



Removal of *Escherichia coli* from synthetic turbid water using titanium tetrachloride and zirconium tetrachloride as coagulants

Ahmad Jonidi Jafari^{a,b}, Mona Mahrooghi^c, Mehrdad Moslemzadeh^{a,b,*}

^aResearch Center for Environmental Health Technology, Iran University of Medical Sciences, Tehran, Iran, Tel. +9886704745;

Fax: +982188622707; emails: mehrdad.moslemzadh@gmail.com (M. Moslemzadeh), jonidi.a@iums.ac.ir/ahmad_jonidi@yahoo.com (A.J. Jafari)

^bDepartment of Environmental Health Engineering, School of Public Health, Iran University of Medical Sciences, Tehran, IR, Iran

^cDepartment of Bacteriology, Faculty of Medical Sciences, Tarbiat Modares University, Tehran 11114115, Iran, email: mona.mahrooghi@gmail.com

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ABSTRACT

Performances of titanium tetrachloride (TiCl₄) and zirconium tetrachloride (ZrCl₄) for removal of *Escherichia coli* from synthetic turbid water were studied. Jar test experiments were conducted at various coagulant doses (10 to 60 mg L⁻¹), pH values (6–8.5) and effect of inorganic ions (Na⁺, Ca²⁺ and Mg²⁺) to determine the optimum conditions based on removal efficiencies of turbidity, *E. coli* and zeta potential. With increase of the coagulant dosages, the coagulation performances increased while the coagulants showed greater capacity for turbidity and *E. coli* removal at near their isoelectric points (40 and 50 mg L⁻¹), where turbidity and *E. coli* removal were 96.96% and 4.69 logs, respectively for TiCl₄ and 92.5% and 3.97 logs, respectively, for ZrCl₄. The pH had different effect on the removal performances, where the best results were in pH = 8.5 for TiCl₄ and pH = 6.5 for ZrCl₄, in which *E. coli* reductions were 4.85 logs and 4.35 logs, respectively, for TiCl₄ and ZrCl₄. Increase in the dose of ions improved coagulation performances, where decrease in the zeta potential revealed that compression of the double layer was the main mechanism for both coagulations. In summary, these results indicate that both TiCl₄ and ZrCl₄ enable adequate removal of *E. coli* from turbid water.

Keywords: *Escherichia coli*; Turbid water; Titanium tetrachloride; Zirconium tetrachloride; Coagulation

1. Introduction

Drinking water quality is closely related to people's health. It is estimated that 1.1 billion people do not have access to healthy water resources. Consequences of inadequate health service and clean water are including nearly 4 billion cases of diarrhea and 2.2 million deaths annually that were observed mostly among children in the developing countries [1]. Natural and wastewater contain colloidal solids and microbial pollutions. Colloidal solids are difficult to remove since they are stable and in result it can complicate water processing. Suspended solid in water led to turbidity

that was followed by shielding pathogens against disinfection processes in the water and wastewater treatment plants. Infectious diseases that stem from waterborne pathogens not only cause loss of life and illness but also have negative effects on the economy related to medical expenses and productivity losses because they can reach natural water sources in large amounts [2]. *Escherichia coli* is the most common enteric pathogen. This species is applied as an indicator of the microbial quality of water and wastewaters, and its presence represents fecal contamination [3]. World Health Organization (WHO) bacteriological criterion for drinking water is less than 1 *E. coli* per 100 mL [4].

* Corresponding author.

To remove turbidity and pathogen “especially *E. coli*”, there are many different methods [5–9]. In these works, the main mechanism to remove the pollutants was based on physical, chemical and physico-chemical processes, which are expensive technologies and they remove only one of the pollutants. Moreover, chlorination is one of the most common methods, which is used for water disinfection. Recent studies have found that the use of chlorine for water disinfection (e.g., two-step chlorination or three-step chlorination vs. one-step chlorination) could also improve the *E. coli* removal. These processes were found to be effective but tend to have high cost associated [10,11]. With respect to chemical oxidation that is conventional method for removal of pathogens, this process is not eco-friendly and some organism is resisted to the applied chemicals [11–13]. Therefore, production of a high quality water before disinfection step in the water treatment plants is crucial to supply a sanitary and economical water.

Among the technologies, the coagulation/flocculation process is the most common and the most effective process in simultaneous removal of the pollutants from wastewater. There are four main mechanisms in coagulation process including charge neutralization, compressing double electric layers, bridging effect and sweeping effect. Generally, two or more mechanisms would work together in actual water treatment because of different factors (such as coagulant dosage, pH, concentration of inorganic salt and so on) [14]. Recently, titanium tetrachloride (TiCl_4) and zirconium tetrachloride (ZrCl_4) have been used as novel coagulant in the water and wastewater treatment studies. The TiCl_4 can be an interesting alternative for conventional coagulants, which was proposed by Shon et al. [15] to solve the sludge disposal problem associated with conventional Fe and Al salt. In addition, TiCl_4 has a higher efficiency in water and sewage treatment compared with conventional coagulants such as $\text{Al}_2(\text{SO}_4)_3$, FeCl_3 , polyaluminum chloride (PAC), and polyester sulfate [16]. Also, flocs produced by TiCl_4 are mostly larger than conventional coagulants and they grow very fast. Finally, low toxicity of titanium salt has been reported in comparison with aluminum salt. For titanium-based compounds, no water quality guidelines have been determined yet. The residual concentration of titanium salt after treatment by TiCl_4 is about $10 \mu\text{g L}^{-1}$, which is in the range of titanium concentration in drinking water ($0.5\text{--}15 \mu\text{g L}^{-1}$) [17]. Recently it has been reported that zirconium tetrachloride (ZrCl_4) showed a good efficiency as a coagulant in the coagulation process with greater positive zeta potential of their flocs than Al-based coagulants. Also, it may enhance organic matter removal and reduce sludge production compared with Al and Fe. Several studies have reported that zirconium (Zr) has a high performance in reduction of waterborne pathogens compared with Al and Fe [18–20]. The Ti and Zr compounds (for use in coagulation) have been reported to be non-toxic and to not pose known risks to health and the environment [17]. However, their efficiency in reduction of waterborne pathogens is scarcely documented.

Meanwhile, determination mechanisms engaging on the coagulation process are important to enhance the removal performance of contaminants. Hence, investigation of zeta potential known as electrostatic charge of suspension is

necessary. The zeta potential demonstrates mobility rate of particles in water solution [21]. Changes in floc zeta potential are not only used to evaluate the destabilization ability of coagulants but also generally regarded as effective tool to investigate coagulation mechanism. Coagulation is generally explained in terms of charge neutralization and sweep flocculation [22]. One of the other factors that has influence on coagulation mechanisms was concentration of inorganic salt such as CaCl_2 , MgCl_2 and NaCl , which could be influenced in double-layer compression mechanism. They also can neutralize electrostatic charge of particles [21]. According to the mentioned issues and the benefits of using TiCl_4 and ZrCl_4 coagulants, the main objective of this study is to investigate removal of *E. coli* bacteria from synthetic turbid water using TiCl_4 and ZrCl_4 in the coagulation process.

2. Materials and methods

2.1. Chemicals

All applied chemicals were of analytical grade and utilized without further purification. *E. coli* (ATCC25922) was provided by Pasteur Institute of Iran. All culture media and chemicals were purchased from Merck Company. A Half McFarland standard solution and Mueller Hinton Broth (MHB) were supplied by Merck (Merck KGaA, Darmstadt, Germany). Titanium tetrachloride (TiCl_4), zirconium tetrachloride (ZrCl_4), calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), magnesium chloride (MgCl_2), sodium chloride (NaCl), hydrochloric acid (HCl) and sodium hydroxide (NaOH) were purchased from Merck, Germany. TiCl_4 and ZrCl_4 solution was prepared following the method described by Hussain et al. [17]. The stock solutions (1.6 g L^{-1} as metal concentration) of TiCl_4 and ZrCl_4 were prepared by dissolving 3.71 mL of TiCl_4 (0.2 M HCl solution) and 4.14 g of ZrCl_4 in high purity water. Also, stock solutions of salt (1 g L^{-1}) were obtained by dissolving 1 g of each salt in deionized water.

2.2. Preparation of bacterial strain

E. coli strain was cultured in nutrient broth medium for 24 h at 37°C (in aerobic conditions). With a sterile inoculating loop, a loopful of the suspension was streaked onto MacConkey agar and further incubated at 37°C for 48 h [23].

2.3. Preparation of synthetic turbid water

In this study, the synthetic turbid water was prepared as follows: in the first step, amount of clay after cleaning and drying in oven was milled and then sieved to obtain uniform clay particles. To sterilize the clay, it was autoclaved. The defined amount of sterilized clay was poured in a 10 L tank and it was settled for 2 h to remove its settling suspended solid. Then, 6 L of the test wastewater was picked up from surface of the suspension and then its content was characterized. In the second step, a 6 L suspension of tested bacteria in the sterile synthetic turbid water with 10^5 CFU/mL were prepared by adding 4,000 μL of bacterial culture in peptone broth (1.5×10^8 CFU/mL), respectively, in the room temperature. In each experiment, this work was carefully conducted to prepare test turbid water.

2.4. Experiments and jar test

The effects of coagulant dosage, pH and salt on the coagulation of turbidity, *E. coli* and the floc zeta potential were evaluated using single-factor experiments. First of all, the effects of coagulant dosage (10, 20, 30, 40, 50 and 60 mg L⁻¹) and pH solution (6, 6.5, 7, 7.5, 8 and 8.5) were investigated on the removal of turbidity and *E. coli*. Then, the effects of concentration of ion (Na⁺ = 10, 20 and 40 mg L⁻¹, Mg⁺² = 20, 40 and 80 mg L⁻¹, and Ca⁺² = 40, 80 and 160 mg L⁻¹) on the removal of turbidity and *E. coli* in coagulation were examined by adding pre-determined amounts of stock solutions of 1 mg L⁻¹ CaCl₂, MgCl₂ and NaCl to the test turbid water. In all the steps, the zeta potential of formed floc, also, was determined. So, for doing these experiments, the prepared test turbid water was coagulated on a programmable jar test using TiCl₄ and ZrCl₄ coagulants. The coagulation procedure involved a rapid mixing at 200 rpm for 1.5 min, followed by a 20 min of flocculation at 40 rpm, and a 20 min settling. Water samples were taken from 3 cm below the water surface.

2.5. Test turbid water quality analysis

Initial concentration of ions (Ca⁺², Mg⁺² and Na⁺) in the test turbid water was analyzed by a flame photometer (AE-FP8200-A). Measurement of zeta potential of the test turbid water and coagulated water was carried out using zeta analyzer (Zetasizer 3000HS Advance, Malvern Instrument GmbH, UK). Counting of *E. coli* bacteria was carried out by plate count method, where the number of colonies grown on the plate containing MHB media was counted before and after each of the experiment. The number of colonies within the range of 30–300 was counted after incubation for 24 h at 37°C. Each experiment was replicated three times. Turbidity was measured using a turbidimeter (Hach 2100P, USA). Removal efficiency of turbidity was calculated by Eq. (1), where C_i is the initial turbidity (before coagulation) and T_f is final turbidity (after coagulation).

$$\frac{T_i - T_f}{T_i} \times 100 \quad (1)$$

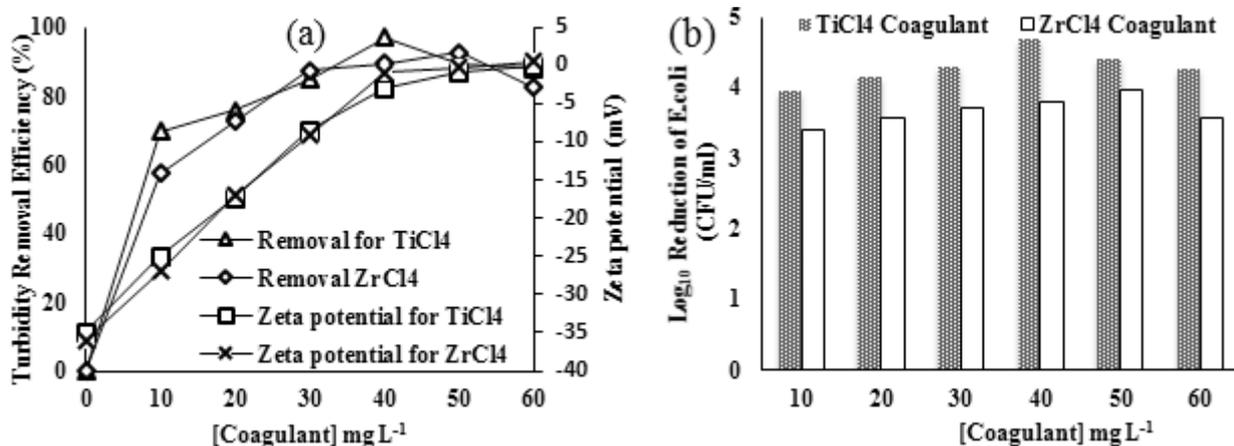


Fig. 1. Effect of coagulant dosage (mg L⁻¹) on the removal of turbidity and zeta potential (a), and the reduction of *E. coli* (b).

Table 1
Characterization of test wastewater

Na ⁺ , mg L ⁻¹	5
Ca ²⁺ , mg L ⁻¹	5
Ng ²⁺ , mg L ⁻¹	6
pH	7.2
Turbidity, NTU	20 ± 3
<i>E. coli</i> , CFU/mL	1.5 × 10 ⁸

All chemical and microbial experiments were performed based on the standard methods suggested by APHA [24], except where noted.

3. Results and discussion

3.1. Characterization of the test turbid water

The characterization of the test turbid water is listed in Table 1. The test turbid water used in the total experiments had approximately the same quality as one used throughout the study.

3.2. Effect of coagulant dosage on zeta potential and the removal efficiency

As known dosage of the coagulant is an efficient variable in the stabilization of colloids. Effect of coagulant dosage on the coagulation efficiency was conducted as pH = 7 and concentration of coagulants (TiCl₄ and ZrCl₄) was in the range of 20–60 mg L⁻¹. Figs. 1a and b present the jar test result of the synthetic water as a function of the coagulant dosage of TiCl₄ and ZrCl₄ coagulants in the concentrations of 2, 5, 10, 15, 20 and 25 mg L⁻¹; they include the simultaneous removal of turbidity (Fig. 1a), reduction of *E. coli* (Fig. 1b), and zeta potential for both the coagulants. For both TiCl₄ and ZrCl₄, the turbidity and *E. coli* removal efficiency increased with the increase in coagulant dose, however beyond certain dosage, 40 and 50 mg L⁻¹ for TiCl₄ and ZrCl₄, respectively, the removal efficiency consistently decreased with the coagulant dose (Figs. 1a and b). In addition, it was observed that TiCl₄

coagulation is more efficient than $ZrCl_4$ in the tested range dosage although both of them showed superior removal efficiency for the pollutants in the tested dosage. This conclusion was in accordance with the study by Hussain et al. [17]. Also, the variations in the reduction of *E. coli* same time the variations in the removal of turbidity show the reduction of *E. coli* can be influenced by the turbidity of water. Further increase in coagulant dosage led to floc charge reversal. The dosage, at which the charge reversal occurs, was defined as iso-electrical-dosage (IED) [25]. Thus, the IED values for $TiCl_4$ and $ZrCl_4$ were about 40 and 50 $mg\ L^{-1}$, respectively, indicating the charge neutralization capability order of $TiCl_4 > ZrCl_4$. The lesser efficiency of $ZrCl_4$ than $TiCl_4$ can be related to the pine floc formed by $ZrCl_4$ that have been reported in the studies by Christensen and Myrnel [18] and Deng et al. [26]. According to Fig. 1a, the zeta potential of coagulated water reached to -25 and -27 mV for $TiCl_4$ and $ZrCl_4$, respectively, at dosage of $10\ mg\ L^{-1}$ while raw tested water was about -36 mV. However, the zeta potential was steadily decreased after dosage of $10\ mg\ L^{-1}$. By compares on $TiCl_4$, $ZrCl_4$ coagulation received to re-stabilized point at dosage of $60\ mg\ L^{-1}$, where the zeta potential was $+0.5$ mV (Fig. 1a), which indicated that re-stabilized ions occurred easily with $ZrCl_4$ dosage increase, resulting in decrease of turbidity and *E. coli* simultaneous removal at higher dosages. It is while, the zeta potential decreased with increase in tested $ZrCl_4$ dosage, where the zeta potential was -0.2 . This appearance was in accordance with study by Zhao et al. [22]. The maximum reduction of *E. coli* by $TiCl_4$ and $ZrCl_4$ coagulants was 4.69 and 3.97 logs (Fig. 1b). According to the study carried out by Zhang and Farahbakhsh [27], the reduction of *E. coli* up to 2 logs during the secondary treatment using coagulant. For both coagulants, the reduction of *E. coli* for a tested water decreased after a pointed dosage of coagulants despite increase of zeta potential (Figs. 1a and b). This behavior is consistent with a sweep flocculation mechanism and adsorption [9]. The microbial removal by $TiCl_4$ and $ZrCl_4$ can be attributed to several factors. Zirconium effectiveness is usually explained in terms of its valence [19], which presumably provides higher charge neutralization power. That is necessary for destabilization of microbial and

other colloids. This also explains the higher $TiCl_4$ and $ZrCl_4$ affinity to organic matter and algal organic matter shown in the previous studies [19,28].

3.3. Effect of pH on zeta potential and removal efficiency

Coagulant chemicals have an optimum pH range in which good coagulation and flocculation occur in the shortest time with a given dosage [29]. Also, charge on hydrolysis products and precipitations of metal hydroxides are controlled by pH of solution. So, pH is an important variation in the chemical coagulation [30]. Effect of pH of solution on the coagulation performance was conducted at concentration of the coagulants in the range of $20\ mg\ L^{-1}$ and pH in range of 6–8.5. The results of turbidity, *E. coli* simultaneous removal efficiencies, and zeta potential in the pH variations for both coagulants were summarized in Figs. 2a and b. As can be seen in Figs. 2a and b, both turbidity removal and reduction of *E. coli* showed steady increase with increased pH for $TiCl_4$ coagulant; the optimum turbidity removal (90%) and the reduction of *E. coli* (4.85 logs) for $TiCl_4$ coagulant occurred at $pH = 8.5$. It is while, the turbidity removal and *E. coli* reduction for $ZrCl_4$ coagulant showed steady increase with pH lower and then beyond the inflection point the coagulation efficiency was either inhibited or even decreased with pH as the optimum turbidity removal (85%) was at 6.5 (Fig. 2a), while the *E. coli* reduction (4.52 logs) was at pH 6 (Fig. 2b). This observation was in agreement with the findings by Deng et al. [26] and Chekli et al. [28], who demonstrated that coagulation of organic matter and turbidity by $TiCl_4$ and $ZrCl_4$ was the most efficient when pH was 9 and 6, respectively. Also, Fig. 2a shows the variation of zeta potential at different solution pH for $TiCl_4$ and $ZrCl_4$ coagulants. The zeta potential of flocs formed after coagulation with the $TiCl_4$ and $ZrCl_4$ increased dramatically with the increase of pH value. With increase of pH, zeta potential decreased from -1 to -28 mV for $TiCl_4$ and from -2 to -32 mV for $ZrCl_4$. This indicated that the charge neutralization effect of $TiCl_4$ and $ZrCl_4$ at acidic condition was superior to that at alkaline and neutral condition. According to the trend of zeta potential with the pH variations, and this fact that

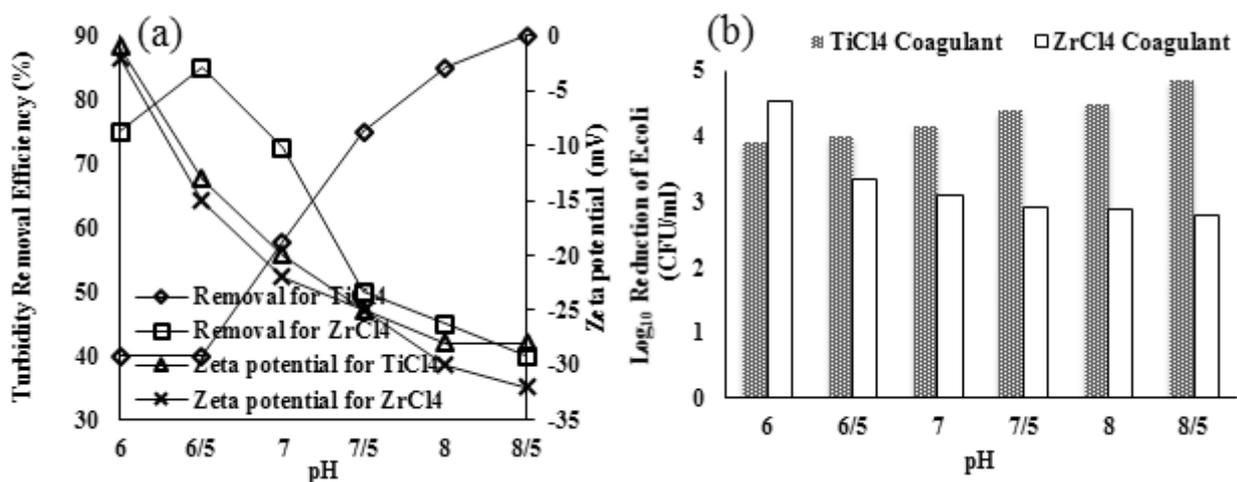


Fig. 2. Effect of pH on the removal of turbidity and zeta potential (a), and the reduction of *E. coli* (b).

the highest coagulation performance achieved at pH 8.5 for $TiCl_4$, it was proved that the coagulation behavior is consistent with a sweep flocculation mechanism but is inconsistent with adsorption and charge neutralization [22]. That is while, the maximum $ZrCl_4$ coagulation performance occurred

at pH = 6.5 and then it reduced by further increase of pH, which clearly demonstrated that clear adsorption and charge neutralization is the main mechanism in this process [31]. So, the difference in the effect of the initial solution pH on floc zeta potential attributes to the coagulant hydrolyzates [32].

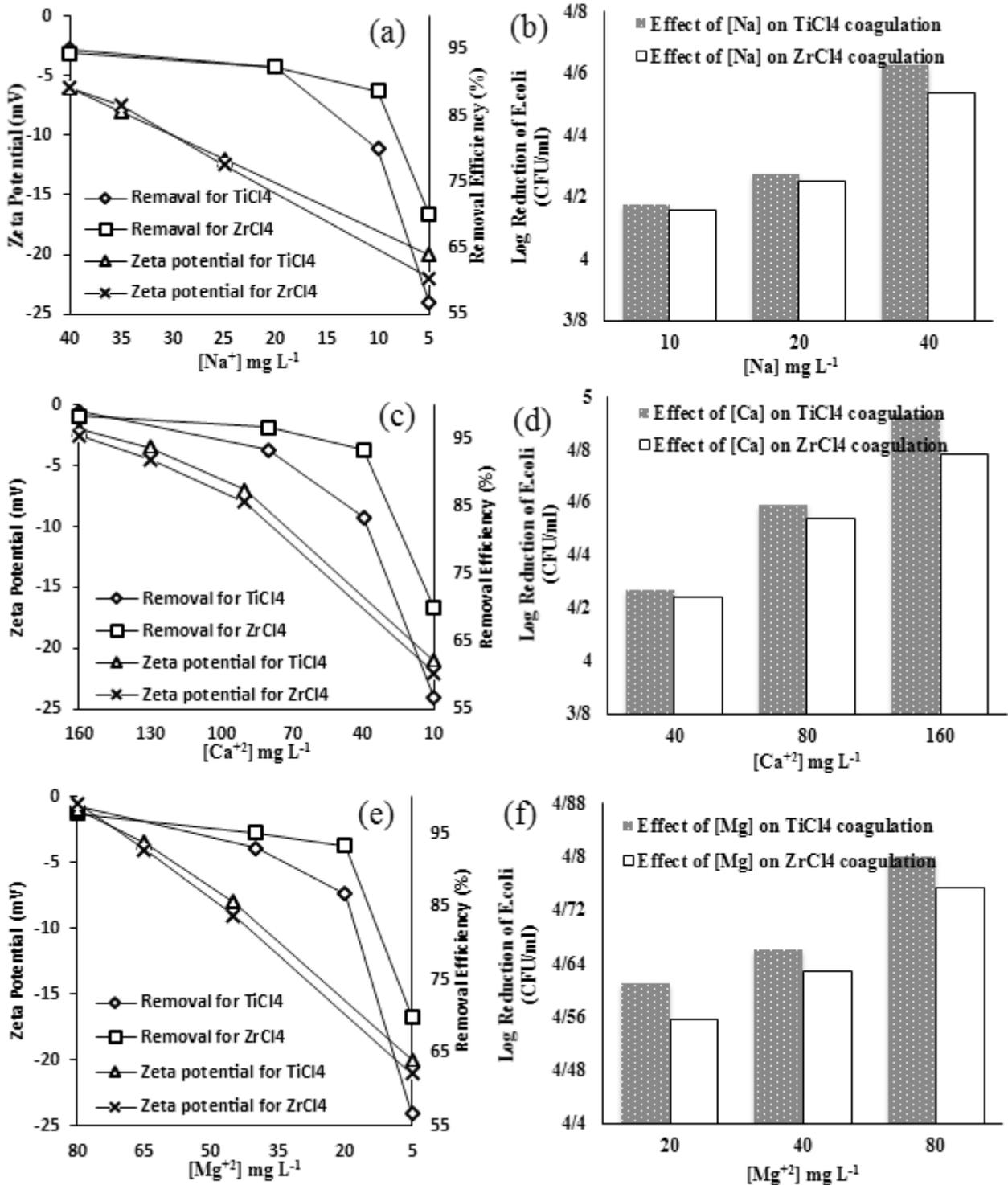


Fig. 3. Effect of Na^+ , Ca^{2+} and Mg^{2+} in the tested water on the coagulation performance of $TiCl_4$ and $ZrCl_4$ (pH = 7, coagulant dosage = 20 mg L⁻¹).

The colloids were easily adsorbed and co-precipitated by the hydrolyzates, which had low solubility and large surface area. When pH was higher than 7, the suspension system was difficult to be destabilized because the hydrolyzates were transformed to metal hydroxyls [32]. These complexes are predominant, when the pH is higher that resulted in simultaneous reduction of the turbidity and *E. coli* for both coagulants. When the pH value is lower, the high positive-charged complexes of TiCl_4 and ZrCl_4 ion could cause the micro flocs formed, which makes the micro flocs re-stabilize resulting in decreased turbidity and *E. coli* removal efficiency.

3.4. Effect of salt concentration on the removal efficiency

As discussed in Section 1, the effects of salt on the turbidity and *E. coli* simultaneous removal were primarily attributed to the double-layer compression effect of the cations introduced through the addition of TiCl_4 by ZrCl_4 tested solution. The effects of Ca^{+2} , Mg^{+2} and Na^+ in the synthetic water on TiCl_4 and ZrCl_4 coagulation were investigated further at pH = 7 with a coagulant dosage of 20 mg L^{-1} for both coagulants. The tested concentration ions, in this study, were in the range of surface water [33]. Fig. 3 shows the effect of concentration of the ions (Ca^{+2} , Mg^{+2} and Na^+) on the turbidity removal efficiency, Zeta potential, and the reduction of *E. coli* by TiCl_4 and ZrCl_4 as coagulants. Figs. 3a, c and e show that increase in the concentration of ions, increased turbidity removal for both coagulants. This increase is more remarkable for TiCl_4 coagulation than ZrCl_4 do that. The turbidity removal increased considerably from less than 56.66% for the TiCl_4 and 70% for the ZrCl_4 , corresponding to the tested water, to 80%, 83.33% and 86.66% for the TiCl_4 and 86.66%, 93.33% and 93.33% for the ZrCl_4 , when the $[\text{Na}^+, \text{Ca}^{+2}$ and $\text{Mg}^{+2}]$ of the tested water were 10, 40 and 20 mg L^{-1} , respectively (Figs. 3a, c and e).

Also, the zeta potential of water treated by both coagulants (TiCl_4 and ZrCl_4) decreased by increasing concentrations of the ions (Na^+ , Ca^{+2} and Mg^{+2}) (Figs. 3a, c and e).

Increase of Na^+ concentration led to decrease in zeta potential of coagulated water from -20.2 mV for TiCl_4 and -22 mV for ZrCl_4 coagulation to -6.1 mV for TiCl_4 and -6 mV for ZrCl_4 coagulation (Fig. 3a). Increase of Ca^{+2} concentration decreased the zeta potential of coagulated water from -21.2 to -1.9 mV for TiCl_4 coagulation. On the other hand, the zeta potential of coagulated water changed from -22 to -2.5 mV for ZrCl_4 coagulation (Fig. 3c). The zeta potential decreased from -20.2 mV for TiCl_4 coagulation and -21 mV for ZrCl_4 coagulation to -0.5 and -1 mV , respectively. These phenomena show, where coagulant dosage and pH were constant, increase of Ca^{+2} and Mg^{+2} concentrations could have reached the zeta potential of tested water close to the point of zero charge of particles in the water that resulted in increase not only in the turbidity but also in the *E. coli* reduction (Figs. 3b, d and f). For both coagulants, increase of Na^+ , Ca^{+2} and Mg^{+2} concentrations improved reduction the *E. coli*. The highest reduction of *E. coli* for TiCl_4 and ZrCl_4 coagulation were 4.62 logs and 4.53 logs, respectively, where Na^+ concentration was 40 mg L^{-1} (Fig. 3a). Also, reduction the *E. coli* up to 4.92 logs for TiCl_4 and 4.78 logs for ZrCl_4 , when Ca^{+2} concentration was 160 mg L^{-1} . In concentration 80 mg L^{-1} for Mg^{+2} , reduction the *E. coli* up to 4.79 logs and 4.75 logs for TiCl_4 and ZrCl_4 coagulation, respectively. The results clear that the turbidity and *E. coli* reduction efficiencies for TiCl_4 coagulation were more influenced than ZrCl_4 coagulation in the tested salt. Also, it shown that Ca^{+2} ion was more effective than other ion (Na^+ and Mg^{+2}) in this coagulation process. All the results show that turbidity and *E. coli* reduction efficiency have been increased with increasing the concentration of salt, where it was approximately near to surface water salt concentration. On the other hand, Wang et al. [21] have reported that high concentrations of the salt, at the limit of synthetic sea water, can decrease turbidity removal efficiency when concentration of salt (Na^+ , Ca^{+2} and Mg^{+2}) exceed the desirable amount due to re-stabilization of particle materials. The existence of salt can cause compression of the double layer, resulting in destabilization of particles

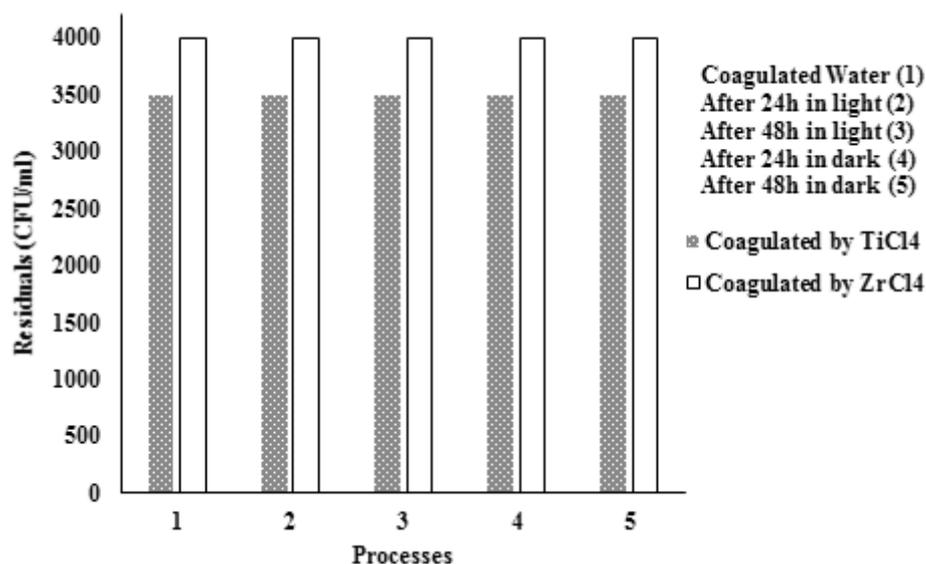


Fig. 4. Bacterial regrowth during storage of the treated samples.

whereby repulsive electrostatic interactions are overcome by attractive van der Waals forces [31].

3.5. Bacterial regrowth during storage of the treated samples

To investigate whether bacterial regrowth occurred during storage of water coagulated by TiCl_4 and ZrCl_4 , tests were conducted with three types of water samples after 24 and 48 h of storage in dark or light at the ambient temperature. The results of the study are presented in Fig. 4. It is obvious from Fig. 4 that no significant growth or decay have occurred during the 2-d storage in each of the samples containing *E. coli* treated by TiCl_4 and ZrCl_4 coagulants. This phenomenon could have occurred because of narrow antimicrobial activity for TiCl_4 and ZrCl_4 [34].

4. Conclusion

The work reported here was aimed to assess the performances of TiCl_4 and ZrCl_4 salt for the removal of turbidity and *E. coli* bacteria from synthetic turbid water. The final results are as follows:

- The TiCl_4 performed somehow better in terms of turbidity and *E. coli* removal than ZrCl_4 at the same dose. The maximum performance of TiCl_4 and ZrCl_4 was in dosage of 40 and 50 mg L⁻¹, respectively.
- The TiCl_4 coagulant showed better efficiency in removing turbidity and *E. coli* compared with ZrCl_4 coagulant at alkaline pH (maximum in pH = 8.5). It is while, the maximum performance of ZrCl_4 was in pH = 6.5.
- The presence of ions (Na^+ , Ca^{+2} and Mg^{+2}) as mono and divalent cations promoting compression of the double layer mechanisms resulted in improving the TiCl_4 and ZrCl_4 performance.
- The neutralization and compression of the double layer were the main mechanisms involved for both TiCl_4 and ZrCl_4 coagulations while sweep coagulation were found to be the main mechanism at high pH volume (alkaline pH).
- The results of this study indicate that both TiCl_4 and ZrCl_4 coagulations can achieve turbidity and *E. coli* removal efficiency better than second step in wastewater treatment.

So, the results indicate that these TiCl_4 and ZrCl_4 salt could be used as coagulants in water treatment processes providing no health risks in their application.

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