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Effects of sludge retention time (SRT) and biosurfactant on the removal of polyaromatic compounds and toxicity

Delia Teresa Sponza*, Oguzhan Gok

Dokuz Eylul University, Engineering Faculty, Environmental Engineering Department, Buca Kaynaklar Campus, 35160 Izmir, Turkey

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ABSTRACT

A laboratory-scale aerobic activated sludge reactor (AASR) system was employed to investigate the effects of SRT on the removal of three less hydrophobic and six more hydrophobic PAHs in the presence of rhamnolipid (RD), emulsan (EM) and surfactine (SR) biosurfactants. Among the biosurfactants it was found that RD exhibits a better performance than the others in the removal of PAHs. At a RD of 15 mg l^{-1} aerobic treatment for 25 days SRT was enough to remove over 90% of the total PAHs, 88% of the COD originating from the inert organics (COD_{inert}) and 93% of the COD originating from the inert soluble microbial products (COD_{imp}). At this SRT and RD concentration, about 96–98% of the RD was biodegraded by the AASR system, 1.2–1.4% was accumulated in the system, 1.1–1.3% was released in the effluent, and 1.2–1.4% remained in the waste sludge. The addition of electron acceptors (NO_3^{-1}, SO_4^{-2}) and increasing of temperature up to 45 °C enhanced the PAH yields. The most effective PAH degradation occurred in high-oxygenated and neutral pH conditions. The PAH concentration affecting half of the *Daphnia magna* organism (EC_{50} value) was reduced from EC_{50} = 45.02 ng ml^{-1} to the PAH concentration affecting only 6% of the live *Daphnia magna* (EC_6 = 5.30 ng ml^{-1}) at the end of the aerobic treatment at a SRT of 25 days. Toxicity removals originating from the PAHs were 96%.

1. Introduction

Many PAHs are priority pollutants listed by the US Environmental Protection Agency and they cannot be removed effectively in activated sludge systems. Not many studies have been performed investigating the effects of sludge retention time (SRT) on the treatment of petrochemical wastewaters in aerobic activated sludge reactor systems. Namkung and Ritmann found that the total PAH removal efficiencies varied between 1% and 61% in the activated sludge systems at a SRT of 20 days [1]. Some investigators have considered the yields of PAHs through the biological reaction stage in an aerobic reactor at different SRTs [2,3]. Potential advantages of biosurfactants include their unusual structural diversity that may lead to unique properties, the possibility of cost-effective production, and their biodegradability [4]. These properties make biosurfactants a promising choice for applications in enhancing PAHs degradation.

In Izmir, Turkey, wastewaters from the petrochemical industry are treated with conventional activated sludge systems. Petrochemical industry wastewater treatment plants may have acted as a source of PAH pollution in the environment because high concentrations of PAHs are usually detected in petrochemical industry wastewater treatment plant influent, effluent and dewatered sludge [5,6].The studies performed by our team showed that the PAHs are usually removed by processes such as biodegradation, sorption, and volatilization, etc. in aerobic treatment plants [7]. We reported that volatilization and abiotic hydrolysis of PAHs can be ignored [7]. Therefore, biodegradation in activated sludge systems could be the major mechanism for PAH removal in petrochemical industry wastewater. Since such systems are unable to completely remove the three less hydrophobic PAHs with three benzene rings [(acenaphthene (ACT), flourene (FLN) and phenanthrene (PHE)] and six more hydrophobic PAHs with five and six benzene rings [(benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(1,2,3-cd)pyrene (IcdP), dibenz(a,h)anthracene (DahA) and benzo(g,h,i) perylene (BghiP)] these are released into receiving bodies. In activated sludge systems the SRT should be long enough to provide sufficient retention time for contact of biomass with toxic organics like PAHs and inhibitory substances. The SRT values typically used in full-scale aerobic wastewater treatment plants are in the range of 4–10 days for carbon oxidation [8]. For the treatment of wastewaters containing inert and toxic compounds the activated sludge systems should be operated as long as necessary in order to maintain enough contact time between the microorganism and organic substrates in question.

The studies performed until now have been concerned with the aerobic degradability of low molecular weight hyrophilic PAHs [9].

* Corresponding author. Tel.: +90 232 412 71 19; fax: +90 232 453 11 53.
E-mail address: delya.sponza@deu.edu.tr (D.T. Sponza).

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The fates of more hydrophobic PAHs with high molecular weights have not been investigated in detail for petrochemical wastewaters. On the other hand, high molecular weight compounds may be components of bacterial cells that lysed during the endogenous stage or some extracellular polymeric substances derived from suspended bacteria within the aerobic sludge reactors [10]. A large proportion of PAHs remained in the treatment system until discharged. In the presence of surfactants the solubility and the biodegradability of PAHs were stimulated so that they could be taken up by the bacterial cells, could be used as carbon and energy source or could be used throughout co-metabolism [8–10]. Fast PAH and inert organic substrate diffusion from aqueous media to bacteria cells occurred via increasing mass transfer rates in the presence of biosurfactants. This caused a decrease in the inert fraction of the COD and PAH in the effluent [8,10]. The dissolved COD (COD_{dis}) parameter used for substrate utilization cannot give enough information about the degradation of organic matter [11]. The inert soluble microbial products generated from the biomass decay, from the endogenous respiration and from the hydrolysis of slowly degradable organics in the AASR. The determination of soluble inert COD (COD_{inert}) of influent wastewater and COD_{imp} generated in the biological treatment gains importance for meeting the stringent discharge limits and aquatic toxicity. These fractions become the major constituents of the effluent COD and they by-passed the AASR system without being affected by the biochemical reactions between substrate and bacteria. This is important for refractory wastewater treatment, such as in the petrochemical industry [11].

PAH removal efficiencies are low in the petrochemical industry wastewater treatment plants for activated sludge processes in Izmir. For this reason, in this study, it was aimed to determine the best biosurfactant (among RD, EM and SR) to improve bacterial activity when treating the petrochemical wastewaters. The effects of increasing SRT and RD biosurfactant concentrations on the removals of three less hydrophobic (ACT, FLN and PHE PAHs with three benzene rings) and six more hydrophobic PAHs (BbF, BkF, BaP, IcdP, DahA, BghiP PAHs with five and six benzene rings) (Table 1) and on the removals of COD_{dis}, COD_{imp}, COD_{inert} removals in a real petrochemical industry wastewater were investigated in an AASR system. The fates of RD and PAHs were investigated in the AASR system. The effects of some environmental conditions (dissolved oxygen, temperature, electron donors and pH) on the PAH yields were investigated. Furthermore, the effect of increasing SRTs on acute toxicity removals was investigated using the *Daphnia magna* test.

2. Materials and methods

2.1. Experimental set-up

An aerobic activated sludge (AASR) system made of stainless steel was used in the experimental study. The configuration of the AASR reactor is illustrated in Fig. 1. It consists of an aerobic (effective volume = 9.0 l) and a settling compartment (effective volume = 1.3 l). The AASR was continuously fed from the bottom by a feeding pump with raw wastewater taken from the influent of the aeration tank of wastewater from the petrochemical industry. The AASR was aerated by an air pump and porous diffusers to maintain the DO concentrations between 4 and 6 mg l^{-1}. The effluent wastewater from the aeration tank to the sedimentation tank passed through holes in a plate inclined at 45° to the horizontal axis. Effluent leaving the sedimentation tank was collected in an effluent tank.

2.2. Chemicals

PAHs and solvents used in GC–MS, RD, EM and SRr were purchased from Aldrich Chemical Company and have purities of 99% or greater. A mixture of R1 and R2 RD biosurfactants (commercially known as JBR natural biosurfactant) was used in this study. The second biosurfactant EM is a complex extracellular acylated polysaccharide produced by the Gram-negative bacterium *Acinetobacter calcoaceticus*. SR is a very powerful surfactant commonly used as an antibiotic. It is a bacterial cyclic lipopeptide, mainly known for its exceptional surfactant power. Its amphiphilic properties help this substance to survive in both hydrophilic and hydrophobic environments.

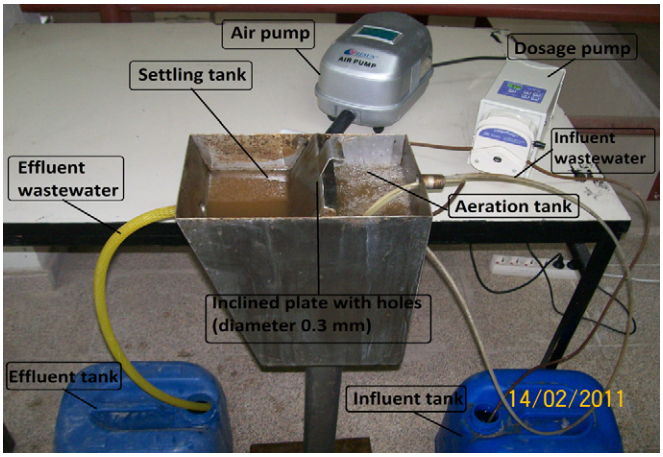

Fig. 1. Configuration of aerobic activated sludge reactor (AASR) system.

2.3. Operational conditions

In this study real wastewater was taken from the influent of the aerobic tank of the petrochemical industry wastewater treatment plant in Izmir, Turkey. The activated sludge was taken from the recycle line of the final settling unit of the aeration tank. The flow rate and hydraulic retention time (HRT) were constant as 2 l d^{-1}, and 5 days, respectively. The dissolved oxygen (DO) in AASR was adjusted to 4–6 mg l^{-1} with an air pump at flow rates of 2.5–4.5 l day^{-1} The SRTs were adjusted to 5, 15, 25 and 40 days by discarding an appropriate volume of activated sludge daily from the aeration tank of the AASR system. With each SRT change the AASR reactor was operated 20–25 days to reach steady-state conditions. Steady-state conditions were defined by stable COD and PAH removals higher than 65–70% for seven consecutive days. The results given in tables and figures are data representing the steady-state conditions. The food to mass (F/M) ratio and organic loading rate (OLR) in the AASR system were measured as 0.14 g COD g^{-1} VSS d^{-1} and 0.34 g COD l^{-1} d^{-1}, respectively. The mixed liquor suspended solid (MLSS) and mixed liquor volatile suspended solid (MLVSS) concentrations in the AASR were 2950 and 2356 mg l^{-1}, respectively.

The OU, OUR tests were performed in 500 ml glass flasks containing mixed samples of wastewater-biomass taken from the AASR. They were capped with silicone suba-seal septa (Sigma–Aldrich) and wrapped with aluminium foil to prevent photolysis.

The flasks were divided into five groups, high-oxygen and low-oxygen, anaerobic and anoxic conditions. For the high-oxygen condition the flask was aerated with an air pump every day to reach dissolved oxygen concentrations of 4–6 mg l^{-1}. For the low-oxygen condition, the flask was treated as that of non-oxygen condition but about 2 ml N_2 gas in the flask was then replaced with purified oxygen gas (>99.9%), and the 2 mg l^{-1} content was obtained by replacing N_2. During these tests the dissolved oxygen was measured frequently. During the biodegradation experiment, the