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Treatment of Industrial Wastewater with High Concentration of Hydrocarbons Using Membrane Reactors

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Abstract: The application of membrane bioreactors for the depuration of wastewater coming from the washing of mineral oil storage tanks is described. Microfiltration hollow-fibre membranes were used in the submerged configuration. Filtration tests were carried out with a biomass concentration of about 15 g/L in order to assess the critical flux of the hollow fibre membrane used. Then particular care was taken in carrying out the performance runs in the sub-critical flux region. The reactor performance was very high, with removal efficiencies ranging between 93% and 97% also when the concentration of hydrocarbon was very high. Some kinetic parameters for the COD and the hydrocarbon removal were estimated.

Keywords: *bioremediation, membrane biological reactor, activated sludge process, microfiltration hollow fibre membrane*

1. Introduction

During the last ten years the number of scientific papers on membrane biological reactors (MBRs) has been steadily increasing [1], as well as the application of the technology to the treatment of domestic wastewater [2-5]. Recently, the attention of the researchers has been shifting to the application of MBR to industrial wastewater. Of particular interest is the treatment of industrial wastewater containing mineral oil [6-7], and hospital and pharmaceutical [8-10], agro-food [11-12] and textile [13] wastewater.

Unlike the conventional activated sludge process, in the MBR process there is not the secondary settling tank which is replaced by a proper microfiltration membrane to avoid the passage of the biomass in the final effluent. The consequent advantage of using a MBR process against a conventional activated sludge process is the possibility to use a wider range of operating conditions. For example, while in the conventional activated sludge process the choice of the sludge concentration in the aeration tank is bound by the settling characteristics of the sludge, in a MBR process high sludge concentration (up to 20 g/L) could be used [2] since microfiltration membranes are selective enough to retain the suspended solids which constitute the biomass. Hollow-fibre membranes can be directly submerged in the bioreactor volume and then the clarified effluent is obtained by means of a dead-end filtration by applying trans-membrane pressure. One of the limiting factors in the MBR could be the biomass adhesion to the membrane surface, and than in order to maintain the operations stable and long-term before the membrane cleaning the permeate flux should be maintained below the critical flux [14].

The paper will show some preliminary data of a submerged polyethylene hollow-fibre membrane bioreactor for the treatment of wastewater containing high concentrations of hydrocarbons coming from the washings of mineral oil storage tanks. The conventional treatment process used by the company is based on a activated sludge aeration tank with a biomass concentration of about 2～4 g/L after the separation of most

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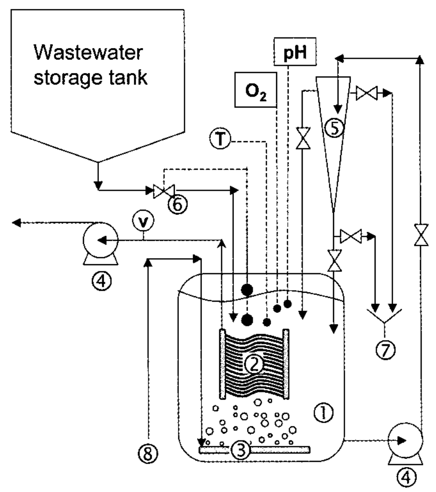

Fig. 1. Experimental set-up used as membrane bioreactor. (1) bioreactor tank; (2) membrane module; (3) air diffuser; (4) peristaltic pumps; (5) settling tank; (6) electro-valve driven by a level-meter; (7) sludge and clarified water drain; (v) vacuometer; (O_2) oxygen sensor; (pH) ph-meter; (T) thermocouple.

of the oil in a skimming tank. The biological process is followed by a chemical-physical treatment.

2. Experimental

Wastewater was generated by a local company from the washings of mineral oil storage tanks in the industrial port of Genoa and it contains high concentration organic compounds, mainly hydrocarbons. Wastewater used in this work was sampled in the conventional treatment plant after the skimming tank. The organic compound composition depends on the type of products stored in the tanks and both the frequency and quality of the washings. Some of the organic compounds are very soluble in water (e.g. cyclohexanone) while others are almost insoluble (e.g. xylenes). The pH was in the range of 6.5~8.5. The hydrocarbon concentration was between 33 and 9000 mg/L and the chemical oxygen demand (COD) varied from 700 to 10000 mg/L. Nitrogen was present only as ammonia and in concentrations ranging from 114 to 330 mg/L. Phosphorus as phosphate was absent.

Fig. 1 shows the experimental rig. The MBR was composed of a hollow fibre membrane module sub-

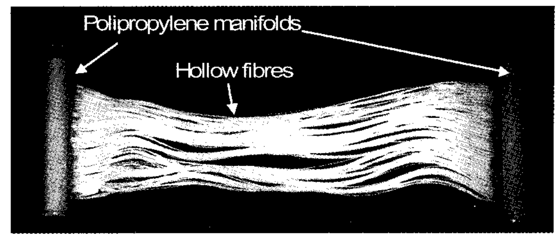

Fig. 2. 0.2 m^2 hollow-fibre membrane module.

merged in a reactor (V = 3 L) fed by gravity with wastewater contained in a storage tank. Oxygen and the turbulence to suspended the biomass was provided by an air diffuser located under the membrane modules. When necessary, part of the activated sludge could be wasted or recycled in the reactor by a peristaltic pump and a settling tank. The treated wastewater effluent was recovered through the microfiltration membrane, where the driving force was provided by a peristaltic pump located after the membrane module. The level in the reactor tank was kept constant using a level sensor coupled with an electro-valve on the feed stream.

The activated-sludge was obtained by the inoculation of a sample of the same activated sludge from the conventional treatment process used by the company in Genoa. Nitrogen and Phosphorus were added in the mixed liquor as NH_4NO_3 and KH_2PO_4 respectively, using the concentrations suggested by the supplier of the micro-organism.

The hollow-fibre microfiltration membranes used were made of polyethylene and their structure was symmetric. Polyethylene membrane were chosen because of their better stability in presence of hydrocarbons and their better resistance during the cleaning procedures, when compared to other materials. The outer and the inner diameters of each hollow fibre were 0.65 and 0.41 mm respectively and the nominal pore size was 0.4 μm. Fig. 2 shows the 0.2 m^2 module made in laboratory using hollow-fibre membranes.

Total hydrocarbons concentration (THC) by CCl_4 extraction, chemical oxygen demand (COD) using the dichromate method, mixed liquor suspended solids (MLSS) by filtration on a 0.2 filter and weight meas-

Table 1. MBR Operating Conditions

Operating condition		1st run	2nd run	3rd run	4th run
Single run operating time	h	160	270	360	1200
Temperature	°C	22	22	22	22
Permeate flux	L/(m^2 h)	0.83	0.42	1.25	1.5
Hydraulic retention time	h	17.7	31.8	11.5	9.7
Average mixed liquor suspended solids (MLSS range)	g/L	5.2 (4.8~7.4)	8.4 (7.4~9)	9.2 (7.3~11)	14 (8~17)
Average COD	mg/L	1300	7964	1800	1400
Average total hydrocarbons	mg/L	1436	7500	1350	900

urements and ammonia using the Nessler method were determined in the feed and in the membrane permeate, following the analytical procedures reported in the APHA standard methods [15]. The concentration of the nutrients as nitrate, nitrite and phosphate ions had been checked in the mixed liquor using an ion exchange chromatograph (DX 120 Dionex equipped with a Ion-pac AS9-HC column).

Table 1 resumes the main operating conditions of the membrane bioreactor during the runs studied. The sludge retention time used in this work was about 50 days. Between the two consecutive runs the membrane module was cleaned in a solution of sodium hypochlorite (500 mg/L as chlorine) at 40°C for 2 h.

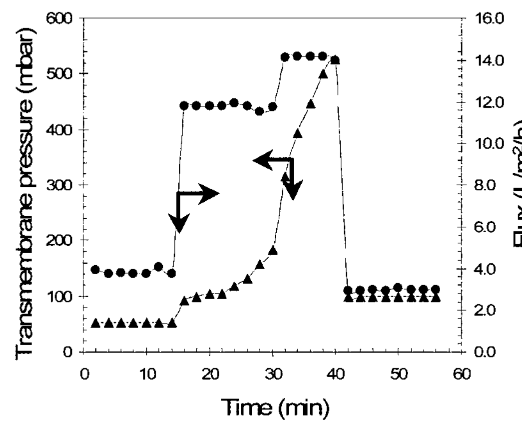

Fig. 3. Critical flux determination. Biomass concentration of about 15 g/L.

3. Results and Discussion

The accumulation of biomass on the membrane surface can strongly affect the membrane performance [16]. Fig. 3 shows a typical test carried out in order to assess the critical flux of the membrane in the used operating conditions. The permeate flux through the membrane was increased with 15 min long constant steps and during each constant flux step the behaviour of transmembrane pressure was observed. The critical flux was estimated when the transmembrane pressure began to increase with time. At the critical flux the accumulation of biomass on the membrane becomes a limiting factor [17-18]. The critical flux for the membrane module used with a biomass concentrations of about 15 g/L was about 12 L m^{-2} h^{-1}. All the other experimental runs were carried out in the sub-critical flux region with permeate flux ranging from 0.4 to 1.5 L m^{-2} h^{-1}.

The membrane module was cleaned between two consecutive runs and the water flux was measured and compared with that of the new membrane. The water flux curve after a cleaning procedure was not dependent on the run conditions in which the membrane operated in the bioreactor.

Fig. 4 shows the substrate concentration in the feed and in the permeate in terms of COD as a function of the operating time. The substrate concentration in each run wasn't always the same, and moreover a little scatter was present in the concentration data, due to the sometimes high dilution ratio used for the analytical measurements. The results are resumed in Table 2 in terms of average substrate concentration for each run period. Almost all the COD was due to the hydrocarbon present in the wastewater. The removal efficiency

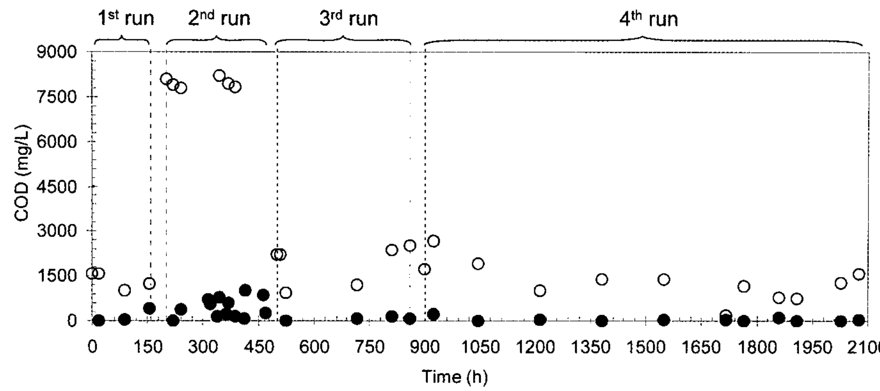

Fig. 4. COD in the feed (○) and in the permeate (●) for 4 consecutive runs.

Table 2. Average Substrate Concentration in the Feed and Permeate of Each Run

Run	Time (h)	Hydraulic retention time (h)	Total wastewater volume (L)	Mixed liquor suspended solids (g/L)	COD			Total hydrocarbon		
					Feed (mg/L)	Permeate (mg/L)	Removal efficiency (%)	Feed (mg/L)	Permeate (mg/L)	Removal efficiency (%)
1st	160	17.7	27.1	5.2	1300	80	93.8	1436	101	93.0
2nd	270	31.8	25.4	8.4	7964	268	96.6	7500	350	95.3
3rd	360	11.5	94.0	9.2	1800	90	95.0	1350	95	93.0
4th	1200	9.7	370.6	14	1400	48	96.4	900	35	96.1

of both COD and hydrocarbons was between 93% and 96% also when the substrate concentration was very high (e.g. 2nd run). The highest and the lowest volumetric organic loadings applied were respectively about 6 kg_{COD} m^{-3} $h^{-1}$and 1.7 kg_{COD} m^{-3} h^{-1}.

The substrate removal efficiency can be defined as

$$\eta = \frac{S_o - S_e}{S_o} \cdot 100$$

and is related to the food to microorganism ratio F/M [19]

$$F/M = \frac{S_o}{HTR \cdot X}$$

where:

S_o = influent substrate concentration (mg/L)

S_e = effluent substrate concentration (mg/L)

X = biomass concentration (mg/L)

HRT = hydraulic retention time (d)

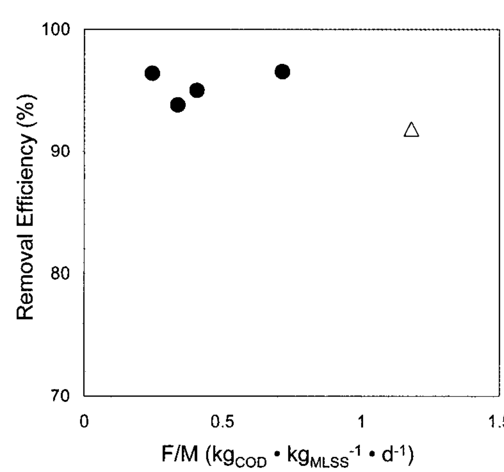

Fig. 5. COD removal efficiency against the F/M ratio for the MBR (●) and the conventional activated sludge process as elaborated from ref. [20] (△).

Fig. 5 shows the behaviour of the COD removal efficiency with the F/M ratio (expressed as kg of influent COD to kg of mixed-liquor suspended solids to day ratio) for both our membrane bioreactor and for an activated sludge process applied to the removal of mineral oil from wastewater from literature [20]. Tellez et al. studied a conventional activated sludge plant for the treatment of a wastewater contaminated by mineral oil and in Fig. 5 is reported the lowest F/M ratio used by them. The removal efficiency of the membrane bioreactor, even if the operating conditions were quite variable, seemed not depending on the F/M ratio and the efficiency reached was comparable with the literature data of the cited authors. Usually, for a domestic wastewater treatment using a conventional activated sludge process the removal efficiency decreases by increasing the F/M ratio and often high F/M ratio are applied because of the lower biomass concentration used (up to 5 g/L).

Assuming the Monod equation for the biomass growth:

$$\mu = \mu^{max} \frac{S}{K_s + S}$$

the maximum specific growth rate, μ^{max}, was evaluated to be 0.024 ± 0.03 h^{-1} and the constant Ks was about 170 mg/L.

Combining the specific utilization rate of COD, U, with the Monod equation and considering a pseudo-first order dependence on the substrate concentration, the kinetic parameter k^I can be calculated and compared with that one reported in literature for the same kind of wastewater.

$$U = \frac{S_o - S_e}{X \cdot HRT} = k \frac{S}{K_S + S} \cong k^I S$$

After selecting the MBR data that verified the pseudo-first order assumption, k^I was evaluated to be 0.0063 and in good agreement with the value reported by Eckenfelder [21].

4. Conclusions

The treatment of wastewater containing high concentration of hydrocarbons was carried out using a membrane bioreactor. The role of the membrane was to clarify by dead-end filtration the mixed liquor. The membrane module realized using hollow-fibre membranes was submerged directly in the bioreactor. The critical flux for the membrane was evaluated to be about 12 L m^{-2} h^{-1} and the following treatment runs were carried out using a permeate flux below the critical flux.

The reactor performance was excellent, with removal efficiencies ranging between 93% and 97% also when the concentration of hydrocarbon was very high. Moreover, the hydraulic retention times used in this work were lower compared to those used in the conventional activated sludge process. Some kinetic parameters for the COD and the hydrocarbon removal were assessed.

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