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Minimizing solid wastes in an activated sludge system treating oil refinery wastewater

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ABSTRACT

Biosurfactants are suitable for application in wastewater treatment systems due to their biodegradability, biocompatibility and low toxicity. In activated sludge systems, they reduce coalescence and disintegrate flakes, enabling more cells to have access to oxygen. At low concentrations, they may act as growth inhibitors. In this study, rhamnolipid was added to a bench scale sequential batch reactor operating in similar conditions as oil refinery wastewater treatment plants. Concentrations from 12 to 50 mg rhamnolipid/L were evaluated, the latter being the minimum concentration necessary to reduce sludge disposal. In this concentration, rhamnolipid reduces sludge disposal of up to 52%, maintaining COD removal of 81–97% and good sludge settling properties (SVI 120 mL/g) and could also reduce area occupied by secondary clarifier of 39–52%. However, biosurfactant application needs to be optimized, because its cost is even higher than the savings obtained with lower waste disposal.

1. Introduction

Activated sludge is the system most widely used in the treatment of domestic sewage and industrial effluents, including those generated in oil refineries. However, despite its high organic matter removal efficiency, it has high sludge production, which, after suitable treatment, is often referred to final disposal in landfills [1,2]. This practice increases the costs for the treatment plant because sludge management can reach 60% of total operation costs, even though its volume accounts for only 1–2% of the total volume of treated effluent [2]. The activated sludge system of the oil refinery in this study generates about 11 daily tones (dry basis) of sludge with a daily disposal cost of USD 770.

In Brazil, a new environmental law on solid waste management was recently implemented (Law No. 12,305, August 2, 2010), establishing a National Policy on Solid Wastes, prioritizing the prevention of waste generation, followed by reduction, reuse, treatment and final disposal. The implementation of this law in the coming years is expected to further aggravate the problem of generation and disposal of sludge in landfills because it adds an environmental aspect to sludge management costs.

Some modifications may be implemented in activated sludge systems to reduce sludge generation such as extended aeration and operation with reduced food/microorganism ratio (F/M ratio) [3,4]. Most Brazilian oil refineries have adopted these changes and are already producing less sludge. Still, the amount of sludge generated is considerably high due to the high water consumption and, consequently, high generation of effluents [5].

According to Mahmood and Elliot [6], excess sludge reduction approaches fit into two categories: (a) post treatment of the sludge generated in order to reduce the amount for disposal and (b) changes in the wastewater treatment unit, so that sludge is produced in lower quantities. The second category, i.e., preventing the generation of biomass, can be regarded as a better choice in environmental terms [7]. In terms of integration with wastewater handling units, the existing mechanisms aiming sludge reduction are cell lysis/cryptic growth (most studied technique), uncoupled metabolism, endogenous metabolism and microbial predation, and each one of them consists of a set of technologies. Several technologies have been studied and even implemented on a pilot and industrial scale, although some studies are still restricted to the laboratory scale [2,8].

As the problem of sludge generation is a subject that is in evidence all over the world, the search for new technologies to reduce excess sludge production is still necessary. The application of biosurfactants to reduce sludge production is one of these new

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alternative, still little discussed in literature, and should be studied in oil refineries. Biosurfactants are molecules with chemical properties similar to surfactants, frequently obtained by microbial means. The interest in these substances has increased mainly because they are considered environmentally compatible, since they have low toxicity and are biodegradable [9,10]. In wastewater treatment, biosurfactant can be used to reduce coalescence, disintegrate biological flakes and allow more cells to have access to oxygen in aerobic biological processes, thus improving the treatment efficiency [11]. However, depending on the concentration, biosurfactants can inhibit cell growth or act as biocides [12]. Studies have shown that rhamnolipid-type biosurfactants have biocidal and inhibitory effect on algae and may even affect cell organelles [13]. The effect of biosurfactants as microbial growth inhibitor or biocide has been very little studied and there are no reports in literature about their use in wastewater treatment systems in order to reduce sludge generation by changing microbial metabolism.

The aim of this study was to evaluate the sludge disposal reduction in the treatment of oil refinery effluent by activated sludge operating in sequential batch with and without addition of biosurfactant. The study also aimed to verify whether this alternative has potential for application in reducing one of the greatest environmental and economic problems today in treatment plants of oil refineries and other types of industry. The reduction in sludge generation allows processes intensification as it offers opportunities for use of equipment already known but in reduced size (in the case of sludge sedimentation tanks) and environmental benefits (lower emissions of pollutants during transport and lower amount disposed in landfills).

2. Material and methods

2.1. Origin of effluent and sludge

The bioreactor operation used a mixture of effluents from an oil refinery, collected and stored at room temperature until time of use, and a synthetic medium containing substances typically found in oil refinery wastewaters, whose composition is based on the study of Brookes [14]. The NaCl concentration in the medium was adjusted to salinity value close to that found in Brazilian oil refineries (600 mg Chloride/L).

The sludge used as inoculum in bioreactors was obtained from the activated sludge system of an oil refinery, being collected and stored at 4 °C until time of use and characterized as mass of volatile solids by waste mass (74 mg VS/g wet weight).

2.2. Biosurfactant production

The production of the rhamnolipid-type biosurfactant was performed according to method described by Santos et al. [15], using *Pseudomonas aeruginosa* PA1, a strain previously isolated from oil wells [16], preserved in ultrafreezer (−80 °C) with glycerol 10% (w/v). The pre-inoculum (1 g biomass/L) was cultivated in a rotary shaker at 30 °C and 170 rpm for 40–44 h in medium with the following composition (g/L): $NaNO_3$ 1.0; KH_2PO_4 3.0; K_2HPO_4 7.0; $MgSO_4{\cdot}7H_2O$ 0.2; yeast extract 5.0; peptone 5.0 and glycerol 30.0. At the end of this period, cells were recovered by centrifugation (5000 g for 15 min) and used as inoculum (1 g/L) in 1 L erlenmeyer flasks containing 500 mL of medium with the following composition (g/L): $NaNO_3$ 1.4; KH_2PO_4 3.0; K_2HPO_4 7.0; $MgSO_4{\cdot}7H_2O$ 0.2 and glycerol 30.0. Fermentation was conducted at 30 °C for 168 h.

The culture medium derived from fermentation containing rhamnolipids was centrifuged to remove cells (5000 g), autoclaved (121 °C/15 min) and maintained under refrigeration (4 °C). The cell-free broth used in this study contained 7.9–10.2 g/L of rhamnolipids (crude rhamnolipid solution). After purification, a 0.75% (w/v) aqueous solution was characterized according to methodologies described in Araújo et al. [17], with surface tension of 29.8 mN/m and critical micelle concentration (CMC) of 67 mg/L.

2.3. Feeding of bioreactors

The feeding of bioreactors consisted of a mixture of oil refinery wastewaters and synthetic medium calculated to obtain COD around 1000 mg/L. To maintain an ideal COD:N:P ratio of 100:5:1, there was need for supplementation with 2 mL solution composed of (g/L) $Na_2HPO_4{\cdot}12H_2O$ 40.42 e KH_2PO_4 6.58 (mixture of effluents had sufficient nitrogen concentration) per L of feed. In order to improve the sludge settleability, 5 mL of $FeCl_3{\cdot}6H_2O$ 6.66 and $Al_2(SO_4)_3{\cdot}18H_2O$ 4.0 solutions (g/L) were added per L of feed, as recommended by Novak et al. [18]. The feed pH was adjusted to average values of 7.2 ± 0.2.

2.4. Operation of bioreactors

Two 1-L bioreactors with 500 mL working volume were used: Control (without addition of biosurfactant) and Test (with addition of biosurfactant). To ensure adequate oxygen supply, compressed air was injected through a porous diffuser located at the bottom of bioreactors. Aeration along with magnetic stirring allowed maintaining the sludge in suspension and the supply of dissolved oxygen necessary to the process.

Bioreactors started with the addition of 20 g of sludge used as inoculum and feeding to complete the working volume of the reactor (500 mL) to an initial VSS (volatile suspended solids) concentration of about 3000 mg/L. Control and Test bioreactors were monitored for a total period of 266 days in sequencing batch, simulating operating conditions of oil refinery continuous reactors: 5.5 h reaction time, sludge age of 20 d, volumetric organic load (VOL) of 1.2 kg COD/m^3 d and F/M of 0.4 kg consumed COD/kg VSS. Two daily medium exchanges were made. In the first exchange, aeration and agitation were shut down, sludge was left to sediment for 30 min and half the supernatant (130 mL) was replaced by a new feed with COD of 1000 mg/L, so as to simulate a recycle ratio equal to 1 (one). In the second exchange, 5.5 h after the 1st medium exchange, an aliquot of 25 mL of the mixed liquor was collected to maintain the sludge age at 20 d and again aeration and agitation were shut down. After sedimentation for 30 min, the supernatant (260 mL) was replaced by new feeding to maintain the biomass until the next day. The mixed liquor aliquot collected was analyzed for volume of settled sludge, concentration of VSS and TSS (total suspended solids), pH and centrifuged COD.

Initially, the biosurfactant was added to the Test bioreactor feed to obtain the desired concentration. As this operation mode does not take into account the product biodegradation, it began to be added directly to the Test bioreactor in two daily medium exchanges, so that the entire reactor content presented the desired rhamnolipid concentration, which ranged from 12 to 50 mg/L.

2.5. Analytical methods

To determine the sludge volume index (SVI), a modification of the standard method was used with sedimentation of 12.5 mL of mixed liquor in 25 mL measuring cylinder for 40 min. The other parameters (TSS, VSS, pH and centrifuged COD) were determined according to standard methods [19]. The operation of bioreactors was divided into periods based on the rhamnolipid concentration used and the results for each period were reported as mean ± standard deviation of 8 (period with 45 mg/L of rhamnolipid into the reactor), 11 (period with 40 mg/L of rhamnolipid into the