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# Particle size distribution characterization of swine wastewater using membrane treatment process for resource recovery

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## ABSTRACT

Treatment of swine wastewater using membrane bioreactor (MBR) was attempted in this study, and detailed measurement of different parameters, including chemical oxygen demand (COD), total phosphorus (TP), total nitrogen (TN), ammonia nitrogen ($NH_4^+$–N) and protein, was also conducted. It has been reported that the membrane fouling phenomenon is related to the characteristics of pollutants in wastewater based on particle size distribution (PSD), therefore, clarifying the particle size range of pollutant components can help to design more efficient and targeted water treatment processes. In this article, the PSD in the swine wastewater is the primary focus, in order to select suitable membrane units for designing an advanced treatment and attaining various resource recovery. This study results revealed that the MBR influent contained majority fractions of COD, TP, and protein in both the super colloidal (accounting for 44.3%, 45.4% and 44.9%, respectively) and dissolved (accounting for 30.5%, 36.1% and 37.7%, respectively) state. Whereas, the majority of $NH_4^+$–N (72.9%) and TN (69.8%) were classified as the dissolved portion in the MBR influent. The COD and TP could be removed partly using a sedimentation unit in the particle state (>100 μm), super colloidal state (100–0.8 μm), and dissolved state (<0.22 μm). MBR process, which was followed by a set of composite membranes comprised of the antifouling membrane and the desalination membrane, displayed an effective removal of TN and TP in all size ranges, especially those attributed to colloid and super colloid for all above 90% elimination abilities. The composite membranes played a vital part in the complete removal of particulate and dissolved matters. Therefore, a compensation treatment of particle and the dissolved matter was essential to wastewater disposal and to maintain a healthy water cycle. In this study, a three-dimension excitation emission matrix fluorescence spectroscopy was performed to assess dissolved humic-like substances in the filtered wastewater.

*Keywords:* Particle; Wastewater characterization; Swine wastewater; Membrane separation; Chemical oxygen demand

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## 1. Introduction

Swine wastewater is mainly comprised of livestock urine, feces, and rinsing water, with a characteristic of high concentration of organic wastewater because of its abundant content of nitrogen (N), phosphorus (P), organic matter, and suspended solids. Inappropriate and untreated discharge of swine wastewater will cause serious threats to environmental health like polluting the surface and groundwater [1], causing eutrophication [2], killing aquatic animals, even resulting in the emergence of human disease [3]. As reported by the First National Pollution Source Census in China [4], livestock breeding is a vital source for environmental pollution: chemical oxygen demand (COD), total nitrogen (TN), and total phosphorus (TP) emissions accounting for 95.78%, 37.89% and 56.34% of the total emissions of agricultural pollutants, and accounting for 41.87%, 21.67% and 37.90% of the total emissions of major pollutants in China, respectively. The concentrated animal feed production units developing from small-scale to large-scale operations [5] are highly associated with causing a severe agricultural non-point source pollution, where an excess amount of highly concentrated wastewater is discharged to land or streams with far excess limit than what receiving water bodies and environment can withstand. Such events cause the accumulation of concentrated pollutants in the environment. Therefore, it is necessary to treat the swine wastewater preferably by strengthening the quality of treated water and resource recycling and to achieve environment-friendly and energy-saving operations.

Recent studies reported that swine wastewater is a rich source of nutrients and the ammonia and phosphate in swine wastewater can be recovered and used in various applications, such a process offers an eco-friendly waste recycling option [6,7]. A detailed characterization of swine wastewater is necessary and useful to design the treatment and simultaneous resource recovery process. The commonly used conventional treatment technologies to treat livestock waste are solid-liquid separation, anaerobic digestion [8,9], and aerobic treatment [7]. Besides, ecological treatments like wetland [10] were also performed to enhance the pollutants removal rate. However, a few conventional processes have a series of obstacles and limitations, such as the unsatisfactory removal of N and P from treated water [11,12], requirement of high operational cost, complexity in processing [13], and low removal efficiency of TN due to the lack of available carbon source for denitrification in the traditional nitrification-denitrification process [14]. To counter these drawbacks, there is a need to explore an alternative treatment process for better disposal solutions with a new perspective for efficient wastewater treatment. Such a process needs to be designed and evaluated to develop a novel generation of a treatment system that meets the standards of effluent discharge [15,16].

Nowadays, membrane bioreactor (MBR) treatment is increasingly popular and drawing the attention of wastewater treatment plant operators for its efficient pollutant removal and discharging high-quality treated water into the environment [17]. Besides, the contaminant's removal efficiency, energy-saving and nutrient recovery provide added advantages in implementing the MBR process for wastewater purification.

The filter pore size of 0.45 μm is commonly used to differentiate between particulate and soluble components [18]. However, the detailed classification method employed in partitioning pollutant fractions has attracted wide attention. The particle size distribution (PSD) based characterization of components has significant importance in better understanding biodegradability [15,16] and solving membrane fouling problems [19,20]. Several researchers studied the PSD in both industrial (e.g., textile wastewater, petrochemical wastewater, and tannery wastewater) and municipal wastewater originated from rural and urban areas [16,18,21–23]. To date, the swine wastewater has not been extensively studied for PSD, which contains a significant number of large particles (i.e., suspended solids) that could easily hamper the reactor operations. This leads to difficulty in reactor designing, high operational costs, and subsequent environmental issues due to the discharge of poor water quality. Therefore, an investigation of PSD in swine wastewater is necessary for successful process operation and to evade associated environmental problems.

This research aims to better understand the nature of swine wastewater, advance efficiency in agricultural wastewater treatment and agricultural resource utilization, and enhance the environmental and agricultural sustainable development from the perspective of engineering. In this study, PSD-based characterization of COD, TP, TN, ammonia nitrogen ($NH_4^+$–N), and protein presents in the swine wastewater was investigated. Size distributions of COD/protein, COD/TN, and TN/TP in MBR influent, and variation of $NH_4^+$–N/TN with the narrowing aperture fractions were evaluated. Also, the variety of PSD features when the wastewater flowing through the membrane units was discussed. And, a three-dimension excitation emission matrix fluorescence spectroscopy (3D-EEM) test was performed to better monitor the quality of filtered swine wastewater.

## 2. Materials and methods

### 2.1. Sampling

Swine wastewater samples were taken from a swine farm at Jiading District, Shanghai, China. Sampling points and the treatment systems of the animal farm were shown in Fig. 1. Samples were collected from ① MBR influent, ② MBR influent after settling, ③ MBR effluent, ④ the final effluent, and ⑤ the concentrated liquid. The raw wastewater was initially treated using MBR and followed by a set of composite membranes comprised of the antifouling membrane and the desalination membrane. The MBR treatment tank was designed as an A/O treatment system: in the front section, the influent water was fully mixed with the return water in the back section for biological denitrification and denitrification, and in the back section for biological degradation and nitrification. Effluent discharged from the composite membrane was divided into a final (to be discharged safely in receiving water bodies) and concentrated liquid (to be used for agricultural purposes). The samples were collected from the 5 collection points. At each sampling site, three replicates were collected. Each replicate was a 4 L water sample.

Sampling equipment and sampling bottles were cleaned and dried beforehand by following standard procedures for accurate sample collection. Thus, collected samples were transported without any collision or vigorous shaking activity. The samples that arrived in the laboratory were decanted immediately and chemical characteristics were performed within 3 d. The samples (both unfractionated and fractionated) were stored at 4°C to prevent biodegradation.

The composition of swine wastewater was reported to vary from one site to another, which mainly depends on site-specific operational conditions and manure collection methods [13]. However, the swine wastewater characteristics of this study were within the range of samples collected from previous studies [24–26], which are shown in Table 1.

### 2.2. Separation

The fractionated substances in wastewater had been grouped into four main categories based on their particle size, which included (i) settleability, (ii) super colloidal, (iii) colloidal, and (iv) soluble matters. With reference to the classification of particle size [27,28] in wastewater were classified as (i) particle state >100 μm; (ii) super colloidal ranged from 0.8 to 100 μm; (iii) colloid substance ranged between 0.22 and 0.8 μm; and (iv) soluble matters <0.22 μm.

To obtain different particles, a series of filtration steps were performed using membranes with different pore sizes, 100, 10, 0.8, 0.45, and 0.22 μm, respectively, as represented in Fig. 2 [21]. The classical membrane filter method [23,28] was referred for the classification of particle size. Furthermore, Buchner funnels were used for filtration of membrane disc sizes of 100 and 10 μm aperture, and suction filters were used for other filters (0.8, 0.45, and 0.22 μm). Thus, obtained filtrates were chemically characterized.

Table 1
Compositions of the swine wastewater obtained from previous studies compared with the swine farm samples used in this study

| Parameter (mg L$^{-1}$) | Previous studies | This study (MBR influent) |
|---|---|---|
| COD | 5,000~25,000 | 5,098~6,240 |
| TN | 600~3,000 | 959~1,431 |
| $NH_4^+$–N | 400~2,500 | 892~1,340 |
| TP | 20~300 | 123~135 |

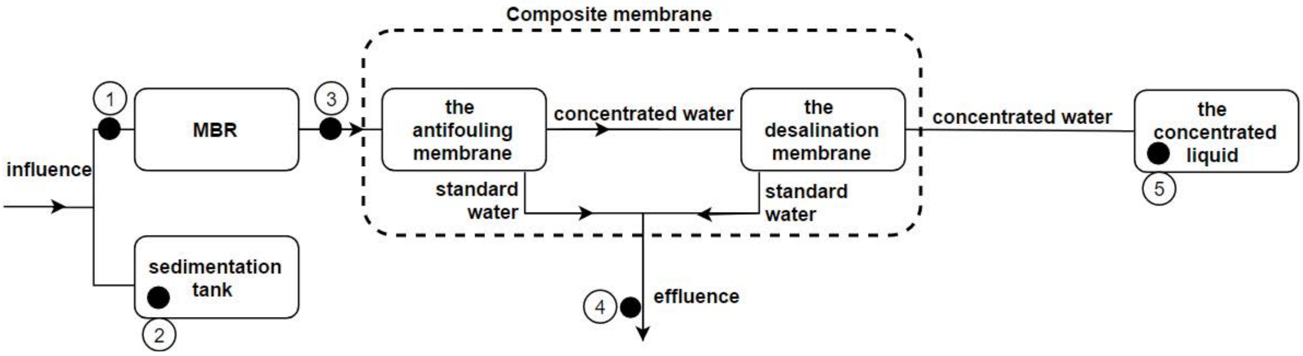


Fig. 1. The craft of the livestock wastewater treatment applicated in a swine farm at Jiading District, Shanghai, China. The full line denotes the wastewater flows while solid points represent the sampling points.

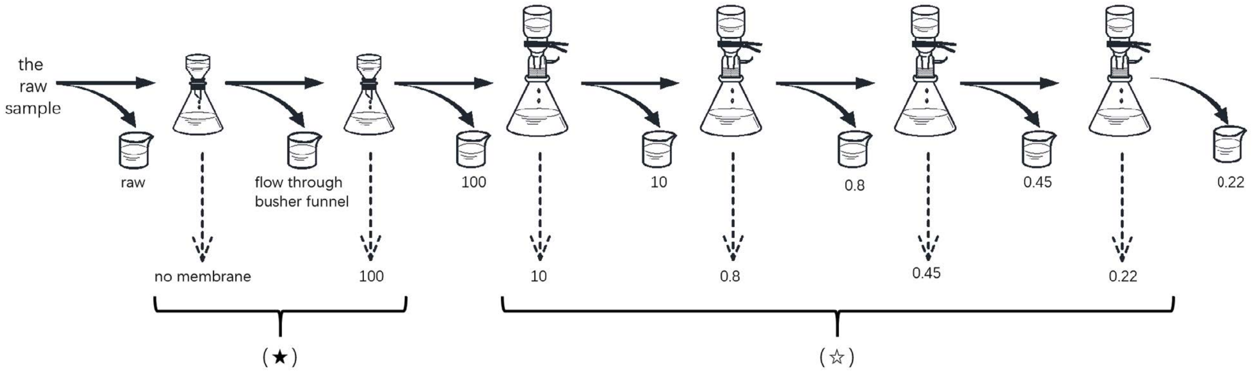


Fig. 2. Operation of series filtrations. The raw sample representing the raw wastewater from five different sampling points. Numbers under the beakers representing the theoretical maximum particle size of inclusions in obtained solutions. Numbers under dotted arrows representing the pore sizes of membranes in devices used for filtration. Solid arrows representing the flow direction and filtration order of samples, the sample filtered from the previous step was divided into two parts, a part subject to chemical measurements, and the rest subject to subsequently finer filtration. (★) representing filtration with Buchner funnel; (☆) representing filtration with suction filter.

All the membranes used in this study were suitable for aqueous solution, which were made of nylon (pore sizes of 100 and 10 μm) and mixed cellulose ester for pore sizes between 0.8 and 0.22 μm. The membrane and its units were rinsed thrice in running tap water and then rinsed thrice in 70% ethanol. The final cleaning was performed in distilled water and then the oven-dried unit was cooled down before use.

After the particle size classification, contaminants distribution infiltrate from four different filter sizes was calculated as mentioned in Table 2.

### *2.3. Chemical analysis*

Chemical characterization and quantification were conducted in triplicates for filtrates collected in each filtration step [29]. The average value obtained with standard deviation [30] was reported as an experimental result and all the analyses were performed as per the Standard Methods [11,28]. Wherever the high concentration of organic compounds and suspension solids presents in the swine wastewater were suitably homogenized by diluting in water before chemical quantification.

#### *2.3.1. COD and protein measurement*

COD was measured based on the Dichromate method (GB11914-89).

Protein measurement was conducted using a modified Lowry method [27,31]. A 5 mL Lowry reagent was mixed well with the 1 mL sample and the solution was incubated at room temperature for 10 min. Then, 0.5 mL Folin-phenol reagent was added and mixed immediately. Until a blue color developed another 30 min, the incubation was done, then samples were analyzed in a spectrophotometer at 750 nm wavelength. The blank was prepared using a similar method except saline was used instead of the sample. The standard curve was obtained using bovine serum albumin as a sample.

#### *2.3.2. TN and $NH_4^+$–N*

TN measurement in all wastewater fractions was conducted using alkaline potassium persulfate digestion-UV spectrophotometric method (GB11894-89). A series of known concentrations of potassium nitrate was used to plot a TN standard curve. The accuracy of TN data measurement required high purity potassium persulfate (Merck, GR). In the preparation of alkaline potassium persulfate solution, the aqueous solution was heated in a water bath (<50°C) and stirred well to prevent decomposition of the reagent.

Table 2
Calculation of contaminants distribution based on particle size

| Partition | Interval content |
|---|---|
| Particle | $V_{total}$–$V_{100}$ |
| Super colloidal | $V_{100}$–$V_{0.8}$ |
| Colloid | $V_{0.8}$–$V_{0.22}$ |
| Soluble | $V_{0.22}$ |

$V_{total}$–$V_{100}$: Particle size > 100 μm; $V_{100}$–$V_{0.8}$: 100 μm > Particle size > 0.8 μm; $V_{0.8}$–$V_{0.22}$: 0.8 μm > Particle size > 0.22 μm; $V_{0.22}$: 0.22 μm > Particle size.

Ammonia nitrogen ($NH_4^+$–N) measurement was performed based on the Nessler's Reagent (Shanghai Macklin Biochemical Co., Ltd., China) spectrophotometry assay. A series of known concentrations of ammonium chloride was used to plot the standard curve of $NH_4^+$–N.

#### *2.3.3. Total phosphorus*

TP measurement was conducted using the ammonium molybdate spectrophotometric method (GB11893-89) as described by Sophonsiri and Morgenroth [27]. To investigate the interference of large particles for the spectrophotometer, contrast experiments were conducted before the measurement to show the stability of TP values among several batches.

#### *2.3.4. Three-dimension excitation emission matrix fluorescence spectroscopy*

A 3D-EEM spectrum of humic-like substances in swine wastewater was measured using a luminescence spectrometer (Hitachi F-4600) [32,33]. Before the analysis, samples were firstly filtered through 0.22 μm filters. The EEM spectra were obtained in scanning emission spectra from 300 to 500 nm at 4 nm increments, and by varying the excitation wavelength from 200 to 450 nm at 4 nm increments. During the measurements, both the excitation and emission slits were set at 5 nm at the scanning speed of 12,000 nm/min. The spectrum of distilled water was used as the blank. Data of EEMs were processed using software origin 9.0 and represented by contour lines. The X and Y-axis represented the emission spectra from 300–550 nm and excitation wavelength from 200 to 450 nm, respectively.

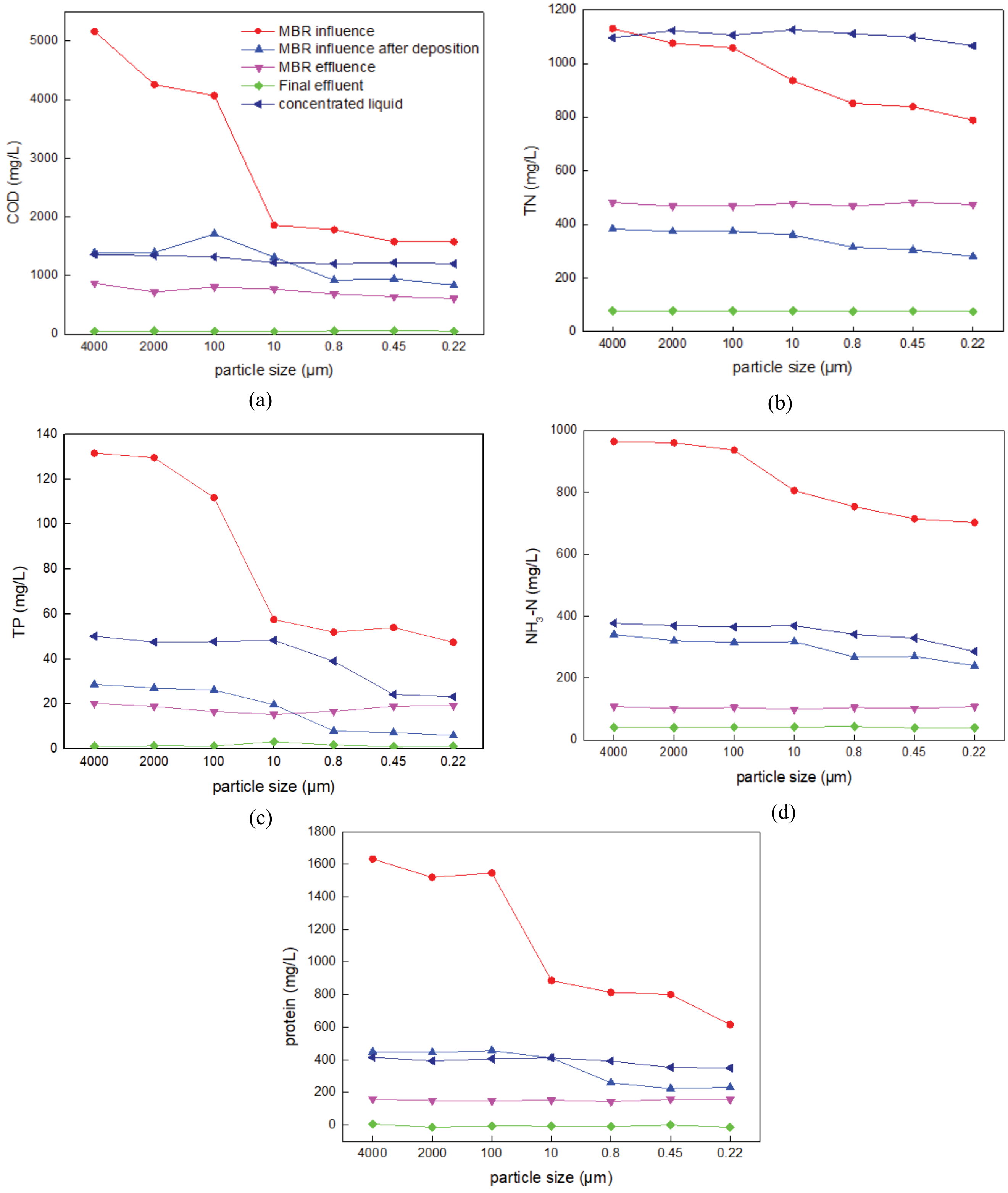
## 3. Results and discussion

### *3.1. PSD of COD, TN, TP, $NH_4^+$–N, protein in swine wastewater*

#### *3.1.1. PSD of COD in swine wastewater*

The COD characteristics in the swine wastewater were significantly different among different size fractions in Fig. 3a. The MBR influent displayed a decrease in COD concentration from 4,066.2 to 1,780.9 mg of COD $L^{-1}$ in the filtrates obtained from 100 to 0.8 μm. This result suggested that the super colloidal COD accounted for 44.3% in MBR influent. Whereas the dissolved state COD (collected using 0.22 μm filter) accounting for 30.5% in MBR influent COD (1,576 mg $L^{-1}$) was also nonnegligible. The comparison of COD value in MBR influent and settled wastewater revealed that the sedimentation unit effectively removed the COD of each particle size to a certain extent, especially >100 μm.

Within the operation of precipitation, the proportion of COD measured as the super colloidal and dissolved state also increased significantly compared with the precipitable state and their sum accounted for more than 90% of the overall COD, becoming the two dominant components of MBR-influent-after-settling.



(a) (b) (c) (d) (e)

Fig. 3. PSD of different chemical compositions for swine wastewater. Unfiltered samples and filtered by Buchner funnel (without any membrane) are drawn as 4,000 and 2,000 μm, respectively. Other samples filtered by various membranes are plotted as corresponding aperture sizes.

This study found that low COD value in colloidal particle size fractions (0.8~0.22 μm) was obtained from the swine wastewater. The reason for the presence of lower COD value could be due to coagulation and flocculation of colloids, or degradation during the filtration process due to shear stress and enzymatic degradation [16]. Also, the presence of high COD in the soluble range (<0.22 μm) might be speculated as caused by the degradation of COD and in the shift of COD distribution caused by the hydraulic retention [16]. More and more studies optimized the removal of organic pollutants from the perspective of their particle size. Several studies reported that pre-treatment of wastewater by solid–liquid separation was an efficient and economical process for the removal of COD presents in large particles, and physical entrapment and adsorption were efficient for the removal of refractory compounds [34] and substance distributed in the colloidal form [18].

The PSD of COD is closely related to the biodegradability and energy footprint [35] of the wastewater treatment system. The smaller size particles usually can be easily consumed by biomass, while the larger particles require hydrolysis before biomass utilization [36]. The carbon and energy footprint of the wastewater treatment system was found to be altered by the soluble COD/COD ratio and particulate COD/COD ratio [35]. The biodegradation kinetics was also found to affect pollutant treatment efficiency [37], oxygen transfer, and subsequent increase the operational cost. Therefore, relationships between COD size distribution, biodegradability, and energy footprint require further investigation, in future studies.

### 3.1.2. PSD of TN in swine wastewater

The TN measurements from samples are presented in Fig. 3b. The soluble matters (particles < 0.22 μm) contained the majority of TN, where 97%, 96% and 96% of the TN were observed in the form of soluble in MBR-effluent-tank, final effluent, and concentrate pool, respectively. The distribution of TN in MBR-influent-tank, which was best distributed over all size fractions, had a slight bend at 100 μm. The particle size (>100 μm), super colloidal (100–0.8 μm), and colloidal (0.8–0.22 μm) accounted for only 6.4%, 18.3% and 5.5%, respectively, and remained 69.8% TN in dissolved state (<0.22 μm). This study results demonstrated that in the swine wastewater, the majority of compounds containing nitrogen elements were soluble. Thus, the TN use, applications, and removal must be focused on the dissolved state.

### 3.1.3. PSD of TP in swine wastewater

The distribution of phosphorus is plotted in Fig. 3c. The highest TP fractions in the MBR influent were in the super colloidal state (45.4%) and then in the dissolved state (36.1%). Interestingly, 63.9% of TP was found removed by suction filtration unit with an aperture of 0.22 μm. However, all the phosphorus detected in the MBR effluent and final effluent could be attributed to soluble form (<0.22 μm). Little suspended matters were found in the concentrated liquid, of which the dominant particles were in the dissolved (46.3%) and colloidal (31.5%) states. Results presented in Fig. 3c indicated that the sedimentation process achieved an excellent TP removal from swine wastewater, as a result, the TP value reduced significantly from 131.5 to 28.7 mg $L^{-1}$. This study indicated that in addition to conventional biological treatment, a simply equipped sedimentation process in the swine wastewater could also act as an effective tool in TP removal for the MBR influent.

### 3.1.4. PSD of $NH_4^+$–N in swine wastewater

The PSD-based $NH_4^+$–N fractionation obtained from different processes is shown in Fig. 3d. This study results suggested that the variation in $NH_4^+$–N concentration with different size fractions exhibited a similar trend with TN (Fig. 3b). PSDs of $NH_4^+$–N in both MBR-effluent-tank and the final effluent run in parallel and showed a minuscule reduction, both containing more than 90% soluble fraction (<0.22 μm). Plots of MBR influent after settling and the concentrated liquid may not look as declining as that of the MBR influent. But comparing the percentage of the soluble (<0.22 μm) and the filtered matters, including the particle, super colloidal and colloidal, it could be seen that the above 3 processes had similar soluble fractions (72.9% for MBR influent, 70.3% for MBR influent after settling, 75.8% for concentrated liquid). In Fig. 3d it can also be seen that a larger proportion of the $NH_4^+$–N is in the soluble form compared to that proportion of COD, TP, and protein. Hence, the removal of $NH_4^+$–N should also be achieved in the concentrated liquid in a dissolved state. Similar operation of lowering $NH_4^+$–N by solid-liquid separation would not act as effectively as filtration used to remove TP although there was a difference value, which could be speculated as adsorption function and microbial utilization, plotted in the amount of $NH_4^+$–N in MBR influent before and after precipitation (Fig. 3d). Based on the soluble state of $NH_4^+$–N, transferring excess $NH_4^+$–N from wastewater into solid-state for use as nutrition is to be studied, such as fixing $NH_4^+$–N on large particles through adsorption and precipitation process.

### 3.1.5. PSD of protein in swine wastewater

Size distribution of protein in the swine wastewater treatment processes is shown in Fig. 3e. This study results indicated that protein constituted a significant portion comparing to other compounds (mentioned in Fig. 3a–d) in all the swine wastewater. The MBR influent contained 1,632.2 mg $L^{-1}$ of protein, by converting proteins to COD using conversion factors based on assumed typical composition as suggested by Li et al. [28], roughly 45%–50% of COD in the MBR influent before and after settling was measured as protein.

The particle size variation was observed in the MBR influent before and after precipitation, whereas in the concentrated liquid, MBR effluent, and the final effluent the particle size was found almost unchanged. In the MBR influent, the super colloid state was regarded as a dominant portion which occupying 44.9% of overall protein, on the other hand, the dissolved state was also quite important for occupying 37.7% of overall protein distribution. After settling the MBR influent, the dominant fractions of protein were still measured as super colloidal and soluble state as 41.5% and 51.5%, respectively. As a component of COD, the trend of protein in this aspect was very similar to COD.

It is also widely accepted that protein is one of the major components of soluble microbial products (SMP) [38], which plays an important role in the formation of gel layer in membrane fouling [39], biofouling [40], and organic membrane fouling [41]. Moreover, the particle size has also been reported to be involved in membrane blockage [40]. Fouling and its different mechanisms cause difficulties in membrane cleaning and engineering costs. Swine wastewater has the property of containing rich particulate matters, which are reported to contribute to the resistance filtration induced by fouling comparing to colloids and dissolved molecules (DM) [42], and usually induce membrane blockage in the early stage.

Therefore, pre-filtration of the wastewater containing high content of suspended solids is recommended to reduce the MBR operational cost and membrane-shelf-life. The use of composite membranes in this study is speculated to get fouling by the dissolved substance [43], which needs chemical cleaning [41] to eliminate the membrane blockage. The rich nutrients (e.g., N, P) existing in the MBR effluent also provide a suitable living condition for microbial bacteria. Thus, the relationship between membrane blockage and PSD in terms of protein requires detailed studies.

#### *3.1.6. Summarize of PSD features*

As above indicated, overall features of pollutants did not always follow the same pattern. COD, TP, and protein contained particles ranging from small colloids up to quite large particles, while $NH_4^+$–N and TN containing more soluble components, didn't have occurrence tendency as distinct as others. Profiles for the concentrating liquid, even presented high in chromaticity and pollutant concentration, were all relatively flat because wastewater from such a procedure had less visible particulate matter and, conversely, also less matter retained by the membrane.

### *3.2. COD/protein, COD/TN and TN/TP between different size fractions in swine wastewater*

The ratio of COD/protein, COD/TN, and TN/TP observed in the MBR influent is shown in Fig. 4. Based on the proportion of ammonia nitrogen in swine wastewater, the COD/protein ratio was calculated to explore the characteristics of proteinaceous organic matters (Fig. 4). Overall, the COD/protein ratio was decreased with decreasing size fractions. More proteinaceous material was detected in the smaller matter, and a similar trend was observed in domestic sewage [16] as indicated in Fig. 4 and Table 3. The maximum portion of protein content was in colloidal organics (0.8–0.22 μm) and a less protein proportion was observed in particle states (>100 μm). The overall lower ratio observed in the swine wastewater (Table 3) indicated that the proteinaceous organic compounds occupying a greater proportion in COD of swine wastewater than municipal wastewater.

The large particle and super colloidal (>0.8 μm) possessed a high C/N ratio, whereas the smaller substances (<0.8 μm) could be denoted to contain low C/N value (Fig. 4). Therefore, nitrification and denitrification of swine wastewater treatment, which is closely related to the C/N ratio, will unfavorably decrease with the excessive proportion of small size substances and the reduction of solid particles.

It is well documented that struvite precipitation [44] and wetland operation could serve as promising technologies to recover nutrients such as N and P from the swine wastewater [45]. However, the N/P value observed in all fractions was >3 (Fig. 4), which was higher than the expected molar ratio for struvite precipitation (1:1) [46]. Such a scenario might cause an additional cost of extra phosphate addition. To address the problem, adsorption technology aiming at soluble N can be combined with struvite precipitation [47] to be used as a complementary approach to remove the excess nitrogen elements in the swine wastewater. Wastewater treated with land application usually cannot be completely remediated by crops due to different N/P ratio

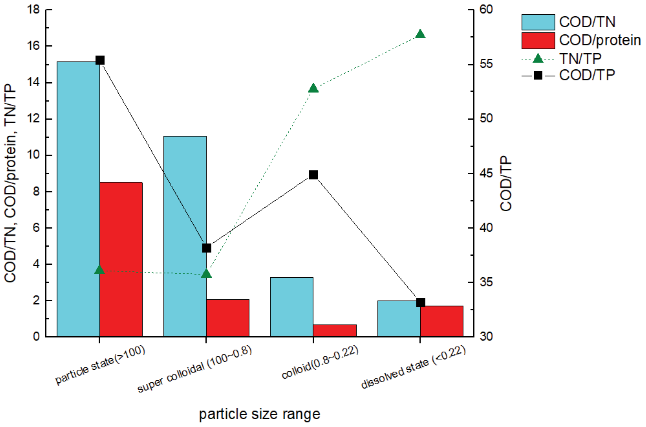


Fig. 4. Comparison of COD/TN, COD/protein, TN/TP, COD/TP and their size distributions in MBR influence of swine wastewater.

Table 3
Comparison of proteinaceous organic matters in COD between swine wastewater and municipal wastewater

| | | | | | |
|---|---|---|---|---|---|
| | Range (μm) | >100 | 100~0.65 | 0.65~0.1 | <0.1 |
| Municipal wastewater | Ratio | 9.8~262 | 30~74 | 15.5~21 | 11.1~400 |
| | Reference | (Ravndal et al. [16]) | | | |
| | Range (μm) | >100 | 100~0.8 | 0.8~0.22 | <0.22 |
| Swine wastewater | Ratio | 8.5 | 2.1 | 0.7 | 1.7 |
| | Reference | This study | | | |

requirements and nutrient availability [45], and adsorption properties of some materials in wetland treatment could be artificially improved to weaken such a difference.

### 3.3. Variation of $NH_4^+$–N/TN

The comparison of $NH_4^+$–N in TN (Fig. 3b and d) percentage in 5 sampling sites is presented in Fig. 5.

Fig. 5 indicates that the ratio of $NH_4^+$–N to TN in all fractions was lesser than particle size. It could be due to more nitrogenous substance existing in the dissolved state made every curve of the $NH_4^+$–N/TN ratio remain constant. The difference between TN and $NH_4^+$–N could be denoted as other forms of nitrogen that existed in organic form in agricultural wastewater [45]. The $NH_4^+$–N to TN ratio decreased significantly after the MBR procedure from 85% to 22%. In the effluent from the swine wastewater treatment system, the relative proportion of $NH_4^+$–N and TN was again large to about 54.6%. But comparing the numerical value of these compounds from MBR effluent (Fig. 3b and d), it was observed that the composite membranes (the antifouling membrane the desalination membrane) reduced the $NH_4^+$–N value from 108.3 to 42.5 mg $L^{-1}$, TN from 481.6 to 77.8 mg $L^{-1}$. Thus, the MBR could serve as a promising technology to strip $NH_4^+$–N from the swine wastewater through nitrification. However, the low C/N ratio (≈4.6 in MBR influent) than the recommended value of 7 [48] might cause depleted carbon source, which was a challenge for denitrification of such wastewater. So, in such a process, the transformation of nitrate was not enough, and accumulation of nitrate occurred in the MBR effluent. The TN was significantly eliminated through the composite membranes, thus the proportion of ammonia nitrogen in total nitrogen was increased. As indicated in Fig. 5, the settling and filtration were not effective in the conversion of $NH_4^+$–N to other forms of nitrogenous compounds, but the MBR operation and biochemical reaction played a significant role in nitrogen transformation.

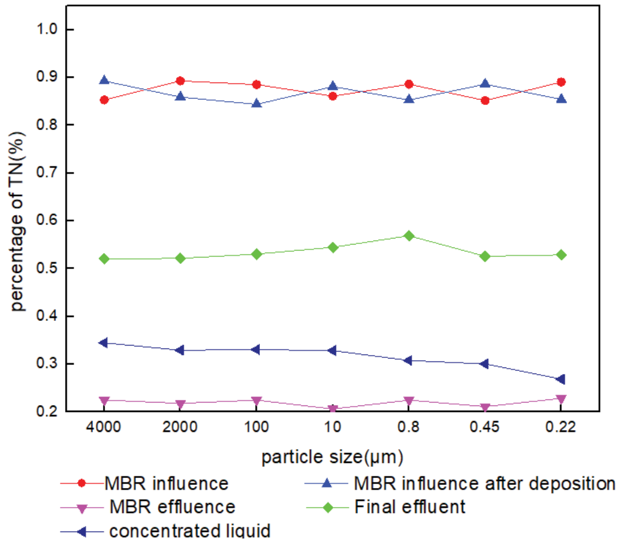


Fig. 5. $NH_4^+$–N/TN of livestock wastewater when it flowing through different treatment structures. Both $NH_4^+$–N values and TN values were calculated as total measured content in the overall range of less than particular particle size, other than the interval existing.

The concentrated liquid containing abundant nitrogen and phosphorus was produced as a potential fertilizer. The nitrogen-to-protein conversion was calculated based on the common determination using a 6.25 factor [49]. The concentrated liquid contained high TN (1,115.1 mg $L^{-1}$) but low $NH_4^+$–N value (377.2 mg $L^{-1}$), where nearly 6.0% of the TN resource existed in the form of protein and nearly half of the TN resource existed in the form of nitrate radical, nitrite. It is reported that soluble nitrogen [50] is readily available to the plants, thus the use of concentrated liquid as a fertilizer is a good choice.

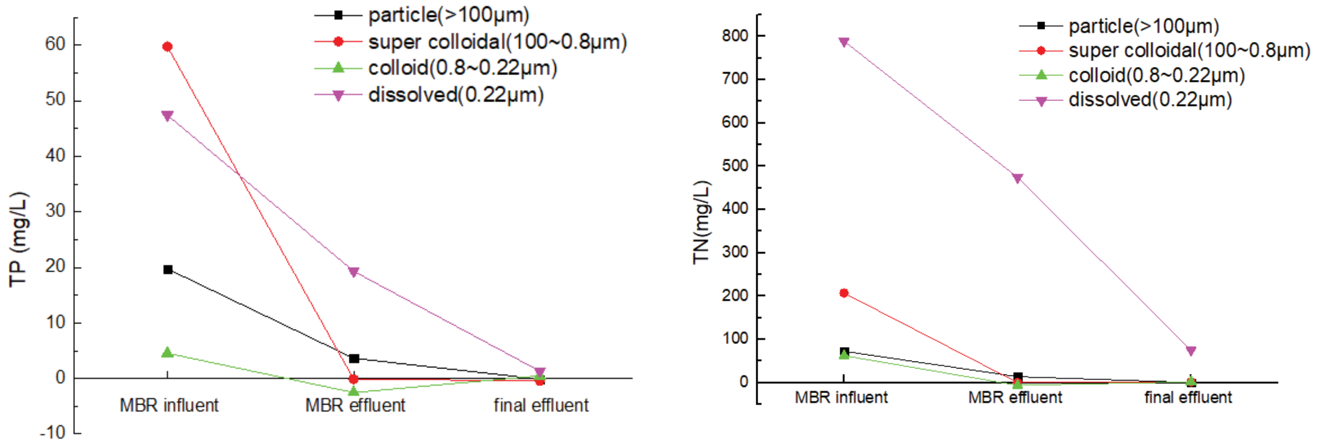
### 3.4. Effects of water purification process on PSD

Fig. 6a and b represent the nutrients (TP and TN) removal efficiency in the membrane flow process through size distribution. The change of TP concentration in the particulate state (>100 μm) during treatment is mentioned in Fig. 6a. Most particulate TP was found before the biological treatment, after biofilm treatment nearly 82.1% was removed. The remaining 17.9% of residue was eliminated by the composite membranes and no particulate TP was detected in the final treated water. Also, the removal of TP in the super colloidal and colloidal states from swine wastewater revealed excellent elimination ability (≈100% elimination of super colloidal and 90% of colloidal TP). This study results suggested that the MBR equipped in the wastewater treatment system for livestock farms had an excellent performance in these two states of TP removal. Furthermore, MBR operation prevented the membrane fouling in the composite membrane. Remarkable soluble phosphate removal was observed from 47.4 to 16.3 mg $L^{-1}$ by MBR, and then from 16.3 to 1.3 mg $L^{-1}$ by the composite membranes. The use of a composite membrane in this process significantly reduced the dissolved TP in the final discharge and maintained the effluent standard.

Similarly, a similar result was obtained by PSD-based TN experiment (Fig. 6b), the most granular (81.0%), super colloidal (≈100%), and colloidal states (≈100%) of TN could be removed by the biological treatment. The soluble TN accounting for 69.8% in the MBR influent was not effectively removed by the MBR process (only 59.3%). However, the composite membrane achieved a steady removal of the dissolved TN from 467.9 to 74.7 mg $L^{-1}$, and a concomitant small amount removal (18.6%) of TN larger than 100 μm was observed, suggesting that the composite membrane handled a positive function in MBR compensation and an essential role in final qualified discharge.

In this process, effective removal of TN and TP in all fractions was observed in the MBR process especially from the colloidal and super colloidal states of pollutants. However, the stringent effluent discharge standards demand a tertiary treatment or polishing step to augment the process performance and to achieve the complete removal of both soluble TN and TP.

A better comprehension of this feature can result in a more purposeful and efficient system for wastewater treatment and resource recovery. For example, if the swine



(a)

(b)

Fig. 6. Particle, super colloidal, colloid, and dissolved nutrients (TN and TP) fingerprints of the MBR influent, the MBR effluent, and the final effluent.

wastewater is subsequently treated for reuse, further treatment after biological treatment can be weakened, and the utilization will be focused on the collection of dissolved and granular nutrients. If the swine wastewater will ultimately be discharged, tertiary treatment is needed to the reduce content of soluble TN and soluble TP, which can induce the nuisance consequences of excessive nutrient pollution and consequently aggravate the risk of water eutrophication, particularly in concentrated breeding areas. This implies that consideration on how to optimize the polishing process of the swine wastewater to reduce the economic cost in this procedure is essential to engineering and practice. On the other hand, optimizations of the MBR process to be applied in swine wastewater should focus on further strengthening the removal efficiency of particulate (>100 μm) and dissolved (<0.22 μm) nutrients.

### *3.5. 3D-EEM of humic-like substances in swine wastewater*

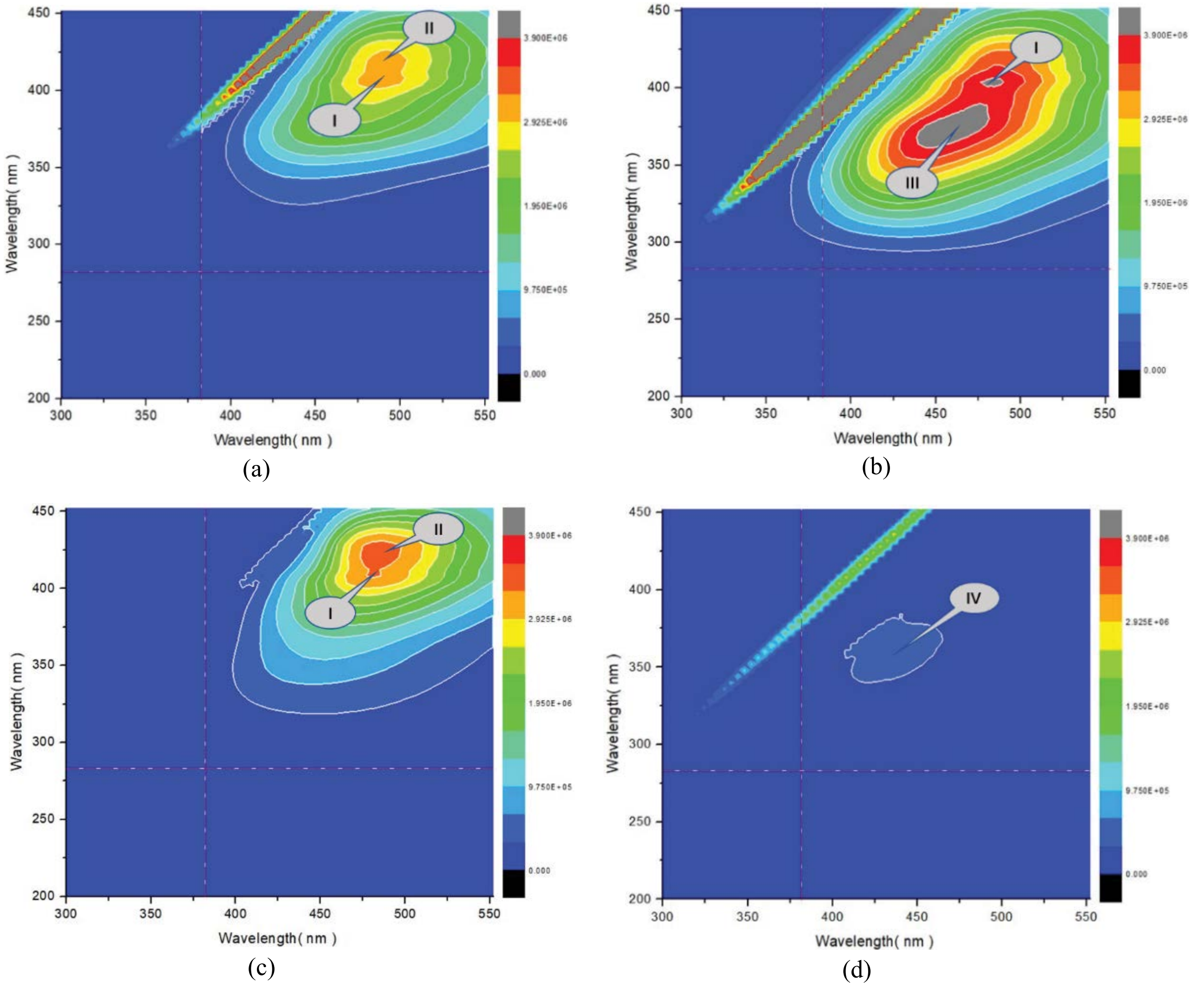
Based on the results obtained from Fig. 3a–e, a large portion of dissolved organic matter (DOM) was still observed in the filtered wastewater. The detailed variation in the dissolved humic-like substance, which was classified as a significant part of DOM, was analyzed using 3D-EEM fluorescence spectroscopy (Fig. 7). The four marked fluorescence peaks were recorded in different experimental stages (Fig. 7) at the Ex/Em of 408/484 (peak I), 416~424/488~492 (peak II), 372/460 (peak III), and 356/436 (peak IV) representing the humic-like substances. However, it displayed different Ex/Em characteristics and fluorescence intensities. In the raw swine wastewater, the peaks I and II were observed (Fig. 7a), after settling (Fig. 7b) the peak II was disappeared and another fluorescence with a strong intensity was seen near peak III. At the end of MBR biological treatment (Fig. 7c), the fluorescence signal remained unchanged as compared to the MBR influent (Fig. 7a). The reason for the increase in signal strength may be due to the decomposition of macromolecules during biological activities [51]. At the effluent water after the purification using a composite membrane (Fig. 7d), only peak IV was observed with low fluorescence intensity. The shift in humic-like substances in the swine wastewater was probably associated with (i) the filtration of smaller substances, (ii) the reduction of condensed aromatic moieties, (iii) conjugated bonds formed through microbial reactions during residence time, and (iv) the degradation of large molecules [52,53].

A fluorescence index ($FI_{370}$) was calculated to distinguish the source of isolated aquatic fulvic acids, and the fluorescence intensity ratio was determined as an emission wavelength of 450 nm divided by 500 nm, both excited at 310 nm [54]. For all the samples, before the composite membrane treatment, the values of $FI_{370} < 1.4$ (1.154, 1.296, and 1.250 for MBR influent, MBR influent after settling, and MBR effluent, respectively) indicated the fulvic acids derivatives originated from the terrestrial environment. Therefore, peaks I, II, and III represented the humic substances from terrestrial sources [55], which was by the literature [56], that stated the bacterial fluorescence couldn't be observed at higher excitation (>300 nm) wavelength. Due to the composite membrane filtration, the $FI_{370}$ of the final effluent increased to 1.846 dramatically due to microbial-derived fulvic acids. Through this process, the eutrophic nature of raw wastewater was treated and a clean final effluent (Fig. 7d) was produced. The $FI_{370}$ was increased due to the increase of autochthonous contribution from the chromophoric dissolved organic matter [54].

## 4. Conclusion

We investigated the correlation between PSD and chemical characteristics of swine wastewater, and detailed removal efficiency of membrane units. The results from this study demonstrated as follows:

- The majority fractions of COD, TP, protein in MBR influent were all in the super colloidal state, accounting for 44.3%, 45.4% and 44.9% of overall content,



(a) (b) (c) (d)

Fig. 7. 3D-EEM of humic-like substances in swine wastewater: (a) MBR influence, (b) MBR influence after precipitation, (c) MBR effluence, and (d) final effluence.

respectively. On the other hand, the dissolved state COD, TP, protein were also quite important for proportions of 30.5%, 36.1% and 37.7%. Both COD and TP could achieve highly effective removal in each particle range by sedimentation units.

- $NH_4^+$–N and TN contained larger portions of soluble components. In the MBR influent, 72.9% of $NH_4^+$–N and 69.8% of TN were classified as soluble portions, respectively.
- More proteinaceous material was detected in the smaller size matter; the C/N ratio of swine wastewater would unfavorably decrease with the excessive proportion of small size substances and the reduction of large solid particles; PSD-based N/P measured in every fraction was >3 and some suggestions on wastewater purification process were summarized to address that.
- $NH_4^+$–N/TN ratio remained constant over gradually diminishing size ranges. The $NH_4^+$–N to TN ratio was significantly decreased from 85% to 22% after the MBR treatment and again increased to 54.6% in the effluent from the swine wastewater treatment system. The possible use of the concentrated liquid as a fertilizer would be a good option for resource recovery from swine wastewater.
- MBR process achieved effective removal of TN and TP in all size ranges when treating swine wastewater, especially contaminants attributed to colloid and super colloid states (>90% elimination ability). The qualified removal rate of nutrient content in particle and dissolved matter required further treatment on the basis of MBR.
- 3D-EEM fluorescence spectroscopy of dissolved humic-like substances was conducted, a slight shift in fluorescence location, a variety in intensity, and a migration to microbial-derived fulvic acids were observed.

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