### 2.1. Wastewater preparation, biomass acclimation and immobilization, and reactor start-up

The synthetic wastewater containing phenol and formaldehyde, supplemented with the elements required for bacterial growth ($NH_4Cl$, $KH_2PO_4$, $K_2HPO_4$, and trace elements), was prepared by dissolving aliquots of 1% stock solutions of each compound in tap water. A formalin solution containing 38% formaldehyde was used for preparing formaldehyde stock solution. The pH of the feed wastewater was regulated at the value of $7.3 \pm 0.2$, which is in the range of optimum value for the bacterial growth. At the beginning of the experiment, the preparation and acclimation of biomass was conducted as follows: 1 L of activated sludge from a lab-scale bioreactor, in prior use efficiently treating a synthetic wastewater containing high concentrations of formaldehyde (Moussavi et al., 2009b), was mixed with 1 L of activated sludge from a lab-scale bioreactor efficiently treating a synthetic wastewater containing high concentrations of phenol (Moussavi et al., 2009a) in an aerated stirred vessel. The suspension contained $11 \pm 0.5$ g mixed liquor suspended solids (MLSS) $L^{-1}$. The biomass was acclimated and enriched for the removal of mixture of phenol and formaldehyde while being fed in batch mode with a daily exchange volume of 1 L of synthetic wastewater solution containing required nutrients, and formaldehyde and phenol each 100 mg $L^{-1}$. When the removal of phenol, formaldehyde and COD increased to 95%, the biomass was considered to be acclimated and enriched for the degradation of compounds. Following biomass acclimation, the reactor was operated as an SBR with a 24-h cycle time (detailed in Table 1) and fed with synthetic wastewater containing 100 mg $L^{-1}$ each of formaldehyde and phenol. The concentration of these compounds was progressively increased to 400 mg $L^{-1}$ over 50 d. In order to shorten the start-up phase, the immobilization of the acclimated biomass on the media (open-pore polyurethane foam) described below was attempted in a separate secondary vessel in parallel to the suspended biomass acclimation. To do this, a procedure similar to acclimation of suspended biomass was undertaken except that media were added to the reactor. After attaining at pseudo-steady-state performance in the primary reactor, the media with the acclimated biomass attached were added to the bioreactor on day 35 of operation, and it was operated continuously until pseudo-steady-state was reached, at which point the start-up phase was considered to be complete.

### 2.2. Experimental setup and operation

A bench-scale experimental setup was constructed and operated in this work, consisting of a cylindrical glass column as the bioreactor, an aeration system with a stone diffuser supplying air to maintain the dissolved oxygen at around 3 mg $L^{-1}$ in the mixed liquor during the aeration cycle time, a feeding system with a distributor installed at the bottom inside of the reactor, a decant system, a time-control automatic operation system, tubing, valves and other accessories. The bioreactor had an internal diameter of 14.5 cm and total height of 40 cm. A decant automatic time-controlled valve was located at a height of 10 cm from bottom of the column giving a constant 1.6 L remaining volume (volume of mixed liquor remaining in the reactor at the end of the decant phase) in each operating cycle. Following the attainment of biomass acclimation and enrichment, the operation of the bioreactor was switched to continuous mode at day 35 of operation, with a changing the feed from batch to continuous mode (flow rate of 1.6 L $d^{-1}$) as well as adding the biofilm-containing media. The operation of the MSCR comprised aerating, settling and decanting cycles, occurring sequentially, while the reactor was fed continuously. Open-pore polyurethane foam cubes (8 mm × 8 mm × 8 mm, with a specific surface area of 600 $m^2$ $m^{-3}$ and a density of 35 kg $m^{-3}$; Zander, Germany) were used as media. It has been previously shown that the sponge can be suitable media for biofilm formation (Guo et al., 2009). The volume of media added to the reactor was held at 10% of the working volume. The fill and/or decant volume, i.e., the volume of raw wastewater fed into the bioreactor or volume of effluent decanted from the bioreactor at each cycle, was fixed at 1.6 L $d^{-1}$ unless otherwise noted. The experimental schedule of the study and phase timing are given in Table 1. The experimental setup was operated at room temperature (23–25 °C) during the overall course of the investigation.

### 2.3. Analysis

The concentrations of phenol, formaldehyde and COD were measured at the feed and decant streams as required. The samples taken from decanted supernatant were filtered with a 0.45 μm filter and the filtrate was analyzed. All these parameters except formaldehyde, and suspended solids were analyzed according to Standard methods (APHA, 1998). The concentration of formaldehyde was determined according to the Nash's method (Nash, 1953). The DO and pH of the mixed liquor were checked frequently using electrodes.

## 3. Results and discussion

### 3.1. Bioreactor start-up

As mentioned previously, the bioreactor was started up as an SBR by injecting synthetic wastewater at a 24-h cycle period. The inlet phenol and formaldehyde concentrations were each increased from 100 to 400 mg $L^{-1}$ over 50 d. Fig. 1 depicts the results of start-up study; as shown here, after passage through the bioreactor, the concentrations of both compounds, phenol and formaldehyde, each at concentrations of up to 300 mg $L^{-1}$, as well as COD, were removed at efficiencies greater than 99% and 97%, respectively. This indicates a successful start-up, which can be related to the use of a concentrated biomass pre-acclimated to phenol and formaldehyde removal as the initial seed. On day 30 of start-up, the inlet concentrations were further increased to 400 mg $L^{-1}$; this caused a deterioration of the effluent quality in terms of COD concentration and turbidity. As seen in Fig. 1, the removal of contaminants, in particular COD began to decrease following this increase of inlet concentrations. For instance, the removal efficiency of COD dropped to below 90% after four cycles of changing inlet concentrations had passed. The greater reduction in removal of COD compared to that of phenol and formaldehyde upon increasing the inlet load implies a partial degradation of compounds and generation of intermediates which contribute to COD. At this point, it was decided to switch the SBR bioreactor to MSCR by changing the