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Performance of Membrane Bioreactor (MBR) in High Phosphate Wastewater

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***Abstract*—**This study presents the performance of membrane bioreactor in treating high phosphate wastewater. The laboratory scale MBR was operated at permeate flux of 25 L/m^2.h with a hollow fiber membrane (polypropylene, approx. pore size 0.01 - 0.2 μm) at hydraulic retention time (HRT) of 12 hrs. Scanning electron microscopy (SEM) and energy diffusive X-ray (EDX) analyzer were used to characterize the membrane foulants. Results showed that the removal efficiencies of COD, TSS, NH_3-N and PO_4^{3-} were 93, 98, 80 and 30% respectively. On average 91% of influent soluble microbial products (SMP) were eliminated, with the eliminations of polysaccharides mostly above 80%. The main fouling resistance was cake resistance. It should be noted that SMP were found in major portions of mixed liquor that played a relatively significant role in membrane fouling. SEM and EDX analyses indicated that the foulants covering the membrane surfaces comprises not only organic substances but also inorganic elements including Mg, Ca, Al, K and P.

***Keywords*—**Membrane bioreactor (MBR), membrane fouling, phosphates, soluble microbial products (SMP).

I. Introduction

PHOSPHORUS is one of the key nutrients causing eutrophication and water pollution problems. Continuous elevated level of phosphate in water system stimulates the growth of photosynthetic algae and toxic cyanobacteria. The unbalance nutrient would lead to the increase in purification costs, decrease in conservation value of impoundments and loss of livestock which eventually will upset the ecosystem.

Domestic wastewater has typical phosphate concentration ranging from 10 to 15 mg/L [1]. Agricultural, industrial, household items and many other human activities are the major sources of phosphate in natural water bodies.

Many methods of phosphate removal were investigated using electro-coagulation, chemical precipitation [2], membrane bioreactor and nanofiltration. Some novel techniques have also been developed such as electrodialysis and reverse osmosis [3]. However, most of these technologies are at disadvantage because of poor operational stability or high economic cost.

Membrane bioreactors (MBRs) are being increasingly used as MBRs allow high concentrations of mixed liquor suspended solids (MLSS) and low production of excess sludge; enable high removal efficiency of biological oxygen demand (BOD), chemical oxygen demand (COD), and water reclamation.

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However, the reduction of permeability caused by membrane fouling is still a major problem and remains as the main constrain in the wide use of membrane treatment.

In wastewater treatment technology, MBRs has developed in recent years due to the stringent discharge criteria, increasing space constraints and desired flexibility for future expansion and upgrade [4]. In general, membrane permeability is influenced by membrane properties such as pore size, porosity, hydrophobicity, and surface charge and by filtration conditions like trans-membrane pressure, cross-flow velocity/aeration, and module geometry. One of the most effective impact of MBR operating parameters on fouling is the hydraulic and solids retention times (HRT and SRT), sludge age and loading rate [5].

A number of attempts have been made to correlate flux with biomass concentration, flocculants size, and sludge rheology [6]. The differences of experimental methods incorporate with the complex nature of the biological process often result in inconsistency and contradictory [7].

The goal of this research is to study the performance of MBR treating wastewater containing high phosphates. The other major focus of this work related to membrane fouling which was analyzed through the changes of trans-membrane pressure (TMP) and scanning electron microscope (SEM) of membrane.

II. Materials and Method

A. Description of MBR

A laboratory-scale submerged membrane bioreactor was constructed and installed at the Civil and Environmental Engineering Laboratory of SEGi University College, Kota Damansara. The overview of the MBR system is shown in Fig. 1. The MBR tank has an effective working volume of 40L, in which a hollow fibre membrane module (Table I) was submerged in the central compartment.

A coarse air bubble diffuser was installed and the air was supplied by compressed air below the membrane modules. The MBR was aerated from beneath the ultrafiltration module through a diffuser to provide the cross flow effect, the oxygen requirement for the biological process, and to mix the mixed liquor in the reactor. The pH value in the MBR tank was maintained at 7.2 ± 0.1 by adding NaOH - $NaHCO_3$ solution, and the dissolve oxygen (DO) concentration was controlled at 2.0 mg/L.

Fig. 1 The overview of the membrane bioreactor during the start-up process

The membrane flux of the MBR was kept constant during the experiment at about 25 – 30 L/m^2.h, which is lower than critical flux value as determined by step-wise method. The membrane permeate was extracted intermittently with a negative pressure pump connected to the membrane module. The MBR was operated (Table I) at temperature within the range of 25 to 35^{o}C.

TABLE I
OPERATING CONDITIONS OF MBR REACTOR DURING SEEDING

Parameter	Value
Sludge volume index	194 mg/L
Mixed liquor suspended solid	3678 mg/L
Volatile suspended solid	735 mg/L
Hydraulic retention time (hrs)	12
Flow (L/d)	80

B. Activated Sludge Sample

The sludge samples were taken from the return sludge tank of Taman Tun Dr Ismail (TTDI) municipal wastewater treatment plant in Kuala Lumpur, Malaysia. The sludge was stored in plastic container during the transportation from the plant site to the laboratory.

C. Wastewater

Synthetic wastewater was used in this study to control variable nature of nutrient concentration in raw wastewater. The feed ingredients and compositions of wastewater are included in Table II. The concentrations of the chemicals were taken from OECD guideline 301 C modified MITI tests (1). The synthetic wastewater was prepared periodically and stored in a refrigerator at temperature of 4^{o}C to hinder its decomposition. The acclimatization period for the sludge was approximately 40 days.

The synthetic wastewater constituted of glucose, NH_4Cl, KH_2PO_4, K_2HPO_4 and $Na_2HPO_4.12H_2O$ as primary nutrients, while $MgSO_4.7H_2O$, $FeCl_3$, and $CaCl_2.H_2O$ as trace nutrients. Sodium bicarbonate ($NaHCO_3$) was added to adjust pH between 7 and 8.

TABLE II
COMPOSITION OF SYNTHETIC WASTEWATER (g/L)

Composition	Concentration
KH_2PO_4	8.50
K_2HPO_4	21.75
$Na_2HPO_4.12H_2O$	44.60
NH_4Cl	1.70
$MgSO_4.7H_2O$	22.50
$CaCl_2$	27.50
$FeCl_3.6H_2O$	0.25
$C_6H_{12}O_6$	1.00

D. Analytical Methods

1. Wastewater Quality Analysis

Chemical Analysis

All activated sludge characteristics including COD, ammonia nitrogen, phosphates, suspended solids (SS) and volatile suspended solids (VSS) were measured according to Standard Methods [8]. The turbidity and SS were measured as indication of sludge flocculation performance. The sludge volume index (SVI) was used to evaluate the settleability of the flocculants. A turbidity meter (HACH, Model 2100 AN) measured the turbidity.

Extraction of SMP and EPS

The soluble microbial product (SMP) was extracted by centrifuging the activated sludge samples at 5000 g for 5 min. The SMP was summed by adding the concentration of carbohydrate, protein and humic substances. Polysaccharides were determined using the phenol-sulphuric acid assay, developed by Dubois *et. al.*[9], using glucose as a standard. Proteins and humic like substances were determined using the method of Lowry *et. al.* [10], modified by Frolund *et. al.* [11], using bolvine serum albumin (BSA) as standard. The extracellular polymeric substance (EPS) was extracted by heating up the supernatant of the centrifuged activated sludge at 80^{o}C for 10 min followed by centrifuge at 8000 g for 8 min, as describe in Judd [4]. The concentrations of carbohydrate, protein and humic substances were analyzed using same procedure as SMP analysis. All samples were analysed in triplicates.

Sludge Particle Size

The particle size was determined by a Malvern Mastersizer instrument with a 300 mm lens which enables the measurement of particles in the range of 0.9 – 546 µm. The activated sludge samples were continuously recycled through the sample cell of the Malven with a peristaltic pump to be exposed at a 2 mW He-Ne laser (wavelength 633 nm) at a speed of 500 m/s. The scattered light is detected by means of a detector that converts the signal to a size based on volume. The average size of the flocculants given as the mean based on the volume equivalent diameter.

2. Membrane Fouling Analysis

Scanning Electron Microscopy with an EDX probe (SEM-EDX)

The membrane fouling was observed with scanning electron microscope coupled with energy dispersive X-ray

spectroscopy (SEM-EDX) (Thermo Scientific, accelerating voltage of 20 kV, Universiti Putra Malaysia). Before SEM-EDX analysis, samples were Au-Pd coated. TMP values were also measured. Most of the results were taken from the average duplicate samples.

III. Result and Discussion

A. Overall Performance of the MBR System

The MBR were unstable during the start-up period, resulting in substantial fluctuations of TMP and mixed liquor suspended solid (MLSS). However, the MBR reached a steady state after approximately 60 days and relatively constant MLSS were observed. Chemical cleaning was not performed during the entire period of operation. Table III shows the characteristics of influent, effluent, and the removal efficiencies of various parameters.

TABLE III
Characteristics of Wastewater

Water quality parameters	Concentrations (mg L^{-1})		Removal percentages (%)
	Influent	Effluent	
Total COD	1200	96	93
Suspended solid	3060	20	98
NH_3-N	15.0	1.0	80
PO_4^{3-}	299.8	219.5	45

The chemical oxygen demand (COD) and total suspended solid (TSS) were monitored for the removal efficiency of organic matter. The retention of particles in the MBR tank leads to non-detectable suspended solids in the effluent with a COD and TSS removal rate of approximately 91 - 93% and 90 - 98%, respectively when the COD concentration of influent fluctuated at 506 – 1499 mg/L. However, the removal of ammonia nitrogen and phosphates were very poor. The concentration of PO_4^{3-} in the influent and effluent were around 300 and 220 mg/L, respectively giving 30% removal efficiency only. This shows that phosphate size is smaller than the molecular weight cutoff (MWCO) of membrane.

B. Effect of Biomass Concentration on SMP Production and Components

MBR biomass always consists of a combination of particulate, colloidal, microbial deposited, organic and inorganic precipitates and dissolved fractions. The importance modifications of biomass composition (solubilisation of minerals and organics) and structure (floc size) are likely to induce a shift of both floc surface properties and soluble fraction reactivity.

Throughout the study, polysaccharides (PS) concentration ranged from 2 to 146 mg/L in the sludge filtrate and 0 to 8 mg/L in the permeate. The main fractions of SMP are PS, proteins, nucleic acids and humic substances arising from cell lysis, secretion or already presence in the influent. The SMP production is a microbial response to the external environmental conditions. Unfavourable conditions (such as nutritional parameter, C/N ratio, operational, environment, etc) will produce more SMP which will increase membrane fouling rate. Table IV shows the size of particle and turbidity of MLSS over time for this study. Large size flocs, low turbidity and low SS content imply good flocculating ability of the sludge.

TABLE IV
Particle Size and Turbidity of MLSS Over Time

Week	Particle size (μm)	Turbidity (NTU)
1	350.2	21.5
2	274.3	1978
3	280.3	792.5
4	274.1	115
5	175.6	1398
6	134.3	1600
7	172.3	1975

C. Fouling of Membrane

The membrane fouling of the MBR was demonstrated by an increased of trans-membrane pressure (TMP). The TMP increased from 27 kPa to 82 kPa during more than 60 days of operation. The increase was probably due to raised viscosity at high biomass concentration within the reactor (corresponding to a reduction in operating flux under hydraulic pressure operation). MBR was cleaned chemically by mixed solution of NaOCl and NaOH at the 60^{th} day.

The most direct and indirect factor affecting a successful biological phosphate removal process is the correct balance of nutrient, carbon sources and pH of wastewater. In addition, careful consideration must be given to the operating MBR system at the correct F:M, HRT, SRT, temperature and dissolved oxygen concentration to ensure that a healthy sludge population prevails in the reactors.

D. SEM-EDX Analysis of Hollow Fiber Membrane from Membrane Bioreactor

Fig. 2 (a-e) displays examples of images obtained using SEM at magnification of 20,000 times. It revealed that the fouled membrane was covered with slime gel layer. New hollow-fiber membrane surfaces were porous and free of particles as shown in Fig. 2(a). SEM images of fouled membrane were taken on a weekly basis. After one week of operation, at TMP of 43 kPa (Fig. 2b) the membrane pores were not clear where some organics and microorganisms have deposited on the membrane surfaces. Fig. 2(c) show some microorganisms are living actively on the membrane surface after two weeks of operation. It should be noted that there are certain bacteria and organics contributed to membrane biofouling. As a result, the TMP did not drop. After week four of operation as showed in Fig. 2(d), at TMP of 80 kPa, the sludge deposited on the membrane surface had thickened up to 33.1 μm (Fig. 2e) making no visual microbial activity can be viewed.

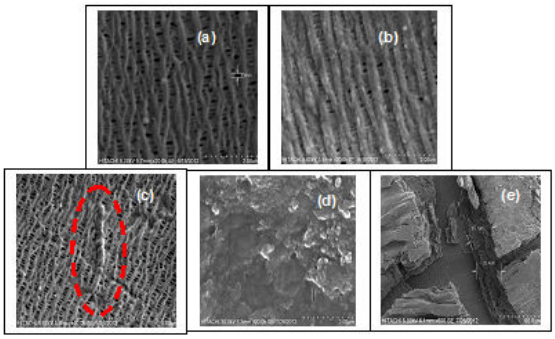

Fig. 2 SEM images: (a) clean membrane, (b) semi-fouled membrane, (c) bacteria attachment, (d) completely fouled membrane, (e) fouled thickness

The elemental analysis was further performed on the surface layer of the membrane in order to identify chemical components of the layer by EDX analysis. Table V shows the chemical composition of some particles present within the hollow fibre membrane. The carbon and oxygen element, which are one of the major components of the organic phase, were not considered for the determination of percentage by weight of each mineral element since it is not quantitative in our case. The main elements found in the hollow fibre membrane in decreasing order are: phosphorus, aluminium, potassium, magnesium, sodium and chlorine. These results confirm that the mineral fraction extracted in the hollow fibre membrane in the MBR reactor is present under more than one form.

Wang *et al*. [12] and Meng *et al*. [13] investigated that the fouling layers containing small amount of inorganic elements such as Mg, Al, Si, Ca and Fe formed on the membrane surface could bridge the deposited cells and biopolymers, which is difficult to eliminate even by chemical cleaning [14].

TABLE V
CHEMICAL COMPOSITION OF MEMBRANE BY EDX

Element	C	O	Na	Mg	Al	P	Cl	K
%	50.28	44.82	0.52	0.52	1.39	1.50	0.33	0.63

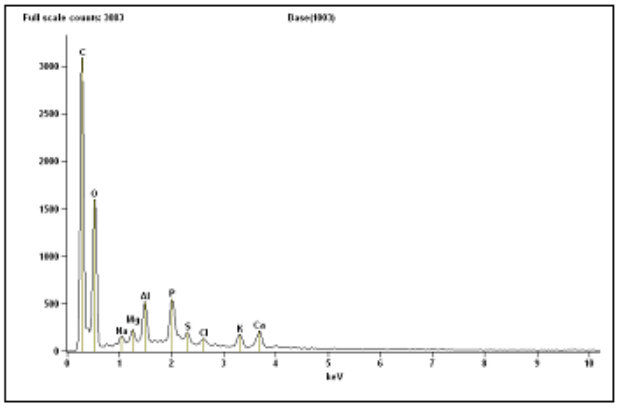

Fig. 3 EDX analysis membrane foulants on the membrane surface (our own data)

As shown in Fig. 3, there was existence of phosphorus, aluminum, magnesium and potassium on the membrane layer after 60 days of operation, which could provide favourable binding sites for heavy metals as functional groups. Phosphate could not penetrate into the membrane interior because it combines with SMP in the MBR reactor.

IV. Conclusion

The submerged MBR was steadily operated for more than 60 days. At the end of the operation, a large area of foulants was observed on the membrane surfaces. The main components of organic matters including SMP were partly removed in the MBR processes. SMP of sludge flocs played a relative significant role in membrane fouling. SEM and EDX analysis demonstrated that membrane surfaces were covered with a large amount of organic substances and inorganic elements such as Mg, Ca, Na, Al, K and P. It should be noted that phosphate could not penetrate into the membrane interior because it might combines with SMP in the MBR reactor. It is concluded that SMP could be an important cause of membrane fouling.

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