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### **Paper:**

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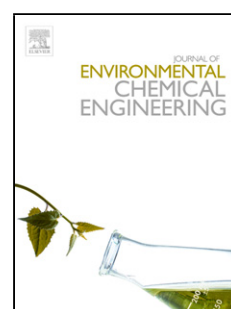
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## Accepted Manuscript

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**CHITOSAN AS NATURAL COAGULANT IN HYBRID  
COAGULATION-NANOFILTRATION MEMBRANE PROCESS  
FOR WATER TREATMENT**

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**Highlights**

- Water treatment industry is exploring the opportunity for sustainable development.
- Chitosan (natural coagulant) can be used with membrane process for water treatment.
- Performances of hybrid chitosan-nanofiltration membrane processes were studied.
- Chitosan affected the charge interaction between foulants and membrane surface.
- Compatibility between chitosan and NF membrane for water treatment was evaluated.

**ABSTRACT**

Water treatment industries are exploring the possibility to use environmental friendly chemicals and to discover the potential of advanced treatment technology in order to achieve sustainable development. Hybrid coagulation-membrane process has been introduced and proven to be a reliable water treatment process. In this study, the potential of chitosan as natural coagulant in hybrid coagulation-NF membrane process was studied. Three synthetic humic acid (HA) solutions with different ionic strength and composition will be used; without salt (Set 1), with NaCl only (Set 2), and with NaCl, CaCl<sub>2</sub>, and NaHCO<sub>3</sub> (Set 3). Our findings indicated that gradual flux decline for Set 1 can be related to the continuous accumulation of neutral charged particles (pH 4.2) on the membrane surface. Formation of compact foulant layer due to further charge suppression of the foulants by dissolved ions (Set 2) resulted in severe membrane flux decline. When the pH of Set 1 and Set 2 supernatant solutions were increased to 7, fouling has been resolved due to the presence of strong electrostatic repulsion between the foulants and membrane. During the initial filtration process for Set 3, the flux has remained constant due to the strong repulsion between negatively charged foulants and membrane (pH 7). It was followed by severe flux decline which could be attributed to the effect of concentration polarization. Hence, this study highlighted that the impact of natural coagulant on the membrane process should be systematically studied in order to prevent unnecessary loss due to the incompatibility between both processes.

**Keywords:** Hybrid coagulation-membrane process; Chitosan; Biodegradable coagulant; Membrane fouling; Water treatment

**1. INTRODUCTION**

Coagulation process has been commonly applied in water treatment system for a long period due to its capability to remove natural organic matter (NOM) and suspended particles in the raw water [1]. It can be divided into three major groups; inorganic type (conventional), organic polymers, and natural coagulant [2]. Conventional coagulants such as ferric chloride (FeCl<sub>3</sub>) and alum have been widely used in water treatment process [1]. However, there are several issues regarding the possible adverse side effects of those residual coagulants on the environment and

living organisms. Excessive coagulants might lead to corrosion problem and result in high concentrations of metal coagulants in treated water which is detrimental to the human health [3–5]. Another drawback of these hydrolyzing metal coagulants is the production of huge amount of sludge, which is non-biodegradable and causing disposal problems to environment [4,6]. For the application of synthetic organic polymers, concerns about the presence of residual monomers which is neurotoxicity and carcinogenic have impeded its use in water treatment process [2]. These issues together with the increase in awareness of sustainable development have driven the water sector to seek for natural coagulants.

Natural coagulants produce much lesser sludge and due to its biodegradability properties, sludge treatment is easier and less harmful to environment [4,6]. Natural coagulants such as chitosan, *Moringa oleifera*, nirmali seeds, *Jatropha curcas* seeds, and Tannin have been proven as effective alternative coagulants for conventional coagulants in removing NOM and turbidity [3,4,7,8]. However, some limitations have prevented the coagulants from being used commercially. *Jatropha Curcas* extract only worked at best when the pH of the water is lowered down to below 4, while extract from chestnut and acorn worked best at pH 9 [2,8]. Most of the freshwater resources have pH around 7, which indicates that pH adjustment has to be carried out in order to obtain the best performance from those coagulants [9]. The production of plant-based coagulants might compete with other agricultural activity for land usage and might encounter the problem of harvesting due to weather/seasonal changes [4]. Hence, chitosan has been selected as the natural coagulant in this study since its optimum working pH is around 6-7 where adjustment of pH is not required and it can be synthesized from chitin, one of the most accessible biopolymers on earth [10]. Besides, there are already studies showing that chitosan has the potential to be used in water treatment coagulation process as it was proven capable to remove turbidity and NOM in the water [10–13].

However, with the deteriorating raw water quality and the implementation of more stringent water quality regulations, coagulation process alone could not secure and achieve the required standard for potable water. Thus, it is being combined with more advanced technology especially membrane process to produce acceptable potable water. Many successful cases have

been reported where coagulation acted as pretreatment process to remove large amount of foulants in the water so that membrane performance can be enhanced and sustained [14].

Even though conventional coagulants and ultrafiltration(UF)/microfiltration(MF) membranes have been commonly used in the hybrid coagulation-membrane processes [6,15–20], the issue on the compatibility of chitosan coagulation with membrane process has not been well studied. Hence, this study aims to investigate the effect of chitosan on the hybrid coagulation-membrane performance. Nanofiltration (NF) membrane will be used in this study since it is suitable for brackish water treatment. Systematic study using different background solutions would be carried out to investigate and inspect how the chitosan changes the characteristics of the solutions, as these changes will affect the performance of the membrane process.

## 2. MATERIALS AND METHODS

### 2.1 Chemicals and Membrane

All chemicals used are analytical grade, unless stated otherwise. Humic acid (HA), chitosan, kaolin, acetic acid, calcium chloride ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ), sodium bicarbonate ( $\text{NaHCO}_3$ ), and sodium chloride (NaCl) were purchased from Sigma Aldrich (Malaysia). Ultrapure (UP) water with a quality of  $18 \text{ M}\Omega\text{cm}^{-1}$  was used for all solution preparation. Chitosan was dissolved in 1 % acetic acid solution. Membrane used in this study was NF 270 (Dow Filmtech, USA) with molecular weight cut-off (MWCO) around 200-400 Da. NF 270 has a smooth and negatively charged surface, with root mean square (RMS) roughness around 9 nm and zeta potential around -41.3 mV at pH 9 [21].

### 2.2 Synthetic Test Water

Synthetically prepared waters with fixed turbidity were used for this work. The HA concentration for each batch of run was 20 ppm. Suitable amount of kaolin was added into the synthetic water to adjust its turbidity to  $30 \pm 0.5$  NTU. The pH of the water was adjusted to 7 by using sodium hydroxide (NaOH) and hydrochloric acid (HCl). The zeta potentials of the

synthetic waters with 3 different background solutions total dissolved solids (TDS) were as below: a) 0 ppm TDS ( $-50 \pm 3$  mV) b) 400 ppm NaCl ( $-50 \pm 3$  mV) c) 400 ppm mixture (80 ppm NaCl, 200 ppm  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , and 170 ppm  $\text{NaHCO}_3$ ) ( $-22 \pm 2$  mV).

### 2.3 Jar Test Coagulation and Cross-flow Process Setup

Coagulation pretreatment prior to NF membrane was carried out in a conventional jar test apparatus (Model ZR4-6, Zhongrun Water, China). The coagulation procedures consisted of three steps: vigorous stirring after the addition of coagulant (100 rpm for 1 minute), mild stirring (30 rpm for 29 minutes), and settling (30 minutes). The dosage of chitosan and  $\text{FeCl}_3$  was varied in order to obtain the optimal dosage which gives the best performance. The supernatant after the coagulation process was then used as the feed water for membrane experiment. The removal efficiency of foulant was calculated using the following equation:

$$R = \left( \frac{C_i - C_f}{C_i} \right) \times 100\% \quad (1)$$

where R denotes to the rejection of foulant,  $C_i$  indicates the initial concentration of HA, and  $C_f$  indicates the final concentration of HA after the coagulation process.

Bench-scale cross-flow membrane experimental setup with recycle loop was used for the membrane experiment and is shown in Fig. 1. Commercial flat sheet NF 270 membrane was cut into rectangular shape and laid on top of the membrane test cell (CF 042, Sterlitech, USA) with membrane effective filtration areas of  $0.0042 \text{ m}^2$  (excluding the area covered by the O-ring) and tightened by a rubber O-ring. During the membrane filtration experiment, the supernatant water from the coagulation process was poured into the feed tank as the model solution and was kept at constant temperature of  $27 \text{ }^\circ\text{C}$ . A flow meter was installed in the feed stream to monitor the flow rate of the feed solution. Applied pressure of the filtration system was generated using the high pressure pump (Blue Clean, BC 610, Italy) and controlled at 10 bars, while the retentate from the membrane system was re-circulated to the feed tank at constant cross-flow rate velocity fixed at  $42 \text{ cm/s}$  to minimize the changes of feed concentration. Two pressure gauges were used to

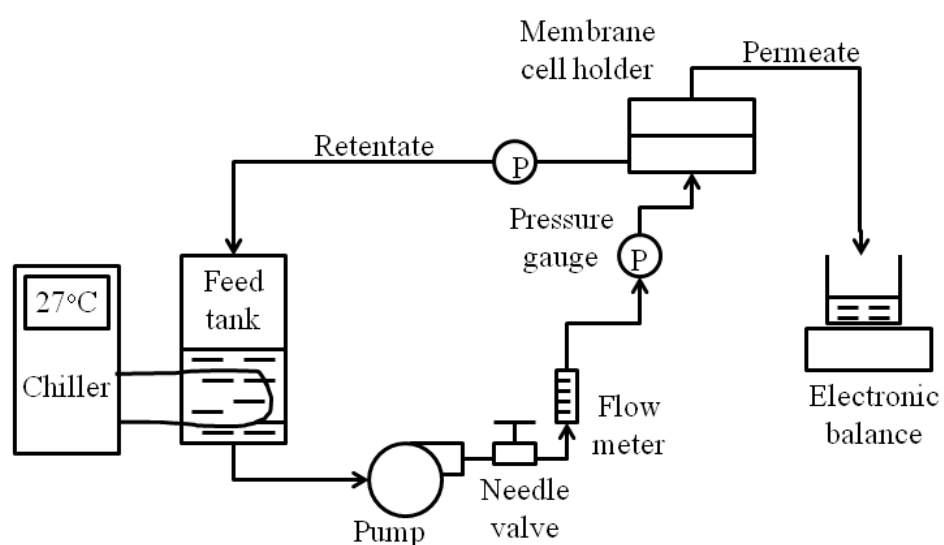


indicate the operating pressure of the feed and retentate streams. This membrane filtration experiment was conducted for 5 hours. Experiments with background solutions of 0 ppm and 400 ppm NaCl were repeated with pH of supernatant water adjusted to 7 in order to study the effect of membrane surface charge and compared with solution of mixture salts.

The performance of the membrane process was presented as normalized flux versus time, where the normalized flux was calculated as in Eq. (2).

$$N_J = \frac{J_t}{J_0} \quad (2)$$

where  $N_J$ ,  $J_t$ , and  $J_0$  represent normalized flux, instantaneous flux, and initial pure water flux, respectively.



**Fig. 1.** Schematic Diagram of Bench-Scale Cross-Flow Process

#### 2.4 Analytical Methods

Humic acid content was measured using UV/Vis spectrophotometer (PerkinElmer, USA) at a wavelength of 254 nm. Zeta-Sizer (Malvern, UK) was used to measure stability of the suspensions; and Master-Sizer (Malvern, UK) was used to determine the particle size in the supernatant. Turbidity of the water was measured using 2100 N Laboratory Turbidimeter

(Hanna, USA). Conductivity and pH of the solution were measured using HI 2550 Benchtop Meter (Hanna, USA). Fouled membrane imaging was carried out using ultra high resolution Field Emission Scanning Electron Microscopy (Merlin Compact, Zeiss, Germany).

### 3. RESULTS AND DISCUSSION

#### 3.1 Coagulation Performance

Table 1 shows the characteristics of each supernatant solution after coagulation process. The background solution of each set was as below: a) Set 1 – 0 ppm (no dissolved salt) b) Set 2 – 400 ppm NaCl c) Set 3 – 400 ppm mixture solution (80 ppm NaCl, 200 ppm CaCl<sub>2</sub>.2H<sub>2</sub>O, and 170 ppm NaHCO<sub>3</sub>) d) Set 4 – 0 ppm (pH of supernatant adjusted to 7) e) Set 5 – 400 ppm NaCl (pH of supernatant adjusted to 7). It can be seen that chitosan managed to remove more than 90 % of turbidity and kaolin-HA in the solution, effectively reducing the turbidity to lesser than 1 NTU. However, the pH of the supernatant solution for Set 1 and 2 had been reduced to around 4 due to no alkalinity in the solution. Near zero zeta potential indicated that the residual particles in both supernatant solutions had neutral charge. With the adjustment of pH, the residual particles in the solutions regained their negative charge as in Set 4 and 5. Supernatant solution for Set 3 remained neutral since it contained alkalinity which offset acidity of the chitosan coagulant.

The mechanisms involved in the coagulation process can be predicted by observing the change in zeta potential of the particles in the solutions. Significant increase in zeta potential for Set 1 and 2 after the addition of chitosan indicated that neutralization was the predominant mechanism here, where the negatively charged particles had been neutralized by chitosan. Such postulation was supported by the finding of Zhao et al. where charge neutralization was proposed as the dominant mechanism when the final zeta potential of polyaluminum chloride (PAC) coagulation approached zero [22]. With weak or nearly none electrostatic repulsion between the particles, agglomeration started to take place and eventually flocs formed will settle down and removed as sludge. For solution with alkalinity and calcium ions, the initial zeta potential was much higher than Set 1 and 2 (-22 mV compared to -50 mV). This probably due to the presence of positively charged calcium ions which bound the negatively charged particles in the solution

and resulted in reduced overall zeta potential [23]. It was postulated that neutralization was not the only mechanism involved in the removal of HA-kaolin for Set 3, as its final zeta potential did not increase much. Indeed, chitosan may partially neutralize the particles and bind them together to form larger flocs via bridging mechanism. The presence of calcium ions possibly enhanced the bridging effect since its positive charge tended to attract negatively charged particles together. In the end, the particles still obtained certain charge due to the partial neutralization and bridging mechanisms. This prediction was based on the finding by Sun et al., where they suggested charge neutralization was not the dominant mechanism since the zeta potential of coagulated water was not higher than -10 mV [24]. For Set 4 and 5, the residual particles in the supernatants regained their negative charge after the pH had been adjusted to 7. It was noticed that with the presence of NaCl in Set 5, the residual particles did not regain as much zeta potential as in Set 4, probably due to the increased ionic strength that suppressed the electrostatic charge of HA-kaolin particles [25].

Overall, chitosan tends to produce neutral charged particles in the supernatant solution if the raw water contains no or low alkalinity. With the presence of alkalinity and calcium ions, bridging mechanism also involved in binding the particles together to form agglomerates. The impact of those residual particles on the membrane performance will be explained in the following section.

**Table 1**  
Characteristics of Supernatant Water for each Solution

Parameters	Set 1	Set 2	Set 3	Set 4	Set 5
pH	4.2 ± 0.1	4.1 ± 0.1	7 ± 0.5	7 ± 0.5	7 ± 0.5
Zeta potential (mV)	-1 ± 2	2 ± 1	-13 ± 1	-30 ± 3	-20 ± 2
UV <sub>254</sub> removal (%)	91 ± 1	91 ± 1	88 ± 1	91 ± 1	91 ± 1
Turbidity removal (%)	98 ± 1	98 ± 1	95 ± 1	98 ± 1	98 ± 1

### 3.2 Membrane Performance and Fouling

Fig. 2 shows the membrane flux and salt rejection performances for each set of hybrid coagulation-NF 270 membrane processes while Fig. 3 portrays the cross-sectional view of the foulant layer formed on the membrane surface using FESEM. Normalized flux for Set 1 (pH 4.2)

as shown in Fig. 2(a) decreased gradually during the whole filtration period. However, when the pH was adjusted to 7 (Set 4), no flux decline was observed. At pH 7, both the membrane and particles regained their negative charges, which effectively slowed down the attachment of foulants (HA-kaolin) onto the membrane surface due to strong electrostatic repulsion forces between them [26]. Hence, severe flux decline was prevented and fouling was under controlled. The foulant layer formed also appeared to be thinner due to the presence of stronger repulsion forces, as shown in Fig. 3(d) compared to Fig. 3(a). At pH 4.2, the particles and membrane nearly lost their surface charge and charge repulsion became weak. This resulted in the increased interaction between the foulants and the membrane surface leading to continuous flux decline [27]. The same scenarios have been observed to occur in hybrid process using 400 ppm NaCl background solution as presented in Fig. 2(b). The flux decreased drastically for Set 2 where the membrane filtration unit was fed with supernatant at pH 4.2. It was believed that concentration polarization due to the accumulation of NaCl further worsened the performance, as the weak electrostatic repulsion between the particles and membrane surface was further reduced and consequently the foulants have smaller macromolecular configuration [27,28]. This resulted in the formation of a thicker and more compact cake layer on the membrane surface compared to Set 1 & 4, which totally hindered the passage of water and salt through the membrane. Such claim was supported by the observed thicker foulant layer as shown in Fig. 3(b).

However, with the pH adjusted to 7 as in Set 5, membrane fouling propensity has been curbed and no flux decline was observed during the experiment. FESEM image as shown in Fig. 3(e) indicated the foulant layer formed on the membrane surface at pH 7 was indeed thinner compared to Fig. 3(b) where it was operated at acidic condition. This may be attributed to the strong electrostatic repulsion between the particles and membrane that prevented the formation of compact foulant layer on the membrane surface [26]. The gradual decrease in conductivity rejection might be due to the effect of cake-enhanced concentration polarization (CECP) [29]. The formation of foulant cake layer hindered the back diffusion of salts from the membrane to the bulk and thus increased the concentration of salts at the membrane surface. Continuous accumulation of salts and greater concentration gradient across the membrane resulted in decreasing salts rejection, in agreement with other findings [30,31]. From the findings in this study, it is suggested that pH adjustment might be required after chitosan coagulation process if

the pH of the supernatant solution decreases too much (low alkalinity solution), so that membrane fouling propensity can be controlled and minimized. Besides, it was discovered that caution has to be taken when coagulation process dominated by charge neutralization mechanism is integrated with NF membrane. This is because electrostatic repulsion plays a vital role in preventing fouling and increasing rejection for charged membrane like NF.

Fig. 2(c) shows that the membrane flux receiving supernatant solution from chitosan coagulation with salts mixture as background solution decreased gradually initially and substantially after a period of filtration time. The salts rejection decreased initially and remained steady at the end of filtration period. As illustrated in the figure, there are two fouling regions according to the trend of membrane flux decline. It was postulated that during the first flux decline section, calcium acted as bridging agent between the membrane and foulants as well formed complex with the foulants in the supernatant solution [32]. Calcium bridged the foulants onto the membrane surface which led to the gradual flux decline phenomena. At the same time, salts rejection was decreasing due to concentration polarization and lower salt back diffusion during the formation of cake layer. After the formation of foulant cake layer, rapid deposition of foulant on the cake layer happened due to the capability of calcium to form complex with carboxylic functional groups of organic molecules [33]. Consequently, the formation of thicker and denser compact fouling layer resulted in severe flux decline while at the same time prevented the passage of salts through the membrane [34]. Indeed, the foulant layer as shown in Fig. 3(c) was the thickest among the processes, which indicated the role played by calcium ions. The reason why conductivity rejection remained constant after the flux started to drop substantially might be due to the equilibrium achieved between the flux decline and the lower salt passage. Electrostatic repulsion failed to prevent fouling from happening because the particles were only slightly negative charged after being neutralized by chitosan (as shown in Table 1 Set 3) and the repulsion between the particles in the supernatant and membrane was not strong enough to prevent the adsorption of foulants onto the surface. Fouling was further aggravated by the presence of calcium ions that bridged the foulants in the solution onto the foulant layer at the membrane surface as well as intermolecular bridging among the foulants in the cake layer [34].

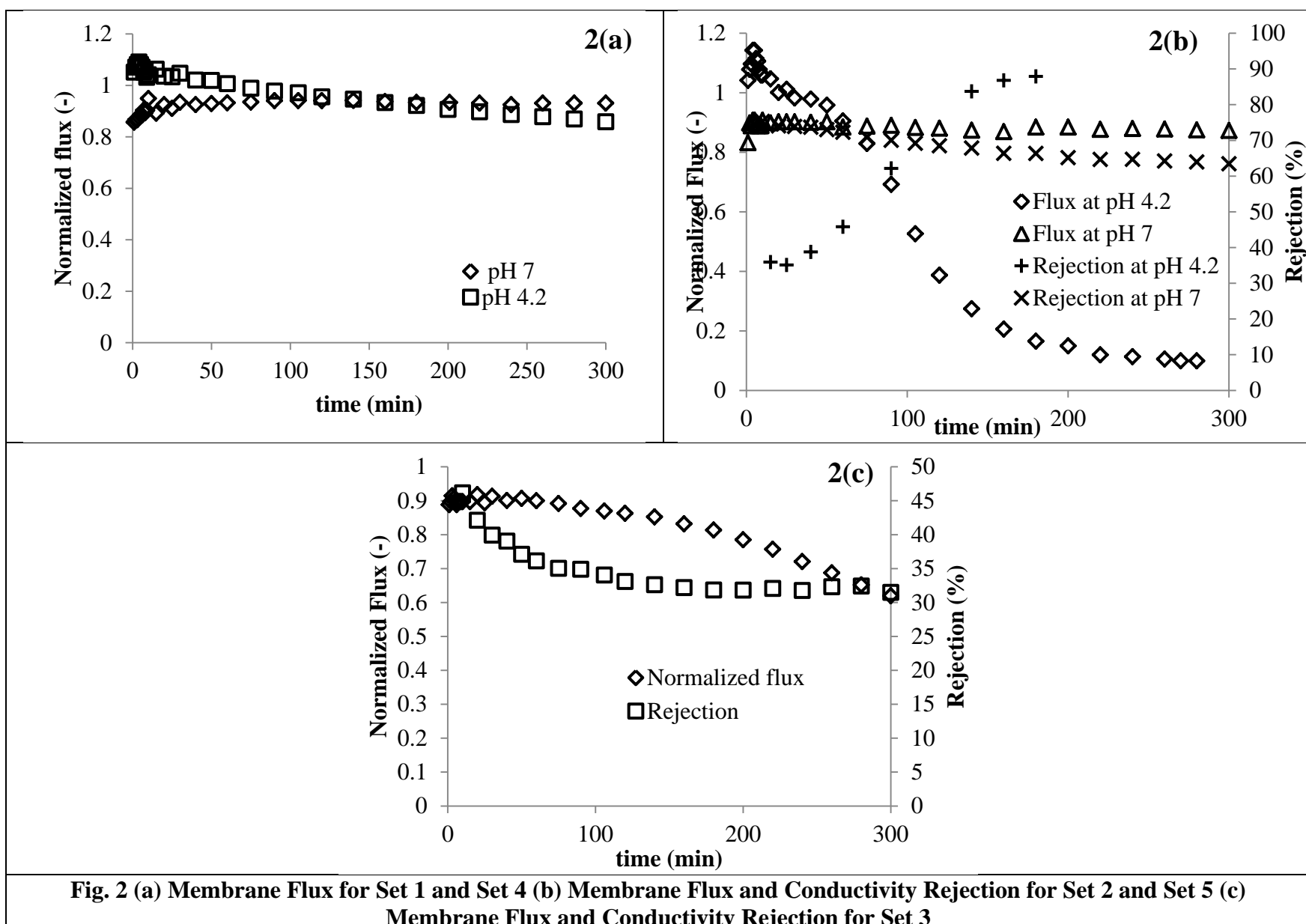
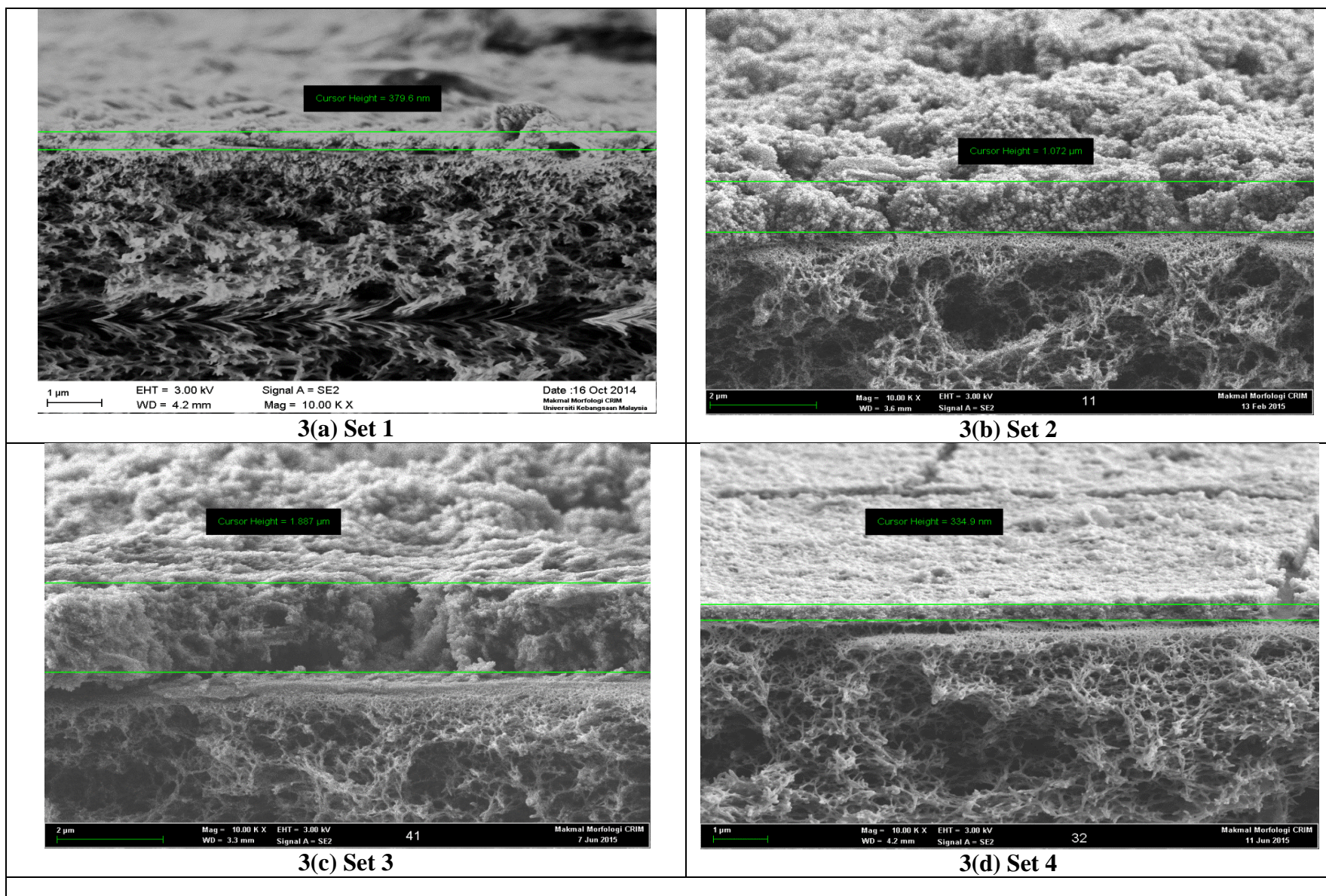
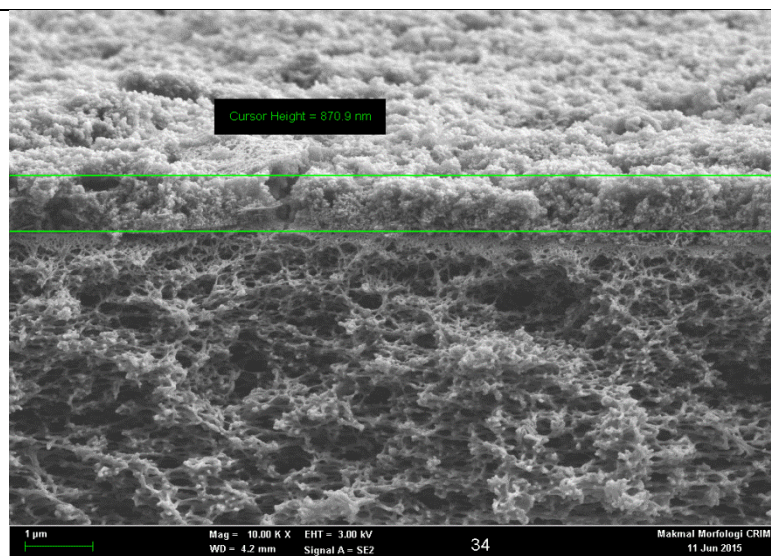


Fig. 2 (a) Membrane Flux for Set 1 and Set 4 (b) Membrane Flux and Conductivity Rejection for Set 2 and Set 5 (c) Membrane Flux and Conductivity Rejection for Set 3





3(e) Set 5

**Fig. 3** Fouled NF 270 membrane autopsy (cross-sectional view) by FESEM according to solutions (a) Set 1 (b) Set 2 (c) Set 3 (d) Set 4 (e) Set 5



#### 4. CONCLUSION

Chitosan was capable to remove the turbidity in the synthetic raw waters mainly by neutralization mechanism for low alkalinity solution while bridging mechanism also played a role when treating solution with higher alkalinity and calcium ions. The production of near neutral charged particles in the supernatant solutions caused a disastrous effect on the membrane performance, especially in the presence of NaCl salt and CECP effect (Set 1 and Set 2). It was found that pH adjustment which had been carried out prior to the membrane process managed to maintain the membrane flux and reduce fouling propensity (Set 4 and Set 5). However, when chitosan was used for high alkalinity and calcium ions solution, the membrane did not perform as well as in Set 4 and 5, even though the membrane possessed its negative charged properties. The flux decline might be attributed to the higher affinity of the particles to adsorb onto the membrane surface. The zeta potential of particles in Set 3 was lower than Set 4 and 5, which resulted in weaker repulsion from the membrane. Besides, it was believed that calcium might increase the tendency of adsorption by bridging the negative charged foulants with the negative charged membrane. Furthermore, calcium might bridge the foulants in the solution onto the foulant layer on the membrane surface. Eventually, the cake layer formed was thicker compared to the rest of the hybrid coagulation-membrane processes. Hence, it can be concluded that chitosan might not compatible with NF membrane because its main coagulation mechanism was charge neutralization, which produced neutral charge particles. For NF membrane, electrostatic repulsion plays a vital role in curbing the fouling propensity. Thus, chitosan coagulation rendered it ineffective and enhanced membrane fouling propensity.

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