



## Removal of copper oxide nanoparticles from aquatic mediums by coagulation-ultrafiltration membrane hybrid continuous system

A.H. Konsowa<sup>a</sup>, M.G. Eloffy<sup>a,c,\*</sup>, W.A. Ibrahim<sup>b</sup>, Y.A. El-Taweel<sup>a</sup>, O.E. Abdelwahab<sup>c</sup>

<sup>a</sup>Chemical Engineering Department, Faculty of Engineering, Alexandria University, Alexandria, Egypt, Tel. +201226150501; email: manal\_elfoffy@yahoo.com (M.G. Eloffy), Tel. +201222162806; akonsowa@alexu.edu.eg (A.H. Konsowa), Tel. +201222220102; email: ytawwil20@gmail.com (Y.A. El-Taweel)

<sup>b</sup>Sanitary Engineering Department, Faculty of Engineering, Alexandria University, Alexandria, Egypt, Tel. +201001679698; email: welbarki76@gmail.com

<sup>c</sup>National Institute of Oceanography and Fisheries, Alexandria, Egypt, Tel. +201221093161; email: olaabdelwahab53@hotmail.com

Received 21 January 2019; Accepted 20 August 2019

---

### ABSTRACT

The overall aim of this work is to investigate the fundamental mechanisms and phenomena governing the removal of engineered nanomaterials in aquatic systems, specifically, copper oxide nanoparticles (CuO NPs) which are expected to have a huge impact in the field of nanotechnology and its applications. Nanofiltration membranes (NF) are very effective in removing nanoscale pollutants. However, high pressures (100–1,000 psi) are required to operate NF membranes. Also, the NF membrane technique is not preferred for use in the treatment of wastewater containing nanoscale particles due to the fouling of membrane problem which results in decreasing treated water production. Conversely, ultrafiltration membranes (UF) require much lower pressures (5–60 psi) and the fouling problem is reduced, but unfortunately, they are not effective in retaining dissolved ions, organic solutes, and nanoscale pollutants. Therefore, in the present study, we used the coagulation/flocculation/sedimentation (CFS) step as a pre-treatment process to enhance the UF process. Experimental work was carried out to investigate the effects of solution chemistry (i.e., pH values, suspended solids concentrations, and turbidity of solution) and the physico-chemistry characteristics of nanomaterials, e.g., shape, size, electrostatic charge on the particles surface and the composition of nano-materials on the removal process, select the suitable kind of coagulants; viz., Magnafloc LT31 as anionic, Magnafloc 10 as cationic or Dynafloc 30 as inorganic polymers and their optimum doses related to the efficiency of CFS processes in the different cases and finally, study the effect of design considerations of CFS systems and operating parameters of the filtration system such as trans-membrane pressure as a function of treated water fluxes and effect of backwashing and chemical cleaning on the membrane fouling and consequently determine their effects on the filtration performance. The removal efficiency of nano-materials and the efficiency of turbidity removal varied according to the coagulant type. The results indicated that the efficiency of CuO NPs removal was 87.4%, 89.33%, and 90.3% in case of CFS process, it was found 94.2%, 97%, and 97.66% in case of CFS/UF process; followed the following order for different types of coagulant, Magnafloc LT31 > Dynafloc 30 > Magnafloc 10. The efficiency of turbidity removal for the CFS process was estimated at 81.7%, 91.0% and 90.0% with Magnafloc 10), Dynafloc 30 and Magnafloc LT31; respectively. Similar to the CFS process, the CFS/UF process indicated that the efficiency of turbidity removal was observed greater than 96% using Magnafloc L31 while 94.3% in the case of Dynafloc 30 and recorded 87.9% only with Magnafloc. That is meaning that the efficiency of turbidity removal and nanoparticle removal in both CFS and CFS/UF processes was more efficient using anionic and inorganic polymers as a coagulant.

*Keywords:* Nano-waste; Copper oxide nanoparticles; Physico-chemical characterizations of nanomaterials; Ultrafiltration membrane; Coagulation process; Wastewater treatment

---

\* Corresponding author.

## 1. Introduction

Nano-materials with different compositions are being manufactured in increasing amounts, including those metal(s) and metal oxide(s) such as copper and copper oxide(s) nanoparticles [1]. Copper, as a red-brown metal, is in high demand with the usage of more than 20 million tons/year. They are both standard materials for the production of electrical cables and coins and also used as active ingredients in biocides (e.g. used in organic farming, in anti-fouling coating processes, and for wood impregnation). In consumer products such as pillowcases and socks. Copper oxide is a *p*-type semiconductor with a bandgap of ~ 1.7 eV [2]. It is used for its anti-microbial properties. Besides copper is also an essential trace element needed for the proper functioning of many enzymes in biological systems and the adult need is between 1 and 1.5 mg copper/d. CuO can be reduced to metallic copper when exposed to hydrogen or carbon monoxide under high temperatures. While the many positive benefits that nanotechnology and engineered nanomaterials (ENs) will likely provide to mankind, there are also numerous uncertainties in the science community regarding its potential negative impacts [3]. In the modern era, nanoparticles synthesis causes a lot of toxic by-products [2]. Examples of a metal oxide nanomaterial that has been detected in wastewater treatment effluent are copper oxide nanoparticles (CuO NPs), Copper is one of the substances known to be eco-toxic. They are graded harmful to humans and as dangerous for the environment with an adverse effect on aquatic life. There are several hot spots in the water cycle for ENs and their interaction with other water constituents. Engineered nanoparticles (ENPs) are inevitably released into the soil and waterways and eventually reach the ocean [4,5]. As their applications in science and technology expand, the need to understand the eco-toxicological impacts of ENPs on marine ecosystems will become increasingly important [6]. Humans can have regular contact with copper and copper oxide through its many applications [7]. It is important to keep in mind that copper oxide is a skin irritant and that its oral use (as an essential micro-element) should be limited. Also, the handling of copper and copper oxide powder (also, as a nano-pesticide) should be done with great care. Nanomaterials material must be removed before discharge because of the nature of the colloidal suspension these particles will not sediment or be separated with conventional physical methods (such as settling or by membrane Nanofiltration (NF) because fouling) unless they are agglomerated through coagulation [8]. Ultrafiltration

(UF) membranes have rapidly become an efficient alternative to conventional treatment in water production. The primary problem encountered in the application of membrane technology is membrane fouling [9]. Fouling can cause flux decline, resulting in an increase in cost for the production of treated water and even replacement of membranes. Coagulation is more widely applied and studied due to low cost and being easy to use. It was shown that coagulation could improve flux indeed [10]. However, some research work indicated that although coagulation could remove nanomaterials (NMs) and decrease the resistance of membrane filtration, the rate and extent of fouling could not be mitigated by coagulation [11]. Coagulation is used as a primary process for both drinking water and wastewater treatment, but combining coagulation with other processes could improve overall performance for various environmental remediation tasks [12]. Many studies on UF membranes in water treatment have been conducted or are currently in progress to improve the performance of this process. The present investigation gives a summary of these studies and deals with pre-treatment options, membrane types, as well as process and water parameters, membrane fouling, membrane cleaning procedures and operational experiences with UF membranes.

## 2. Materials and methods

Coagulation/flocculation/sedimentation (CFS) was used as a pre-treatment process of hollow fibers ultrafiltration membrane (HF-UFM) unit which used to treat wastewater containing different concentrations of CuO NPs. Magnafloc LT31 Magnaafloc 10 and Dynafloc 30 polymer were used as coagulants in the CFS process and their characterizations were provided by the supplier. Table 1. CuO NPs were used to prepare the synthetic suspension solution of nanoparticles and some of their physical and thermal characterizations were provided by the supplier Table 2. The morphological and stability of nanoparticles were investigated in this study. The optimum doses of coagulants needed to neutralize the charge of nanoparticles and the optimum pH values for each type of coagulants were the most important operating parameters for the CFS process and were determined using the Jar test. The efficiency of turbidity removal and nanoparticle removal were the indicators for the performance of the CFS process also that, fluxes and transmembrane pressure were studied to follow CFS/UF process. An integrated system of CFS/UF was required UF membrane unit with specific characterizations in Table 3.

- Efficiency of turbidity removal is calculated from Eq. (1)

$$\text{Efficiency of turbidity removal\%} = \frac{\text{Initial turbidity of solution before CFS(NTU)} - \text{Final turbidity of solution after CFS(NTU)}}{\text{Initial turbidity of solution before CFS(NTU)}} \times 100 \quad (1)$$

- Efficiency of nanoparticle removal is calculated from Eq. (2)

$$\text{Efficiency of nanoparticles removal\%} = \frac{\text{Initial concentration of solution before CFS} \left( \frac{\text{mg}}{\text{l}} \right) - \text{Final concentration of solution after CFS} \left( \frac{\text{mg}}{\text{l}} \right)}{\text{Initial concentration of solution before CFS} \left( \frac{\text{mg}}{\text{l}} \right)} \times 100 \quad (2)$$

Table 1  
Physical and chemical properties of coagulants

Items	Magnafloc LT31	Dynafloc 30	Magnafloc 10
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		2,500–4,900 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

Table 2  
Physico-chemical and thermal properties of copper oxide nanoparticle (CuO NPs)

Item	Description
Appearance (color)	Dark Brown
Chemical symbol	CuO
Appearance (form)	Powder
Chemical composition (% content)	Copper: 79.87 Oxygen: 20.10
Solubility	Suspended in water, dissolve slowly in alcohol or ammonia solution. Soluble in dilute acids.
Density (g/cm <sup>3</sup> )	6.31
Molar mass (g/mol)	79.55
Average size (TEM, nm)	70–100
Surface area (m <sup>2</sup> /g)	>18
Moisture content	<1.5% water
Shape (TEM)	Multiple shape
Melting point (°C)	1,201
Boiling point (°C)	2,000

Table 3  
Characterizations of membrane unit

Membrane character	Description
Membrane type	Ultrafiltration hollow fiber membrane (UF-HFM)
Membrane material	Poly vinyl chloride (PVC)
Surface area	0.125 m <sup>2</sup>
Molecular weight cutoff (MWCO)	50,000 Da

## 2.1. Materials

### 2.1.1. Properties of coagulants

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

### 2.1.2. Characterizations of nanoparticles (CuO NPs) containing wastewater

The CuO NPs suspension solution used was supplied by NanoTech Egypt Company for Photo-Electronics. It has been prepared via the sol-gel technique. This technique offers

some advantages in stabilizing the as-prepared nanoparticles. In the aforementioned method, CuO NPs involves the addition of an aqueous +NaOH solution to the solution of CuCl<sub>2</sub> to form a precipitate. The physicochemical and thermal characteristics of CuO NPs and their suspension provided by the producer are summarized in Table 2.

### 2.1.3. Characterizations of membrane unit

The experiments were carried out using a membrane with characterizations summarized in Table 3.

### 2.1.4. Jar testing of coagulants

The optimum coagulant concentration (OCC) which is needed to neutralize the charge of the nanoparticles was estimated using jar testing. Also, the optimum pH values were determined. The experimental matrix investigated is made up of three coagulants selected. For each coagulant, conditioning was done at rpm 90 for 1–2 min and then at 30 rpm for 30 min. The same stirring rate was used in the 6 beakers of the jar test. The OCC was determined after stirring had been stopped by measuring the turbidity in the supernatant in the suspensions after 30 min of settling, it is the quantity of coagulant that results in the lowest turbidity.

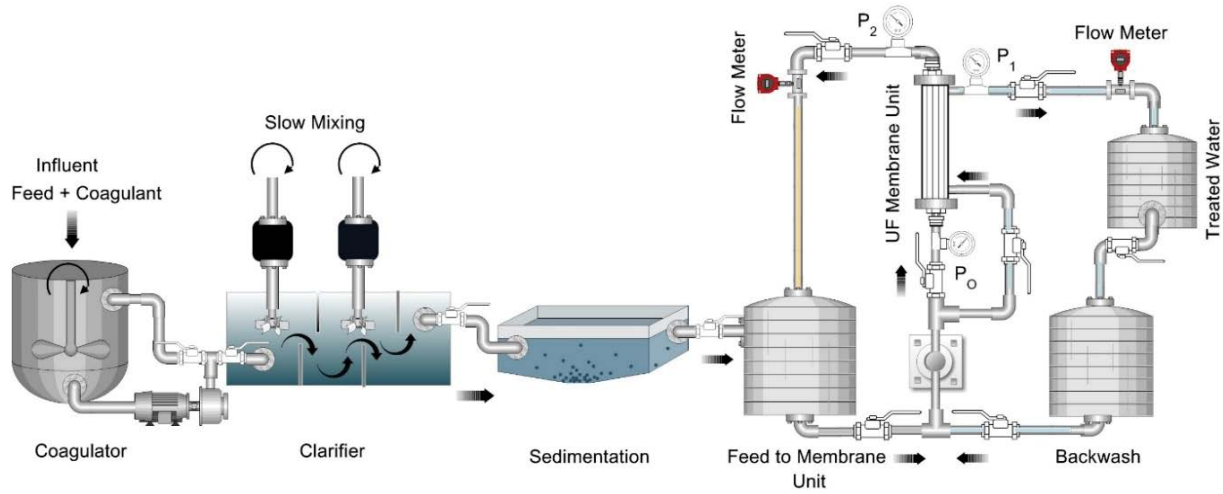


Fig. 1. Coagulation-ultrafiltration membrane hybrid continuous system.

2.2. Experimental work

The treatment system involved two main processes Fig. 1. The first is CFS. The primary purpose of the CFS process is the removal of turbidity from the water. Coagulation is achieved by adding different types of chemicals (coagulants) to the wastewater to promote the destabilization of the nanoparticles and agglomeration of the resulting individual colloidal particles. The coagulant doses and the optimum pH values are determined and performed using jar tests as a preparation process for the treatment operation.

- *Flocculator*: is designed perpendicular to provide enough interparticle contacts to achieve particle agglomeration so that they can be effectively removed by sedimentation. Agglomeration of colloids by collisions to form separable flocs.
- Slow and gentle mixing.
- *Vertically baffled tank*: The water flows vertically. The baffle walls help to create turbulence and thus facilitate mixing Figs. 2a and b.
- *Mechanisms*: collisions from Brownian motion-induced collisions through stirring.
- Detention time: for floc formation is recommended to be 30 min.
- Volume = flow rate × detention time.
- Velocity gradient =  $[\rho \times g \times \Delta H / \mu \times t]$ . Where,  $\rho$  = water density ( $\text{kg/m}^3$ ),  $g$  = acceleration of gravity =  $9.81(\text{m/s}^2)$ ,

$\Delta H$  = head loss through tank (m),  $\mu$  = dynamic viscosity ( $\text{N sec/m}^2$ ) ( $\text{kg/m sec}$ ) and  $t$  = detention time (sec).

3. Results and discussion

3.1. Membrane permeability

The transport properties of the unused membrane were tested using deionized water (DW) under constant operating conditions to determine the pure water flux ( $J_{dw}$ ), refer to Fig. 3, which was compared with the values of flux after using the membrane.

3.2. CuO NPs characterizations

3.2.1. Zeta potential distribution

Zeta potential of CuO NPs was measured using Malvern Zetaseizer ZS Fig. 4, it is found of  $-35.1 \text{ mV}$ , this result means the stability of nanoparticle is moderate according to table by Riddick [15]. The stability ratio of a dispersion, which is closely related to the interactions between two dispersed entities, is one of the most significant properties of the dispersion. For example, unstable suspensions with a tendency to flocculate may produce less compact cakes at the membrane surface with increased permeability [13]. To mitigate membrane fouling, a membrane system combined with chemical/physical processes such as coagulation/sedimentation, sand filtration, ozonation, and

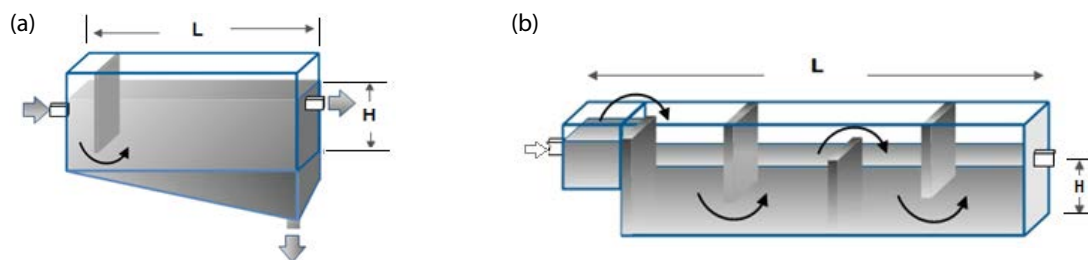


Fig. 2. (a) Configuration of flocculation and (b) Sedimentation tank.

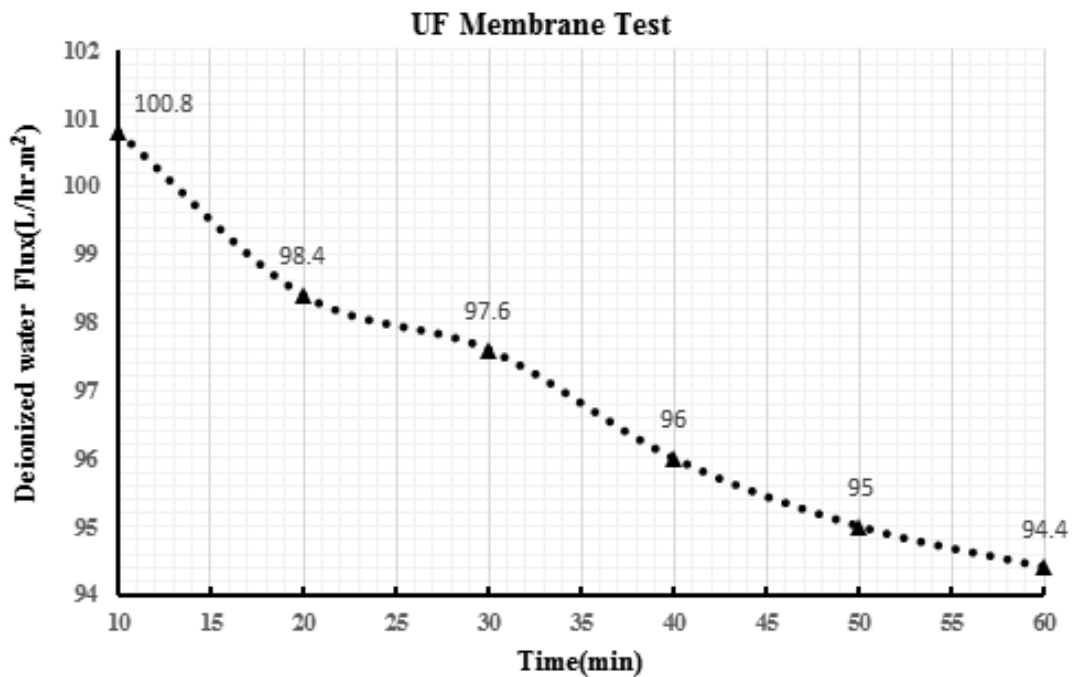


Fig. 3. Membrane permeability test.

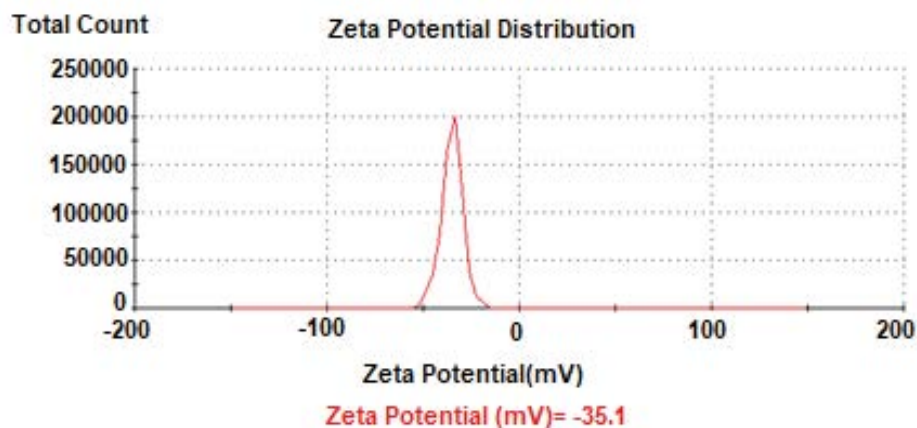


Fig. 4. Zeta potential distribution of CuO NPs.

chlorination needs to be adopted [14]. Most particles suspended in water and wastewater, e.g., clays, silica, hydrated metal oxides, paper fibers, biological cells, etc., possess negative surface charges in the neutral pH range. The stability of suspensions related to their Zeta potentials was mentioned in Table 4.

### 3.2.2. Morphological characterizations CuO NPs

Transmission electron microscopy (TEM) was performed on JEOL JEM-2100 high-resolution TEM at an accelerating voltage of 200 kV, respectively. The TEM clearly shows that the prepared copper oxide NPs have an average size between 60–100 nm with multiple shapes; cf. Figs. 5a and b. The image of CuO NPs was carried out by scanning electron microscopy

Figs. 6a and b show the image of CuO NPs before and after the coagulation process. The shape of the particle was “multiple shapes”.

### 3.2.2. Size distribution of CuO NPs

Nanoparticle solution used for particle size determination was prepared by adding 5.0 mg CuO NPs into 1 L double distilled water. The solution was sonicated and stirred for 20 min to disperse the NPs. The size distribution determination was conducted using Malvern Zetaseizer ZS to measure mean particle size distribution, zeta potential. Copper oxide NPs can be dispersed in liquids under several forms. The nature of such dispersions depends on the size of the solid particles. Copper oxide NPs have average an size between

Table 4  
Stability of suspensions with relation to zeta potential

Stability characteristics	Average zeta potential (mV)
Maximum agglomeration and precipitation	0 to +3
Range of strong agglomeration and precipitation	+5 to -5
Threshold of agglomeration	-10 to -15
Threshold of delicate dispersion	-16 to -30
Moderate stability	-31 to -40
Fairly good stability	-41 to -60
Very good stability	-61 to -80
Extremely good stability	-81 to -100

Adopted from Riddick [15].

60–100 nm in dispersion case and about 600–900 nm in aggregation status Fig. 7 and 8.

### 3.3. Operating parameters

#### 3.3.1. Determination of the optimum coagulant dose

In the present study, jar tests were performed to evaluate the effectiveness of the coagulants; Magnafloc 10, Dynafloc 30 and Magnafloc LT31 on CuO NPs removal. Figs. 9a–c shows the results of turbidity reduction from the coagulation/flocculation experiments versus the corresponding coagulant dosage. Results indicate that similar removal trends were observed using three different coagulants. Higher turbidity reduction efficiency was observed when Magnafloc LT31 (cationic) was used as the coagulant. Results show that the turbidity removal efficiencies reached 2.21, 2.86, 3.21, 3.64, 4.71 and 7.55 when 10, 15, 15, 20, 25, and

25 mg/L were added to 10, 20, 30, 40, 50, and 60 mg/L of CuO NPs solutions.

#### 3.3.2. Determination of the optimum pH value

The influence of pH on the coagulation process was investigated for each type of coagulant. The experiments were performed for the three coagulants at the same operating conditions; the same dose of coagulant and the same rpm of jar test at room temperature. The residual turbidities were estimated at different pH values for each coagulant type and were recorded in Fig. 10.

Jar test procedures for determine the optimum pH values of coagulation process are; Adjust pH of the jars while mixing using HCl (1 N) and NaOH (1 N) at room temperature, add same dose of the selected coagulant type to each jar, rapid mixing for 1 min, then reduce the speed of stirring to 30 rpm for 15 min. Turn off the mixers and allow flocs to settle for 30 min. The residual turbidity at a certain dose of each different polymer types; viz., anionic organic polymer addition (Magnafloc 10), inorganic polymer (Dynafloc 30), cationic organic polymer addition (Magnafloc LT31) and different pH values are displayed in Fig. 10. The results showed that the values of residual turbidity at a certain dose of coagulant were varied with different values of pH. The higher turbidity removal efficiency was observed when the pH was acidic to neutral and a lower dosage of the polymer was used. The lowest turbidity dropped when the pH value was 2 to 7. Gohary and Tawfik [16] reported that higher coagulation efficiency can be obtained if the initial pH is less than 8. Thus, the pH should be appropriately controlled to enhance coagulation efficiency.

#### 3.3.2. Efficiency of CuO NPs removal

Atomic absorption spectroscopy was used to determine the concentration of CuO NPs suspension solution

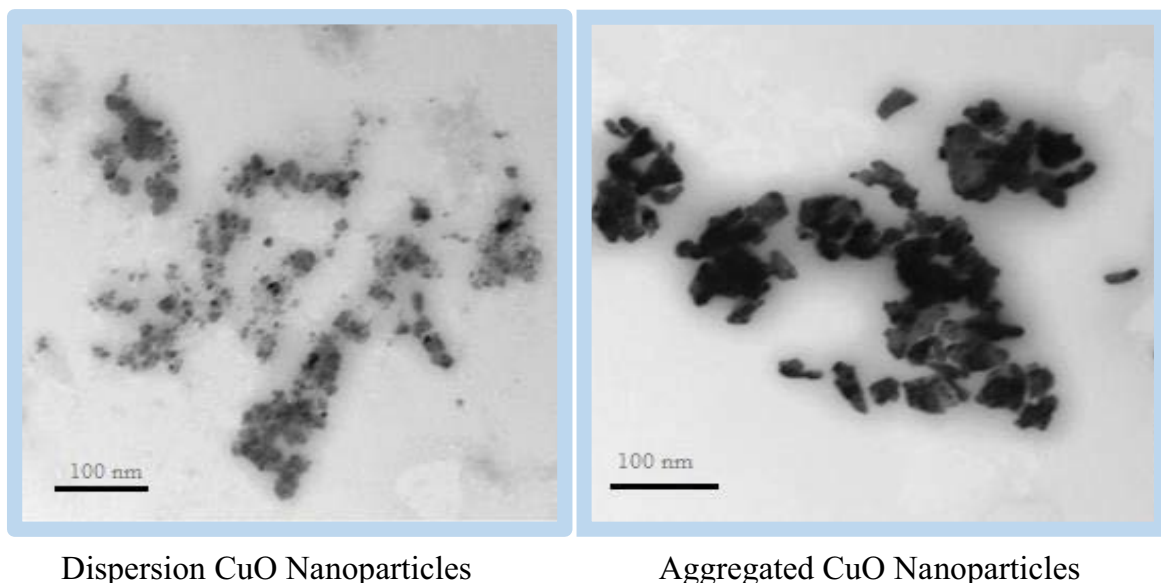


Fig. 5. (a,b) Transmission electron microscope (TEM) image of copper oxide NPs.

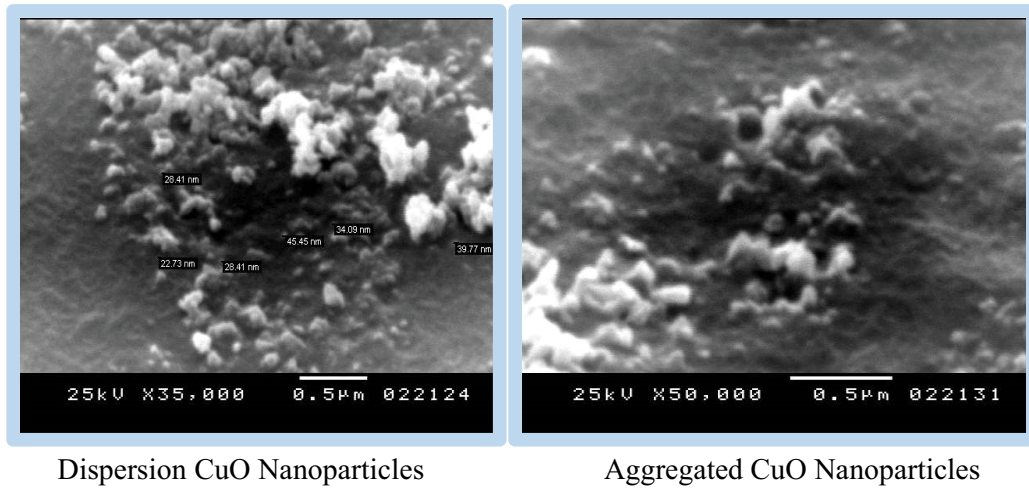


Fig. 6. (a,b) Scanning electron microscopy (SEM) image of copper oxide NPs.

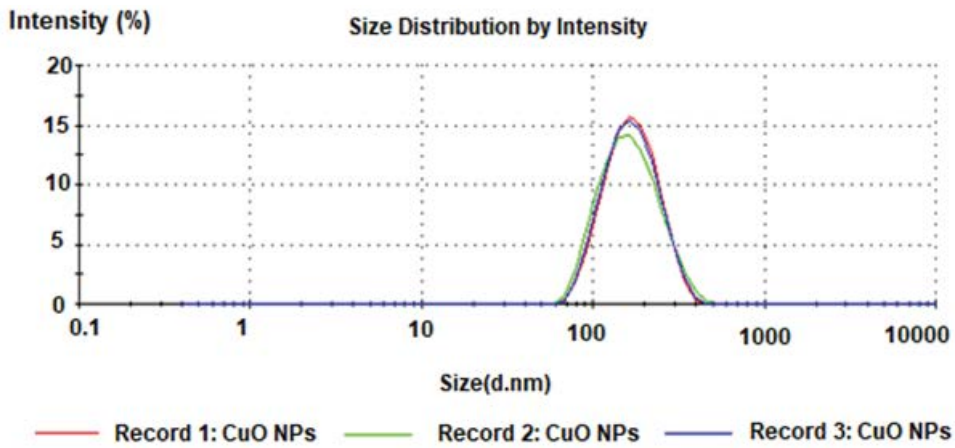


Fig. 7. Size distribution of dispersed CuO NPs.

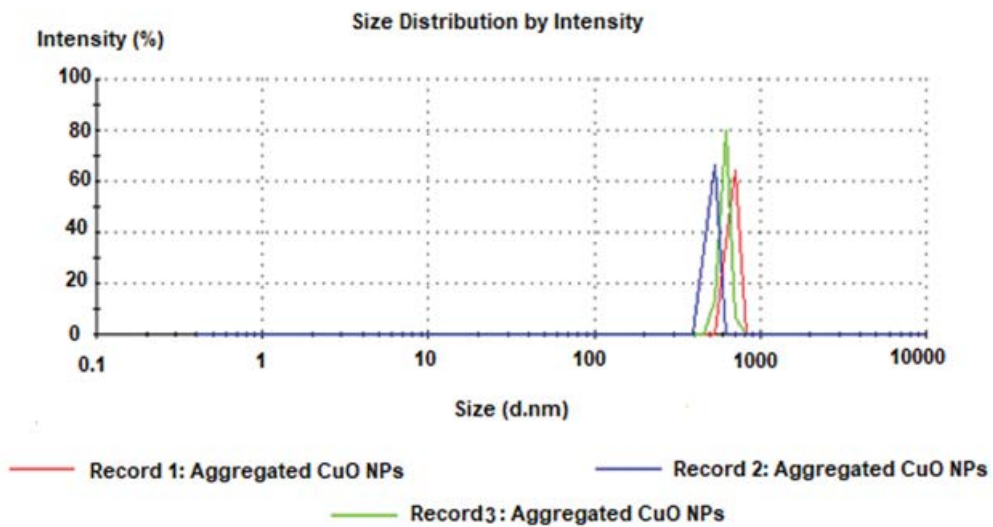


Fig. 8. Size distribution of aggregated CuO NPs.

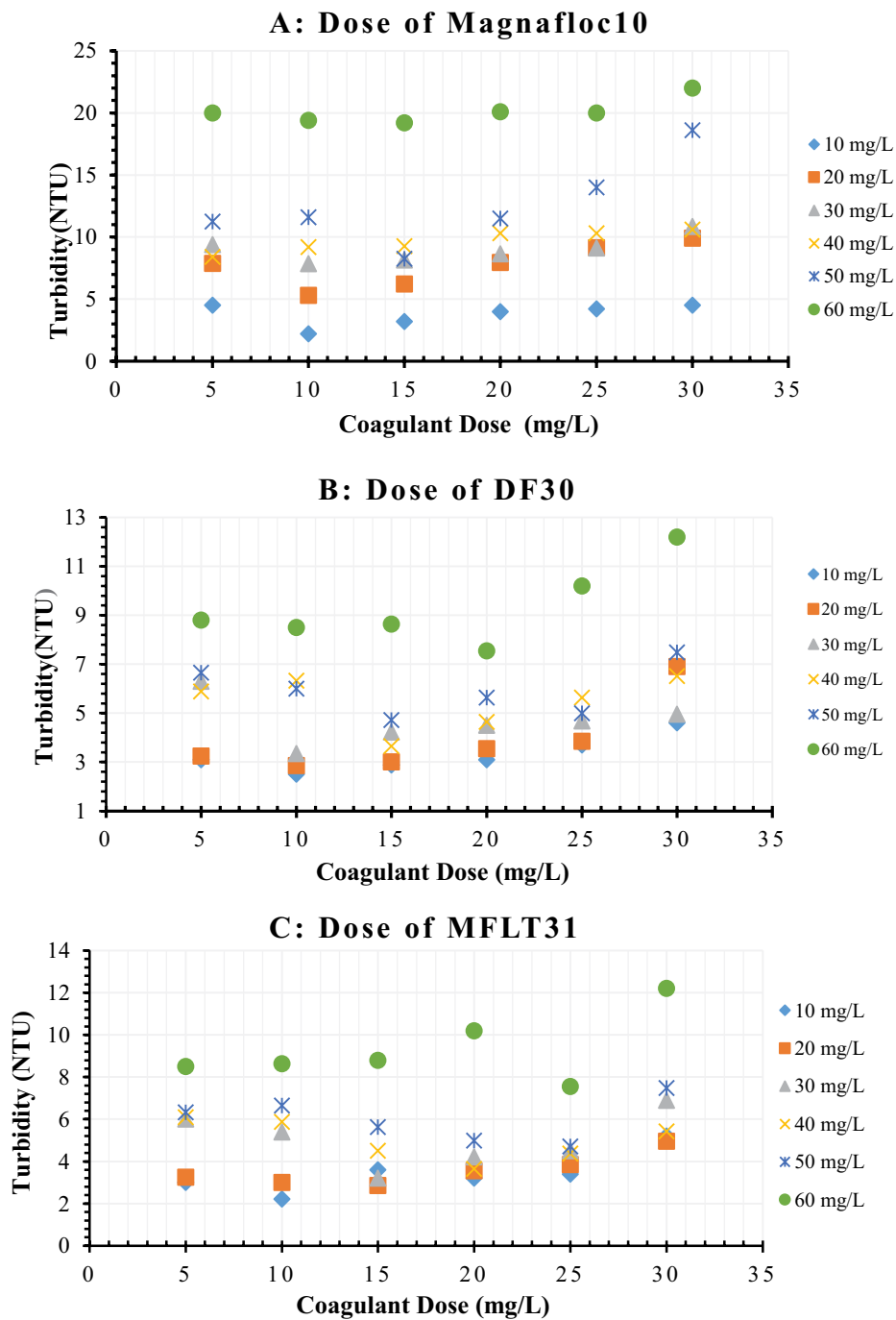


Fig. 9. (a,b,c) Optimum coagulant dose of CFS process for different concentration of CuO NPs.

before and after the coagulation and UF process with different initial concentrations of NPs and different types of coagulants.

Fig. 11 presents the efficiency of NPs removal after coagulation and UF at an initial concentration of 60 mg/L of CuO NPs. The results indicated that the efficiency of removal was 87.4%, 89.33%, and 90.3% in the case of CFS process while CFS/UF was found 94.2%, 97%, and 97.66%; followed the following order Magnafloc LT31 > Dynaflo c30 > Magnafloc 10. This result is in disagreement with

the fact that cationic polyelectrolytes are typically used to coagulate particles that are negatively charged (the most common type). The mechanisms involved in the destabilization of the particles by cationic polyelectrolytes are charge neutralization, but in the present case, the mechanism of the coagulation process was by bridging of particles. Nonionic and anionic polyelectrolytes can also be used to destabilize negative colloids. But in the case of an inorganic polymer, we used a bigger amount of coagulant more than with cationic or anionic polymer. Traces of particles with different



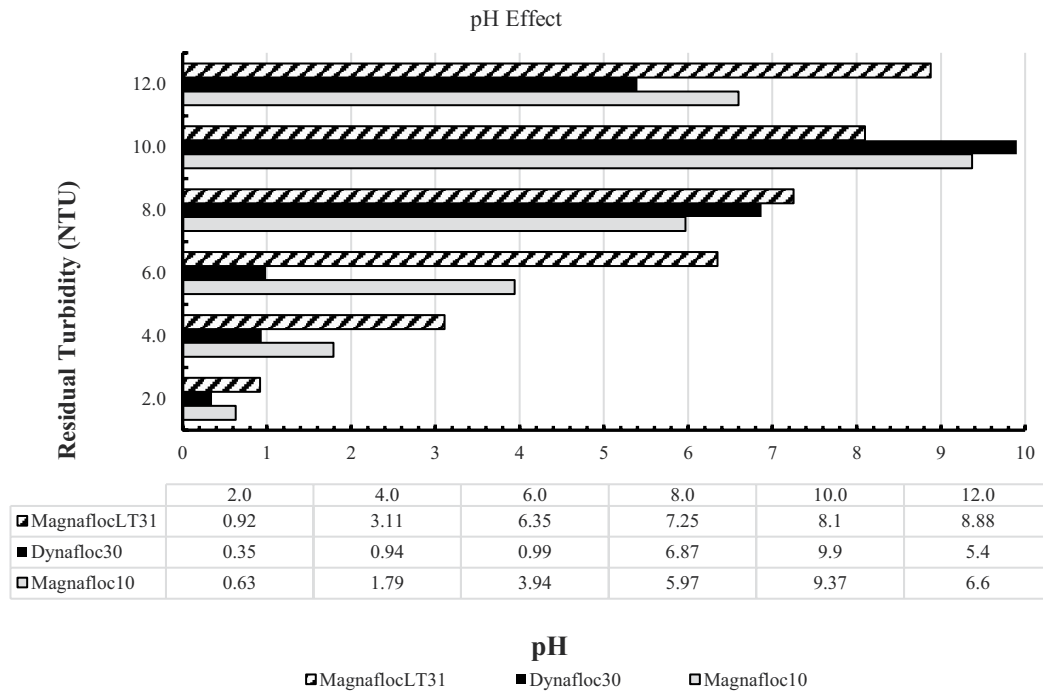


Fig. 10. Determination the optimum pH value of CFS process with different type and constant dose of coagulant.

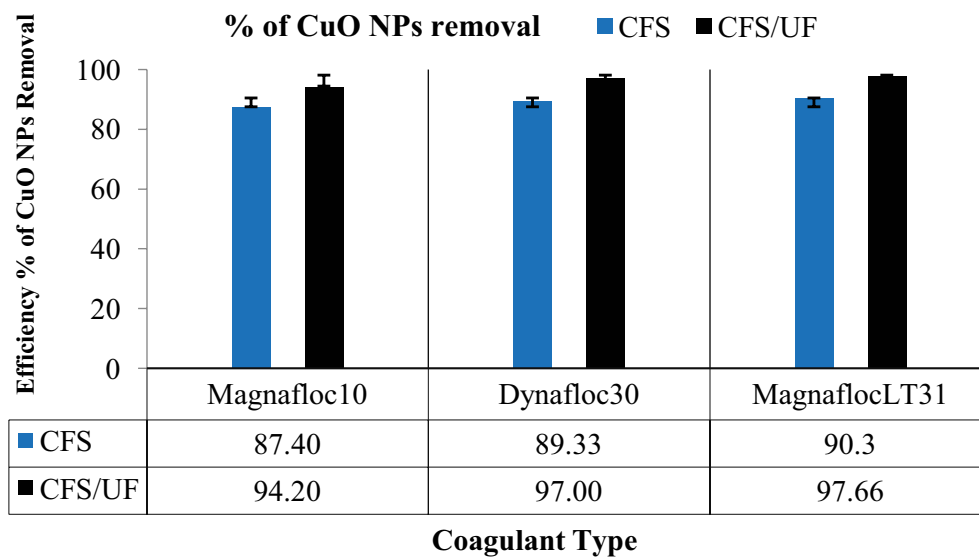


Fig. 11. Effect coagulant type on the efficiency % of CuO NPs removal from wastewater.

sizes remained in the solution to discern why the removal of particles did not reach 100%.

Two hypotheses have been put forward to explain the phenomenon of selective solute removal by UF membranes. The hypothesis of Urease et al. [17,18] states simply that the membranes have abnormally large pores that are not included in the main pore size distribution of the UF membranes, but there is insufficient direct evidence to support this hypothesis. Also, the hypothesis does not explain why the removal of particles is incomplete. The second hypothesis rests on the presence of physical defects and the lack

of membrane integrity manifested as pinholes in the membrane [19] or the efficiency of coagulation/clarification/sedimentation process was not enough to coagulate all particles causing to the penetration of non-coagulated particles through the membrane.

### 3.3.3. Efficiency of turbidity removal

More than 95% of the remaining turbidity after the coagulation process can further be removed after the following UF treatment. Results indicate that the UF membrane

system is very effective in turbidity removal during the water reclamation process. An in-line system backwash is required after periods of operation to maintain an efficient removal rate. The results showed that the efficiency of turbidity removal in both CFS and CFS/UF was more efficient using anionic and inorganic polymers as coagulant where it was estimated in case of CFS process 81.7%, 91.0% and 90.0% with Magnafloc 10 (anionic organic polymer), Dynafloc 30 (inorganic polymer) and Magnafloc LT31 (cationic polymer); respectively. CFS/UF was indicated similar results; the efficiency of turbidity removal was observed greater than 96% using Magnafloc L31 while 94.3% in the case of Dynafloc 30 and recorded 87.9% only with Magnafloc Fig. 12.

3.4. Filtration experiments

Several key operational conditions that control membrane performance include the operating flux, [20] backwash interval, and pretreatment processes, such as coagulation. Furthermore, the UF productivity can be significantly deteriorated by membrane fouling which results from the mass loading of solid and contaminants present in the feed water. The changes in flux with time for a polyvinyl chloride membrane used for the UF at Transmembrane pressure (TMP) of 0.5–1 bar are presented in Figs. 13a–c.

3.4.1. Permeate flux at different CuO NPs concentrations and different types of coagulants

Membrane flux (Jdw) is the first tested membrane flux with DW.

To study the effect of coagulant pretreatment on the UF membrane performance, several experiments were conducted in which the feed water was dosed with the following coagulants: cationic Magnafloc LT31, inorganic polymer (Dynafloc 30) and anion organic polymer (Magnafloc 10) before membrane filtration. The coagulants were continuously injected into the source water at the beginning of the

feed storage tank to the feed pump. The dosage and the type of coagulant used in a study provide different results about flux decline. For all the coagulants, the extent of flux decreased with the time increase due to the increase of fouling. The results indicate that size exclusion is the main mechanism for the filtration of aggregated CuO NPs by UF membranes. The flux was found a decrease in the following order; Magnafloc LT31 > Dynafloc 30 > Magnafloc 10 due to the increasing the operating time. Figs. 13a–c. Partial penetration of the UF membranes by CuO NPs is likely facilitated by the enlargement of the particles that accumulated on the membrane surface thus inevitably resulting in the decrease in flux with time.

3.4.2. TMP at different CuO NPs concentrations and different types of coagulants

Figs. 14a–c depict the trans-membrane pressure values when plotted vs. time of filtration for different types of coagulants: (a) cationic polymer addition, (b) inorganic polymer, and (c) anionic polymer addition. The results indicated that the TMP increased during the filtration process due to the accumulation of the coagulated particles on the membrane surface and fouling formation. Pretreatment and coagulation have been studied and were proven to be effective in reducing membrane fouling. The key point is to deposit a cake layer from the coagulated flocs on the membrane surface as protection to the membrane, instead of removing the flocs away. On one hand, due to the “protective effect” of the cake layer towards membrane fouling, backwash could be carried out after long filtration times, on the other hand, the fouling formed by the accumulated cake layer is reversible, which can easily be removed. In the coagulation and UF membrane, cake layer formation is an important cause of TMP increase under a constant flux filtration.

Among different coagulant types, were found to be closely related to cake layer formation. The difficult problem is that the rapid TMP increasing after each backwashing

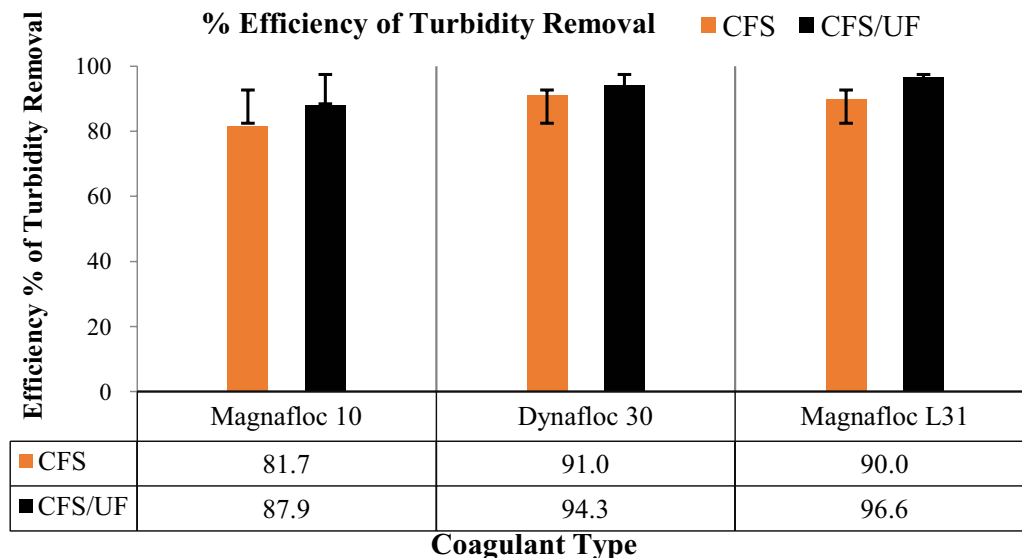


Fig. 12. Effect of coagulant type on the turbidity removal efficiency.

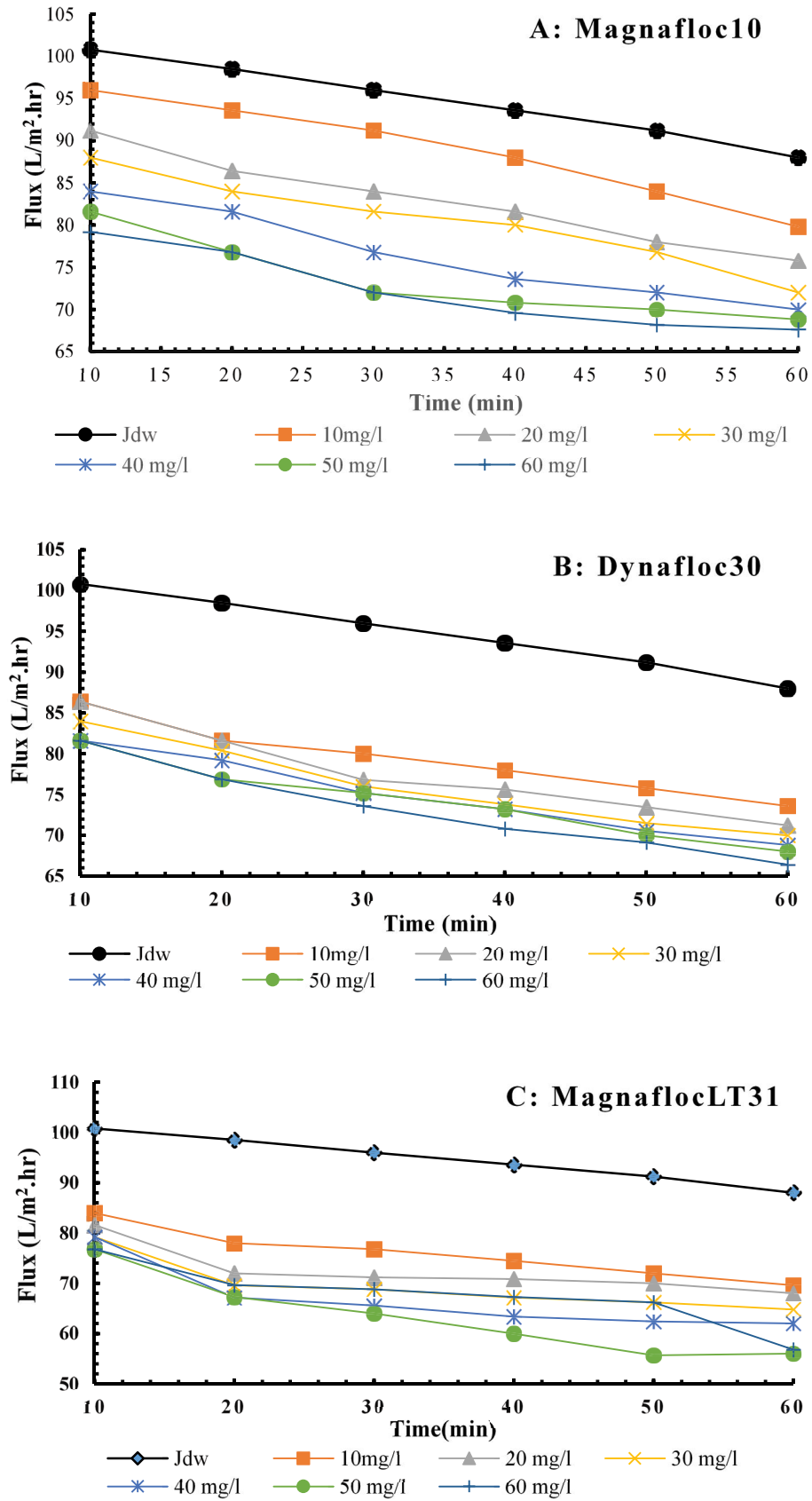


Fig. 13. (a,b,c) Permeate flux at different CuO NPs concentrations and different types of coagulants.

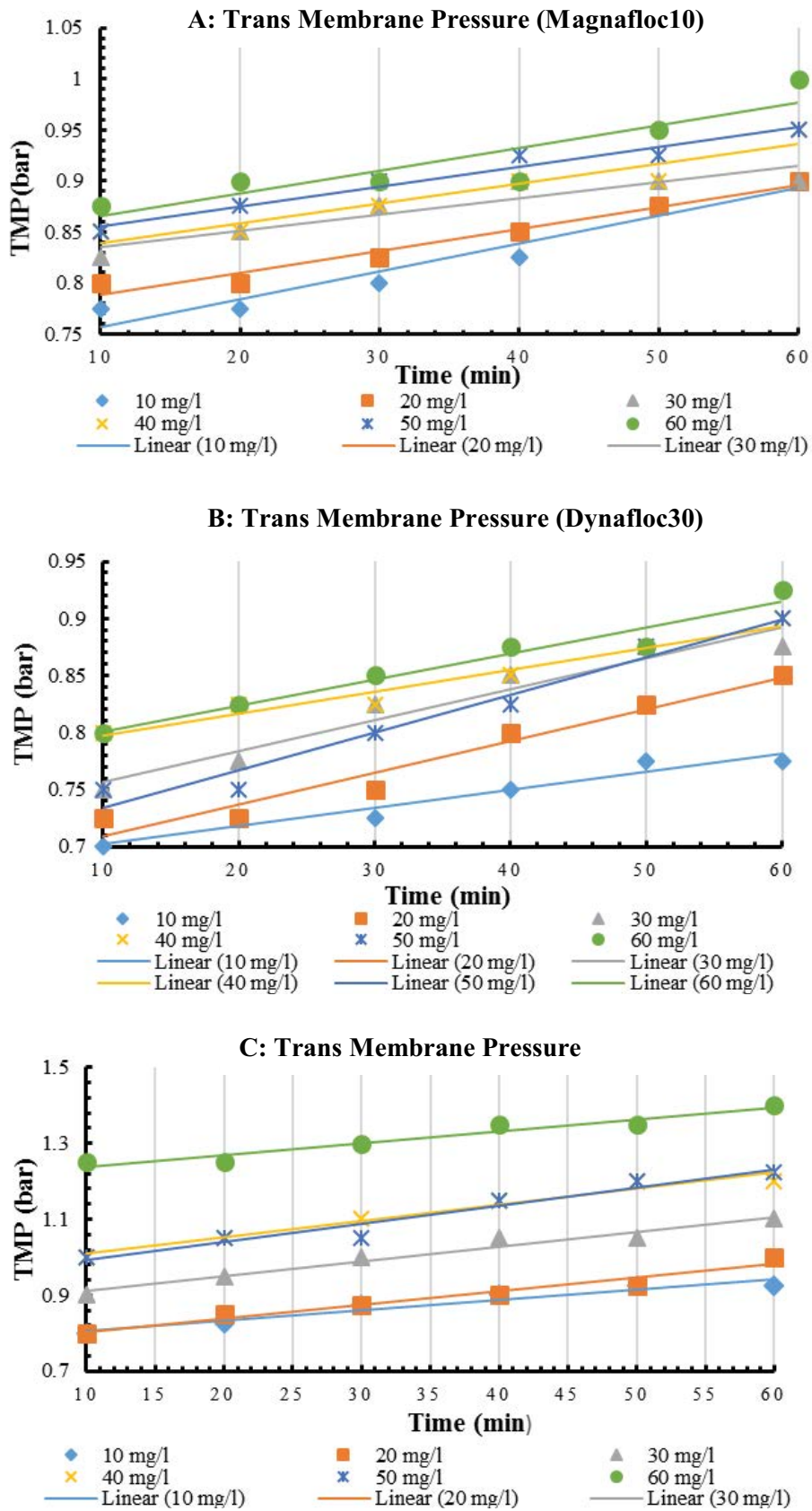


Fig. 14. (a,b,c) TMP at different CuO NPs concentrations and different types of coagulant.

time reduces the backwashing effect. The figure shows that TMP increased sharply in the first few hours after which the rate of increase is smooth and linear. It can be explained that during the first period, fouling was due to pore blocking caused by the physical deposition of large particles on the membrane surface and in the pores. Increasing TMP produces a linear increase in the permeate flux. The limiting point is where the maximum flux value is obtained under some operating conditions and it cannot be increased by varying TMP. Therefore, to keep a continuous process; the TMP selected must be lower than the critical value, this means work under the critical zone in which the fouling effect is minimum [21].

### 3.4.3. Effect of the initial concentration of CuO NPs on the UF membrane rejection

Fig. 15 shows that the rejection of coagulated particles increased with increasing the initial concentration. To find a more satisfying explanation, the current study focused on the retention of nanoparticles as a function of the initial concentrations of NPs. Earlier studies indicated that increases in the initial concentration led to increases in the aggregation of nanoparticles, membrane compaction and thus ultimately resulting in the formation of a denser membrane with smaller pores. This is in agreement with the case for CuO NPs and the membranes employed in the current study which showed the expected increase in particle retention as the initial concentration is increased.

### 3.5. Chemical cleaning

As suspended solids accumulate near, on, and within the membrane lumen they may reduce the permeability of the membrane by blocking or constricting pores and forming a layer of additional resistance to flow across the membrane leading to reduction in permeate flux over time [22], periodical cleaning is a necessity for membrane systems to

ensure optimal operation, the membrane cleaning efficiencies were termed as flux recovery percent. UF permeate was used for backwashing and suitable chemical reagent for the type of pollutant and material of the membrane. Metal ions often cause inorganic fouling, which could be removed by citric acid. A low pH cleaning solution of 2.0% (w) citric acid ( $C_6H_8O_7$ ) was used.

How long can I expect membranes to last in my system? Informatics of the results of flux as a function of time answered this question in the form of the equation between  $y$  as a flux,  $x$  as the time: Figs. 16a–c.

$$\text{For Magnafloc 10; } y = -0.6107x + 90.281 \quad (3)$$

$$\text{For Dynafloc 30; } y = -0.2683x + 80.741 \quad (4)$$

$$\text{For Magnafloc LT31; } y = -0.4061x + 76.665 \quad (5)$$

## 4. Conclusion

In conclusion, the study of hybrid continuous coagulation/flocculation/sedimentation-membrane process for removal of CuO NPs from aquatic mediums showed that design considerations play an important role and multiple feed points for coagulants and other chemicals can be provided to obtain a higher quality of treated water [23]. This pre-treatment system is suitable for the treatment of nanoparticle-contained wastewater instead of the use of a nanofiltration membrane for further water purification [23]. The low-pressure needed for UF membrane processes is recommended to be used to treat the nano-pollutant effluents. It is more economical than NF and reverse osmosis (RO), the foregoing techniques are characterized by high energy consumption and one of the main challenges associated with the processes remains early-stage design of techno-economically optimized purification [24], at the lower initial concentration of CuO NPs, the efficiency of removal of is considered low. Much lower

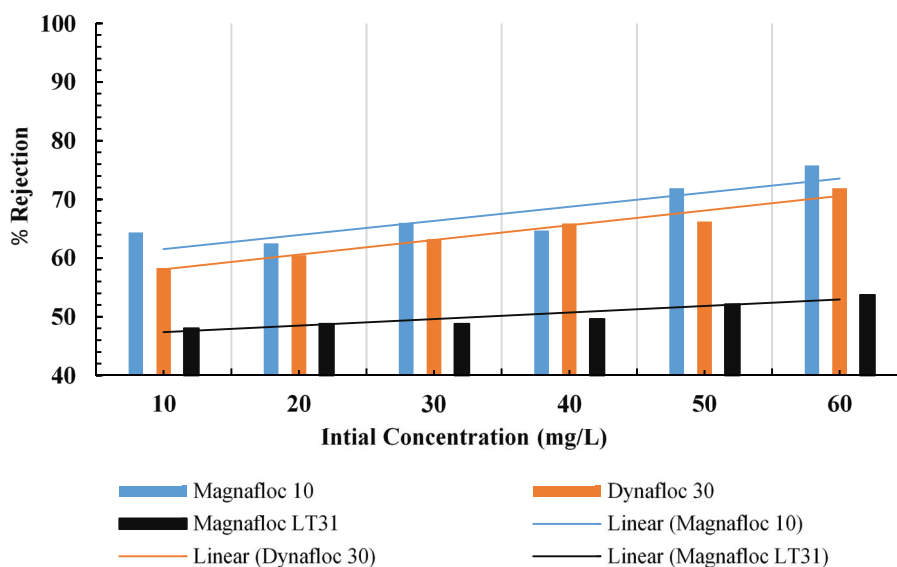


Fig. 15. Effect of initial concentration of CuO NPs on the UF membrane rejection.

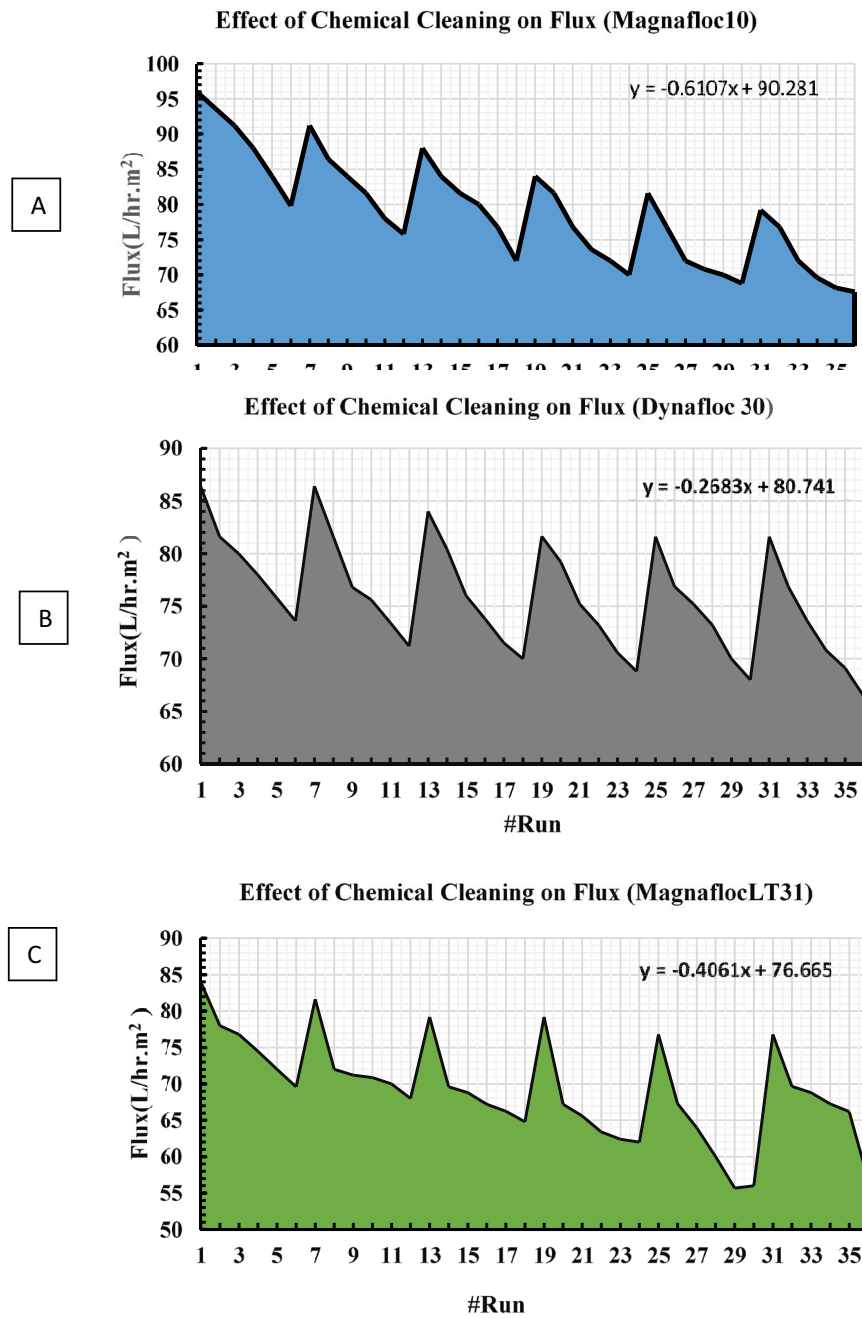


Fig. 16. (a,b,c) Membrane cleaning efficiencies with different coagulants.

concentrations of CuO NPs need to be investigated. In the case of SiO<sub>2</sub>NPs, the reverse needs to be investigated, in large scale practical work, RO membranes can be employed as a third stage to remove any remaining traces of nano-waste.

**References**

[1] I. Khan, K. Saeed, I. Khan, Nanoparticles: properties, applications and toxicities, *Arabian J. Chem.*, (2017) 1–24, <https://doi.org/10.1016/j.arabjc.2017.05.011> (In Press).

[2] A. Rajendran, S.E. Dhanraj C, S. Senthilkumar, A Green and Facile approach for the synthesis copper oxide nanoparticles using hibiscus rosa-sinensis flower extracts and it's antibacterial activities, *J. Bioprocess Biotechnol.*, 8 (2018) 3–8.

[3] S.J. Klaine, P.J.J. Alvarez, G.E. Batley, T.F. Fernandes, R.D. Handy, D.Y. Lyon, S. Mahendra, M.J. McLaughlin, J.R. Lead, Nanomaterials in the environment: behavior, fate, bioavailability, and effects, *Environ. Toxicol. Chem.*, 27 (2008) 1825–1851.

[4] R.D. Handy, R. Owen, E. Valsami-Jones, The ecotoxicology of nanoparticles and nanomaterials: current status, knowledge gaps, challenges, and future needs, *Ecotoxicology*, 17 (2008) 315–325.

[5] RCEP, Royal Commission on Environmental Pollution, *Novel Materials in the Environment: The Case of Nanotechnology*, The Stationery Office, Norwich, UK, 2008, 147 p.

- [6] Y. Ju-Nam, J.R. Lead, Manufactured nanoparticles: an overview of their chemistry, interactions and potential environmental implications, *Sci. Total Environ.*, 400 (2008) 396–414.
- [7] M. Walkowicz, P. Osuch, B. Smyrak, T. Knych, E. Rudnik, Ł. Cieniek, A. Róžańska, A. Chmielarczyk, D. Romaniszyn, M. Bulanda, Impact of oxidation of copper and its alloys in laboratory-simulated conditions on their antimicrobial efficiency, *Corros. Sci.*, 140 (2018) 321–332.
- [8] S. Golkhah, H.Z. Mousavi, H. Shir Khanloo, A. Khaligh, Removal of Pb(II) and Cu(II) ions from aqueous solutions by cadmium sulfide nanoparticles, *Int. J. Nanosci. Nanotechnol.*, 13 (2017) 105–117.
- [9] J.-M. Laíne, C. Campos, I. Baudin, M.-L. Janex, Understanding membrane fouling: a review of over a decade of research, *Water Sci. Technol. Water Supply*, 3 (2003) 155–164.
- [10] B.-z. Dong, Y. Chen, N.-y. Gao, J.-c. Fan, Effect of coagulation pretreatment on the fouling of ultrafiltration membrane, *J. Environ. Sci.*, 19 (2007) 278–283.
- [11] Y.H. Li, J. Wang, W. Zhang, X.J. Zhang, C. Chen, Effects of coagulation on submerged ultrafiltration membrane fouling caused by particles and natural organic matter (NOM), *Environ. Eng.*, 56 (2011) 584–590.
- [12] J.-Q. Jiang, The role of coagulation in water treatment, *Curr. Opin. Chem. Eng.*, 8 (2015) 36–44.
- [13] M. Wu, D.D. Sun, Characterization and reduction of membrane fouling during nanofiltration of semiconductor indium phosphide (InP) wastewater, *J. Membr. Sci.*, 25 (2005) 135–144.
- [14] S.-R. Chae, H. Yamamura, B. Choi, Y. Watanabe, Fouling characteristics of pressurized and submerged PVDF (polyvinylidene fluoride) microfiltration membranes in a pilot-scale drinking water treatment system under low and high turbidity conditions, *Desalination*, 244 (2009) 215–226.
- [15] T.M. Riddick, Control of Colloid Stability Through Zeta Potential, Livingstone Pub. Co., 1968, p. 372.
- [16] F. El-Gohary, A. Tawfik, Decolorization and COD reduction of disperse and reactive dyes wastewater using chemical-coagulation followed by sequential batch reactor (SBR) process, *Desalination*, 249 (2009) 1159–1164.
- [17] T. Urase, K. Yamamoto, S. Ohgaki, Effect of pore size distribution of ultrafiltration membranes on virus rejection in crossflow conditions, *Water Sci. Technol.*, 30 (1994) 199.
- [18] T. Urase, K. Yamamoto, S. Ohgaki, Effect of pore structure of membranes and module configuration on virus retention, *J. Membr. Sci.*, 115 (1996) 21.
- [19] M. Kitis, J.C. Lozier, J. Kim, B. Mi, B. Marinas, Evaluation of Biologic and Non-Biologic Methods for Assessing Virus Removal by and Integrity of High Pressure Membrane Systems, in: Proceedings of the 5th Conference, Germany, 2002, p. 143.
- [20] R. Ramli, N. Bolong, Effects of pressure and temperature on ultrafiltration hollow fiber membrane in mobile water treatment system, *J. Eng. Sci. Technol.*, 11 (2016) 1031–1040.
- [21] A. Cassano, C. Conidi, R. Ruby-Figuero, R. Castro-Muñoz, Nanofiltration and tight ultrafiltration membranes for the recovery of polyphenols from agro-food by-products, *Int. J. Mol. Sci.*, 19 (2018) 351.
- [22] A.H. Konsowa, M.G. Eloffy, Y.A. El-Taweel, Treatment of dyeing wastewater using submerged membrane bioreactor, *Desal. Wat. Treat.*, 51 (2013) 1079–1090.
- [23] A.H. Konsowa, M.G. Eloffy, W.A. Ibrahim, Y.A. El-Taweel, O.E. Abdelwahab, Use of coagulation-ultrafiltration membrane continuous system for treatment of wastewater containing silica nanoparticles, *Desal. Wat. Treat.*, 148 (2019) 60–69.
- [24] M.N. Koleva, E.M. Polykarpou, S. Liu, C.A. Styan, L.G. Papa-georgiou, Optimal design of water treatment processes, *Desal. Wat. Treat.*, 57 (2016) 26954–26975.