Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2019.23793

148 (2019) 60–69
April

Use of coagulation-ultrafiltration membrane continuous system for treatment of wastewater containing silica nanoparticles

A.H. Konsowa[a], M.G. Eloffy[a,c,*], W.A. Ibrahim[b], Y.A. El-Taweel[a], O.E. Abdelwahab[c]

[a]*Chemical Engineering Department, Faculty of Engineering, Alexandria University, Alexandria, Egypt, Tel. +201222162806, email: akonsowa@alexu.edu.eg (A.H. Konsowa), Tel. +201226150501, email: manal_eloffy@yahoo.com (M.G. Eloffy), Tel. +201222220102, email: ytawil20@gmail.com (Y.A. El-Taweel)*
[b]*Sanitary Engineering Department, Faculty of Engineering, Alexandria University, Alexandria, Egypt, Tel. +201001679698 email: welbarki76@gmail.com (W.A. Ibrahim)*
[c]*National Institute of Oceanography and Fisheries, Alexandria, Egypt, Tel. +201221093161, email: olaabdelwahab53@hotmail.com (O.E. Abdelwahab)*

Received 17 April 2018; Accepted 10 January 2019

ABSTRACT

This present work investigated the use of membrane filtration in conjunction with coagulation process for improving the removing of nano-sized materials from wastewater with low cost of energy and high removal efficiency. A continuous coagulation-flocculation-sedimentation (CFS) pre-treatment process - hollow fiber ultrafiltration membrane (HF-UFM) system was designed and carried out to evaluate the treatment efficiency of wastewater containing silica nanoparticles (SiO_2NPs). Synthetic wastewater containing different concentrations of SiO_2 NPs was used to estimate the efficiency of this system. Furthermore, different kinds of coagulants were used for the treatment process respectively, cationic polymer (Magnafloc LT31), anionic polymer (Magnafloc10), and inorganic polymer (Dynafloc30). Coagulant dosages and pH values were controlled. Turbidity and concentrations of SiO_2 NPs were measured before and after each stage. Flux and transmembrane pressure were followed and measured during the treatment process. It is clearly seen that, chemical coagulation was found to be effective for turbidity and concentration removal of SiO_2 NPs by using of Magnafloc LT31 and Dynafloc30. Filtration process was enhanced to a significant degree. According to the result values of experimental work, the efficiency of SiO_2 NPs removal reached 100 % when the initial concentration of SiO_2NPs was equal to 10 mg/l. The efficiency of removal increased dramatically at pH values from 4 to 7. The results involved the efficient improvement of coagulation pretreatment on UF membrane filtration expressed in the permeate flux and trans-membrane pressure (TMP) consequently, the decrease of required energy for treatment process was nearly 10 times lower than the use of conventional nano-filtration process.

Keywords: Wastewater treatment; Impact of engineered nanomaterials; Ultrafiltration membrane; Silica nanoparticles; Coagulation process

---

1. Introduction

Nowadays, nanotechnology is considered as a new revolution in science and technology. Nano-scale particles and colloids have always been part of our environment [1]. It plays an essential role in the development of innovative methods to produce new products, substitute existing production equipment and reformulate new materials and chemicals with improved performance resulting in less consumption of energy and materials and reduced harm to the environment as well as environmental remediation [2]. These products created a high interest by virtue of their unusual mechanical, electrical, optical and magnetic properties. It is inevitable that nano-scale products and

---

*Corresponding author.

by-products will reside at some level in our recreational and drinking waters [3]. From accidental spillages or permitted release of industrial effluents, nanoparticles could accumulate into the human body via skin contact, inhalation of water aerosols, direct ingestion of contaminated drinking water, or indirect exposure from ingestion of vegetables and aquatic organisms such as fish, molluscs and crustaceans as a part of the human diet [4,5]. The most essential nanoparticles used for common products are metallic nano-oxides (SiO_2, ZnO, CeO_2, Al_2O_3, TiO_2, etc.). Nano-silica is the common name for materials composed of nano-silicon dioxide (SiO_2) and occurs in crystalline and amorphous forms. Today, nanoparticles of SiO_2 are already produced in very large quantities, it is a multi-functional ceramic material that is used in various industries to improve surfaces and mechanical properties of diverse materials. It is used as a filler, performance additive, rheological modifier or processing aid in many products formulations, such as paints and coatings, plastics, synthetic rubber, adhesives, sealants, or insulation materials. A particular silica fume (amorphous silicon dioxide) or micro-silica is added to concrete in order to improve the concrete strength and durability. Silica fume is also used in refractory concretes to reduce porosity and to improve the bond strength of the paste-aggregate interface. In addition, nano-silica is developed for a host of biomedical and biotechnological applications such as cancer therapy, DNA transfection, drug delivery, and enzyme immobilization [6,7].

Recently, the impact of nano-silica on basic biology, medicine, and agro-nano-products are reviewed. With the growing commercialization of nanotechnology products, human exposure to SiO_2NPs is increasing, and many aspects related to the size of these nano-materials raised concerns about safety [8]. The unique physico-chemical properties of nano-sized silica make them attractive for industry may present potential hazards to human health, including an enhanced ability to penetrate intracellular targets in the lung and systemic circulation.

The important issue is the development of specific treatments (e.g. coagulation, flotation or filtration) and suitable additives (if necessary) for water containing nano-particles. Recently, [9] Bizi (2012) investigated the coagulation and flocculation of SiO_2NPs by some organic polymers. The development of a three-stage system for the treatment and reclamation of wastewater containing nano-scale particles was studied by B.M. Yang (2011) [10].

In recent years, membrane filtration technologies were studied and applied to improve the quality of reclaimed water [11]. Compared to traditional physical/chemical treatment methods, membrane processes have the advantages of improving water quality, conserving space, saving chemical dosage, reducing sludge, and selectively eliminating physical, chemical, and micro-biological contaminants from wastewater [12,13]. One of the major problems in pressure-driven membrane processes is the reduction of the permeate flux due to membrane fouling, resulting in increased operating costs, so nanofiltration (NF) membrane technology cannot be applied for the purification of nano-scale particle-containing wastewater due to membrane fouling/clogging problems. In this study, ultrafiltration membrane was applied instead of nano-filtration membrane to decrease the trans-membrane pressure (TMP). Furthermore, the application of coagulation /flocculation as a pre-treatment process was studied to control the fouling of ultrafiltration membrane and enhance the efficiency of filtration process [14–17].

2- Materials and methods

2.1 Materials

2.1.1 Characterization of nano-particles containing wastewater

The silica nano-particle suspension used was supplied by NanoTech Egypt for Photo-Electronics. It is marketed under the name (NT-SiO_2 NP). A sequential method was used, to prepare mono-disperse and uniform-size silica nanoparticles (>50 nm) using ultra-sonication by sol–gel process, where the silica nanoparticles were obtained by hydrolysis of tetraethyl ortho-silicate (TEOS) in ethanol medium. Other specifications are: surface area (200 m^2/g) and moisture content (<1.5% of water). Size and shape of SNP were further characterized by JEOL JEM-2100 high resolution transmission electron microscope (TEM) at an accelerating voltage of 200 kV. The TEM clearly showed that, the silica NPs average size is > 50+10 nm with spherical-like shape (Fig. 1a) for disperses SiO_2 NPs; (Fig. 1b) for aggregated SiO_2 NPs.

The image of silica NPs was carried out by scanning electron microscopy (SEM) (Figs. 2a, b) show the image of SiO_2 NPs before and after coagulation process.

The mean particle size and zeta potential distributions (ZPDs) were determined by dynamic light scattering technique using a Zetaseizer Nano ZS from Malvern Instrument, using a dilute suspension of nanoparticles in deionized water (Figs. 3 a, b).

Nanoparticle solution used for particle size determination was prepared by adding 5.0 mg SiO_2 NPs into 1 L DDI water. The solutions were sonicated and stirred for 60 min to disperse the NPs. Zeta potential of SiO_2 NPs was measured using Malvern Zetaseizer ZS, it was found of - 50.9 (mV), this result means that the stability of nanoparticle is fairly good as shown in Fig. 4.

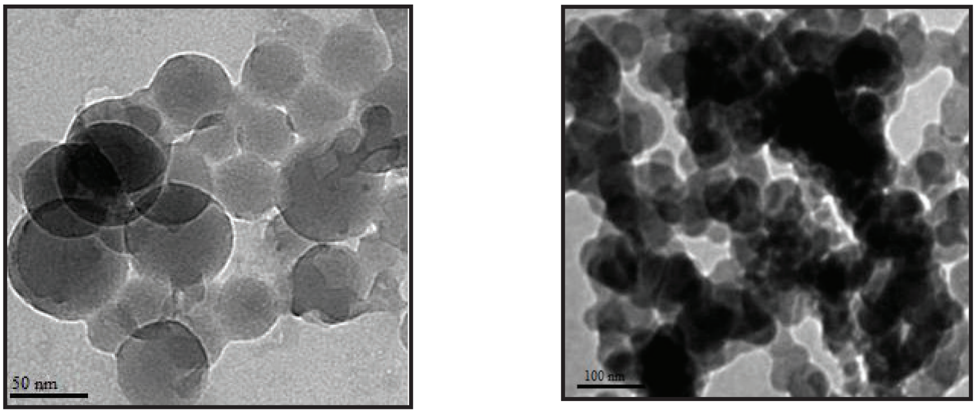
The FTIR analysis was carried out to study the characteristic spectral bands of prepared nano-silica by sol–gel process using Perkin-Elmer 400 FTIR in the wavenumber region between 4000 and 500 cm^{-1} (Fig. 5).

2.1.2. Specifications of membrane unit

The experiments were performed using ultrafiltration hollow fiber membrane (UF-HFM). The UF membrane was made of polyvinyl chloride (PVC) with a total surface area of 0.125 m^2 and molecular weight cut–off (MWCO) equals 50000 Dalton.

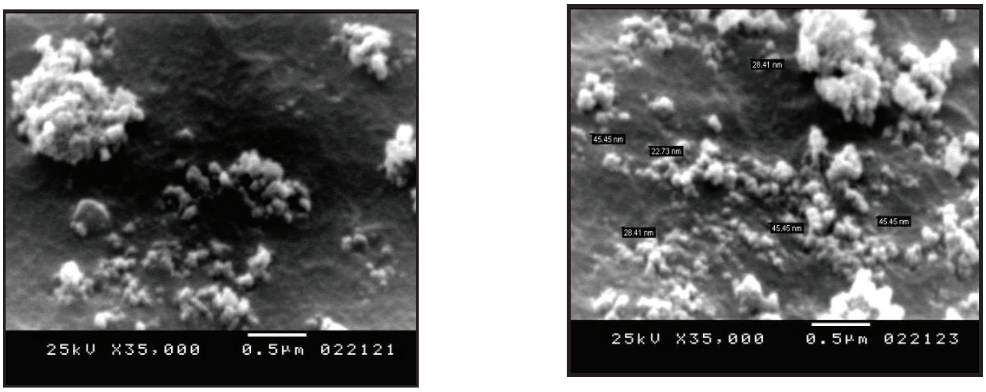
2.1.3. Physiochemical properties of coagulants:

Physical and chemical properties of the coagulants were provided by the producer (BASF SE Company for Chemicals, Germany) and are summarized in Table 1.



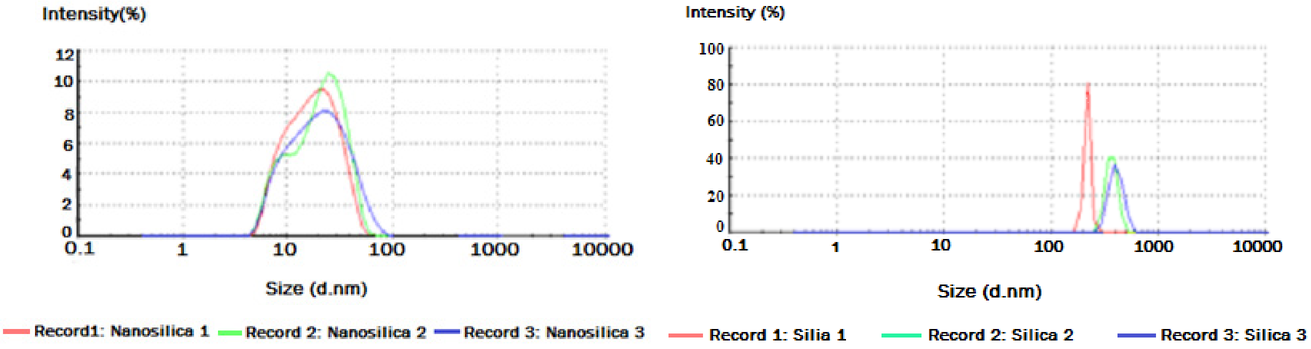
(a) Dispersed SiO_2 Nanoparticles (b) Aggregated SiO_2 Nanoparticles

Fig. 1. a, b Transmission electron microscope (TEM) image for silica NPs.



(a) Dispersed SiO_2 Nanoparticle (b) Coagulated SiO_2 Nanoparticle

Fig. 2. a, b Scanning electron microscopy (SEM), image for silica NPs.



(a) (b)

Fig. 3. a, b. Mean particles size distribution before and after coagulation process.

2.2. Experimental set-up

A schematic diagram of the experimental setup is illustrated in Fig. 6. In this system, effluent from the wastewater treatment plant containing SiO_2NPs was first pretreated by coagulation/Flocculation system followed by UF membrane module.

The following flow direction was used for the treatment process: feed tank (influent) → pump → clarification tank → sedimentation tank → peristaltic pump → pressure gauge → UF-HF membrane module → flow meter → effluent tank. All tubing materials that were used in contact with solution were made of Teflon.

Water samples from sedimentation tank and from the system outlets were collected and analyzed for water quality. This system was operated in continuous-feed mode. Flows and pressures were controlled by adjusting the feed, recycle of concentrate, and permeate valves.

2.2.1. Procedures

- In this study, wastewater containing different concentrations of silica NPs was used to evaluate the effectiveness of this proposed process for the removal of nano-scale particles. Wastewater containing silica NPs was prepared by dispersion of the nanoparticles in distilled water in the concentrations of 10, 20, 30, 40, 50, and 60 mg/l, respectively.

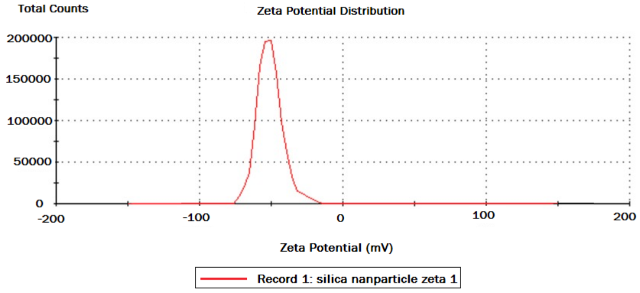


Fig. 4. Zeta potential distribution of SiO_2 NPs.

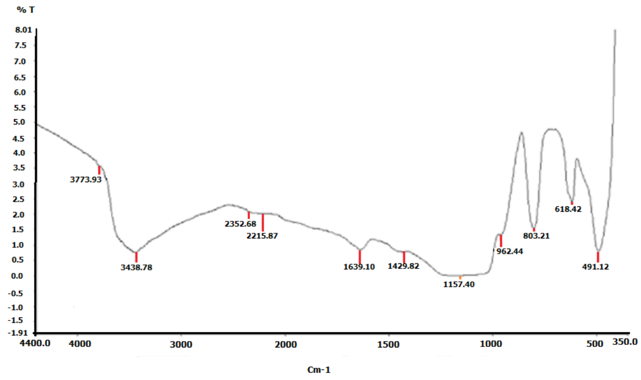


Fig. 5. FT-IR spectroscopy of SiO_2 NPs.

- Jar tests were used successfully to optimize coagulant dosages, pH and concentration of SiO_2NPs. Three coagulants were used: (a) Anionic polymer (Magnafloc 10), (b) Inorganic polymer (Dynafloc30), and (c) Cationic polymer (Magnafloc LT31).
- The optimum dose of coagulants was added directly to the continuous feeding tank of wastewater to neutralize the charges on dispersed non-settable particles while applying a rapid mechanical stirring for 30–60 s, and a medium and slow stirring for the flocculation and clarifier tanks, then the flow was moved to the sedimentation tank, for one hour until the UF system was applied (Fig. 7). After membrane filtration process, the membrane was backwashed by distilled water and chemically cleaned with 0.1% by weight NaOH solution.
- The time needed for coagulation process was estimated to be 30–60 s at 200 rpm mechanical mixing, 30 min for clarification process at 30 rpm, and 60 min for sedimentation process. All these times were controlled by the design equations of tanks and the pump capacity. The concentration of SiO_2 was determined by Molybdosilicate standard method (4500-SiO2 C) [18]. The pH values were controlled by using HCl (1 N), NaOH (1 N). The residual turbidity was estimated using Hach 2100 laboratory turbidity meters and the residual amount of SiO_2NPs was estimated by using spectrophotometer after each stage, the efficiency of coagulation process and the efficiency of the total process were calculated to determine the effect of each process of the treatment process.

2.3. Ultrafiltration performance tests

In the ultrafiltration tests: TMP varied within the range of 0.2–0.6 bar, flow rate varied within the range of 5 to 10 L/h, and temperature varied within the range of 25 ±1°C. Summary of permeability results of the new membrane unit showed in Table 2. In all the performed UF experiments, TMP, and temperature were kept constant during the entire

Table 1
Physical and chemical properties of the coagulants

Items	Magnafloc LT31	Dynafloc30	Magnafloc10
Appearance	Clear viscous liquid	Powder	Powder
Chemical nature	Polyelectrolytes, cationic		Polyacrylamide, anionic
Color	Colorless to yellow	Yellow	Off-white
Solids content	Nominally 50%	–	–
Specific gravity	Approx. 1.2		Approx. 0.70
pH as supplied	Approx. 4.5–6.5	6–9	6.5
Viscosity as supplied	Approx. 400–600 cps		2500–4900 cps
Solubility in water	Infinitely soluble	Infinitely soluble	Forms a viscous solution
Freezing point °C	Approx. –3°C		Ignition temperature: 350°C
Freeze thaw stability	Good	Good	Good

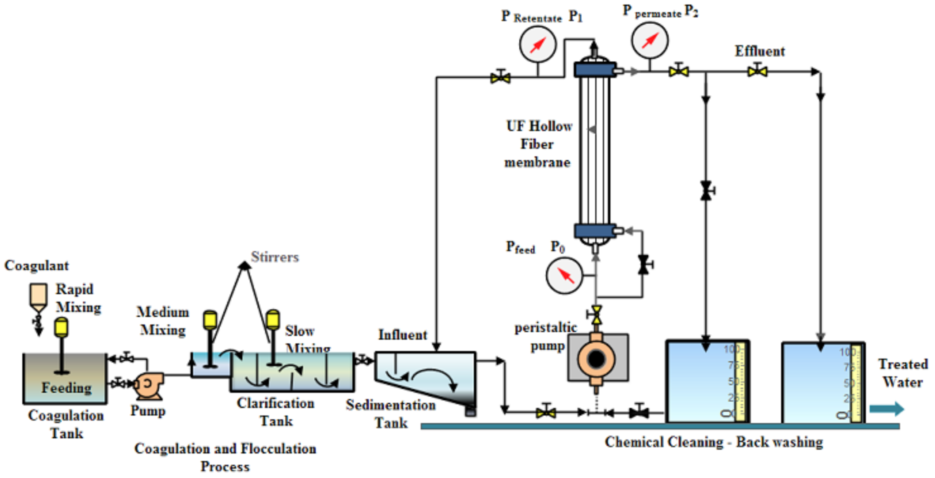


Fig. 6. Schematic diagram of pre-treatment coagulation/flocculation/UF-HF membrane system.

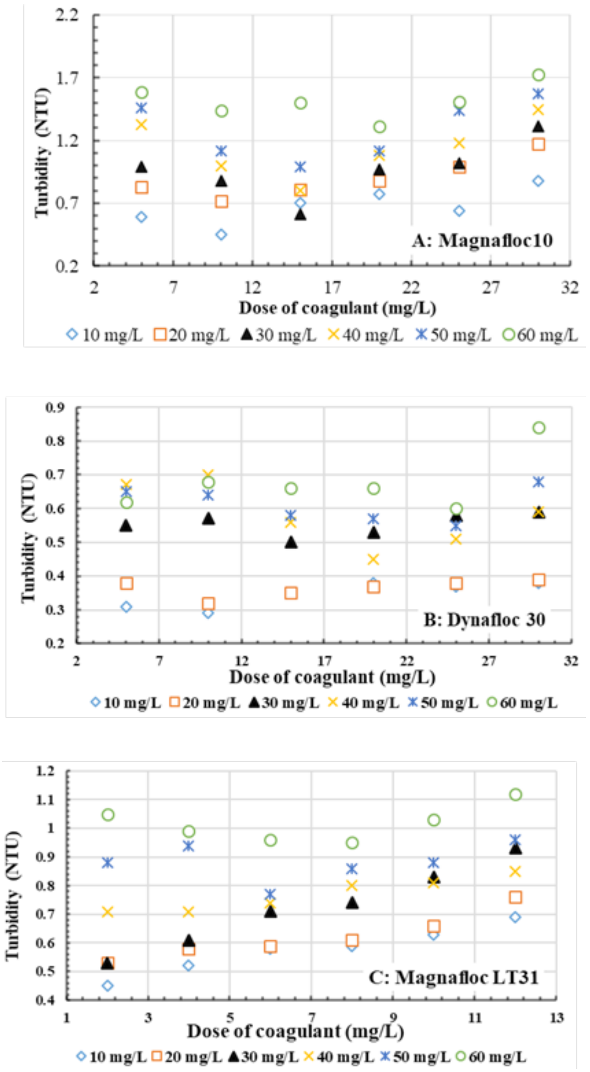


Fig. 7. Effect of coagulant dose on the turbidity for different initial concentrations of SiO_2NPs using (a) Magnafloc10, (b) Dynafloc30 and (c) MagnaflocLT31.

run. The schematic diagram of the experimental setup is shown in (Fig. 6). It consists of two circuits: one for the circulation of the feed solution and the other one for the circulation of the cleaning solution.

2.4. Membrane cleaning protocol

The transportation properties of the unused membrane was tested using deionized water under constant operating conditions to determine the water flux (J_w) and time to compare them with the values of flux after using the membrane. The fouled membrane was cleaned using the following steps: (1) Rinsing with distilled water (30 min); (2) Cleaning with an aqueous NaOH solution of 0.1% by weight in distilled water, pH 11 for 3 h; (3) Rinsing with distilled water (30 min). Once the cleaning process was finished, the water permeability of the membrane was measured using distilled water at a temperature of 25°C, a TMP of 0.6 bar. The results showed that the initial permeability of the membrane was nearly recovered after the cleaning cycle.

3. Results and discussion

The use of coagulation as a pretreatment alternative to improve the performance of membrane filtration process for nano-materials removal from wastewater was studied with cross-flow ultrafiltration membrane filtration apparatus. Various processes and operating conditions of the treatment process were examined, including coagulant type and dosage, pH, and trans-membrane pressure. The results were highly positive and the coagulation/flocculation/sedimentation (CFS) process improved the performance of filtration process and reduced the flux decline by decreasing the fouling of the membrane.

3.1. Coagulation and flocculation system

3.1.1. Determination of the coagulats dose

The description of the effect of different doses of different polymers on turbidity removal from wastewater at dif-

Table 2
Summary of permeability results of the new membrane unit

Test parameter	Value
Feed pressure (P_f), bar.	0.4
Permeate pressure (P_p), bar.	0
Concentrate pressure (P_c), bar.	0.45
Trans-membrane pressure (*TMP*), $TMP = \left(\frac{P_f + P_c}{2} - P_P\right)$; bar	0.425
Flow rate (*Q*), (L/h)	11.8
Area of membrane (A_m) m^2.	0.125
Specific flux, initial permeate flux (J_o), ($J_o = Q/A_m$) L/h·m^2	94.4
Specific permeability (*SP*), $SP = J_{o/}TMP$; L/h·m^2·bar.	222.1
Membrane resistance (R_m), $R_m = \left(\frac{TMP}{J_{dw}}\right)$; 1/m	$4.5*10^{-3}$

ferent initial concentrations of SiO_2NPs is shown in Figs. 7a, 7b, and 7c. It can be clearly observed that with different types of coagulants and different concentrations of SiO_2NPs, the turbidity gradually decreased with the increase of the coagulant dose and started to upward trend again. The minimum value of turbidity corresponds to the optimal dose of coagulants. As the presented results in the figures, the optimum doses were found respectively; 11, 10 and 6 mg/l for Magnfloc10, Daynafloc30 and Magnafloc LT31. Turbidity removal was not increased when higher doses of coagulants were added. This might be due to the fact that the excess coagulant caused a re-stabilization of the suspension [19].

3.1.2. *Effect of pH value on turbidity of wastewater*

SiO_2NPs are stable at pH > 9 and the decrease in size beyond pH 9 is due, to some extent, to the compression of the diffuse double layer and, considerably, to a partial solubility of the particles. These NPs that have a very small diameter and a high surface tension are therefore particularly sensitive to dissolution phenomena. This point corresponds perfectly to the beginning of silica solubilization [20]. Adjusting the pH to the basic range is a common way to disperse SiO_2NPs in water. According to the following formula, increasing the pH leads to increase the negative surface charges of particles and consequently results in higher level of repulsive electrostatic forces between particles to overcome the attractive Van der Waals forces [21].

$$\text{Si-OH} + \text{H}^+ \rightarrow \text{SiOH}_2^+ \quad (1)$$

$$\text{Si-OH} + \text{OH}^- \rightarrow \text{Si-O}^- + \text{H}_2\text{O} \quad (2)$$

Fig. 8 presents the variations of pH measurements under different doses of three coagulants in jar tests. The optimum pH values in jar tests with addition of Magnafloc10, Dynafloc30, and MagnaflocLT31 were 4, 6 and 4, respectively. This indicates that coagulation of SiO_2NPs with Magnafloc10 and Magnafloc LT31 occurred in the acidic medium due to the negative charge of SiO_2NPs.

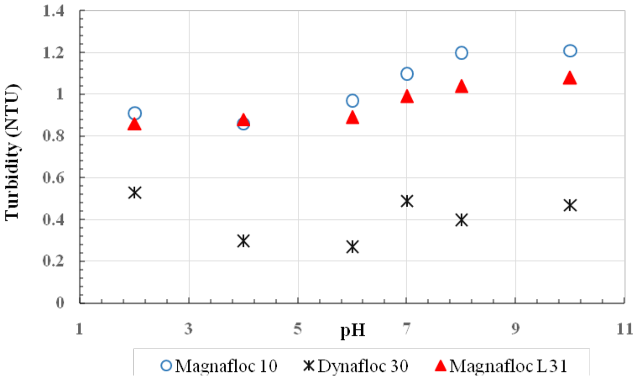


Fig. 8. Variations in turbidity of wastewater containing SiO_2 NPs at different pH values and different coagulant kinds.

3.2. *Ultrafiltration treatment system*

In this section, the effectiveness of the UF membrane system after coagulation of wastewater was examined. The experiments were performed using different concentrations of SiO_2NPs. Percentage removal of SiO_2NPs and percentage turbidity removal of solutions were evaluated.

3.2.1. *Effect of initial concentration of SiO_2 NPs on the removal process*

Different initial concentrations of SiO_2NPs were used to evaluate the efficiency of coagulation and ultrafiltration membrane processes with different kinds of coagulant. The results indicated that for initial concentration of SiO_2NPs (10, 20, 30, 40, 50 and 60 mg/l), the residual concentrations in case of Magnafloc10 after coagulation process were respectively, 2.1, 3.5, 5.5, 9, 11 and 15.5 mg/l, after ultra-filtration treatment were 0.3, 0.91, 2, 3.5, 5.5, and 6.9. As for Dynafloc30 were 1.5, 2.1, 3.2, 4.3, 4.8, and 5.56 mg/l after coagulation, after ultrafiltration treatment were 0, 0.2, 0.35, 0.355, 1.73, and 2.88 mg/l. Where MagnalocLT31 were concerned 2.5, 5.4, 6.06, 8.08, 11.1, and 11.78 mg/l after coagulation, 0.11, 0.578, 1.2, 2.25, 2.5, and 3.5 mg/l after ultrafiltration treatment. The % removal efficiency for different initial concentrations of SiO_2NPs after coagulation process and after ultrafiltration treatment with different kinds of coagulants is presented in Fig. 9 indicating that the efficiency decreased with the increase in initial concentration. Moreover the maximum efficiency occurred by using Dynafloc30 and Magnafloc LT3. This result was expected due to the negative charge of SiO_2NPs suspension solution and the nature of the cationic coagulant where the first step of coagulation process is the de-stabilization of the particle's charges. Coagulants with charges opposite those of the suspended solids are added to the water to neutralize the negative charges on dispersed non-settable solids such as SiO_2NPs [22]. De-stabilization involves the reduction of repulsive forces between particles thereby permitting the van der Waals attractions which lead to coagulation. For insoluble particles such as SiO_2NPs, particle repulsion is usually due to electrical double layer interaction, which can be controlled by changing the magnitude of the surface potential which depends on the concentration of suspended particles. At high concentrations, ions are close together

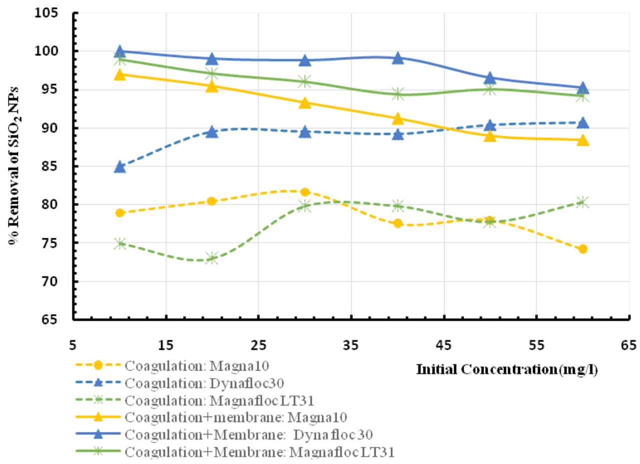


Fig. 9. The effect of initial concentration of SiO_2 NPs on % efficiency of treatment with different coagulants.

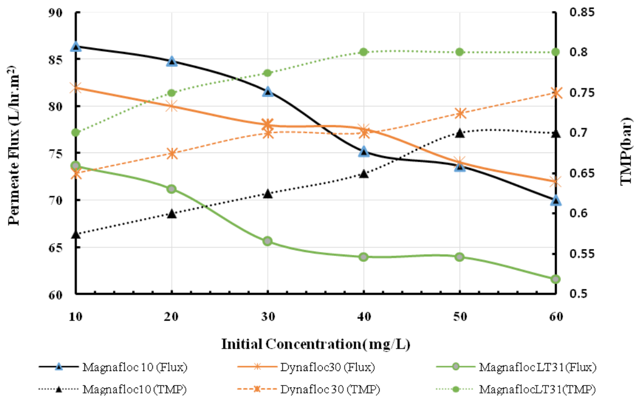


Fig. 10. The effect of initial concentration of SiO_2NPs on % efficiency of turbidity removal with different coagulants.

and the surface charge can be balanced over a relatively short distance from the surface the double layer is said to be compressed. Conversely, at low ionic strength, ions are far apart and the double layer extends a considerable distance from the surface [23].

3.2.2. Effect of initial concentration of SiO_2NPs on the turbidity removal process with different kinds of coagulants

Turbidity of SiO_2NPs solutions of different initial concentrations with different kinds of coagulant was measured and the efficiency of turbidity removal was calculated. Fig. 10 represents the effect of initial concentration of SiO_2NPs on % efficiency of turbidity removal using Magnafloc10, Dynafloc30 and MagnaflocLT31. The results reveal that the % turbidity removal decrease slightly with the increase of initial concentrations of SiO_2NPs. It was also noticed that the efficiency of turbidity removal increased with Dynafloc30 and decreased with magnafloc10. As for Magna flocLT31 the efficiency of turbidity removal increased with the increase of initial concentration of SiO_2NPs.

This complies with the fact that extremely small particulates suspended in a solution will often have a surface charge. Flocculants, containing particles with the opposite charge, can be added to neutralize this charge. When the overall surface charge is balanced, the suspended particles will then bind with the flocculants and settle out [24].

By comparing the performances of the three coagulants which were used in the study, it was found that the performance varied according to the principle of coagulation and flocculation process. The SiO_2NPs particles are stabilized (kept in suspension) by the action of physical forces on the particles themselves. One of the forces is playing a dominant role in stabilization results from the surface charge present on the particles. Most solids suspended in water possess a negative charge and, since they have the same type of surface charge, they repel each other when they come in contact. Therefore, they will remain in suspension rather than clump together and settle out of the water. Once the charge is neutralized, the small suspended particles are capable of sticking together. The slightly larger particles, formed through this process are called microflocs, and are not visible to the naked eye. The water surrounding the newly formed microflocs should be clear.

3.3. Ultrafiltration membrane performance parameters

3.3.1. Permeability results

Transportation properties of the unused membrane were measured using deionized water under constant operating conditions to determine water flux (J_o) and to compare it with the values of flux after using the membrane. The initial permeate flux was determined using the following equation Table 2. Where Q is the quantity of permeate collected (l), J_o is the specific water flux (L m^{-2} h^{-1}), t sampling time (h) and A_m is the area of membrane (m^2). The flux of permeate for different concentrations of SiO_2 NPs suspension solution was tested. The results indicated that the permeate flux decreased with the increasing of operating time for the different initial concentrations and different coagulants for the initial concentration 10 mg/l, after 10 min the permeate flux was 96 (L m^{-2} h^{-1}), after 60 min was 86.4 (L m^{-2} h^{-1}), the same result was repeated with the different concentration of SiO_2 NPs and for the other coagulant kinds.

3.4. The flux and trans-membrane pressure declined during the filtration process at different initial concentrations of SiO_2 NPs with different kinds of coagulant

To determine the effect of SiO_2 NPs concentration on maintainable flux, three coagulants were used in the experiments, the flux decreased and the Trans-membrane pressure (TMP) was increased as solids accumulated on the membrane surface (Fig. 9). The solids content of the water had a direct effect on the decrease in membrane flux and increase in TMP over the course of a production period. When the initial concentration of SiO_2 NPs was 10 mg/l the TMP was 0.5 bar and the flux was 96 L/h·m^2 and when it was 60 mg/l the TMP was 0.65 bar and the flux was 72 L/h·m^2, no constant trend in the decrease in flux and increase in TMP was observed over the course of a production period. The rate at which the flux decreased and TMP increased was depending on the quality of the influent and the effectiveness of the backwash period in preventing progressive membrane fouling. Membrane fouling is caused by deposition and accumulation of feed components on the membrane surface and/or within the membrane pores [25]. Flux and TMP are the best indicators of membrane fouling. Under constant pressure operation, flux declines as a result of membrane fouling. Fig 9 shows that the permeate flux increased with TMP, but with a different relationship to that obtained for pure water flux. Furthermore, higher TMPs caused faster initial flux declines as a result of the large driving force. Membrane fouling did not always increase with TMP. At the beginning of UF membrane, a high TMP gave a lower resistance, but a low TMP caused more serious fouling [26].

3.5. The effect of rejection performance ultrafiltration membrane by SiO_2 NPs

Fig. 12 shows the influnence of the UF membrane by the SiO_2NPs. As the SiO_2NPs concentration increased, the salt rejection decreased while the flux first increased and then decreased. The comparison of rejection in case of Magnafloc10, Dynafloc30 and MagnaflocLT31 indicates that the highest rejection performance was in the case of Dynafloc30 and the lowest in the case of Magnafloc31. This result comply with the obtained result of the coagulation step. As the initial concentration of SiO NPs increased from 10 mg/l to 60 mg/l, the observed rejection was reduced from 100% to 70.3% with Dynafloc, 95.6% to 70.3 with MagnaflocLT31 and from 88% to 55.5% with Magnafloc10. This result comply with the fact that the rejection can be increased at a higher pH and lower ionic strength [27].

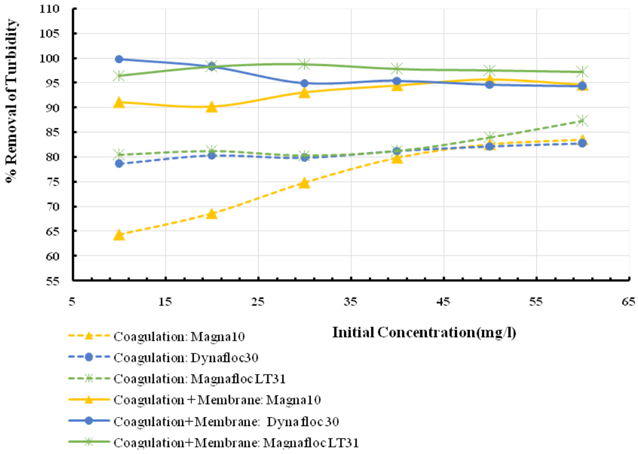


Fig. 11. The effect of initial concentration of SiO_2NPs on the flux and TMP with different coagulants.

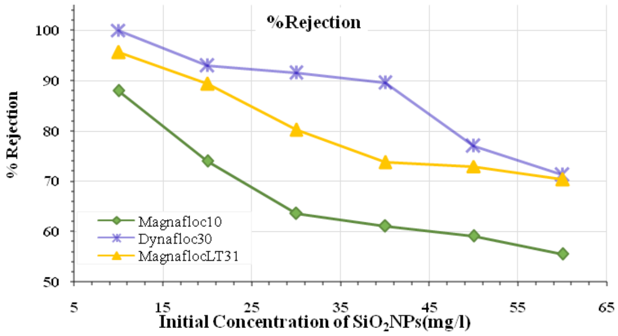


Fig. 12. The effect of initial concentration of SiO_2NPs on the rejection with using different cogulants.

3.5.1. The effect of backwash and chemical cleaning on the production of permeate

The cleaning of the membrane is performed regularly to prevent the accumulation of foulants and reverse the degrading effects of fouling on permeability and selectivity. Regular backwashing (BW) is often conducted every 10 min for some processes in order to remove cake layers formed on the membrane surface. Backwash on fouling and sustainable flux is illustrated in Fig. 13a the point at which the membrane is completely clean, flux increases as the TMP increases. The maximum achievable flux is limited by the maximum allowable TMP that can be applied to the membrane. Over the course of a typical production period, material accumulates on the membrane surface. If the backwash does not remove all the deposited material on the membrane surface during the production period, there is a net accumulation of solid material. The solids accumulation causes the system to start operating at a higher initial TMP during the next production period. Chemical cleaning of membrane were used after each coagulant Fig. 13b. The type of chemicals used depended on the kind of pollutant and the material of membrane. Washing the membrane, either hydraulically or chemically, may remove some of the accumulated materials and partially restore permeate flux [28].

As a summary of our results

- It was found that for different particle concentrations the efficiency of SiO_2NPs removal at initial concentration (10–60 mg/l) of SiO_2NPs suspensions with: a) anionic polymer (Magnafloc10), was 97% at 10 mg/l and 88.5% at 60 mg/l, b) inorganic polymer (Dynafloc30), was 100 % at 10 mg/l ,95.2% at 60 mg/l, and c) cationic polymer (MagnaflocLT31), was 98.9% at 10 mg/l, 94.17% at 60 mg/l.
- It was found that for different particle concentrations the efficiency of SNPs turbidity removal at initial concentration (10–60 mg/l) of SiO_2NPs suspensions with: a) anionic polymer (Magnafloc10), was 91% at 10 mg/l and 94.2 at 60 mg/l, b) inorganic polymer (Dynafloc30), was 99.8% at 10 mg/l and 94.2 at 60 mg/l, and c) cationic polymer (MagnaflocLT31), was 96.4% at 10 mg/l and 97.11% at 60 mg/l.
- The optimum pH values for the maximum turbidity removal were 4, 6, and 4 with: a) anionic polymer (Magnafloc10), b) inorganic polymer (Dynafloc30), and c) cationic polymer (MagnaflocLT31), respectively.
- The permeate flux decrease with the increasing of initial concentration of SNPs.
- The Trans-membrane pressure (TMP) increase with the increasing of initial concentration of SiO_2NPs.

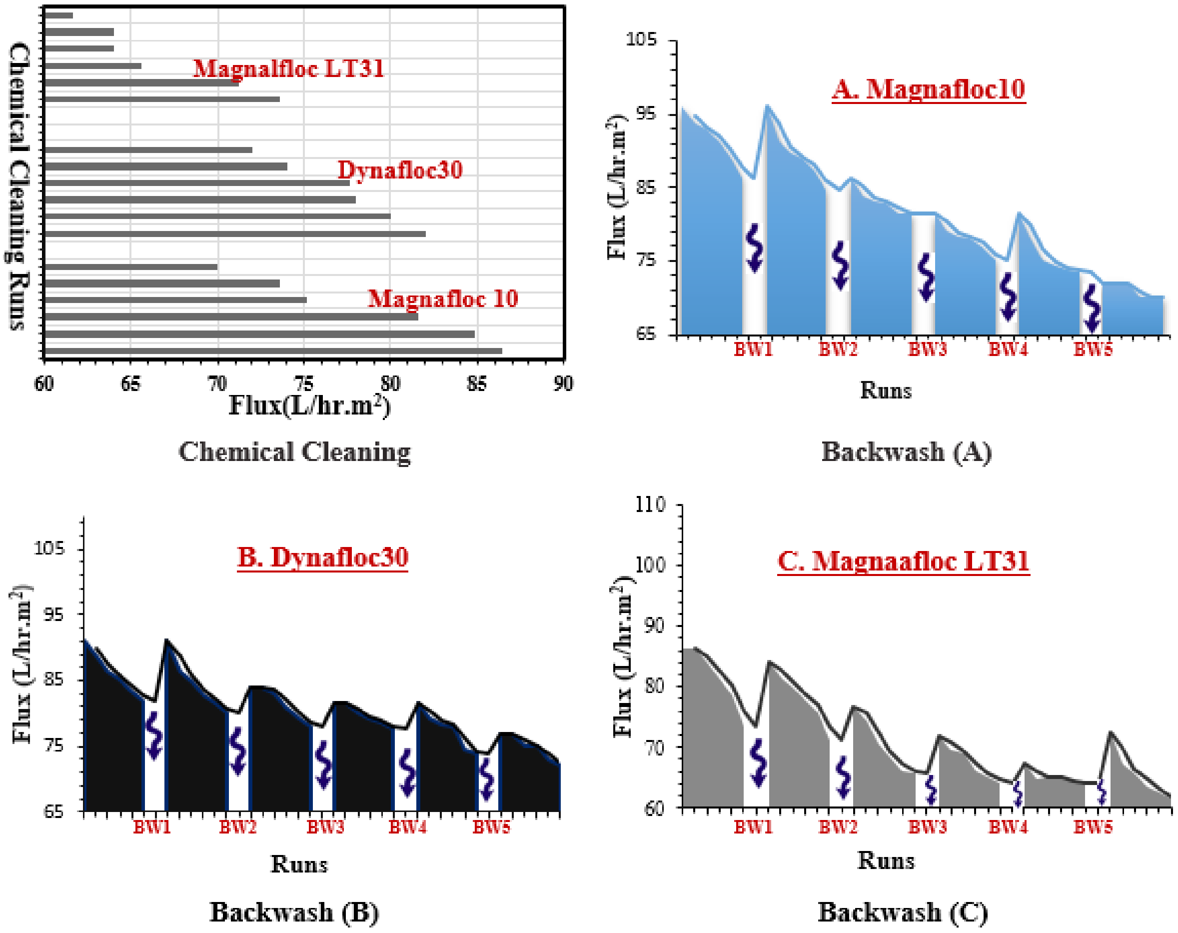


Fig. 13. Influence of chemical cleaning and backwash (BW) on permeate flux in cross flow ultrafiltration with different coagulants.

4. Conclusions

By using this continuous coagulation/flocculation system followed by HF-UF membrane unit and using different kinds of coagulants for treating wastewater containing silica nanoparticle scale, the results from study indicated that:

- Design considerations play an important role and multiple feed points for coagulants and other chemicals can be provided to obtain higher quality of treated water.
- In coagulation/flocculation-UF process, the application of coagulants for wastewater pre-treatment improved the permeate quality and decrease fouling and, consequently, the needed energy, the membrane has an excellent ability to remove nano-particle from wastewater.
- This pre-treatment system is suitable for the treatment of nano-particle-contained wastewater instead of the use of a nano-filtration membrane for further water purification.
- For good performance, it is preferable to use cat-ionic organic polymer, and inorganic polymer. These have advantages compared to common reagents like iron or aluminum salts. They are used in low concentrations and have a low impact on the pH of the suspension.
- This study will be effective in scaling-up system for practical applications.
- Retentate of coagulation-ultrafiltration membrane can be recycled and reused for the same industrial unit or considered as pretreatment of surface water, seawater and biologically treated municipal water upstream of the reverse osmosis unit.
- However, the phenomenon of membrane fouling continues to impede the application of membranes in water treatment, and its prevention or mitigation remains a subject of continuing research [29,30].

After a review of a few papers dealing with the potential hazards of nanoparticles released in the water resources, we observed that there is still a significant lack of knowledge about the treatments of engineered nanomaterials (ENM) in aquatic mediums and it would be an important challenge for the recovery of nano-particles from water in the near future.

References

[1] F. Part, G. Zecha, T. Causon, E.-K. Sinner, M. Huber-Humer, Current limitations and challenges in nano-waste detection, characterization and monitoring, Waste Manage., 43 (2015) 407–420.

[2] G.A. Mansoori, T. Rohani Bastami, A. Ahmadpour, Z. Eshaghi, Environmental application of nanotechnology, Annual Rev. Nano Research, 2008, Vol. 2, Chap. 2.

[3] M.N. Moore, Do nanoparticles present ecotoxicological risks for the health of the aquatic environment?, Environ. Int., 32 (2006) 967–976.

[4] S.K. Brar, M. Verma, R.D. Tyaqi. R.Y. Surampalli, Engineered nanoparticles in wastewater and wastewater sludge – evidence and impacts, Waste Manage., 30 (2010) 504–520.

[5] S. Haruehansapong, T. Pulngern, S. Chucheepsakul, Effect of nanosilica particle size on the water permeability, abrasion resistance, drying shrinkage, and repair work properties of cement mortar containing nano-SiO_2, Adv. Mater. Sci. Eng., 2017 (2017) 1–11.

[6] V. Vijayanathan, T. Thomas, T.J. Thomas, DNA nanoparticles and development of DNA delivery vehicles for gene therapy, Biochemistry, 41 (2002) 14085–14094.

[7] T.K. Barik, B. Sahu, V. Swain, Nano-silica-from medicine to pest control, Parasitol Res., 103 (2008) 253–258.

[8] A.D. Maynard, R.J. Aitken, T. Butz, V. Colvin, K. Donaldson, G. Oberdorster, M.A. Philbert, J. Ryan, A. Seaton, V. Stone, S.S. Tinkle, L. Tran, N.J. Walker, D.B. Warheit, Safe handling of nanotechnology, Nature, 444 (2006) 267–269.

[9] M. Bizi, Stability and flocculation of nano-silica by conventional organic polymer, Nat. Sci., 4 (2012) 372–385.

[10] B.M. Yang, C.J. Huang, W.L. Lai, C.C. Chang, C.M. Kao, Development of a three-stage system for the treatment and reclamation of wastewater containing nano-scale particles, Desalination, 284 (2012) 182–190.

[11] J.J. Qin, M.H. Oo, M.N. Wai, F.S. Wong, Effect of feed pH on an integrated membrane process for the reclamation of a combined rinse water from electro-less nickel plating, J. Membr. Sci., 217 (2003) 261–268.

[12] S.K. Kang, K.H. Choo, Use of MF and UF membranes for reclamation of glass industry wastewater containing colloidal clay and glass particles, J. Membr. Sci., 223 (2003) 89–103.

[13] L.C. Juang, D.H. Tseng, H.Y. Lin, Membrane processes for water reuse from the effluent of industrial park wastewater treatment plant: a study on flux and fouling of membrane, Desalination, 202 (2007) 302–309.

[14] H.K. Shon, S. Vigneswaran, I.S. Kim, J. Cho, H.H. Ngo, Fouling of ultrafiltration membrane by effluent organic matter: a detailed characterization using different organic fractions in wastewater, J. Membr. Sci., 278 (2006) 232–238.

[15] J. Haberkamp, A.S. Ruhl, M. Ernst, M. Jekel, Impact of coagulation and adsorption on DOC fractions of secondary effluent and resulting fouling behavior in ultrafiltration, Water Res., 41(17) (2007) 3794–3802.

[16] L.H. Fan, T. Nguyen, F.A. Roddick, J.L. Harris, Low-pressure membrane filtration of secondary effluent in water reuse: pre-treatment for fouling reduction, J. Membr. Sci., 320 (2008) 135 –142.

[17] J.R. Huang, B.M. Yang, K.S. Chen, C.C. Chang, C.M. Kao, Application of membrane technology on semiconductor wastewater reclamation: a pilot-scale study, Desalination, 278 (2011) 203–210.

[18] Standard methods for the examination of water and wastewater, American Public Health Association, American Water Works Association, Water Environment Federation, 1999.

[19] J.M. Sielechi, B.S. Lartiges, G.J. Kayem, C. Foochow, J. Thieme, J. Ghanbaja, J.B. d'Espinose de la Caillerie, O. Barrès, R. Kamga, P. Levitz, L.J. Michot, Changes in humic acid conformation during coagulation with ferric chloride: implications for drinking water treatment, Water Environ. Res., 42 (2008) 2111–2123.

[20] S. Chen, G. Oye, J. Sjoblem, Effect of pH and salt on rheological properties of aerosil suspensions, J. Dispers. Sci. Technol., 28 (2007) 845–853.

[21] T. Tripathy, D.E., B.R., Flocculation: A new way to treat the waste water, J. Phys. Sci., 10 (2006) 93–127.

[22] H. Stechemesser, B. Dobias, Coagulation and Flocculation, 2nd ed., CRC Press 2005, pp. 820–821.

[23] S. Xia, X. Li, Q. Zhang, B. Xua, G. Li, Ultrafiltration of surface water with coagulation pretreatment by streaming current control, Desalination, 204 (2007) 351–358.

[24] M. Cheryan, Ultrafiltration and Microfiltration Handbook, Technomic Publishing Co Inc, Lancaster, PA 1998.

[25] A.K. Rizvi, A.M. Pabby, Sastre, S.H. Syed, eds., Handbook of Membrane Separations: Chemical, Pharmaceutical, and Biotechnological Applications. Boca Raton, Fla.: CRC Press 2007.

[26] J.-H. Huang, L.-J. Shi, G.-M. Zeng, X. Li, S.-B. He, F. Li, Y.-L. Xiong, S.-H. Guo, D.-M. Zhang, G.-X. Xie, Effects of feed concentration and trans-membrane pressure on membrane fouling in Cd^{2+} removal by micellar-enhanced ultrafiltration, Desalination, 294 (2012) 67–73.

[27] G.L. Amy, NOM Rejection by, and Fouling of NF and UF Membranes, AWWA Research Foundation, USA 2001. TD442.5.N38.

[28] A.H. Konsowa, M.G. Eloffy, Y.A. El-Taweel, Treatment of dyeing wastewater using submerged membrane bioreactor, Desal. Water Treat., 51 (2013) 1079–1090.

[29] W.Z. Yu, L.C. Campos, N. Graham, Application of pulsed UV-irradiation and pre-coagulation to control ultrafiltration membrane fouling in the treatment of micro-polluted surface water, Water Res., 107 (2016) 83–92.

[30] M. Park, T. Anumol, J. Simon, F. Zraick, S.A. Snyder, Pre-ozonation for high recovery of nanofiltration (NF) membrane system: membrane fouling reduction and trace organic compound attenuation, J. Membr. Sci., 523 (2017) 255–263.