

Evaluation of efficiency of membrane submerged reactor in water treatment using ferric chloride (FeCl_3) coagulant with flocculation agents of polyelectrolyte and lime (CaO)

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ABSTRACT

The present study was conducted to investigate the efficiency of water treatment through the coagulation–flocculation process using a membrane submerged reactor (MSR). In this study, first, for treatment of water with different turbidities (10, 50, 100, 200, 500, and 1,000 NTU) and total organic carbon (TOC) (1, 3, and 5 mg/L), the content of ferric chloride coagulant was evaluated along with that of lime and polyelectrolyte for coagulation and flocculation at each of turbidity and TOC levels by Jar test. In the next step, the MSR was designed. Parameters of flux, turbidity and TOC removal (%), and concentration of iron in the treated water, were also investigated. The results of the Jar test showed the pH = 8 was selected as the optimal pH with the highest percentage of turbidity and TOC removal. MSR tests had the best performance in terms of flux at turbidity level less than 100 NTU so that, flux was decreased by only 15% within 8 h of operation time and reached from 40 to 36 L/m² h. While, at a high turbidity level of 200 NTU, flux reduction was up to 50% and reached 21.9 L/m² h. After increasing the operating time of membranes, turbidity removal percentages were constant and higher than 99.5%. The highest percentage of TOC removal by MSR occurred at the turbidity of 100 NTU and TOC 5 mg/L (72%). The results showed that the removal percentages of TOC have also increased by increasing turbidity and TOC concentration; hence, there was a further decrease in flux so that at turbidity of 100 NTU and a concentration of 5 mg/L of TOC after 8 h, flux decreases by more than 27%. The total removal rate of iron by membrane process was more than 99% and the type of membrane fouling was surface sediment with reversibility. Our results showed that MSR combined with coagulation and flocculation can be used as an efficient and flexible method to treat water with different turbidity levels from water sources.

Keywords: Coagulation and flocculation; Membrane submerged reactor; Turbidity; Ultrafiltration; FeCl_3

1. Introduction

In recent years, membrane technologies, such as microfiltration, ultrafiltration, nanofiltration, and reverse osmosis have been used in water treatment processes due

to low energy costs and high elimination of pollution. Also, these technologies require less space and are easy to install [1]. Even today, water treatment with different turbidity levels is extensively done using ultrafiltration membrane because most of the pollutants making up

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this type of water have a high molecular weight and can be easily separated by ultrafiltration membrane filtration. In fact, these systems not only have good performance in terms of purification and water quality but also they are considered as the main option in recycling water from wastewater in the areas where there is low access to surface water [2].

Ultrafiltration submerged membranes have been developed as one of the most important systems in the industry of water and wastewater treatment in the last decade. In these systems, ultrafiltration membranes are placed inside the reactor tank. Membranes can be in the form of flat sheets and tubular or a combination of both. The backwash is also done by aerating the surface of the membrane and a backwash system, done reversely into the membranes using the purified water-reducing fouling on the surface of the membranes [3]. In general, submerged membrane systems are used at low and high pressures, each of which is used based on quality and hydraulic characteristics of flow [4]. Important applications of membrane submerged reactors (MSRs) are as follows: Firstly, removal of turbidity, bacteria, viruses, and similar contaminants in municipal water treatment plants having low inlet water with low pollution load, therefore; they can be used with high current flux and long membrane life. Secondly, they are used in municipal and industrial wastewater treatment plants, for wastewater treatment. However, the widespread use of submerged UF in drinking water treatment is still limited due to two major drawbacks, membrane fouling and insufficient removal of disinfection by-products (DBPs) precursors [5]. Furthermore, several studies on the membrane treatment of the surface, lake, and river waters have demonstrated that the DBPs precursors of natural organic matter (NOM) were one of the major foulants of the membranes [2–6]. To overcome such problems caused by NOM in UF applications, conjunctive use of coagulation and flocculation and membranes is thus becoming more attractive for water treatment because the coagulation and flocculation can capture and retain NOM before it reaches the membrane surface [7]. For addressing the basic problem of membrane fouling and longer operations, the quality of output flow, coagulation, and flocculation processes should be improved before the flow enters the membranes [8]. The coagulation process has a special place in water treatment so that, many studies have been done on the type of optimal coagulant to remove turbidity. A Jar test is used to select appropriate coagulant and also proper dose in the purification process under different conditions. In the chemical purification process, metal ions, such as $\text{Al}_2(\text{SO}_4)_3$ and FeCl_3 are produced by providing the necessary mixing energy, adjusting alkalinity and pH of the solution, and adding appropriate coagulant and flocculation agents including mineral coagulants, ferric chloride, polyaluminum chloride, polyelectrolyte, and hydrated lime to raw water and as a result of decomposition of these substances in water, eventually disturbing negative electrostatic charge of colloidal particles is neutralized [9]. In this study, cationic polyelectrolytes are used. Cationic polyelectrolytes are water-soluble polymers bearing positive ionic groups along back-bone or inside chains. These cationic polymers are synthesized

by free radical polymerization of acrylamide and their derivatives through the copolymerization method, involving solution, precipitation, and emulsion techniques [10].

The use of ferric chloride salts as coagulants at the concentrations where iron hydroxides are dissolved in water more than their solubility limit causes the production of iron hydroxide deposits. Hydroxide deposits trap these particles and cause their deposition while playing a key role in neutralizing the disturbing electrostatic charge of colloids [11]. Accordingly, in process of coagulation and flocculation of organic matter, turbidity and small colloids accumulate in a large volume of flocs and form a layer of sediment easily washed from the surface of the membrane, greatly reducing the deposition of the membrane. However, coagulation and flocculation systems along with the current membrane filtration are mainly used in raw water treatment with low turbidity [12]. Purification of water through coagulation and flocculation using low-pressure MSRs has not been completely investigated so far. In addition, the use of air bubble injection near the membranes increases shear stress and reduces the need for energy and thus, turbulence required to control and remove particles from the membrane surface will have a positive effect [13]. This method shows a better positive and significant effect to increase infiltration flux over a long filtration period. Bilad et al. [14] studied the use of low-pressure submerged membrane filtration for the potential reuse of detergent and water from laundry wastewater. They found that low ΔP as low as 0.05 bars offered the highest permeability of $297 \pm 15.3 \text{ L m}^2/\text{h bar}$ without significant membrane fouling. Increasing ΔP leads to a decreasing trend in permeability especially in the early stages of filtration. Aeration was found to be effective in enhancing hydraulic performance by 60% at rates $>1 \text{ L}/\text{min}$, below which it offers an ineffective foulant scouring effect. Guigui et al. [15] investigated the effect of coagulation in the simultaneous process of flocculation and ultrafiltration on the treatment of surface water. They indicated that this process could also be used in low-quality water treatment so that, the amount of treated water and membrane deposition was significantly reduced compared to the usual state (no use of flocculation). Their results showed that the use of coagulation and flocculation before ultrafiltration increases the quality of diffusion and the removal rate of dissolved organic matter is controlled by the coagulation step. Xiangli et al. [16] studied the role of pretreatment (coagulation and flocculation) in the treatment of lake water by a pressurized ultrafiltration system and they found that the use of coagulation and flocculation process as a pretreatment not only produced high-quality drinking water from lake water with different turbidity levels, but infiltration flow flux from the pressurized membrane was about $190\text{--}200 \text{ m}^3/\text{m}^2 \text{ h}$ and period of chemical descaling of the membranes were greatly prolonged.

In the present study, the effect of using ferric chloride coagulant along with the flocculation agents of polyelectrolyte and lime is investigated in water treatment with different turbidity and total organic carbon (TOC) levels using MSR (without pressure) for simultaneous coagulation, flocculation, and membrane filtration.

2. Materials and methods

2.1. Jar test

In this study, for water treatment with different turbidity levels (10, 50, 100, 200, 500, and 1,000 NTU), first, parameters of optimal pH and contents of ferric chloride coagulant and flocculation agents of polyelectrolyte and lime and also their effect on turbidity removal process were evaluated by Jar test. For preparing water with different turbidity levels, clay was cut into small particles after sieving in a mortar. Then, it was weighed by a Sartorius Practum 213-1S scale with 0.001 g of accuracy and was dissolved in water. After half an hour of settling, its surface water was used as a solution to prepare various water turbidities. Diluted turbidity solutions were prepared from this stock solution using distilled water [17]. Then, half a liter of the test sample with certain turbidity was poured into all 6 beakers of the Jar test device and the parameters of pH, optimal contents of coagulants and flocculation agents were measured as process response.

In the first step, for determining optimal pH, the Jar test was performed using the solution with 10 NTU of turbidity. For this purpose, 500 mL of the solution with 10 NTU of turbidity was added to the first to sixth beakers. Then, pH level was adjusted at values of 5, 6, 7, 8, 9, and 10 by HACH HQ40 multimeter. ferric chloride coagulant with a specific concentration of 5 mg/L was added to the first to sixth beakers. Then, the sample was placed under the DAIHAN WiseStir JT-M6 Jar test device and fast mixing was performed at 120 rpm for 1 min followed by slow mixing at 30 rpm for 10 min. After gentle mixing, the sample was kept at rest for 30 min to be deposited and a sample was taken from each of the beakers and turbidity of the sample was measured using a WTW Turb 355 turbometer. This test was repeated for the solution with 50 NTU of turbidity to confirm the test results. After determining optimal pH, in the next step, optimal content of coagulant materials was identified at different turbidities. Jar tests were performed in the range of 1–50 mg/L of ferric chloride in the presence of optimal pH obtained for turbidity levels of 1000, 500, 200, 100, 50, and 10 NTU according to the mentioned method to determine optimal ferric chloride content for the mentioned turbidity values. For determining the effect of polyelectrolyte flocculation agents and investigating their effect on turbidity removal percentages in the presence of optimal content of ferric chloride and optimal pH at two turbidity levels (50 and 10 NTU), Jar test was done using polyelectrolyte concentrations of 0.1, 0.3, 0.5, 0.7, 1, and 2 mg/L. In the last stage of Jar tests in turbidity removal, the flocculation agent of lime was investigated. Having obtained optimal content of ferric chloride and optimal pH at different turbidities from previous Jar tests, simultaneous addition of flocculation agents (lime and polyelectrolyte) in the presence of optimal main coagulant content (ferric chloride) was investigated.

Different concentrations of lime and polyelectrolyte were determined at 0.5, 1, 3, 5, 10, and 15 mg/L and also at 0.1, 0.3, 0.5, 0.7, 1, and 2 mg/L, respectively, to identify the lowest concentration of lime and polyelectrolyte flocculation agents (optimal content) among them for removing turbidity. So that, 6 stages of testing for each of turbidity

levels and a total of 36 stages of testing were performed. First, a concentration of 0.5 mg/L of lime was used in the presence of concentrations of 0.1, 0.3, 0.5, 0.7, 1, and 2 mg/L of polyelectrolyte. Similarly, in the remaining 6 stages, other concentrations of lime were combined in the presence of the specified concentrations of polyelectrolyte and ferric chloride at optimal pH in the Jar test to determine optimal content of ferric chloride along with polyelectrolyte and lime at the highest turbidity removal percentages.

Jar test experiments were continued to remove the TOC with different concentrations of water turbidity of 10, 50, and 100 NTU. A useful standard for TOC testing is Potassium hydrogen phthalate (KHP) [12]. KHP made by the German company MERCK was prepared at the concentrations of 1, 3, and 5 mg/L, and Jar test were performed at turbidity values of 10 to 100 NTU to evaluate TOC removal rate by ferric chloride coagulant optimization and polyelectrolyte as flocculation agent. TOC concentrations were measured using SM5910 B Ultraviolet Absorption method with DR/6000 spectrophotometer made by HACH Company in the United States. Samples were analyzed for UV absorbance at 254 nm. Light absorbance at 254 nm, which is associated with the aromatic groups in NOM, is used as a surrogate parameter for monitoring the concentration of TOC in a fast and easy manner during water treatment [18].

2.2. MSR tests

MSR was designed for coagulation and flocculation, simultaneous sedimentation, and membrane filtration and was made by Rashab Tarh Company with technical specifications shown in Table 1. Coagulation and flocculation process was used as a batch system based on optimal contents of coagulants and flocculation agents at different turbidity levels

Table 1
Technical specifications of MSR

| Pilot technical specifications | | |
|------------------------------------|---|-----|
| Dimensions (cm) | L | 78 |
| | W | 20 |
| | H | 50 |
| | Thickness | 0.5 |
| Material | Plexiglass | |
| Membrane volume (L) | 35 | |
| Height (cm) | 7 | |
| Dimensions of membrane plates (cm) | L | 35 |
| | W | 25 |
| | Thickness | 1 |
| Membrane material | PESU with 0.04 μ of pore size | |
| Type and number of air blowers | 7 deep tubular aerators of large bubbles | |
| Air supply source | HAILEA ACO-308 model of air pump | |
| Pressure gauge | Vacuum pressure in suction and membrane fouling | |

obtained along with membrane filtration. The parameters of flux, turbidity and TOC removal (%), content of iron during coagulation and flocculation process and in the purified water output and type of membrane fouling in water treatment with different turbidity levels were also investigated. In the MSR, the total content of iron was measured by a HACH DR/6000 spectrophotometer in coagulation and flocculation process (before flow into the membrane) and after membrane

filtration process as the mentioned spectrophotometer has the ability to measure iron in the range of 0.3–3 mg/L [19].

After determining optimal content of ferric chloride along with polyelectrolyte and lime by Jar test for different turbidity levels, the experiments continued in the MSR (Fig. 1). At first, water with different turbidity levels was prepared at proportional volume of the reactor according to the previous instructions and was poured into the reactor.

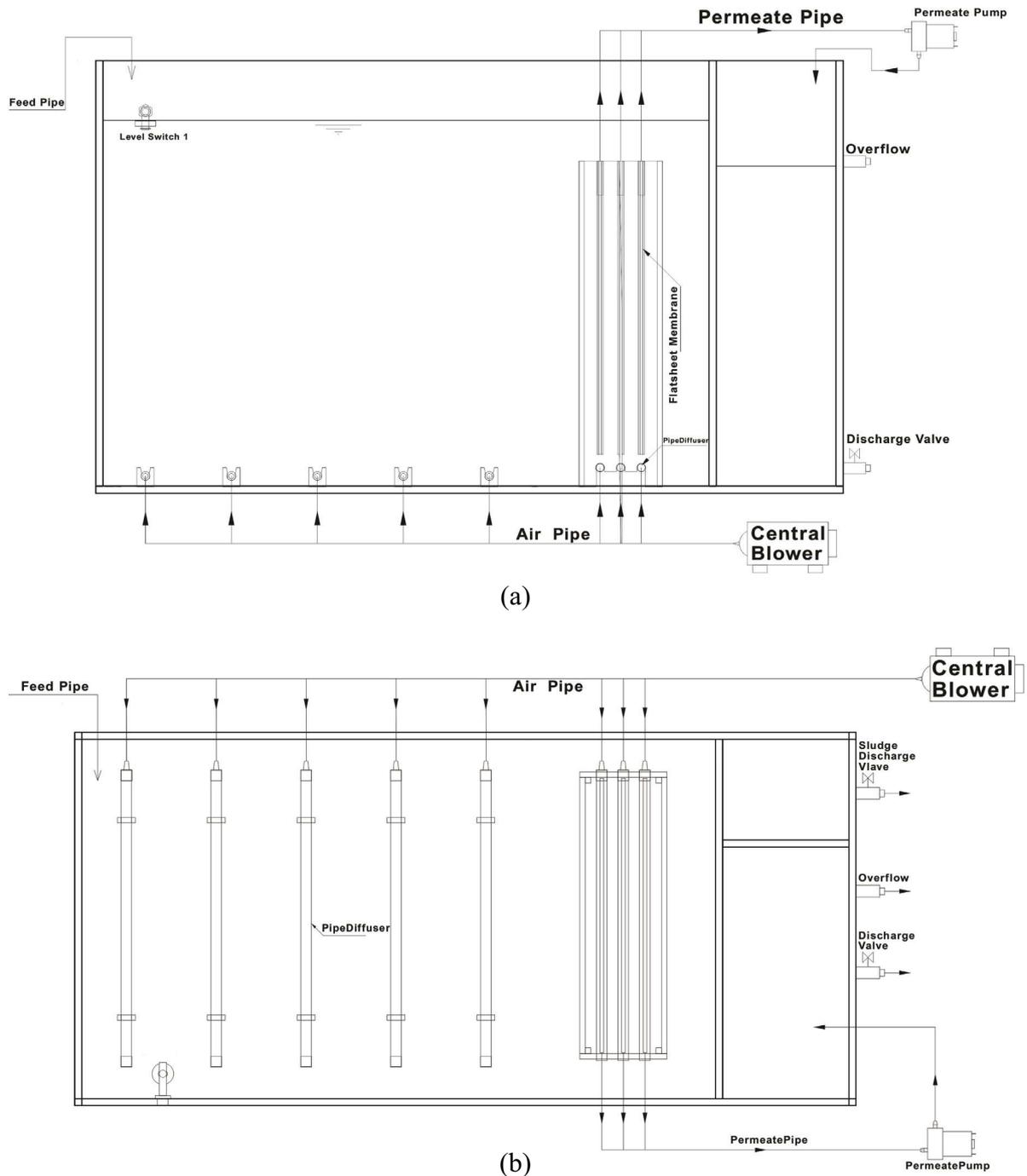


Fig. 1. Schematic of the MSR: (a) View from the front of the pilot and (b) view from inside the pilot.

Then, coagulation, flocculation, and membrane filtration processes were performed to evaluate performance of the membrane reactor in water treatment.

Experiments were performed with different water turbidity levels (10, 50, 100, 200, 500, and 1,000 NTU). In the following, the removal of TOC (1, 3, and 5 mg/L) in turbidity levels (10, 50, and 100 NTU) were also investigated. Water with the desired turbidity (NTU) and TOC (mg/L) was prepared based on volume of the membrane and was poured into the reactor. Then, the air pump was turned on and simultaneous with rapid mixing in the reactor containing optimal content of ferric chloride, proportional amount of flocculation Agents obtained for the desired turbidity and TOC of the Jar test was added to the water.

At this stage, the considered materials were mixed with water for 1–2 min (rapid mixing stage) to mix the coagulants well with water and, complete disintegration occurred. Then, the amount of air for slow mixing step was reduced by air regulating valves. Slow mixing step continued for 10 min until the flakes from coagulation stage were formed and were slowly coarsened (slow mixing step). In the last stage, the air was cut off to determine the amount of input turbidity after clotting at inlet to the membranes.

In the last stage, the water was adjusted by 3 suction pumps installed for each flat sheet membrane in a constant flux (100 mL/min) to determine and analyze the final output turbidity, membrane flux rate, membrane fouling rate, and the related parameters by comparison of diagrams. For measuring flux, membrane filtration was performed first with distilled water then, flux was measured at appropriate intervals at each turbidity level and was calculated according to Eq. (1),

$$J = \frac{Q}{A} \quad (1)$$

where J is the flux of the treated water, Q is the flow of outlet water, and A is the cross-section of the membranes.

For determining flux curve over time, flux was measured at short intervals and these intervals were increased over time. After 8 h of membrane filtration and cutting off filtration flow, the membranes were reversely washed with clean water. Thus, the surface of the membranes was first washed by establishing airflow. Then, water was introduced in the opposite direction and was rinsed with city tap water for 1–2 min to open fouling pores. The percentage of membrane fouling was calculated using Eq. (2), where the J_{initial} is the maximum flux flowing through the membranes and J_{final} flux is the effluent of the treated water.

$$\% \text{Flux removal} = \frac{(J_{\text{initial}} - J_{\text{final}})}{J_{\text{initial}}} \quad (2)$$

Finally, percentage of turbidity and TOC removal was calculated by Eqs. (3) and (4).

$$\% \text{Turbidity removal} = \frac{\text{Turb}_{\text{initial}} - \text{Turb}_{\text{final}}}{\text{Turb}_{\text{initial}}} \quad (3)$$

$$\% \text{TOC removal} = \frac{\text{TOC}_{\text{initial}} - \text{TOC}_{\text{final}}}{\text{TOC}_{\text{initial}}} \quad (4)$$

where $\text{Turb}_{\text{initial}}$ and $\text{TOC}_{\text{initial}}$ are the turbidity and TOC of the coagulated flow before entering the membranes and $\text{Turb}_{\text{final}}$ and $\text{TOC}_{\text{final}}$ are the final turbidity and TOC of the flow in the filtered outlet water.

3. Results and discussion

3.1. pH

The results of the Jar test regarding determining optimal pH are shown in Fig. 2 at turbidities of 10, 50, 100, 200, 500, and 1,000 NTU. As observed, the highest percentage of turbidity removal belonged to a pH level of 8, which was selected as optimal pH. Fig. 3 also showed that the highest percentage of TOC removal in constant turbidity of 10, 50 and 100 NTU was in the pH range of 7–8.

The results showed at low pHs, the amount of H^+ ions increases, which acts as a competitor to the positive ions of organic compounds, thus reducing the removal of organic compounds [13]. The pH of the feed solution is an important factor influencing the permeability of ultrafiltration membranes, especially with polyelectrolytes. For example, polyacrylic acid with ultrafiltration membranes is often well excreted at pH levels around 5 and above, but is quite permeable through the same membranes at pH levels around 3 and below. This desorption behavior with a change in pH is due to a change in the structure of the polyacid. In membranes with a polyethersulfone (PESU) structure, ultrafiltration membranes have the best performance typically at neutral pH, as confirmed in this study. Guigui et al. [15] investigated the effect of coagulation and flocculation with ferric chloride in membrane water treatment systems. In Jar tests, a pH range of 5–8 was tested, with pH = 7.5 having the highest removal percentage at turbidity level of 24.5 NTU and dissolved organic carbon concentration of 54 mg/L. In another study, Xiangli et al. [16] used coagulation and flocculation as pre-treatment in surface water, which led to the best-reported pH level in removing turbidity and organic matter from water, which is consistent with the results of this study

3.2. Optimal content of ferric chloride coagulant

Fig. 4 shows the percentage of turbidity removal at different contents of ferric chloride in the Jar test. According to Fig. 4, the content of the consumed coagulant was naturally increased by increasing turbidity level.

Optimal content of ferric chloride coagulant for turbidity levels of 1,000, 500, 200, 100, 50, and 10 NTU was equal to 5, 5, 7.5, 10, 15, and 20 mg/L, respectively. For determining optimal content of ferric chloride coagulant, not only removal percentage was considered, but also other factors, such as the appearance of the formed flocs and sedimentation rate of its use were also evaluated. As shown in Fig. 4, at turbidity levels of 500 and 1,000 NTU, the amount of coagulant consumption reached 15 and 20 mg/L, which was twice the amount used at 200 NTU of turbidity. Also, increasing coagulation concentration increased removal percentage, especially at a high turbidity level of 200 NTU, which can be attributed to the increase in the level of turbidity and colloidal materials such that,

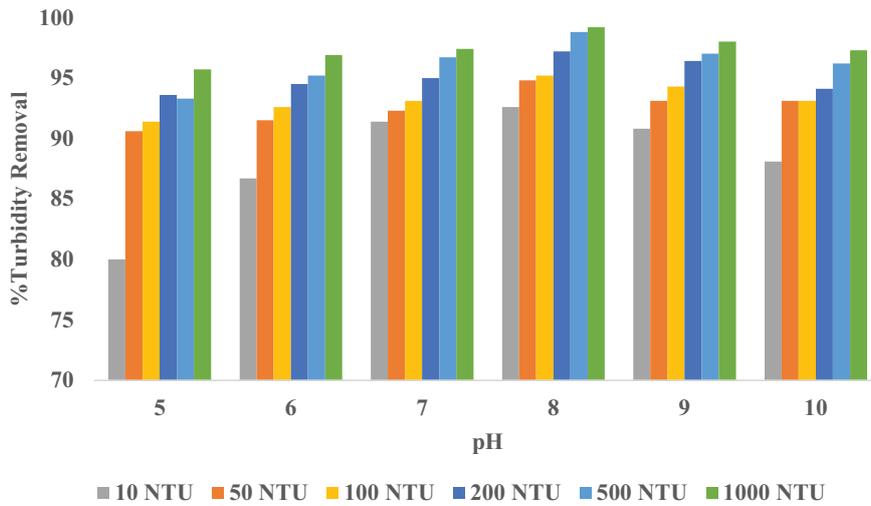


Fig. 2. Determination of optimal pH by Jar test in 10, 50, 100, 200, 500, and 1,000 (NTU) turbidity.

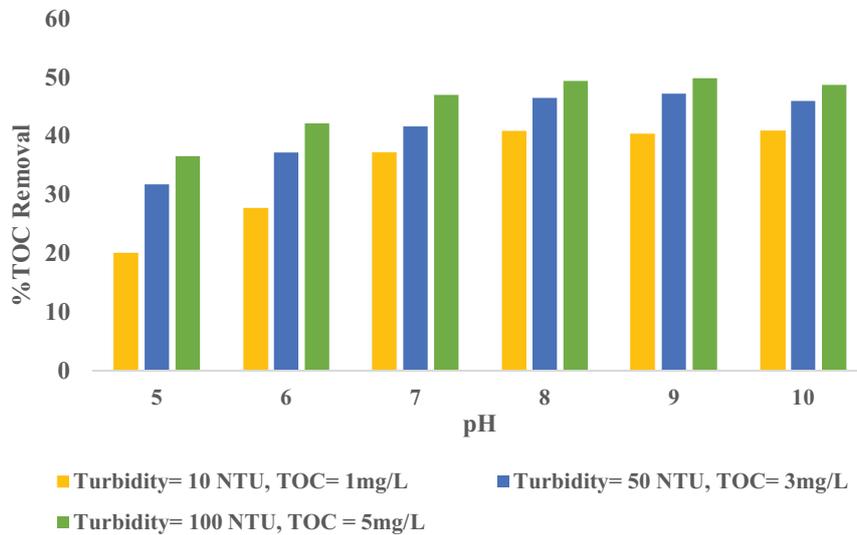


Fig. 3. Determination of optimal pH by Jar test in the simultaneous removal of turbidity (NTU) and (mg/L).

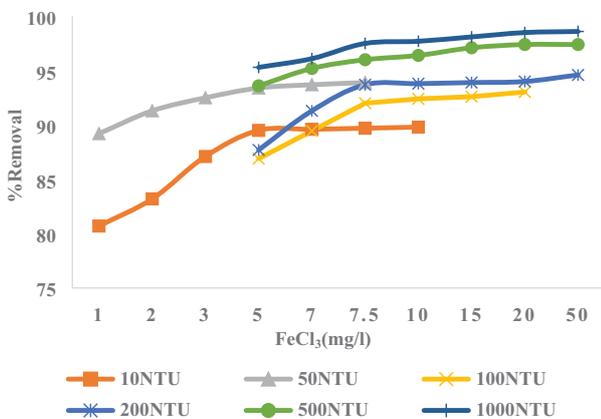


Fig. 4. Results of Jar test for turbidity 10, 50, 100, 200, 500, and 1,000 (NTU) in determining the optimal concentration of FeCl₃ coagulant.

the amount of particles colliding with each other was more during the process of coagulation and flocculation, and more and heavier flocs were formed [20].

Fig. 5 shows TOC removal percentages at the turbidity of 10, 50, and 100 NTU in the presence of different ferric chloride concentrations. The results of Jar test experiments showed that the presence of organic matter along with the turbidity had little effect on the optimal determination of coagulant, and the results obtained are consistent with the turbidity tests alone. At the turbidity of 10 NTU, the highest percentages of TOC removal at the concentrations of 1, 3, and 5 mg/L were 39%, 43%, and 45%, respectively, which occurred in 5 mg/L ferric chlorides. Furthermore, at the turbidity of 50 NTU, the removal percentages at the concentrations of 1, 3 and 5 mg/L of TOC were reported at 42, 47, and 51, respectively, and at the turbidity of 100 at the same concentrations 45%, 50%, and 54% in 10 mg/L of ferric chloride, respectively. Although by increasing the concentration of coagulant, the removal percentages of TOC have increased,

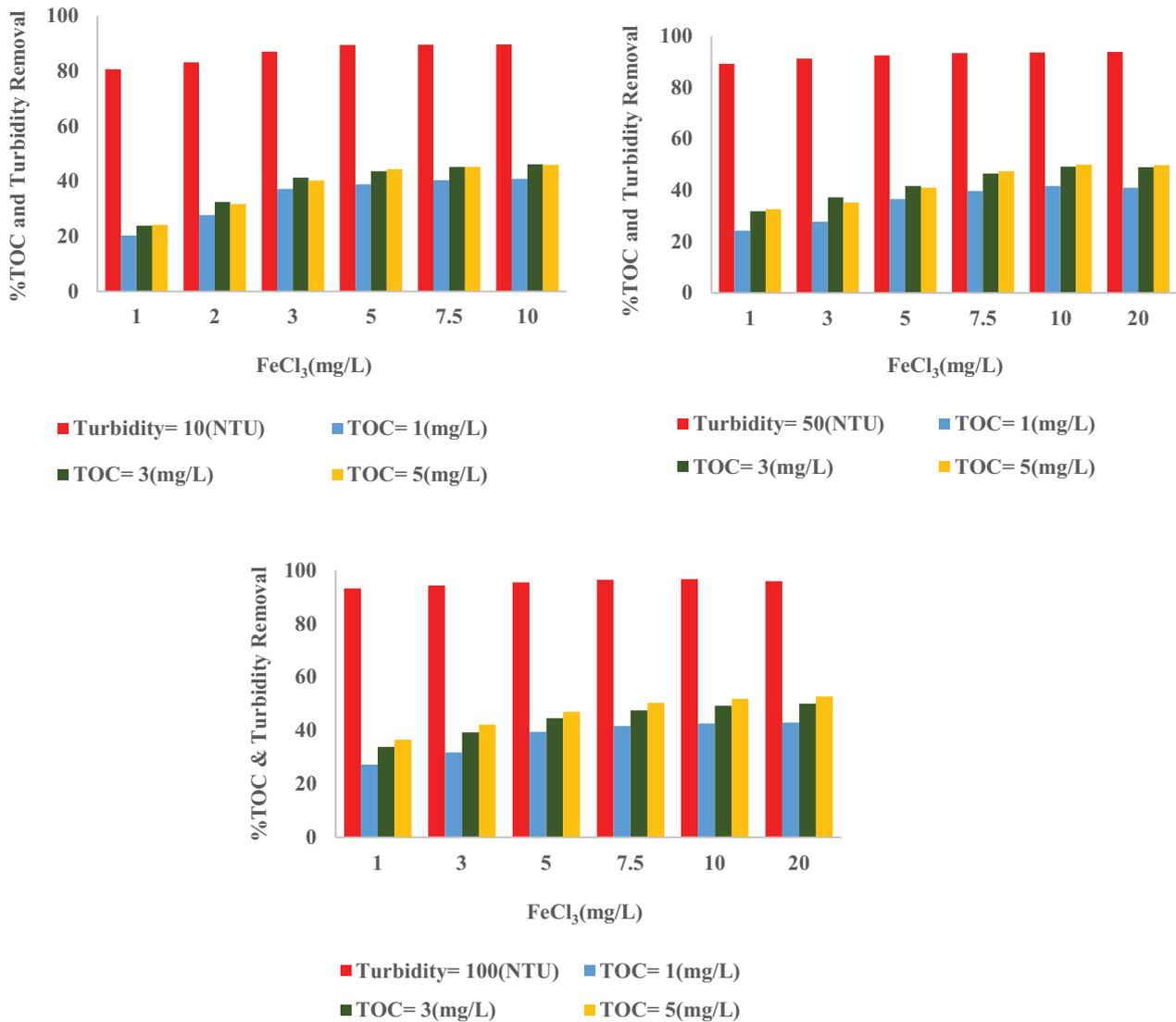


Fig. 5. Results of Jar test experiments to determine the optimal ferric chloride concentration in the simultaneous removal of turbidity (NTU) and TOC (mg/L).

this increase has been about 1%, and the removal percentage has become constant even at the turbidity of 10 NTU. In general, Fig. 5 shows that the TOC removal percentage has also increased by increasing turbidity. Considering the low amount of colloidal material and colloidal core sites at low turbidity rates, the complex of soluble metal ions and functional groups present in the organic matter will form very small flocs. The absence of large and heavy flocs as a result of lack of flocs sedimentation limits TOC removal [16]. For this reason, by increasing turbidity from 10 to 100, the removal rate of different TOC concentrations has also increased.

3.3. Optimal concentrations of polyelectrolyte and lime with ferric chloride

Jar tests were performed to determine the optimal content of polyelectrolyte and lime using the optimal amount

of ferric chloride. Table 2 presents the results obtained from the Jar tests. As expected, the highest removal percentages occurred at high concentrations of polyelectrolyte and lime by increasing turbidity levels.

Fig. 6 shows the diagrams for removal of different turbidities to determine the optimal concentration of polyelectrolyte and lime by Jar test (Table 1 summarizes the results). The results showed that using lime and polyelectrolyte increased turbidity removal percentages but this increase was not significant (1%–3%). Notably, turbidity removal percentage was decreased from the specified optimal value so that, at all turbidities, after addition of lime and polyelectrolyte and increasing percentages of their removal and optimal determination, increasing concentrations of lime and polyelectrolyte not only had no effect on increasing removal percentage, but it also reduced it, which can be due to turbidity caused by the addition of lime and

Table 2

Optimal results of Jar test for turbidity 10, 50, 100, 200, 500, and 1,000 NTU in determining the optimal concentration of FeCl_3 coagulant with lime (CaO) and PE

| Turbidity (NTU) | pH | Optimal FeCl_3 (mg/L) | Optimal PE (mg/L) | Optimal CaO (mg/L) | %Removal |
|-----------------|----|--------------------------------|-------------------|--------------------|----------|
| 10 | 8 | 5 | 0.1 | 1 | 91.3 |
| 50 | 8 | 5 | 0.1 | 3 | 94.1 |
| 100 | 8 | 7.5 | 0.3 | 5 | 95.2 |
| 200 | 8 | 10 | 0.3 | 5 | 96 |
| 500 | 8 | 15 | 0.5 | 10 | 98.8 |
| 1,000 | 8 | 20 | 0.7 | 10 | 99.5 |

polyelectrolyte itself. At turbidity level of 1000 NTU in the presence of ferric chloride, polyelectrolyte, and lime, (at concentrations of 20, 0.7, and 10 mg/L, respectively), 99.5% of removal was obtained, which did not happen at other turbidities. The results of the Jar test showed that the presence of lime and increasing its content caused the environment to become alkaline (the coagulation and flocculation environment reached a pH level of 8) and helped to remove turbidity. As a result, there was no need to adjust pH and the lime itself acted as a pH adjuster and caused the pH level to be adjusted between 7.5 and 8. The results are consistent with the research conducted by Ahangari et al. [21] who investigated the effect of coagulants on membrane fouling in the pre-reverse osmosis effluent treatment process. In the reverse osmosis coagulation process, salts of aluminum sulfate, aluminum chloride, ferrous sulfate, and ferrous iron chloride were used to treat synthetic effluents before entering the membranes. The results showed that the best performance in the coagulation process was related to ferrous sulfate with lime at a concentration of 100 ppm, confirming the results obtained in the present study. Also, Neamati et al. [22] in another study entitled “The Effect of Chemical Coagulation Process and Increasing Lime Concentration on Improving Quality of Effluent from Stabilization Ponds of the Kashan University of Medical Sciences” investigated the effect of different flocculation agents and lime on improving quality of effluent from stabilization ponds of the Kashan University of Medical Sciences (Kashan, Isfahan Province, Iran). The effect of three coagulants including alum, ferric sulfate, and ferric chloride along with lime at different doses on factors, such as turbidity and suspended solids was investigated and analyzed by Jar test. The highest removal percentage was related to ferric sulfate at a dose of 20 mg/L, with 94.5% and 92.1% of removal for suspended solids and turbidity, which is consistent with the results obtained in the present study, and the iron-based coagulant had better performance.

Fig. 7 shows the diagrams of the removal percentage results of different TOC concentrations at the turbidity of 10, 50, and 100 NTU to determine the optimal concentration of polyelectrolyte in the presence of optimal ferric chloride by Jar test. The results showed that polyelectrolytes increased TOC removal by 2%–8%. The optimal polyelectrolyte in the simultaneous removal and different concentrations of TOC and constant turbidity of 10, 50 and 100 NTU was reported at 0.1, 0.5, and 0.7 mg/L, respectively. By increasing turbidity and polyelectrolyte concentration, TOC removal

percentages also increased, so that at the turbidity of 100 and concentration of 5 mg/L, TOC in the presence of optimal ferric chloride (10 mg/L) and polyelectrolyte (1 mg/L), percentage of TOC removal has increased by 8%–61%. This is due to the presence of more colloidal and flocculation agent particles which have contributed to the formation of ionic complexes on a surface of organic matter [12].

3.4. Removal of turbidity and TOC by MSR

MSR experiments were performed on the simultaneous removal of turbidity and TOC. Fig. 8 shows the removal percentage of TOC and turbidity according to the operating time of membranes at the turbidity of 10, 50, and 100 NTU at the TOC concentrations of 1, 3, and 5 mg/L in the presence of optimal ferric chloride coagulants and polyelectrolytes. In general, the results showed that the removal percentages of TOC have also increased by increasing turbidity and TOC concentration. During 8 h of membrane operation, the removal rate of TOC and turbidity was almost constant. The highest percentage of TOC removal by MSR occurred at the turbidity of 100 NTU and TOC 5 mg/L (72%). This is while the lowest percentage of TOC at the turbidity of 10 NTU and TOC of 1 mg/L is equal to 46%. Therefore, it can be said that the natural turbidity of water provides a ready source of colloidal core sites for flocs formation, and if such a source is available, these flocs act as sites to absorb the soluble NOM [23]. The removal of turbidity and TOC by ferric chloride and polyelectrolyte can be attributed to the groups obtained by the hydrolysis of FeCl_3 and polyelectrolyte. When the ferric chloride is added to aqueous solutions, it is hydrolyzed to $\text{Fe}(\text{OH})_2$, Fe^{3+} , $\text{Fe}(\text{OH})_3$ groups at the optimal pH, which according to research the most dominant species among these are in the pH range from 7 to 8 and $\text{Fe}(\text{OH})_2$ [22]. As a result, by trapping colloidal organic particles in the flocs as well as simultaneous membrane filtration, they remove the turbidity and TOC from the water. In the case of low-turbidity waters, such sites are necessary to form a flocs-forming site which is provided by increasing the coagulant concentration.

3.5. Flux

Flux is a very important factor in determining the condition and operation of the membranes. Membrane fouling can be predicted and reverse rinsing time of the membranes can be estimated by obtaining flux changes.

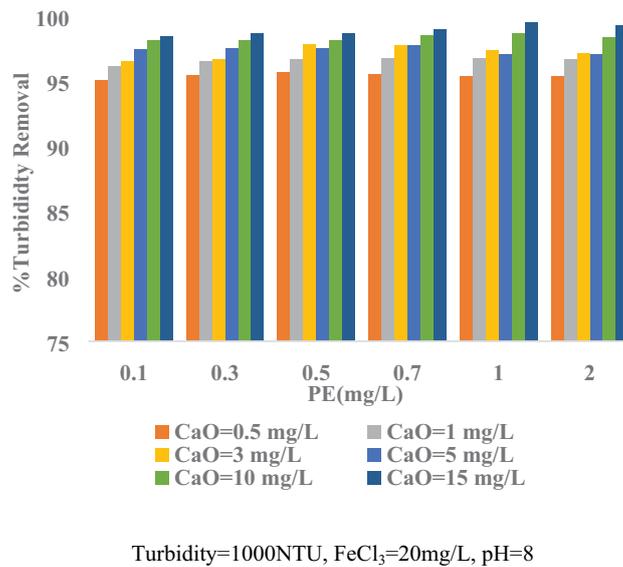
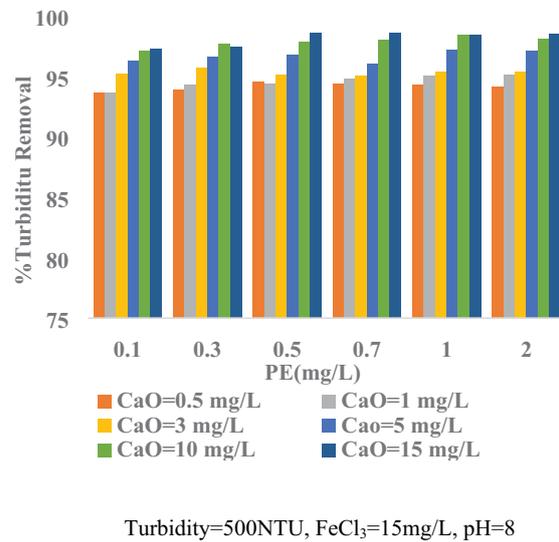
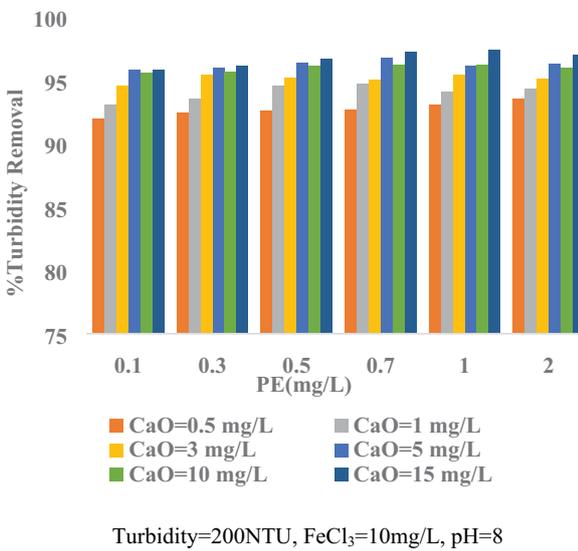
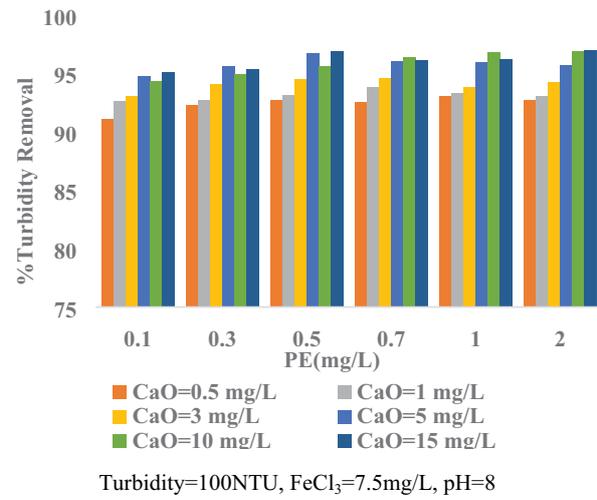
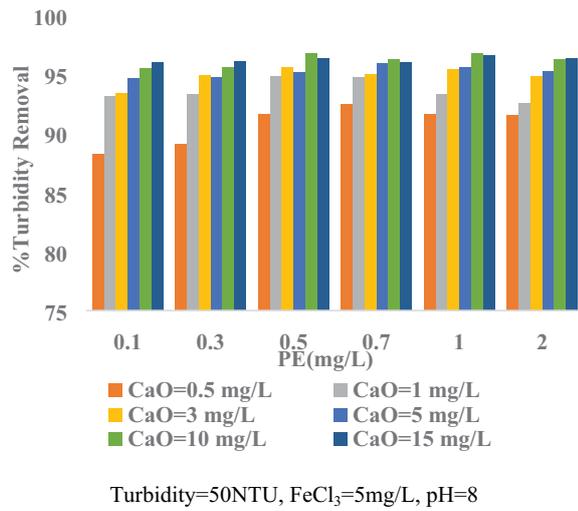


Fig. 6. Percentage removal diagrams of different turbidity to determine the optimal concentration of PE and CaO (in the presence of optimal FeCl₃ and pH = 8).

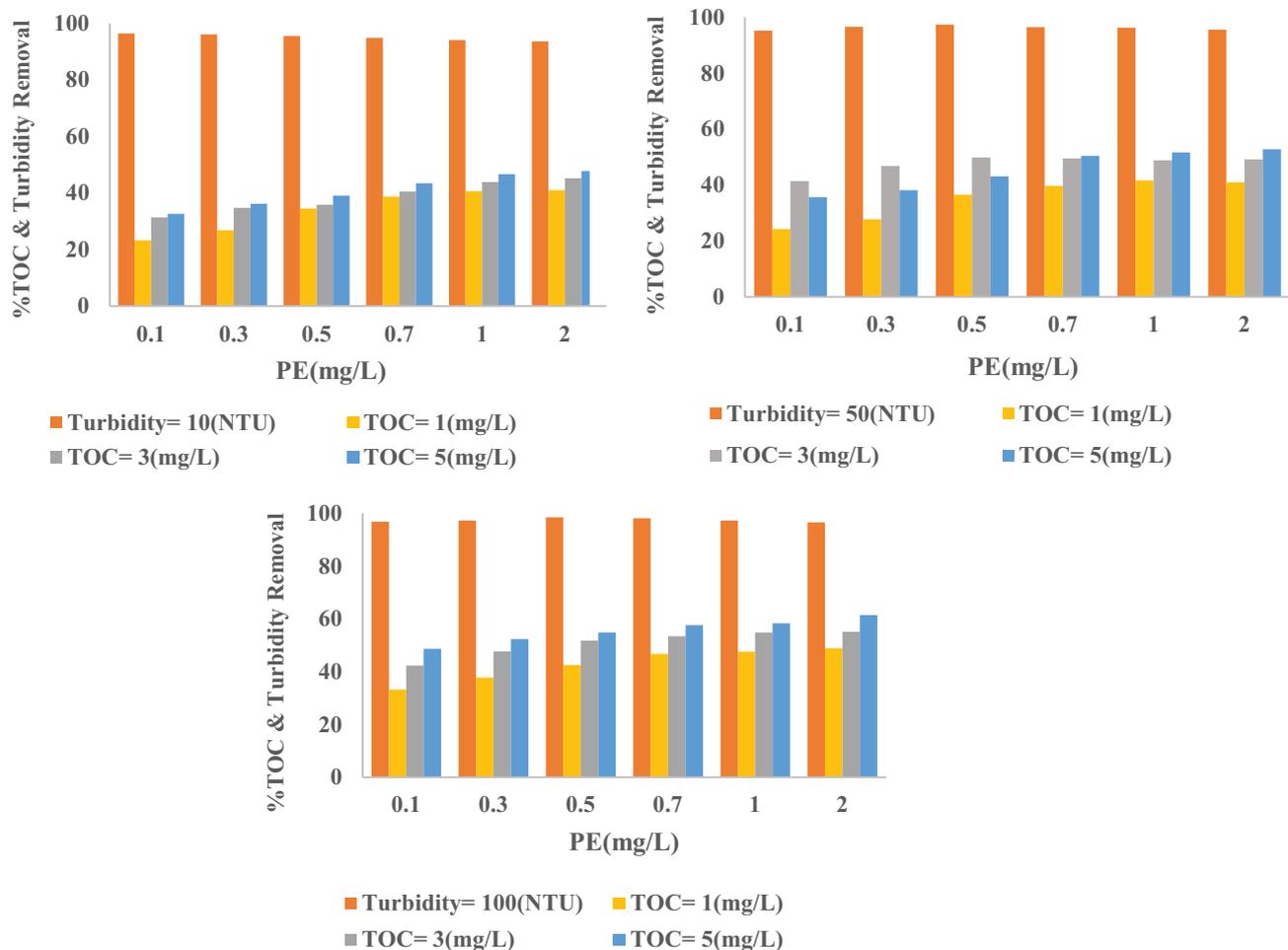


Fig. 7. Results of Jar test experiments to determine the optimal concentration of polyelectrolyte in the simultaneous removal of turbidity and TOC (in the presence of optimal ferric chloride, pH = 8).

For obtaining changes in flux at various turbidity values, the membrane filtration process was continued for different turbidities at a constant output flow rate (100 mL/min for each membrane), and the changes in output water flow rate from the membranes were regularly measured during 8 h. Fig. 9 shows flux changes with respect to the membranes operation time at different turbidities in the presence of ferric chloride coagulant along with lime and polyelectrolyte. As depicted in Fig. 9, flux was decreased slightly over 8 h at turbidity values of 10 and 50 NTU and reached from the maximum flow rate of 40 L/m² h to about 39.5 L/m² h and good performance of the membrane filtration process was observed in the removal of low turbidity in the presence of ferric chloride coagulant with polyelectrolyte and lime.

Flux reduction was started from 100 NTU of turbidity during the desired period so that, after 8 h, flux was decreased by 49%, 38%, 17%, and 15% at turbidities of 1,000, 500, 200, and 100 NTU, respectively. Flux reduction occurred with more slope at turbidities of 1,000 and 500 NTU, indicating accumulation of sediments on the membrane surface. As flux is decreased, feed pressure or circulating feed rate is increased to compensate for lower flux or a larger surface area of the membrane is used, and the system is stopped

when the flux is greatly reduced, the membranes are washed and cleaned by air, and the process begins again. Also, turbidity removal percentages were constant and equal to 99.5% in the membrane filtration test. The results of the present study are consistent with those of the study entitled "Investigation of Drinking Water Treatment by the Pressurized Ultrafiltration System and Its Application in China" where different water samples with different characteristics were tested by membrane ultrafiltration, but the applied reactor was under pressure. Flux diagram was plotted at 20, 110, and 450 NTU of turbidity within 60 min, and the obtained flux reduction was similar to the results obtained using MSR [23]. Also, in another study entitled "Optimization of Operating Conditions in an Ultrafiltration Membrane System", the performance of the ultrafiltration system by the polymer membrane was evaluated under optimal conditions and total suspended solids (TSS), turbidity, and TOC were tested. The results showed a 98% removal at 90 NTU of turbidity and a 56% reduction in flux over 480 min, which is consistent with the results obtained in this study using MSR [24]. In a study, Baptista et al. [25] investigated the role of natural coagulants in removing turbidity from water by submerged ultrafiltration. They found

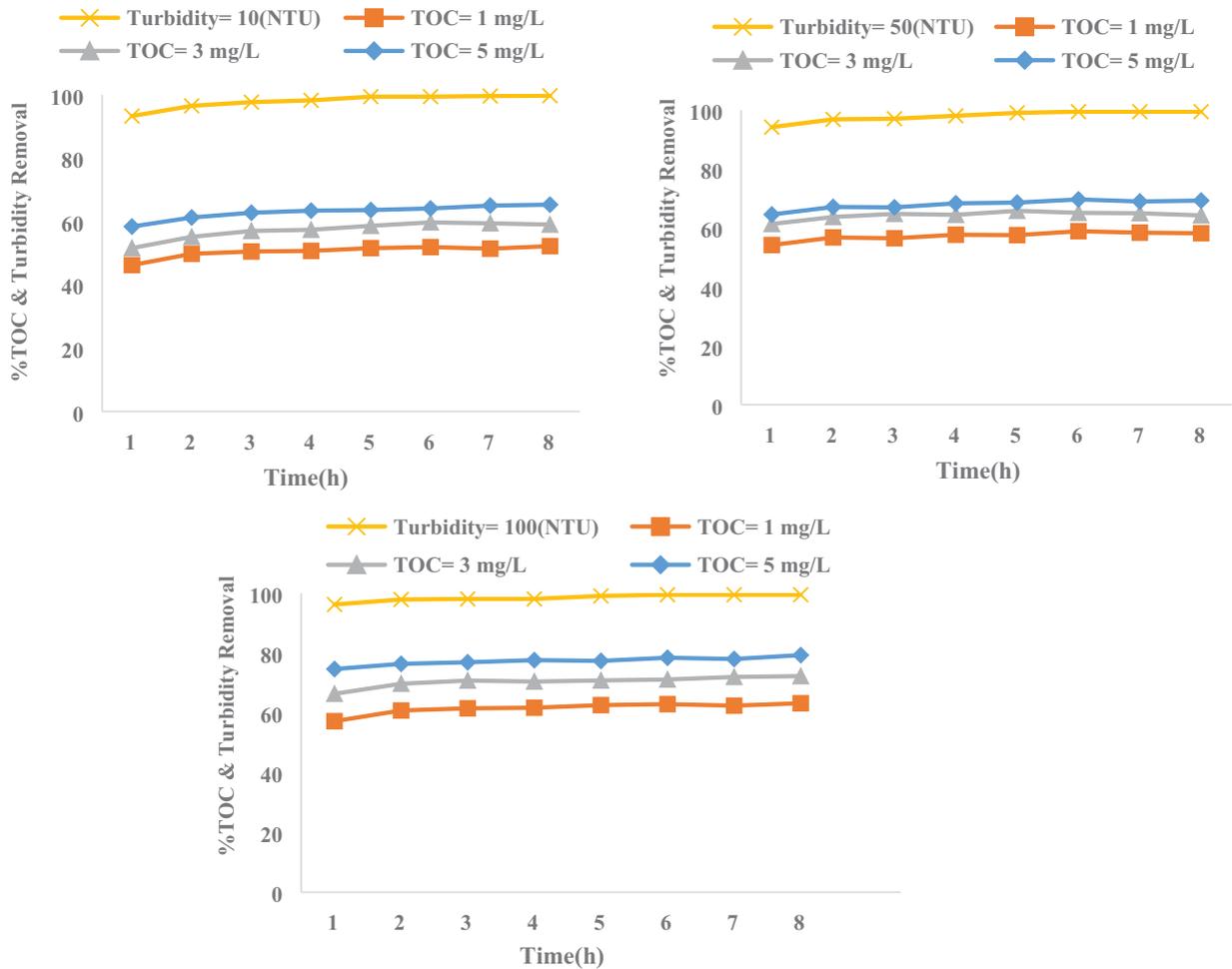


Fig. 8. Turbidity and TOC removal (%) vs. operation time (in the presence of optimal ferric chloride and polyelectrolyte, pH = 8).

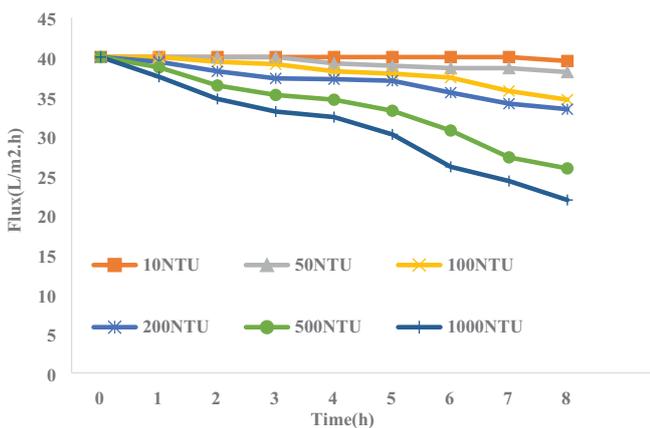


Fig. 9. Flux changes vs. operation time in different turbidities (in the presence of optimal FeCl₃, CaO and PE, pH = 8).

that removal percentage was more than 98% at 68 NTU of turbidity and the flux decrease occurred by 50% after one h of operation time. However, due to the lack of pressure in the MSR, the flux drop was achieved by 50% at 1000 NTU of turbidity and the time for flux drop was longer.

Fig. 10 shows the flux changes due to the operating time of MSR pilot operation at different turbidity and different TOCs with the optimal presence of ferric chloride coagulant with polyelectrolyte. However, the results showed the removal percentages of TOC increased by increasing turbidity and TOC concentrations; hence, there was a further decrease in flux so that at turbidity of 100 NTU and a concentration of 5 mg/L of TOC after 8 h, flux decreases by more than 27%. One of the main problems to remove the soluble NOM from water samples is the inability to create a flocs that can be easily deposited which was done in the presence of turbidity in the process of coagulation and flocculation along with the membrane filtration [7]. Compared to the turbidity results alone (Fig. 9), the presence of organic matter reduced the flux further (12%). However, the greatest reduction in flux is less than 50% which is acceptable after 8 h of membrane operation. The most important reasons for postponing the clogging of membranes include; (1) not using pressure in membrane filtration and (2) the determining role of coagulation and flocculation before the membrane filtration.

In experiments performed on a MSR, the initial pressure applied along the membrane is very low and about

zero at initial times. Over time, membrane filtration causes a flux drop due to the formation of a gel-like layer as a result of surface deposition of residual solutes on the membrane surface. Fig. 11 shows the membranes used in the experiments in the clean and fouling state. This gel layer forms a secondary barrier against the flow through the membrane, thus the pressure required for flux survival is increased. When flux is decreased, a membrane filled with surface sediment is considered. In this study, the reverse membrane washing method was performed using aeration on the surface of ultrafiltration flat sheets and also reversed clean water flow for 1–2 min, to remove membrane surface deposits and adhesion forces at any turbidity.

The flux of pure water was equal to 20 L/m² h in the ultrafiltration membranes used for each flat sheet membrane. When membranes were used to separate macromolecular

or colloidal solutions of clay particles, flux was decreased with time and it reached about 8 L/m² h in approximately 10 h at 1000 and 500 NTU of turbidity. Flux drop was only by 20% after 10 h until turbidity of 100 NTU.

As mentioned in Section 3.1, solution pH is an important factor in ultrafiltration membrane fouling. At pH = 8 (optimal), due to the process of coagulation and flocculation, heavy and large flakes of clay particles are formed along with ferric chloride, polyelectrolyte, and lime creating a gel-like layer of clay so that, in this study, it was excreted by periodically cleaning the membrane and the cleaned membrane was re-exposed to the solution at different turbidity levels. Another important point is the type and shape of the clay particle molecule, which has a multifaceted structure and it is not able to move in a spiral way through cavities

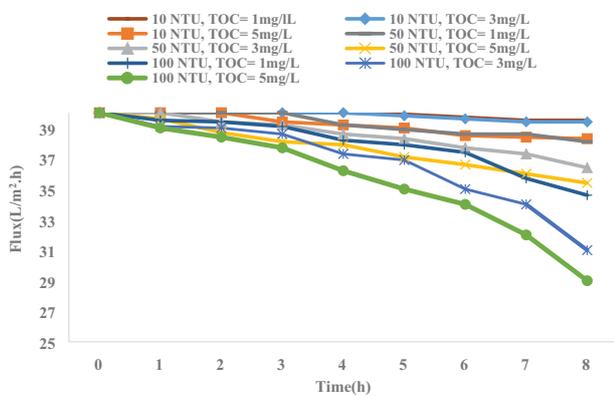


Fig. 10. Flux changes vs. operation time at different turbidity values and TOCs (in the presence of optimal ferric chloride and polyelectrolyte, pH = 8).

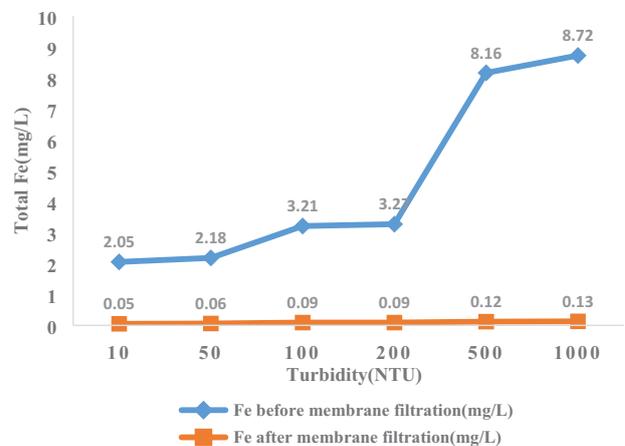


Fig. 12. Changes in the amount of total Fe in the flocculation stage and after membrane filtration in different turbidity.

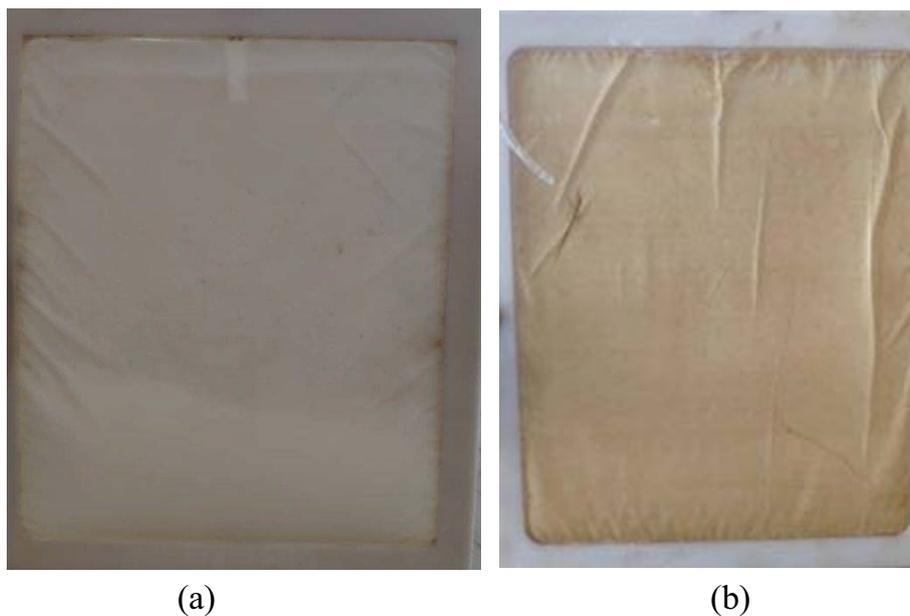


Fig. 11. Ultrafiltration flat sheet membrane used in MSR pilot. (a) Membrane in a clean state and (b) membrane in fouling condition and surface sediments.

Table 3
Comparison of MSR pilot operation results with similar research

| Source of water (Feed) | System/membrane type | Steady-state permeability (Lm ² /h) | %Turbidity removal | Membrane fouling | Ref. |
|--------------------------------|--|--|--------------------|--|------|
| Water with different turbidity | Coagulation, flocculation + LP submerged ultrafiltration (MSR) | 50–60 | 99.9 | Without significant membrane fouling | - |
| Industrial laundry | Combined coagulation, flocculation, sedimentation and UF | 12.5–92.2 | 99.1 | Use of coagulants reduces membrane fouling | [29] |
| Sewage contains detergents | LP submerged ultrafiltration | 297 ± 15.3 | 97 | Without significant membrane fouling | [14] |
| Industrial wastewater | Coagulation + MF | 160–450 | 98 | Improved contaminant removals, decreased fouling | [30] |
| Surface water | Coagulation + UF | 120 | - | Use of coagulants reduces membrane fouling | [15] |
| Surface water | Pressurized UF | 190 | 98 | Irreversible fouling in the long time operation | [31] |

of the membranes. However, other particle molecules with a linear structure, such as polydextran molecules of similar size can pass through the membrane cavities and cause irreversible fouling [26]. Particle charge is another important factor. Many colloidal materials including clay have a negative charge due to having carboxyl, sulfonic, or other acidic groups. Considering the fact that most membranes have a negative surface charge, adhesion of the colloidal gel layer to the membrane is reduced, helping to maintain high flux and prevent surface deposition of the membrane, and a positive charge has adverse effects on the membrane surface [27]. Accordingly, the membranes in this study were retested after backwashing in the experiment. Failure to reduce the maximum (initial) flux at each test showed that the membrane fouling was in the form of surface sediment and flux reduction has not been permanent.

3.6. Changes in total Fe concentration

The solution dilution method was used to measure the total iron content. According to Fig. 12, the total iron output from the membrane at different turbidities ranged from 0.05 to 0.1, which was the highest utilization rate of ferric chloride. According to the standards, the content of iron in drinking water should not exceed 0.3 mg/L [28]. As a result, membrane filtration has the ability to remove iron from an aqueous medium.

4. Conclusion

In this study, the role of ferric chloride and polyelectrolyte flocculation agents was investigated in the coagulation and flocculation process using the MSR for water treatment. Table 3 summarized the main results of the study and were compared them with others in this field.

The results of the Jar test showed that ferric chloride coagulant had a good performance for removing turbidity from water, due to high removal percentages (more than 90% alone) and type of the formed flocs and sludge. Also,

the application of lime and polyelectrolyte caused a 3% increase in turbidity removal percentages. The pH level of 8 was also selected as optimal pH with the highest percentage of turbidity and TOC removal. Coagulation and flocculation process with membrane filtration in the presence of optimal contents of coagulants and flocculation agents at turbidity less than 100 NTU had the best performance in terms of flux so that, flux drop occurred by only 15% within 8 h of operation time and reached from 40 to 36 L/m² h. While, at high turbidity of 200 NTU, flux reduction was up to 50% and reached 21.9 L/m² h. After increasing the operating time of membranes, turbidity removal percentages were constant and higher than 99.5%. The highest percentage of TOC removal by MSR occurred at the turbidity of 100 NTU and TOC 5 mg/L (72%). The results showed that the removal percentages of TOC have also increased by increasing turbidity and TOC concentration; hence, there was a further decrease in flux so that at turbidity of 100 NTU and a concentration of 5 mg/L of TOC after 8 h, flux decreases by more than 27%. The total removal rate of iron by membrane process was more than 99% and the type of membrane fouling was surface sediment with reversibility. Pretreatment with coagulation not only improved the treated water quality, but also enhanced membrane performance, that is, the permeate flux increased and flux decline was reduced. Our results showed that MSR combined with coagulation and flocculation can be used as an efficient and flexible method to treat water with different turbidity levels from water sources.

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