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Comparative assessment of treatment of malathionlaced wastewater by single species (*Pseudomonas Stutzeri*) vs.activated sludge in a submerged membrane bioreactor

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Purification of water containing pesticide namely Malathion in membrane bioreator has been carried out. To understand the complex fouling mechanisms and fouling propensities occurring in a Membrane Bioreactor (MBR), in the current work, comparison of malathion degradation by single species, Pseudomonas Stutzeri, and microbial consortium has been carried out. Extracellular Polymeric Substances (EPSs) and Soluble Microbial Proteins (SMPs) are considered to increase the fouling. Experimental results revealed 85-90% reduction in the COD of the malathion containing synthetic wastewater and degradation kinetics has been reported. Complete reduction of malathion observed within 24 h in both the cases. A key parameter, critical flux is found to be 10 LMH for both the membrane bioreactor systems. Cake and Membrane resistances are calculated thus giving an insight regarding the working of Membrane Bioreactor based on single species and activated sludge.

Keywords: COD reduction, Conventional activated sludge, Malathion degradation, Membrane bioreactor, Membrane fouling, Microbial consortium, Sustainable flux

Myopic use of different chemicals by human beings, such as pesticides, antibiotics, plastics and petrochemicals has put earth in harm’s way. Slowly these chemicals have entered our lifecycle and proved to be lethal to us and other living creatures disrupting the harmony of nature in the long run. They have taken various forms such as endocrine disrupting chemicals (EDCs), micro-pollutants and contaminants of emerging concern (CECs)[1]. The necessary action to eliminate them should, soon be taken at various stages. Use of biological processes to get rid of them or getting them back to an inert state seems a very logical option. Currently a lot of aerobic and anaerobic degradation processes are available for wastewater treatment[2]. Membrane bioreactor is an excellent option for reducing the land footprint of the treatment plants and to achieve better treatment of the wastewater generated. The MBR process is known to degrade different chemicals by microbial action through its activated sludge containing a consortium of bacteria, amoeba, protozoa, algae, fungi and virus and reduce the COD load of a particular waste stream[3]. Membrane fouling and its material of construction is a major concern along with higher power costs as compared to the conventional activated sludge process[4,5]. The fouling of the membrane takes place due to numerous membrane foulants and the complex nature of activated sludge i.e. microbial consortium. The quality and quantity of SMPs (soluble polymeric products) EPSs (extracellular polymeric substances) affect the fouling intensities in MBR[6]. Various options have been tried to reduce the fouling in MBRs such as vibrations or addition of porous biofilm carriers and so on[7,8]. These strategies aim at reducing the cake resistance or adherence of the biomass to the membrane surface, reduction in fouling intensity or foulant concentration.

In the Single Species Membrane Bioreactor (SS-MBR) approach, targeted removal of the pollutant under consideration is carried out by a particular microbial species specially chosen and known to use it as a substrate for its growth. Such a methodology may help in reduction in fouling due to the enhanced ability of the microbe to degrade the pollutant. Hence, in such a scenario lower concentrations of microbe would suffice and it would not have to compete with other microorganisms for nutrients. Fouling is directly attributed to quality and quantity of extracellular polymeric substances and soluble microbial proteins i.e. the carbohydrate fraction/ component of it[9,10]. The reduction in the biomass concentration would help us in reducing fouling and operate at higher fluxes. Hence by reducing the complexity of the activated sludge by a structured approach the problem related to fouling can be handled with simplistic methodologies.

Malathion [(Diethyl 2-dimethoxyphosphinothioyl) sulfanyl]butanedioate is a commonly used organophosphatic insecticide used widely for agricultural as well as pest control purposes. It is stable in the environment and does not readily degrade in oxygen saturated water by molecular oxygen[11]. It binds to cholinesterase irreversibly and is known to cause health issues like nausea, skin and eye irritation, cramps and even death. EPA has suggested a limit of 0.2 mg/L malathion for drinking water[12,13]. Many researchers have worked in the area of pesticide removal from wastewaters and have investigated its concentrations ranging from 0.02 to 100 ppm[14-16].

Pseudomonas stutzeri, a gram negative rod shaped bacterium is well known for its bioremedial capabilities as it can degrade carbon tetrachloride and organophosphorus pesticides[14]. Pseudomonas species is also known to act upon malathion and degrade it into mono and diacid metabolites through carboxylesterase activity[17]. The final product of degradation by the pathway given by Turnbull, 2013 involves the production of phosphates i.e. complete mineralization after oxidative desulfurization or demethylation[18].

The aim of the present study is degradation of malathion from the synthetic wastewater and to compare the SS-MBR approach with Activated Sludge Membrane bioreactor (AS-MBR) operation. Malathion removal was carried out in the two scenarios, SS-MBR and AS-MBR and various parameters were investigated to gain insight regarding fouling, critical flux and COD reduction. Another objection of the present study is to investigate and estimate the membrane resistance reduction due to single species and activated sludge and to know the fouling propensity and its dependency on the MLSS concentration.

Experimental Section

Experimental set up

As illustrated in Fig. 1, the submerged MBR setup consisted of a tank with effective volume of 20L and a Feed Equilization Tank of 5 L. The tank was aerated with a flowrate of 1 L/min and air diffusers were placed at the bottom of the tank. A polypropylene hollow fiber membrane (Membrane P50, Zena Membranes) module with mean pore size of 0.4 micron and total surface area of 0.16 sq. m was used for filtration[19]. Ener Tech Peristaltic Pump Model No.: ENPD 400 Exp was used to create suction pressure and an inline Bourdon Vacuum Gauge was installed to measure the pressure. The setup was provided with a recycle line as shown in Fig. 1 as the dashed line.

Malathion (50% E.C) was procured over the counter locally for the study. Pseudomonas Stutzeri strain (NCIM No. 2562) revived in Medium 41 of the NCIM catalogue was harvested and acclimatized to the synthetic waste water and malathion mixture for 48 h at 120 RPM and 37°C in the shaker incubator. The conventional mixed culture of activated sludge for MBR was obtained from DBESA Central Effluent Treatment Plant (CETP), Dombivli, India[20]. Synthetic wastewater with COD concentration of about 2450 mg/L was prepared with 25 ppm Malathion concentration. 1 L seed culture was prepared as inoculums for the 10 L working volume of the MBR. Hydraulic Retention Time (HRT) was set to be 72 h based on the flask study experiments where the complete degradation of malathion was achieved by the microorganism. No discharge condition was set for the sludge during the operation of MBRs. Mixed liquor suspended solids (MLSS) concentration reached about 715 mg/L for the SS- MBR experiments and about 672 mg/L for the AS-MBR experiments.

Analytical methods

Analysis of malathion was carried out by Knauer HPLC 4.5 × 250 mm C-18 column. The detection wavelength was 230 nm and the mobile phase being 70:30 acetonitrile water system[21]. Total organic carbon content of the samples was analyzed by using SGE ANATOC Series II- TOC analyser. The COD content of the samples was calculated from TOC using the following expression for wastewater effluent streams[22].

$$COD = 7.25 + 2.99*TOC \quad \ldots (1)$$

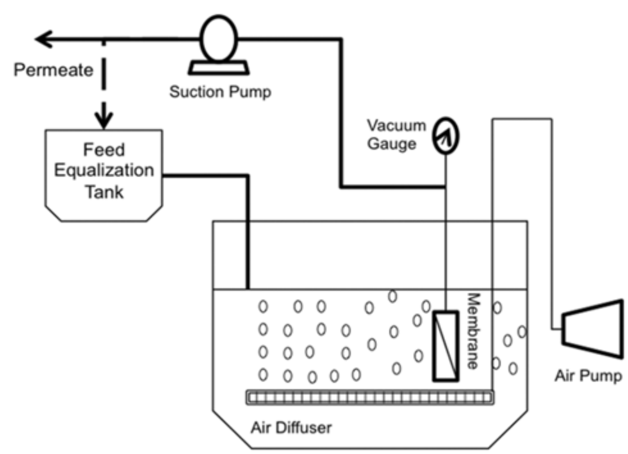

Fig. 1 — Submerged MBR schematic diagram

Results and Discussion

Effect on Malathion removal and COD reduction

Permeate samples were taken at regular intervals to analyse the pollutant and COD levels. As seen in Fig. 2, complete removal of Malathion took place within the first 24 h in the SS-MBR runs with pseudomonas as the selected species. In the MBR setup which was inoculated with the activated sludge from the CETP, the pesticide removal was around 75% for the same duration. The total time required for the AS-MBR to reduce malathion completely was around 48 hr.

Also seen in Fig. 3, in the SS-MBR the COD removal was rapid in the first 24 h compared to the AS-MBR. The COD removal in both the tanks was around 85-90%. Slightly greater COD removal was achieved in the MBR setup at the end of 72 h. The degradation kinetics for the Malathion was calculated from the equation ln (Co/Ct) = k.t where Co is initial concentration at time zero and Ct is the concentration of Malathion at time t of sampling, k is the first order degradation constant[23]. The values of k were found to be 0.12 Hr^{-1} for SS-MBR was and 0.06 $Hr^{-1}$for AS-MBR indicating that pseudomonas are quicker and twice as much efficietnt to degrade the substrate than the mixed microbial consortium.

The plot of ln (Co/Ct) vs Treatment time in Fig. 4 indicates the slope being the rate constant k of degradation as -0.0214 Hr^{-1} for SS-MBR and -0.0304 Hr^{-1} for AS-MBR.

Membrane fouling studies

Studies were conducted to estimate and compare the degree of fouling in both the systems i.e. SS-MBR and AS-MBR. It is known that membranes are more susceptible to fouling as the flux across them keeps increasing. Hence, the aim of the study was to find suitable flux value i.e. the maximum sustainable flux at which fouling would be the least and could be easily tackled. The critical flux is the point at which the fouling increases dramatically with an evident increase in the slope of Trans-Membrane Pressure TMP vs Flux plot. The critical flux study benefits in providing an insight to impose the design flux gradually during the commencement of MBR operation[24]. Also the fouling nature or propensity of the sludge can be judged from such studies which inturn will decide the maximum operation time for a system and the frequency of back flushing[25]. The suction pump was operated at different flux values for a period of 7 min till it attained a steady Trans-

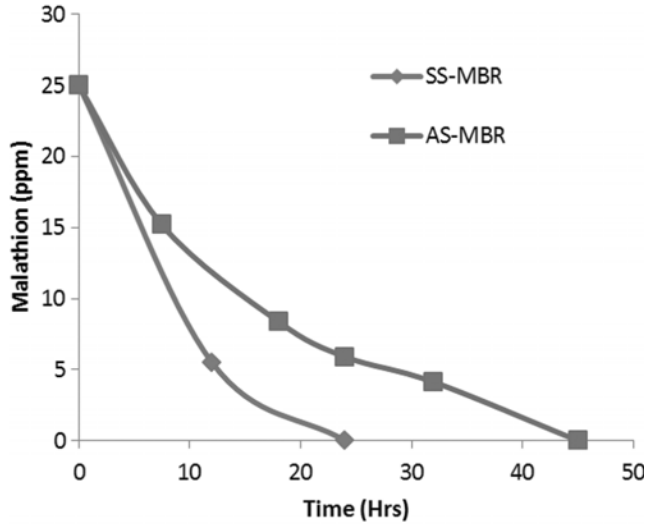

Fig. 2 — Malathion removal by SS-MBR and AS-MBR

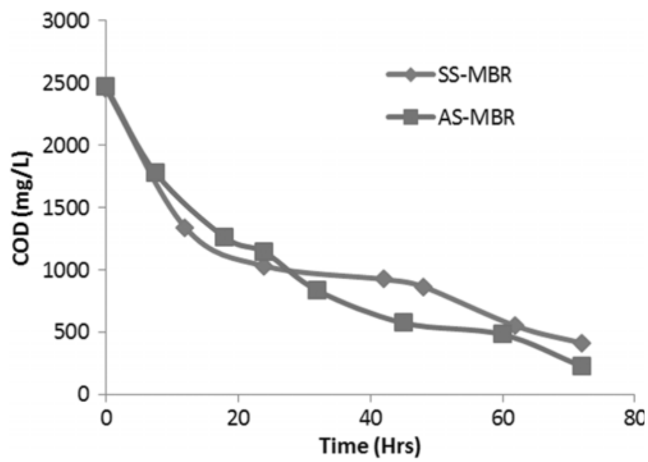

Fig. 3 — COD removal by SS-MBR and AS-MBR

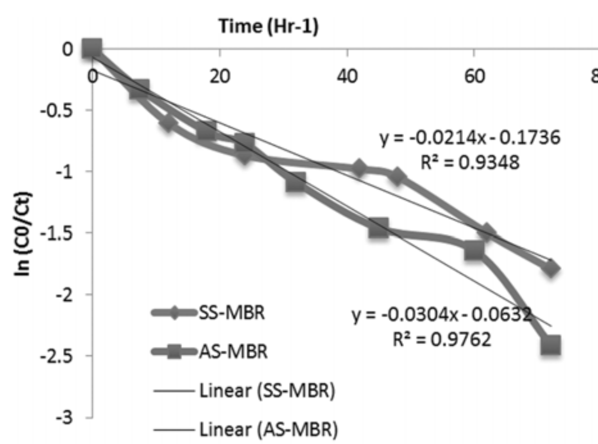

Fig. 4 — The first-order kinetics model for COD reduction

membrane pressure (TMP) value[26]. The Flux vs TMP data have been plotted in Fig. 5 below and a visual analysis of the graph suggests a critical flux value of

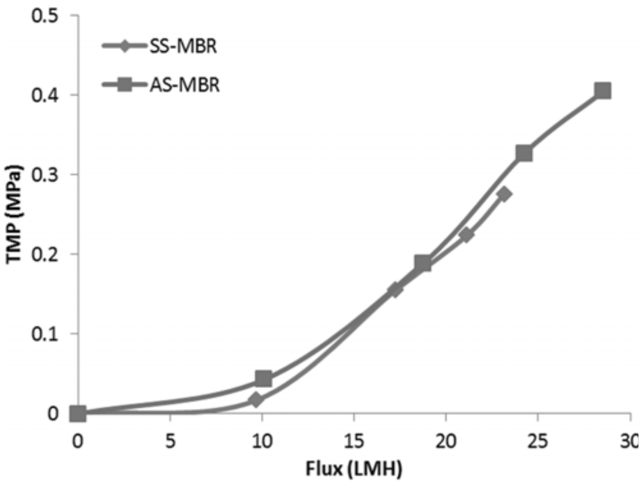

Fig. 5 — Critical Flux test for the hollow fibre membrane module.

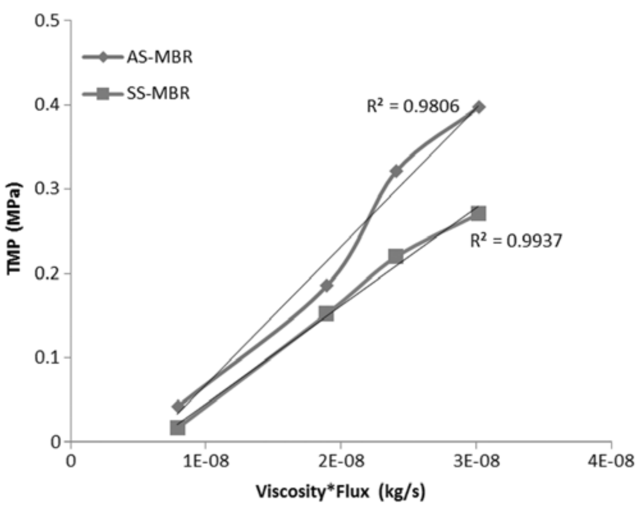

Fig. 6 — Total Resistance for different MBR scenarios.

Table 1 — Overall resistances of the two systems

AS-MBR (R_a)	SS-MBR (R_b)	Post Cleaning (R_m)
1.641E+13	1.16297E+13	6.29013E+11

around 10 LMH. The sustainable flux of a membrane is the flux value at which it can sustain for a long time in operation before the TMP value of the system crosses the desirable limit. The biomass tends to adhere to the membrane surface rapidly after this maximum sustainable flux of 10 LMH. Although the critical flux values are 10 LMH the SS-MBR system has a better sustainable flux value and based on which it can be operated for a longer time. The frequency of back flushing will decrease with longer operation time of the membrane.

The permeation flux for the membrane can be determined as

$$Flux = \frac{\mathrm{TMP}}{\mu * \mathrm{R}} \qquad \ldots (2)$$

where, TMP is trans-membrane pressure value and R is the total resistance for the flow. μ is the viscosity of the watewater which was approximated to be 0.001 kg/(m.s) as of water as the MLSS is very low to affect the suspension viscosity of the solution. Since the suspension viscosity affects fouling only above a concentration of 10 g/L[27]. Simplistic resistance in-series model suggest that the total resistance comprise of the hydrodynamic resistance due to membrane and due to cake layer formation, extracellular polymeric substances and soluble microbial products. From Equation (2), the total resistance R is obtained from the slope of the curve obtained after plotting TMP vs Viscosity*Flux graph. Two separate plots for MBR and SS-MBR and AS-MBR operation can be seen in Fig. 6.

Table 1 presents total resistances during operations for SS-MBR and AS-MBR systems, obtained from the slopes of the curves from Fig. 6. The resistance value for SS-MBR R_b was less than resistance for AS-MBR R_a operation. This decrease in the overall operating resistance was found to be around 30%. As the same membrane was used in both the scenarios the membrane resistance is same and common in both the cases. To find out the membrane resistance, the membrane was cleaned by a combination of sodium hypochlorite 400 ppm and sodium hydroxide 0.1 N solution[28]. On this clean membrane then a clean water flux profile was determined and R_m, the hydrodynamic resistance due to the membrane alone was calculated. Hence the decrease in the overall resistance is attributed solely to the nature of the sludge and different concentration of SMPs and EPSs.

Conclusion

Malathion is better removed by the SS-MBR approach than the AS-MBR system. The complexity of the sludge system is reduced by single species usage for degradation. By using only one bacterial species for biodegradation of malathion instead of complex activated sludge, the maximum sustainable flux of the system increased. Although the MLSS in case of SS-MBR scenario is higher, it witness lesser fouling as compared to regular MBR which leads to the conclusion that membrane fouling is independent of this parameter. The decreased fouling and lower overall resistance in SS-MBR by 30%, result in better critical flux suggesting reduced fouling propensity by the sludge. It can be concluded that an increased operation time and reduced back flushing can be achieved with SS-MBR approach due to its reduced overall fouling resistance and better sustainable flux increasing the efficiency of the process.

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