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Mechanism of bisphenol A removal by a submerged membrane bioreactor in the treatment of synthetic municipal sewage: staged analyses

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ABSTRACT

Bisphenol A (BPA) is a typical endocrine disrupting chemical that potentially jeopardizes body health of human beings. A submerged membrane bioreactor (MBR) has been operated at the laboratory scale for the treatment of synthetic municipal sewage containing BPA. For comprehensive investigation about the effect of hollow fiber microfiltration membrane on BPA removal in membrane bioreactor (MBR) system, staged analyses by environmental scanning electron microscope, BPA filtration tests, and membrane cleaning assessments were conducted. The results showed that BPA, chemical oxygen demand, and ammonia-nitrogen (N-NH_3) were eliminated effectively, at 90.11, 97, and 95%, respectively. With the running time extension of MBR, cake layer on the membrane surface got thicker, simultaneously on which cell-like substances marking biofilm formation accumulated. Staged BPA filtration tests demonstrated that with the aggravation of membrane fouling, the effect of cake layer on BPA interception was improved. And from staged membrane cleaning assessments it was found that the contents of BPA and its main degradation products including 4-hydroxybenzoic acid (p-HBA), 4-hydroxyacetophenone (p-HAP), and 4-hydroxybenzaldehyde (p-HBAL) in fouled membrane followed the same growth trend. Most of BPA was captured by the activated sludge. And the effect of biodegradation was enhanced over the running time of the MBR unit.

Keywords: Membrane bioreactor; Bisphenol A; Staged analysis; Adsorption; Biodegradation

1. Introduction

In recent decades, wastewater reclamation has been drawing tremendous attention as potential countermeasure for assuaging water shortage problems. While as time goes by, the composition of wastewater has changed significantly, with the widespread occurrence of trace organic contaminants (TOrCs) denominated endocrine disrupting compounds (EDCs) defined as exogenous compounds or mixtures that cause adverse health effects in an intact organism, or its progeny, subsequent to changes in endocrine functions [1]. Thus, the presence of these compounds in wastewaters must be taken into account due to their

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linkage with a decrease in the sperm count, an increment of episodes of brain cancer and prostate cancer, and other reproductive disorders in humans, and their potential perniciousness for aquatic species such as feminization and toxicity to fish and invertebrates [2]. Bisphenol-A (BPA) is a typical EDC used in tire production, as a stabilizing agent in polycarbonate, epoxy resins and as the basic chemical in the production of certain flame retardants [3], and discharged in its original form from chemical reaction processes and after thermal depolymerisation [4]. Because of its wide application, BPA has been frequently detected in wastewaters, sewage sludge, water bodies, etc. and reported in many places in the world. It was documented that BPA was identified at higher concentration in leachate from municipal solid waste landfill sites [5]. In municipal sewage sludge, BPA was captured within a concentration range of 30–330 μg/g in Germany [6], 0.033–36.7 μg/g in Canada [7] and 28.3 μg/g in China [8]. Its concentrations in wastewaters vary, ranging from ng/L to μg/L [9]. Besides, the fact that BPA was found in wastewater treatment plant (WWTP) effluents [10] indicates that this compound cannot be completely eliminated in conventional WWTPs.

It has been widely recognized that membrane bioreactors (MBRs) will be the next generation of wastewater treatment processes [11,12]. Combining biological degradation and membrane filtration in a single step, compact process, and allowing for flexibility in the application of different modifications to fine-tune biological performance [13], MBR process can offer the possibility to efficiently oxidize refractory pollutants from wastewaters. Although not becoming commercially available until the late 1990s, the technology has been well improved and can provide superior removal efficiency over many other conventional processes for most basic water quality indicators such as pathogens, suspended solids, and nutrients [14,15]. Several researches elaborated that MBRs had great potential to remove BPA. Kim et al. studied the fate of BPA using a sequencing anoxic/anaerobic-aerobic MBR (SAM) which was fed with synthetic water and operated at SRT of 60 d and categorized the overall BPA's removal into three pathways including discharge with effluent, expulsion with excess sludge, and biodegradation [16]. In their work the removal efficiency of BPA achieved 74.3% on average basis, which was principally attributed to biodegradation (over 80%). Also confirming biodegradation as the overriding mechanism for the removal of BPA, Yang et al. adopted a novel fungal MBR operated under non-sterile conditions to eliminate BPA, which achieved relatively stable removal rate of 80–90% [17]. While Nghiem et al. claimed that both biodegradation and adsorption to the sludge should be responsible for the removal of BPA and demonstrated an excellent performance of MBRs regarding approximately 90% removal of this relatively hydrophobic organic compound [18]. Moreover, from the perspective of technological superiority, Chen et al. [19] proved that compared with conventional activated sludge reactor (CASR) MBR could bear much greater sludge and volumetric loadings and realize a higher and more stable removal rate of BPA which behaved more than 93%, invariably, for which biodegradation played a role of the essence while activated sludge adsorption contributed a little. However, it is necessary to point out that they conducted BPA adsorption test by employing activated sludge through centrifugal processing of which the characteristics differed from that in the MBR to some extent. Although plenty scientific literature has focused on the effect of MBRs on BPA removal, the specific causes for the advantages of MBR over traditional wastewater treatment technologies such as CASR have not been elaborated carefully yet.

Through staged quantitative analyses of BPA and its biodegradation products in the cake layer as well as membrane pores and staged BPA filtration tests of fouled membrane, this study investigates the staged characteristics and staged interception performance of fouled membrane, and categorizes the removal pathways of BPA entering the MBR unit into: (i) adsorption and biodegradation on activated sludge, (ii) adsorption and biodegradation in cake layer, (iii) adsorption, biodegradation, and interception in membrane pores, and (iv) discharge along with the effluent, in order to clearly interpret the migration and transformation ways of BPA in the MBR unit and the effect of hollow fiber microfiltration membrane in MBR on BPA removal.

2. Materials and methods

2.1. Membrane bioreactor unit

A submerged MBR (SMBR) was operated at the laboratory scale. The diagram of the SMBR unit is illustrated in Fig. 1(a). The SMBR unit was composed of a 22.5 L aerobic tank (O) equipped with polyvinylidene fluoride (PVDF) external pressure type hollow fiber membrane (Tianjin Motimo Membrane Technology Co., Ltd., China) of 0.22 μm average pore size, 0.60 and 1.10 mm fiber inner and outer diameters, respectively, and about 0.21 m^2 total filtering surface area, assembled vertically. Raw water in the feed tank was pumped into a 14 L anaerobic tank (A) furnished

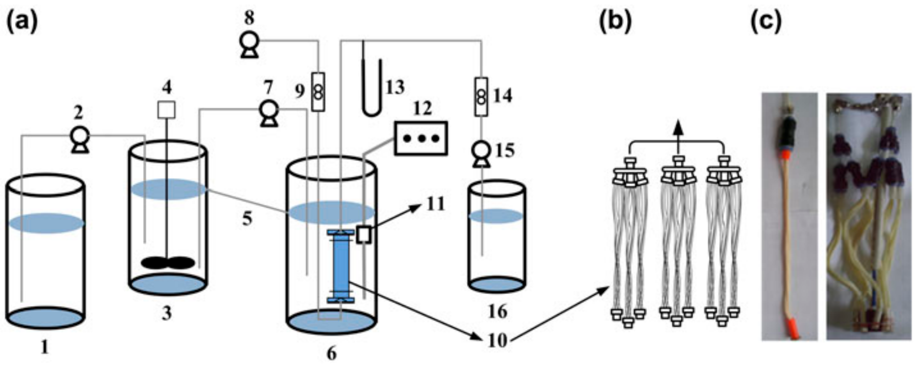

Fig. 1. Schematic diagram of the experimental apparatus: (a) Diagram of the SMBR unit (1—feed tank; 2,7, 15—peristaltic pump; 3—anaerobic tank; 4—stirrer; 5—overflow pipe; 6—aerobic tank; 8—air pump;9—air flowmeter; 10—membrane module; 11—level gauge; 12—PLC; 13—glass-U-tube manometer; 14—liquid flowmeter; 16—effluent tank), (b) Arrangement of the membrane module, and, (c) Photographs of the membrane module.

with a stirrer. After stirring, the mixed liquor was pumped into the aerobic tank in which the operating volume was maintained through a level gage controlled by programmable logic controller (PLC, SIEMENS SIMATIC S7–200). Filtration was achieved by drawing water through membrane with filtration flux at 20 L/(m^2 h) under a slight vacuum generated by a peristaltic pump and measured by a glass U-tube manometer located just after the membrane. Air was supplied through an extended aerator located inside the membrane module and placed vertically as well. The filtration of the treated water was carried out uninterruptedly with continuous air injection in the system. Temperature was preserved around 24 ± 1℃. pH in MBR unit was maintained at 7 ± 1, by adding either HCl or NaOH into the feed tank.

Considering the operability of subsequent experimental analyses, as shown in Fig. 1(b) the membrane module was divided into three equal groups and each group consisted of three equal bundles of membrane fibers (0.023 m^2 average filtering surface area for each bundles). The physical pictures of membrane module utilized in the experiment are demonstrated in Fig. 1(c). Dead-end filtration mode was adopted. Those nine bundles were applied simultaneously at the beginning and kept in parallel under equal pumping pressure guaranteed by the same peristaltic pump.

2.2. Experimental conditions

The MBR unit was initially seeded by a sludge sample collected from certain sewage treatment plant using CASR process in Tianjin, China, of which mixed liquor suspended solids (MLSS), mixed liquor volatile suspended solids (MLVSS), sludge settling ratio, and sludge volume index (SVI) were 3,594 mg/L, 2,878 mg/L, 27%, and 75 mL/g, respectively, performing good settleability. The sludge was acclimated for 15 d with aeration and 1 L supernatant daily discharged. And synthetic municipal sewage was adopted to provide a source of carbon, nitrogen, phosphorus, and trace metal ions required for biomass growth. The synthetic wastewater was prepared freshly each day and fed continuously into the reactor. Composition of this synthetic wastewater is shown in Table 1. For preparing BPA stock solution, solid BPA (chemically pure, Tianjin Damao Chemical Reagent Factory, China) was dissolved to 500 mg/L with alcohol (analytically pure, Tianjin Jiangtian Chemical Technology Co., Ltd, China) and frozen at 4℃. The whole experiment was carried out with synthetic municipal sewage which BPA was spiked into in succession at a concentration of 5 mg/L.

The initial hydraulic residence time of anaerobic tank (HRT_A) was 3.7 h and that of aerobic tank (HRT_O) was 5.2 h. The value of MLSS was kept at 2,800–3,000 mg/L, aeration rate was 1.5 L/min, and reflux ratio was 300%. In view of the fact that activated sludge had high adsorption capacity for BPA

Table 1
Composition of the synthetic wastewater

Compound[a]	Concentration (mg/L)
Glucose	350
$NaHCO_3$	200
NH_4Cl	75
KH_2PO_4	30
NaH_2CO_3	10

[a] All the chemicals listed are analytical reagents (Tianjin Beifangtianyi Chemical Reagent Factory, China).

[20], except some necessary testing usages and the loss with anthropogenic liquid level regulation, sludge was not discharged from the reactor for examining BPA removal efficiency of MBR so as to prevent secondary pollution.

2.3. Experimental protocol

From the start of the running, samples were collected at the inlet, in the mixed liquor of sludge, and at the outlet of the MBR unit every 2 d. The analyses of concentrations of chemical oxygen demand (COD), ammonia-nitrogen (N-NH_3), and BPA were performed. Removal rate is calculated as $R = 100\% \times (1 - c_P/c_F)$, where c_P and c_F are permeate and feed concentrations (mg/L), respectively [21]. Moreover, with the purpose of directly analyzing BPA adsorption and interception performances of cake layer during its development, we conducted BPA filtration tests with membrane fiber bundles in different fouling stages. And staged membrane cleaning assessments were also designed for investigating stage characteristics of cake layer on BPA removal. As the experiment proceeded, every 5 d three bundles (in one group) of membrane fibers were taken out from the MBR unit for analysis by environmental scanning electron microscope (Philips XLSEM, the Netherlands), BPA filtration test, and membrane cleaning assessment, respectively. It is worth mentioning that with the fetch of one group of membrane fiber bundles for above analyses at the end of each stage, the liquid level of aerobic tank was adjusted down accordingly to maintain relatively constant permeate flux of remaining membrane module and correspondingly that of anaerobic tank was driven down via an overflow pipe connecting with the aerobic tank for fear that the experimental design might have an interference on the experimental results.

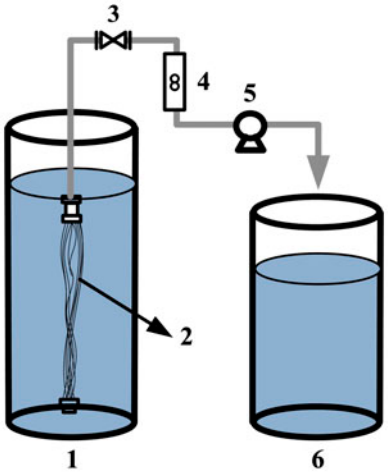

Fig. 2. Filtering unit (1—influent tank; 2—membrane fiber bundle; 3—regulating valve; 4—liquid flowmeter; 5—peristaltic pump; 6—effluent tank).

Device for BPA filtration test has been illustrated in Fig. 2. A bundle of membrane fibers taken out from the MBR unit was installed vertically in the influent tank. With BPA stock solution diluted by DI water to the concentration of 5 mg BPA/L being added in, the filtration was conducted in continuous type by the peristaltic pump, and the filtrate was collected in the effluent tank. Samples were taken from the original and concentrated BPA solutions in the influent tank and at the outlet of the filtering unit every half an hour for detecting the concentrations of BPA using a Waters 2,478 HPLC system equipped with a Symmetry C-18 reversed-phase chromatographic column (5 μm × 4.6 × 50 mm, Waters, the USA) and a UV detector (NC T6 UV–visible Spectrophotometer, China). Test wavelength for BPA was set at 276 nm. An isocratic flow of 1 mL/min of a water: MeOH eluent (5:95, v:v) was used at room temperature for elution. The injection volume was 20 μL. Analyses were carried out immediately after sampling.

Meanwhile, another bundle of membrane fibers in the same group with that used in filtration test was applied in membrane cleaning assessment. The analytical procedure was a modified protocol based on the research work of Jia [22]. The fouled membrane fiber bundle was rinsed by DI water. After standing and stratification for 1 h, the eluate was divided into supernatant part and sediment part. The supernatant part was centrifuged at 6,000 rpm at 24℃ for 10 min, from which new supernatant was obtained. The contents of BPA and its degradation products in the new supernatant were identified by the UV detector (here we call it "Procedure I" and the results are marked "I" in following bar charts). The sediment part was softly washed by DI water and separated by centrifugation (as described above), after which new supernatant and sediment parts were got. Then, Procedure I was repeated, after which we got the contents of BPA and its degradation products in the new supernatant part (II1). The new sediment part was soaked with a solvent mixture of MeOH:DCM (7:3, v:v, chromatographically pure, Tianjin Yingda Rare Chemical Reagents Factory, Tianjin, China) and then separated into supernatant and dehydrated sediment by centrifugation. The contents of BPA and its degradation products in the supernatant (II2) were detected by the UV detector. The sum of II1 and II2 is marked "II" in the following bar charts. Besides, the rinsed membrane fiber bundle was also soaked in the solvent mixture of MeOH and DCM, by which BPA

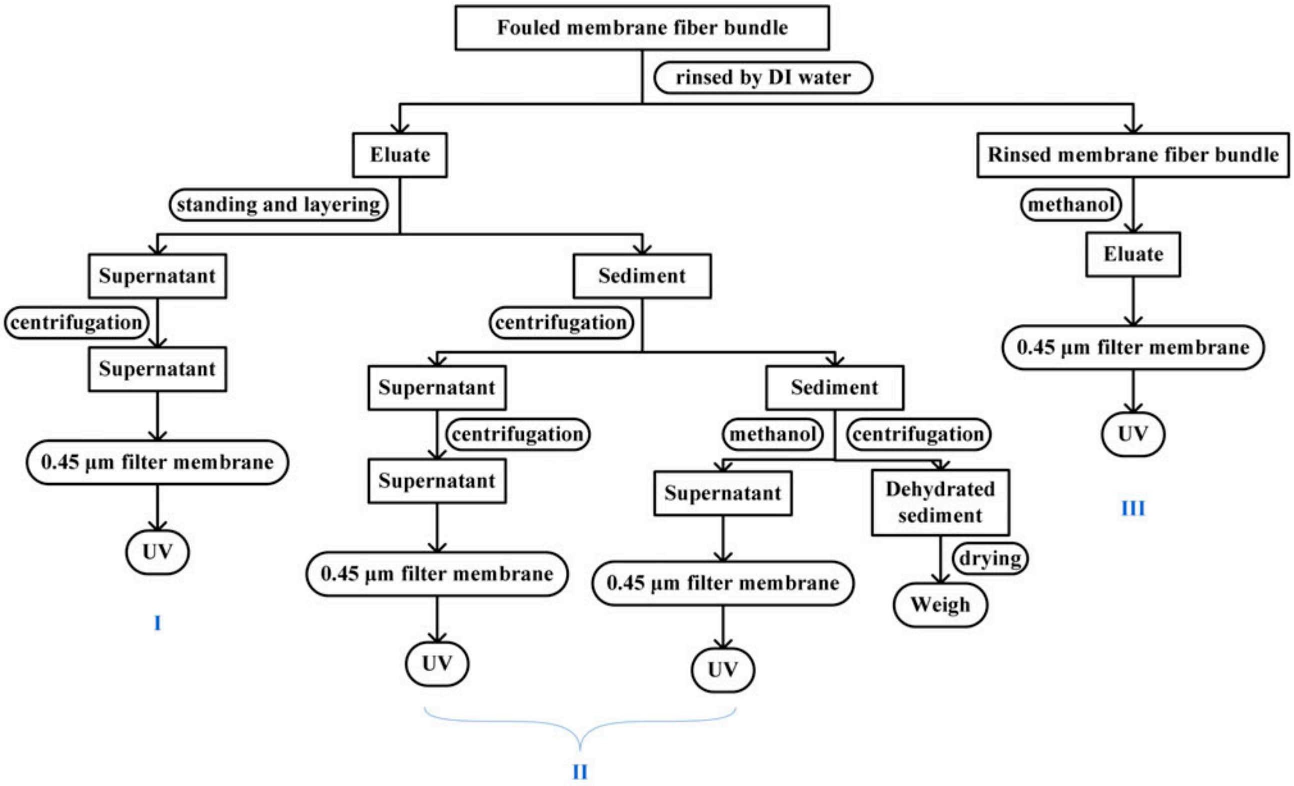

Fig. 3. Testing process of membrane cleaning.

and its degradation products tightly adsorbed on the surface and in the pores of membrane could be extracted into the solvent mixture. The contents of BPA and its degradation products in the eluate (the results are marked "III" in the following bar charts) were examined using the UV detector. The whole testing process of membrane cleaning is pictured in Fig. 3.

Scientific literature suggests that the main degradation products of BPA includes 4-hydroxyacetophenone (p-HAP), 4-hydroxybenzoic acid (p-HBA), and 4-hydroxybenzaldehyde (p-HBAL) which cannot be degraded any more in activated sludge [23–25]. Accordingly, we conducted full wavelength scanning of the methanol solutions of BPA and its three degradation products (analytically pure, Tianjin Institute of Guangfu Fine Chemicals, China) with the UV detector and found their absorption peaks appearing at the wavelengths of 276, 275, 247, and 243 nm, respectively. After that, HPLC system was employed to scan the peak times of BPA and its degradation products at their own characteristic absorption wavelengths. And then, standard solutions with various concentrations of BPA and its degradation products were prepared for mapping their respective standard curves applied in calculating their contents in membrane cleaning assessment through detections with the HPLC system at their characteristic absorption wavelengths.

The third group of membrane fiber bundle was taken out on the 15th running day for carrying out above tests. After that, total content of BPA adsorbed by the activated sludge in the MBR unit was detected (as described above). Since then, pumping was stopped, while devices for stir, aeration, and backflow were kept operating, simultaneously, nutrient substances were added artificially to ensure microbial activity. On the 18th day after stopping pumping, the total content of BPA adsorbed by the activated sludge in the MBR unit was detected again (as described above).

3. Results and discussion

3.1. MBR performance: treatment of synthetic influent containing BPA

The overall performance of the MBR unit has been monitored over a period of 33 d. Treatment performance was evaluated in terms of COD, NH_3-N, and

Table 2
Characteristics of the water in the MBR unit

Parameters	Influent concentration (mg/L)	Effluent concentration (mg/L)	Removal (%)
COD	500	15–28	95.7 ± 1.3
NH_3-N	41.4–159.5	4.5 ± 0.5	＞95
	Total content (mg)	Biodegradation content (mg)	
BPA (Period I[a])	2,828.54	270.40	9.56
BPA (Period II[b])	2,278.52	1,283.02	56.31

[a] Period I corresponds to the first 15 d of operation of the MBR unit.

[b] Period II corresponds to duration after the first 15 d of operation of the MBR unit.

BPA removal. The synthetic influent was characterized by a COD concentration around 500 mg/L. The initial nitrogen (NH_3-N) was between 41.4 and 159.5 mg/L. The initial BPA concentration was set at 5 mg/L. High quality of the treated water was observed with a COD removal around 95.7%. The MBR unit was found to be effective in removing NH_3-N (>95% of NH_3-N was removed) (see Table 2). The results were consistent with those reported in the literature [26–28]. The removal of BPA experienced two periods. The first period was characterized by a low BPA biodegradation, 9.56%, and covered 15 d when the MBR unit was in normal operation. The average residual BPA concentration in anaerobic and aerobic tanks was 62.43 mg/L. This period corresponded to the acclimation stage of micro-organisms for BPA degradation. Actually, when the micro-organisms were exposed to BPA (exogenous substrate) for the very first time, they needed some time to develop new metabolism pathways to oxidize BPA. Meanwhile, there was also selection and multiplication of specialized micro-organisms able to oxidize BPA [29]. The second period (duration after 15 d of MBR operation) was characterized by a BPA removal around 56.31%. The MBR sludge was supposed to be acclimated to BPA.

Fig. 4 indicates the concentrations of COD and NH_3-N in the effluent of the MBR unit during its 15 d operation. From it we can find that the COD concentration of the effluent declined rapidly in the first 4 d, which was followed by a plateau slightly higher than 15 mg/L, whereas the NH_3-N concentration in the effluent always stayed at low level, around 5 mg/L. The concentrations of BPA and its three main degradation products in the effluent of the MBR unit in Period I were detected, and the result was shown in Fig. 5. The BPA concentration of the effluent reduces gradually over time, as shown in Fig. 5, which behaves relatively high falling rate at initial 6 d and tiny fluctuation from the half of Period I (around 0.5 mg/L). However, the concentrations of the degradation products of BPA in the effluent were stabilized at certain levels and hardly conducted great fluctuations, which proved the low biodegradation rate of BPA in Period I mentioned above. In addition, the BPA concentration in supernatant of activated sludge mixture in aerobic tank was 4.57 mg/L, while

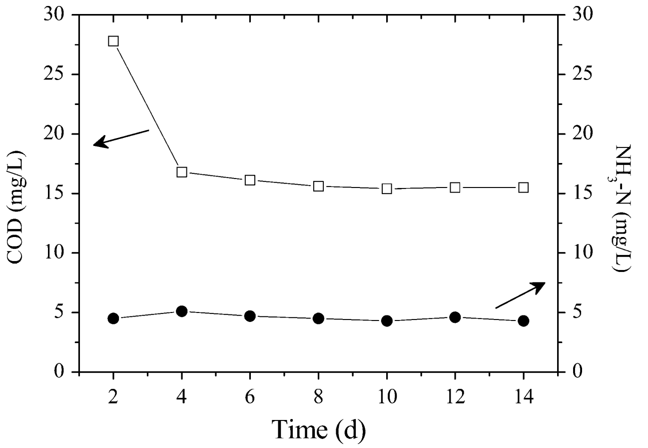

Fig. 4. Concentrations of COD and NH3-N in effluent of the MBR unit.

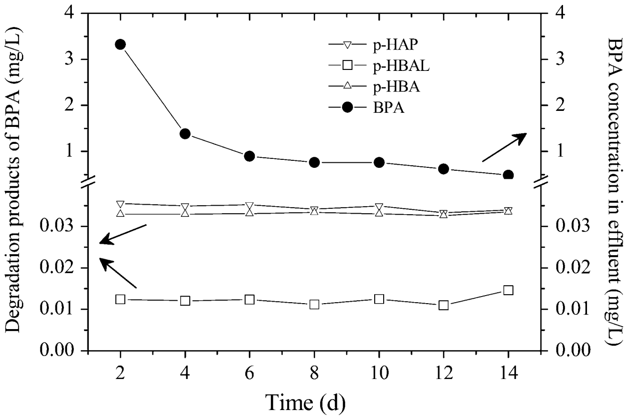

Fig. 5. Concentrations of BPA and its degradation products in effluent of the MBR unit.

through the membrane filter it was declined to 0.5 mg/L. Removal was improved by 81.4%, from which we can conclude that for removing BPA MBR precedes CASR. And this result supported the work of Chen et al. [19].

In each stage (every 5 d) of Period I (first 15 d) one membrane fiber bundle was taken out from the MBR unit for SEM analysis. The photos of membrane surfaces of new bundle and parallel bundles at the ends of Stage 1, Stage 2, and Stage 3 are exhibited successively in Fig. 6. SEM images reveal that with the development of the experiment over time more and more contaminants accumulated on the membrane surface and membrane pores were gradually covered by cell-like substances till invisible. And from those pictures the condition that cell-like substances increasingly form on the membrane surface may account for the gradual generation of biofilm. This developing biofilm could adsorb BPA penetrating the cake layer and membrane surface with the effluent, which explains the decline of BPA concentrations in the effluent (see Fig. 5) to some extent.

3.2. *BPA filtration performance of fouled membrane at different stages*

The designed BPA filtration test aimed to directly investigate the effects of fouled membrane at three different stages during the operation of the MBR unit in Period I on BPA interception. Initial concentration of BPA solution in influent tank for filtration test was detected at 3.19 mg/L, which was made by dilution of the BPA stock solution with DI water. As shown in Fig. 7, for filtering BPA solution with brand new membrane fiber bundle, BPA concentration of the effluent kept growing in the early 3 h. It was noteworthy that after two-hour running the BPA concentration of the effluent achieved 3.19 mg/L which equaled to that of the initial influent. Further, half an hour later the BPA concentration of the effluent reached 3.33 mg/L which exceeded that of the initial influent. And it was also found that after completing the filtration test of the brand new membrane fiber bundle BPA concentration of the concentrated liquid in the influent was 3.67 mg/L, which was higher than that

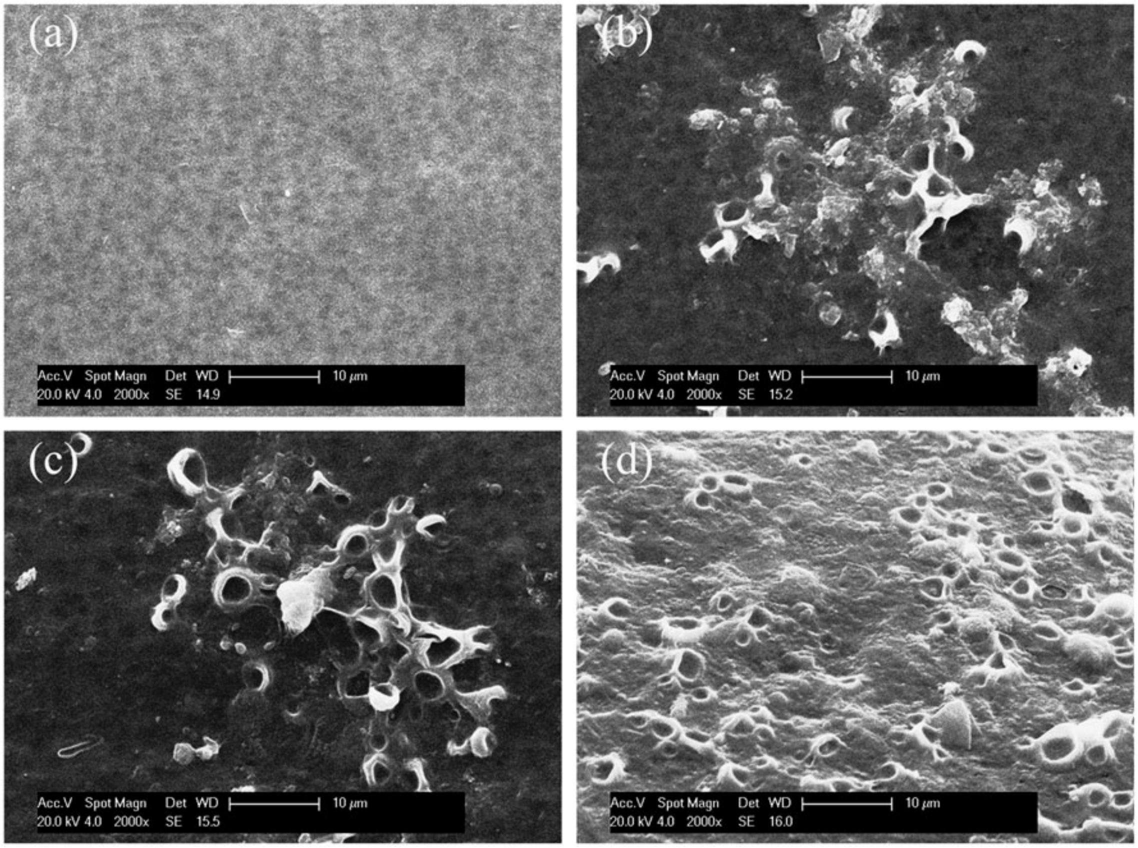

Fig. 6. Membrane surfaces of new and fouled bundles at the ends of different stages pictured in 2,000 times by SEM: (a) Membrane surface of new bundle, (b) Membrane surface of fouled bundle at the end of Stage 1, (c) Membrane surface of fouled bundle at the end of Stage 2, and, (d) Membrane surface of fouled bundle at the end of Stage 3.

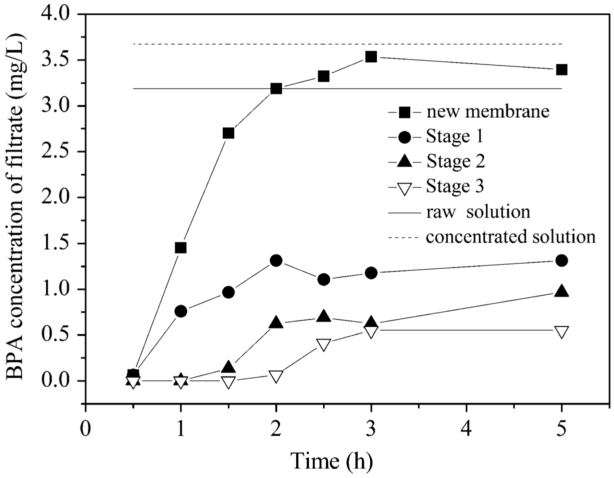

Fig. 7. BPA concentration of filtrate produced by new membrane and fouled membranes at different stages.

of the initial influent. Since the rated pore diameter (0.22 μm as mentioned above) of PVDF hollow fiber membrane utilized in the experiment is much larger than the size of BPA molecular (1.068 nm long as calculated by Nghiem et al. [18]), which intuitively illustrates that membrane pore cannot hold back BPA molecule, we suppose above phenomena can be attributed to consecutive adsorption of BPA on membrane surface and in interior of membrane pores during the filtration. In order to prove that, 100 mL of alcohol was used for steeping clean out of the tested new membrane fiber bundle. It was detected that the concentration of BPA in the eluent reached 0.69 mg/L. In other words, the applied PVDF hollow fiber membrane with an area of 0.0228 m^2 can absorb 0.069 mg of BPA after five-hour operation in the BPA solution of 3.19 mg/L. Thus, with the proceeding of filtration test, the BPA concentration in influent tank continuously rose. Correspondingly, the BPA concentration of filtrate increased. However, because of the absorption and interception function of membrane fibers, the peak of BPA concentration in filtrate still performed lower than the final BPA concentration in influent tank (3.67 mg/L), even though after two-hour filtration the BPA concentration of filtrate exceeded the initial BPA concentration in influent tank (3.19 mg/L) and continued to go up. For the filtration test of fouled membrane fiber bundle at Stage 1 (first 5 d), the BPA concentration of filtrate reached 0.07 mg/L after half an hour. As the extension of time to filtration, the BPA concentration detected rose to a fluctuation around 1.31 mg/L after 2 h. For the filtration test of fouled membrane fiber bundle at Stage 2 (second 5 d), there was not any BPA detected in the filtrate until one hour later. The BPA concentration of filtrate reached 0.62 mg/L after 2 h, which presented obvious increase compared to that after one hour. And after 5 h, the BPA concentration of filtrate achieved 0.97 mg/L, which is lower than that after 5 h at Stage 1. For the filtration test of fouled membrane fiber bundle at Stage 3 (third 5 d), there was still no BPA detected in the filtrate until 1.5 h later. The BPA concentration of filtrate reached 0.55 mg/L after 3 h. And after 5 h, the BPA concentration of filtrate still stabilized at the level of 0.55 mg/L and was inferior to that after 5 h at Stage 2.

From the perspective of the BPA concentrations of filtrate produced with fouled membrane fiber bundles at the three different stages, we can conclude that the longer running, the higher BPA interception rate. With the time extension of BPA filtration by fouled membranes, the BPA concentration of filtrate became an upward fluctuation till 3 h later when certain stabilized level was achieved, which demonstrated the BPA filtration by fouled membranes could be featured by saturation of adsorption after approximate 3 h. With the aggravation of membrane fouling (see Fig. 6), the adsorption and interception capacities of fouled membrane improved. Fig. 7 shows that after the saturation of BPA adsorption by cake layer membrane still has positive effect on BPA interception, which indicates that the existence of cake layer has made the fouled membrane possess interception capacity to some extent.

3.3. *Membrane cleaning assessment for fouled membrane at different stages*

The procedures of membrane cleaning have been described as above. Part I referred to the portion of target substances in the cake layer that can be desorbed to DI water and has vulnerable combination with the cake layer. Part II was the portion of target substances in the cake layer that can hardly be desorbed to DI water so that should be extracted through standing and layering, and even by methanol solution. It consisted of BPA and its degradation products combined tightly with the cake layer. Part III was the portion of target substances adsorbed in the interior of membrane pores and just could be partially extracted by methanol solution because of their difficult desorption. The result of membrane cleaning is illustrated in Fig. 8.

As shown in Fig. 8, with the running time extension of Period I (first 15 d), Contents of BPA and its degradation products in the eluate of fouled membrane bundle samples collected in Stage 1, Stage 2, and Stage 3 increasingly cumulated. The sum of Part I and II is the total content of the portion of target substances

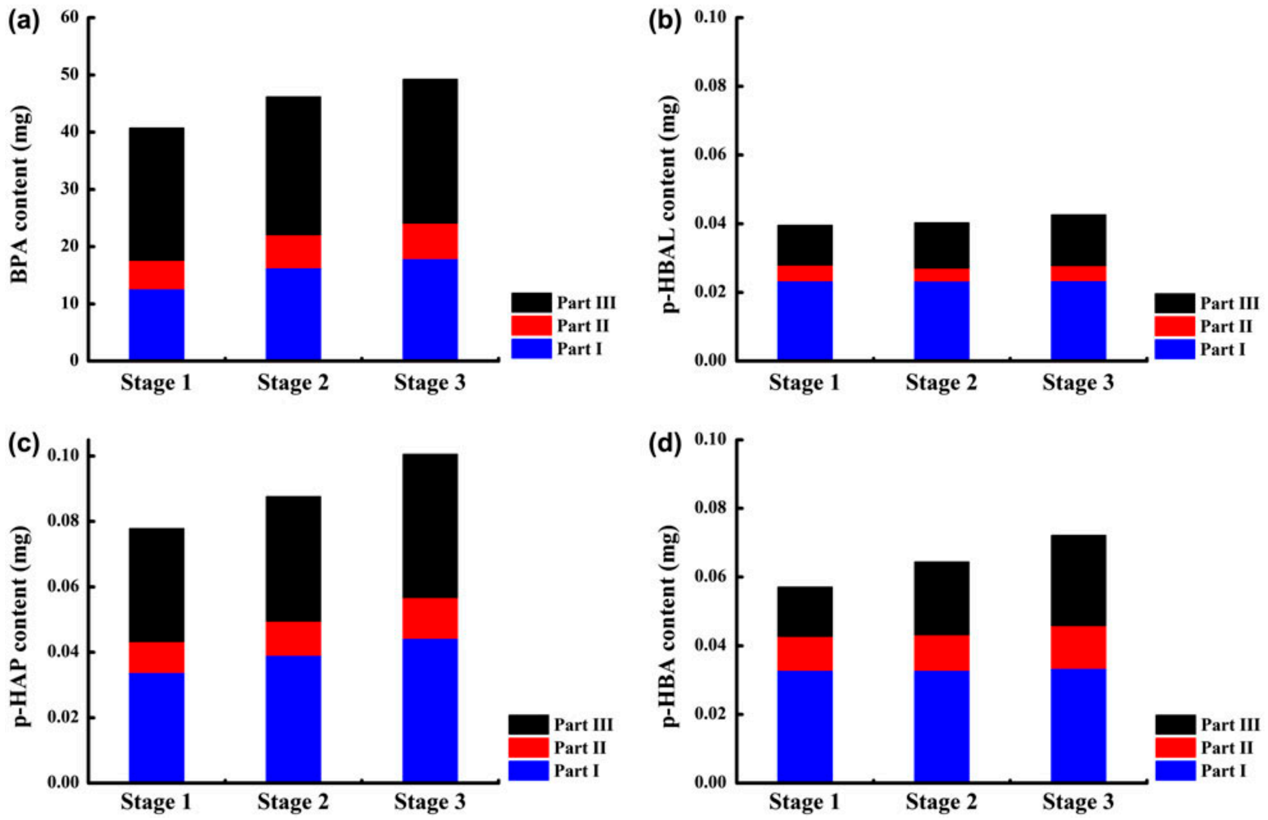

Fig. 8. Contents of BPA and its degradation products in the eluate of fouled membrane bundle at 3 stages in Period I: (a) For BPA; (b) For p-HBAL; (c) For p-HAP; (d) For p-HBA.

in the cake layer, while Part III is the total content of the portion of target substances adsorbed in the interior of membrane pores. In Fig. 8(a), the Part I, II, and III contents of BPA captured by membrane in Stage 1 are detected to be 12.62, 4.94, and 23.19 mg, respectively, from which we can conclude that BPA content in the cake layer of fouled membrane bundle is 17.56 mg (12.62 + 4.94 mg) and the content of BPA adsorbed by the contaminants that block the membrane pores is 23.19 mg. Accordingly, we can also infer that those two portions of BPA in Stage 2 and 3 are 22.01 and 24.19, and 24.04 and 25.24 mg, respectively. It can be deduced that the amount of BPA trapped in the cake layer of fouled membrane was always less than that of BPA adsorbed by the contaminants that blocked the membrane pores in Period I. With the aggravation of membrane fouling featured by the formation of cake layer (as shown in Fig. 6), the contents of BPA and its three biodegradation products trapped by its rose up (see Fig. 8(b)–(d)), which might be attributed to the existence of membrane strengthening the retention rate of (sludge) particles on which BPA is adsorbed as cake layer developed.

3.4. Removal pathways of BPA

In Period I the total amount of BPA inputted to the MBR unit was 2,828.54 mg. By the end of Period I, 279.62 mg BPA was lost with effluent, which occupied 9.89% of the total input. And the sum of BPA amount in anaerobic and aerobic tanks of the MBR unit was 2,278.52 mg which represented 80.55% of the total input, including 190.83 mg (6.75% of the total input) and 217.85 mg (7.70% of the total input) captured in the cake layer and membrane pores, respectively. Since that no-sludge-discharge mode was employed in the experiment, the amount of BPA biodegraded was 270.40 mg which occupied 9.56% of the total input and contained 0.93 mg and 0.56 mg related with the cake layer and membrane pores, respectively, that seemed so small. At the end of Period II the amount of residual BPA detected in the MBR unit was 995.50 mg which made up 35.19% of the total input. The amount of BPA biodegraded by the activated sludge in Period II was 1,283.02 mg. By adding the amount of BPA biodegraded in Period I, totally 1,553.42 mg BPA was degraded by the activated

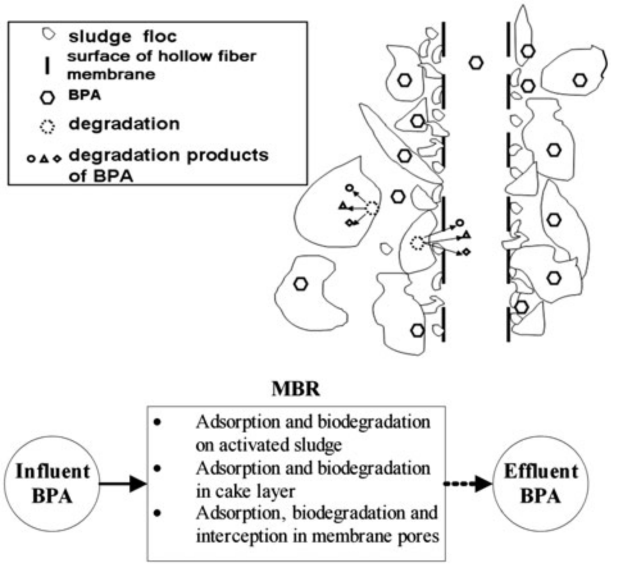

Fig. 9. Graphic representation of BPA removal pathways in the MBR unit.

sludge in the experiment, which made up 54.92% of the total input. Since there was no effluent in Period II (as the peristaltic pump stopped working), The amount of BPA lost with effluent in Period I was definitely regarded as the amount of BPA lost with effluent in the whole experiment.

Considering above data and analysis comprehensively, we can describe the removal pathways of BPA through Fig. 9. The majority of BPA entering the MBR unit was adsorbed on activated sludge, while some free BPA molecules were discharged along with the effluent due to their smaller sizes compared with those of membrane pores. Part of BPA adsorbed on the activated sludge was degraded by the micro-organisms, and the degradation products were also trapped on the activated sludge partially while some free ones left the MBR unit along with effluent as well. With the aggravation of membrane fouling, the cake layer generated gradually, along with which BPA and its degradation products in the sludge liquor could be adsorbed even degraded (extremely weakly), when they landed on the membrane surface and in membrane pores.

4. Conclusions

This study demonstrates the performances of a hollow fiber MBR for the removal of BPA. Totally, 90.11% of BPA was removed from the synthetic influent. The MBR unit was found to be effective in removing COD (up to 97%) and nitrogen (>95% of NH_3-N removed). BPA was adsorbed well onto MBR sludge, and did not accumulate in the sludge liquor because of the oxidization by micro-organisms. With the running time extension of the MBR unit, membrane fouling aggravated since cake layer developed. BPA was adsorbed and degraded by the generated biofilm on the cake layer and the contaminants blocking membrane pores, that is, the aggravation of membrane fouling promoted BPA removal, especially, strengthened BPA adsorption, which can be clarified by the analysis of BPA filtration performance. Membrane cleaning assessment illustrates that the cake layer reinforced the effect of membrane filtration on the removal of BPA. The effect of biodegradation was enhanced over the running time of the MBR unit. Most of BPA was captured by the activated sludge, which might raise people's awareness about the post-processing problem of utilized sludge.

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References

[1] European Commission, European workshop on the impact of endocrine disrupters on human health and wildlife, Report of the Proceedings, Weybridge, UK, EUR 17549, Brussels, 1997.
[2] A.D. Vethaak, J. Lahr, S.M. Schrap, A.C. Belfroid, G.B.J. Rijs, A. Gerritsen, J. de Boer, A.S. Bulder, G.C.M. Grinwis, R.V. Kuiper, J. Legler, T.A.J. Murk, W. Peijnenburg, H.J.M. Verhaar, P. de Voogt, An integrated assessment of estrogenic contamination and biological effects in the aquatic environment of The Netherlands, Chemosphere 59 (2005) 511–524.
[3] C.A. Staples, P.B. Dome, G.M. Klecka, S.T. Oblock, L.R. Harris, A review of the environmental fate, effects and exposures of bisphenol A, Chemosphere 36 (1998) 2149–2173.
[4] J. Roland, W. Meesters, H.F. Schroder, Simultaneous determination of 4-nonylphenol and bisphenol A in sewage sludge, Anal. Chem. 74 (2002) 3566–3574.
[5] R.J. Slack, J.R. Gronow, N. Voulvoulis, Household hazardous waste in municipal landfills: Contaminants in leachate, Sci. Total Environ. 337(1–3) (2005) 119–137.
[6] R.J.W. Meesters, H.F. Schröder, Simultaneous determination of 4-nonylphenol and bisphenol A in sewage sludge, Anal. Chem. 74 (2002) 3566–3574.
[7] H.B. Lee, T.E. Peart, Bisphenol A contamination in Canadian municipal and industrial wastewater and sludge samples, Water Qual. Res. J. Can. 35 (2000) 283–298.
[8] G. Shen, G. Yu, Z.X. Cai, Z.L. Zhang, Development of an analytical method to determine phenolic endocrine

disrupting chemicals in sewage and sludge by GC/MS, Chin. Sci. Bull. 50 (2005) 2681–2687.

[9] W. Körner, U. Bolz, W. Süßmuth, G. Hiller, W. Schuller, V. Hanf, H. Hagenmaier, Input/output balance of estrogenic active compounds in a major municipal sewage plant in Germany, Chemosphere 40 (2000) 1131–1142.

[10] G. Bertanza, R. Pedrazzani, M.D. Dal Grande, M. Papa, V. Zambarda, C. Montani, N. Steimberg, G. Mazzoleni, D.D. Di Lorenzo, Effect of biological and chemical oxidation on the removal of estrogenic compounds (NP and BPA) from wastewater: An integrated assessment procedure, Water Res. 45 (2011) 2473–2484.

[11] W. Guo, S. Vigneswaran, H.-H. Ngo, W. Xing, P. Goteti, Comparison of the performance of submerged membrane bioreactor (SMBR) and submerged membrane adsorption bioreactor (SMABR), Bioresour. Technol. 99 (2008) 1012–1017.

[12] S. Judd, The status of membrane bioreactor technology, Trends Biotechnol. 26 (2008) 109–116.

[13] F.I. Hai, K. Yamamoto, in: W. Peter, 4.16-Membrane Biological Reactors, Treatise on Water Science, Elsevier Science, Oxford 2011, pp. 571–613.

[14] P. Le-Clech, V. Chen, T.A.G. Fane, Fouling in membrane bioreactors used in wastewater treatment, J. Membr. Sci. 284 (2006) 17–53.

[15] T. Melin, B. Jefferson, D. Bixio, C. Thoeye, W. De Wilde, J. De Koning, J. van der Graaf, T. Wintgens, Membrane bioreactor technology for wastewater treatment and reuse, Desalination 187 (2006) 271–282.

[16] K.P. Kim, Z. Ahmed, K.H. Ahn, K.J. Paeng, Biodegradation of two model estrogenic compounds in a preanoxic/anaerobic nutrient removing membrane bioreactor, Desalination 243 (2009) 265–272.

[17] S.F. Yang, F.I. Hai, L.D. Nghiem, L.N. Nguyen, F. Roddick, W.E. Price, Removal of bisphenol A and diclofenac by a novel fungal membrane bioreactor operated under non-sterile conditions, Int. Biodeterior. Biodegrad. 85 (2013) 483–490.

[18] L.D. Nghiem, N. Tadkaew, M. Sivakumar, Removal of trace organic contaminants by submerged membrane bioreactors, Desalination 236 (2009) 127–134.

[19] J.H. Chen, X. Huang, S.Y. Li, X.H. Wen, D.L. Qiao, Comparison of bisphenol A (BPA) and nonylphenol ethoxylate (NPnEO) removal with a membrane bioreactor versus a conventional activated sludge reactor, Acta Scientiae Circumstantiae 28 (2008) 433–439 (in Chinese).

[20] Y.Q. He, J. Wang, B. Sun, N. Luo, The adsorption characteristics of bisphenol A onto activated sludge, 2010 4th Int. Conf. Bioinform. Biomed. Eng. (ICBBE), Chengdu, China, 2010.

[21] J.H. Chen, X. Huang, D.J. Lee, Bisphenol A removal by a membrane bioreactor, Process Biochem. 43 (2008) 451–456.

[22] L.Z. Jia, Study of Bacteria-degradation of Bpa and Degrading Mechanism, Master's Thesis of Academy of Military Medical Sciences, 2004 (in Chinese).

[23] M. Petrović, D. Barceló, Determination of anionic and nonionic surfactants, their degradation products, and endocrine-disrupting compounds in sewage sludge by liquid chromatography/mass spectrometry, Anal. Chem. 72 (2000) 4560–4567.

[24] L.Z. Jia, J.W. Li, Pseudonomas sp. W2 metabolic pathway of bisphenol A, Microbiology 33 (2006) 78–83 (in Chinese).

[25] J.H. Kang, F. Kondo, Bisphenol A degradation by bacteria isolated from river water, Arch. Environ. Contam. Toxicol. 43 (2002) 265–269.

[26] L. Vera, R. Villarroel-López, S. Delgado, S. Elmaleh, Cross-flow microfiltration of biologically treated wastewater, Desalination 114 (1997) 65–75.

[27] P. Battistoni, F. Fatone, D. Bolzonella, P. Pavan, Full scale application of coupled alternate cycles-membrane bioreactor (AC-BRM) process for wastewater reclamation and reuse, Water. Pract. Technol. 1 (2006), doi: 10.2166/wpt.2006.077.

[28] J. Lee, B.C. Lee, J.S. Ra, J. Cho, I.S. Kim, N.I. Chang, H.K. Kim, S.D. Kim, Comparison of the removal efficiency of endocrine disrupting compounds in pilot scale sewage treatment processes, Chemosphere 71 (2008) 1582–1592.

[29] B. Marrot, A. Barrios-Martinez, P. Moulin, N. Roche, Biodegradation of high phenol concentration by activated sludge in an immersed membrane bioreactor, Biochem. Eng. J. 30 (2006) 174–183.