

Investigation of the efficiency of removing turbidity, aluminum, and total organic compounds by using poly-aluminum chloride and chitosan from the water of Karoon River, Iran

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ABSTRACT

This study was conducted with the aim of investigating the efficiency of chitosan in improving the performance of poly-aluminum chloride in removing turbidity, aluminum, and organic compounds, including total organic carbon (TOC) and UV_{254} (absorption of organic compounds by ultraviolet radiation as the wavelength of 254 nm), within the stage of slow mixing of drinking water. This research was conducted on the laboratory scale using a jar test device at the water treatment plant in Ahvaz. The optimal dose of poly-aluminum chloride, together with chitosan, was obtained as 5 and 0.02 mg/L, respectively. The efficiency of the removal of turbidity, TOC, and aluminum, and the absorption of organic compounds by the ultraviolet radiation of a wavelength of 254 nm under optimal conditions of the performance of chitosan, were achieved as 96.59%, 46.15%, 80.49%, and 67.86%, respectively. The governing mechanism for destabilizing colloid particles and removing natural organic compounds can be justified through bridging between the particles—polymers—neutralization of the charge of colloid natural organic compounds, and joint deposition mechanism through adsorption. In addition, the flocs developed by chitosan are larger as they possess greater molecular weight, thereby requiring less time for the deposition.

Keywords: Poly-aluminum chloride; Chitosan; Turbidity; Total organic carbon; Karoon River

1. Introduction

The treatment of water pollutants, especially surface waters, in a manner that is in line with the national standards and regulations of drinking water requires the application of various units and processes [1–5]. Currently,

and in the majority of treatment processes, different chemicals are used to convert colloid forms of the pollutants into sediment able particles [6,7]. In the majority of treatment plants in Iran, alum, and ferric chloride are employed [8–13]. This compound, also known as hydrated aluminum

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chloride, is a pre-polymerized coagulant. In terms of composition, it is a mineral macromolecule, the monomers of which consist of a dual-core complex of aluminum [14,15]. Poly-aluminum chloride introduces some impurities, such as epi-chloroidine—a carcinogenic compound—into the water [16]. Serious damage has occurred in response to the application of aluminum salts which have remained in the water, with the production of a large volume of sludge and its discharge into the environment. The guidelines of the World Health Organization for aluminum and its maximum allowable limit stipulate 0.2 mg/L.

In recent years, a greater tendency has developed toward natural organic polymers instead of artificial compounds. Such coagulants are biodegradable and when they remain in water, it poses no risk to the health of consumers [17,18]. Chitosan was used as a coagulant in Japan in the 1950s. Chitosan, which develops out of deacetylation of chitin, is a polyelectrolyte cation [19]. Therefore, it can act very effectively in the neutralization of negative electric charges [19–21]. Among the most important advantages of chitosan over metal salts in the coagulation process are the low effective injection dose, the lower volume of the sludge, less functional dependence on pH, production of sludge with a better drainage property, higher density, better biodegradability, the property of non-corrosiveness, and convenient displacement. Furthermore, chitosan has fewer adverse effects on the pH and alkalinity when compared to other conventional coagulants. The action mechanism of coagulation and flocculation of this compound involves neutralization of charge, adsorption, and bridging between the colloid particles [21].

Zemmouri et al. [22] investigated the efficiency of chitosan along with alum in removing turbidity. The degree of removal of turbidity by chitosan in conjunction with alum was reported to be as high as 97%. The optimal dose of chitosan was achieved in 0.2 mg/L. Saritha et al. [23] investigated the effect of alum as a coagulant and chitosan as a coagulant aid in removing turbidity, hardness, and E. coli. The optimal dose of chitosan for turbidity of 100 NTU was obtained as 0.5 mg/L. They observed that chitosan significantly decreases the dose of alum required by between 50% and 87.5% [23]. García and Moreno [24] examined the removal of organic compounds, using chitosan and alum. The results suggested that the greater performance of chitosan in comparison with alum in removing turbidity, total organic carbon (TOC), and UV_{254} . They also showed that chitosan, as a coagulant aid together with alum, introduces less aluminum into the water, thereby decreasing the optimal dose of alum by 50%. Rizzo et al. [25] reported the degree of removal of turbidity by chitosan by as much as 85%. The reduction of UV₂₅₄ using chitosan was reported to be around 30%-60% in contrast to using alum and chitosan as a coagulant aid; it has been reported at 85.1%-87% [25]. Sharp et al. [26] reported the degree of removal of turbidity and TOC by chitosan by more than as much as 90%, when compared with alum, which is because of the high molecular weight and presence of amine groups in the chitosan. Mehdinez had examined the efficiency of chitosan and the coagulation protein of Moringa olifera as a coagulant aid together with alum for removing colloid particles, the bacteria of E. coli, and Streptococcus ficalis. The optimal pH was obtained as 7–7.5. The application of the coagulation protein of Moringa and chitosan diminished 12.5%–62.5% and 50%–87.5%, respectively, of the concentration of the alum coagulant across various turbidity and lowered the residual aluminum up to below 0.2 mg/L [27].

The water of the Karoon River in Ahvaz contains various contaminants, including turbidity, aluminum, and organic compounds like TOC, and the amounts of these contaminants vary considerably from seasons to seasons. Thus, a coagulation process through the selection of a suitable coagulant with optimal injection concentration at appropriate pH and alkalinity will be able to remove significant amounts of these contaminants in water, which pose a serious threat to the health of consumers. This research has been conducted with the aim of investigating the efficiency of chitosan as a coagulant aid for improving coagulation in removing turbidity, aluminum, and organic compounds, including TOC, and the absorption of organic compounds and deduction of the dose of the poly-aluminum chloride. It will thereby decrease the economic costs and health effects resulting from the potential release of aluminum into drinking water.

2. Materials and methods

2.1. Chemicals and equipment

This research was carried out on a laboratory scale using a jar test device at the water treatment plant in Ahvaz. The water source of this treatment plant is the Karoon River. This treatment plant provides the major portion of the drinking water for Ahvaz. The commercial poly-aluminum chloride, with a purity of 30% (w/w) from Falizan Tasfiye Company (Tehran), NaOH 0.02% N, chitosan powder with deacetylation degree of 85% from Sigma Aldrich Company (United Kingdom), ascorbic acid, sulfuric acid 0.02 N, and aluminum sodium acetate were consumed during the experiments. The equipment used in the research includes TOC meter (Shimadzu, Japanese, VSH (V model - standalone high sensitivity)), spectrophotometer (Dr-5000) HACH Company (United States), turbidity meter (2100N-HACH), Stirrer (JENWAY-1203, North America), and pH meter (WTW – Wissenschaftlich Technische Werkstätten, Germany).

2.2. Methods

The raw water samples prepared from the intake of the Ahvaz treatment plant were experimented with in terms of the degree of turbidity, pH, temperature, alkalinity, aluminum, UV absorbance (UV-254), and TOC. In order to determine the optimal pH of the coagulant compound - poly-aluminum chloride - this compound was added to all the samples with a constant concentration of 10 mg/L. Thereafter, ajar test was performed on the samples with different pHs of 5, 5.5, 6, 6.5, 7, 7.5, 7.78, 8, 8.5, and 9. To investigate the determination of the coagulant concentration, a jar test was conducted on water samples under optimal pH conditions (pH = 8) with different concentrations of poly-aluminum chloride (3-50 mg Al/L). Following the determination of the optimal concentration of the coagulant, a constant concentration of poly-aluminum chloride (10 mg Al/L) was added to water samples so as to determine the optimal concentration of the chitosan coagulant aid.

A rapid mixing process – with a mixing rate of 120 rpm - was carried out during one minute. At the end of the rapid mixing process, various doses of the coagulant aid chitosan (0.02–10 mg/L) were added to water samples. Next, over the slow mixing stage, the mixing rate was reduced to 40 rpm for 20 min. After that, in order to determine the optimal concentration of poly-aluminum chloride together with the coagulant aid chitosan, a constant concentration of this coagulant aid (0.02 mg/L) and various amounts of the coagulant compound - poly-aluminum chloride (1-20 mg/L) - were added to the samples. The sedimentation duration was considered 30 min. according to the recommendations of valid references [28]. By the end of the experiments, samples were taken to determine turbidity, alkalinity, pH, TOC, absorption of organic compounds, and residual aluminum off 5 cm below the water surface using pipette. For doing the TOC experiment, the samples were poured into dark 250 mL glass bottles with sandpaper caps, then immediately analysed. In order to ensure absence of organic compounds before the application, they were washed by nitric acid 5%. Thereafter, after washing with water, they were placed inside in an oven at 400°C for 1 h.

All the experiments have been carried out, based on standard methods for water and wastewater experiments. Turbidity was evaluated using a turbidity meter HACH, model 2100 N, and according to nephelometric method. Aluminum was measured using spectrophotometer Dr-5000 (3500-Al B. Eriochrome cyanine R method). TOC was measured using TOC meter, Shimadzu, model TOC-V model – combustion standalone high sensitivity (5310-B high temperature method). The UV absorbance (UV-254) was analyzed in accordance with the standard method No. 5910B (ultraviolet absorption method) by using spectrophotometer Dr-5000 and alkalinity was measured by 2320 B. Titration and pH were measured using a digital pH meter, Model 340i (WTW).

In addition, in order to prove the replicability of the analysis method, some of the samples have been prepared in two or three numbers and then analyzed. The total number of the samples over the sampling was 232. Figures were prepared using Microsoft Excel and data were analyzed using Statistical Package for Social Science Software.

3. Results and discussion

Table 1 illustrates chemical and physical specifications of Karoon River water. Fig. 1 represents the trend of changes in the turbidity removal according to pH. The mean input and output turbidity lay within the ranges of 33-34 and 2.08-6.81 NTU, respectively. The efficiency of removal of turbidity has ranged from 80.0% to 93.9%. As can be inferred from Fig. 1, removal of turbidity using poly-aluminum chloride is very sensitive to pH variations, such that the highest mean of turbidity removal (with a confidence interval of 95%) is 93.9% at pH = 8. In other words, in this pH range, the sediment developed during the process - that is, the hydrolysis products of poly-aluminum chloride - have the lowest solubility. According to Fig. 1, with the increase in pH, the percentage of turbidity removal grows. Note that this size of the developed flocs has been cleared in large at the optimal pH, when compared with other pHs. It can be observed that at acidic pHs, the degree of removal of turbidity has diminished. For this reason, charge neutralization cannot be considered the cause of formation of flocs. It seems that the formation of flocs within the optimal pH has occurred mainly through the entrapment of suspended solids in the polymer chains of the coagulant compound, called the swipe coagulation mechanism, and the entrapment of particles in the sediment. Fig. 1 also demonstrates the trend of changes in TOC removal, considering pH. The mean input and output TOC lay within the range of 1.29 mg/L and 0.93– 1.21 mg/L, respectively. The efficiency of removal of TOC has been between 6.2% and 27.9%. The greatest degree of removal of TOC at pH = 8 is 27.9%.

Fig. 2 represents the trend of changes in output aluminum and UV₂₅₄ in relation to pH. The mean input aluminum and UV₂₅₄ have been 0.008 mg/L and 0.038 cm⁻¹, while the mean output aluminum and UV₂₅₄lay within the range of 0.022–0.031 and 0.023–0.031 cm⁻¹. The efficiency of removal of UV₂₅₄ in this period has been within a minimum of 18.42% up to a maximum of 39.5%. In addition, at lower pHs, smaller flocs have been produced with a slower sedimentation time. Bina et al. [21] and Mirzaiy et al. [29] obtained the optimal pH for removing turbidity and organic compounds using poly-aluminum chloride as pH = 8.

Fig. 3 represents the trend of changes in the output turbidity with respect to the dose of the coagulant polyaluminum chloride. The mean input and output turbidity lay within the ranges of 44-45 and 0.89-10.64 NTU, respectively. The efficiency of removal of turbidity has ranged from 75.8% to 97.98%. Overall, the results indicate that with the increase in the concentration of poly-aluminum chloride, turbidity has also increased. The greatest removal efficiency - at 10 and 30 mg/L of the poly-aluminum chloride - was achieved as 93.98% and 97.58%, respectively. According to Fig. 3, it seems that the 93.98% removal is a special point viz. a critical point in the figure. For this reason, the optimal concentration of poly-aluminum chloride for removing turbidity is 10 mg/L. On the other hand, an investigation of the results obtained indicates that the mechanisms that cause lower residual turbidity in water depend on the concentration of the consumed coagulant and pH of water. Under these conditions, dominant mechanisms have been

Chemical and physical characteristics of Karoon River water

Parameter	Value
EC (μs/cm)	1,999
рН	7.99
TDS (ppm)	1,278
TOC (ppm)	5
Turbidity (NTU)	30-132.6
Alkalinity (mg/L CaCO ₃)	139.33–179.4
Aluminum (ppm)	0.004-0.008
Hardness (mg/L CaCO ₃)	492
Calcium (ppm)	135.52
Magnesium(ppm)	36.77
Sodium (ppm)	258.7
Chloride (ppm)	399.3



Fig. 1. Trend of changes in the remaining turbidity and TOC vs. pH (initial concentration of PAC: 10 mg/L, initial turbidity: 33–34 NTU, and temperature: 24.5).



Fig. 2. Trend of changes in the remaining aluminum and UV_{254} vs. pH variations (initial concentration of poly-aluminum chloride:10 mg/L, initial turbidity: 33–34 NTU, and temperature = 24.5).



Fig. 3. Trend of changes in the output turbidity in relation to the dose of poly-aluminum chloride (pH = 8, temperature: 23.9, initial turbidity: 44–45 NTU, and rapid mixing rate: 120 rpm).

mentioned to be of absorption or swipe type, or sometimes a combination of both mechanisms. Fig. 4 demonstrates the trend of changes in output TOC in relation to the dose of the poly-aluminum chloride. The mean input and output TOC lay within the ranges of 1.38 and 0.9–1.28 mg/L, respectively. The efficiency of removal of TOC has been between 7.25% and 34.78%. Based on Fig. 4, with the increase in the dose of poly-aluminum chloride, the removal of TOC also rises. Fig. 4 also represents the trend of changes in the output aluminum with respect to the dose of poly-aluminum chloride. The mean input and output aluminum lay within the ranges of 0.008 and 0.008–1.4 mg/L. Based on this figure, from 1 to 3 mg/L, the trend of changes in aluminum is almost constant. However, from 3 to 30 mg/L, it has an ascending trend, and from 30 mg/L onwards, the increase becomes more dramatic. With the increase in the dose of the coagulant, zeta potential grows, with eventually less metal residuals being removed.

Fig. 5 illustrates the trend of changes in output UV₂₅₄ with respect to the dose of poly-aluminum chloride. The mean input and output UV₂₅₄ lay within the ranges of 0.039 and 0.006–0.029 cm⁻¹, respectively. The removal efficiency of UV₂₅₄ in this period has ranged between 25.64% and 84.62%. Based on this figure, with the increase in the dose of poly-aluminum chloride, the removal of organic compounds also increases. Based on the degrees of removal obtained, it seems that optimal concentration of poly-aluminum chloride for the concurrent removal of turbidity, TOC, and aluminum is 10 mg/L. In the poly-aluminum chloride coagulant, the major parts of aluminum ions are in the form of oligomer and polymer, where only one small proton of aluminum is



Fig. 4. Trend of changes in the output TOC and aluminum with respect to the poly-aluminum chloride dose (pH = 8, temperature: 23.9, initial turbidity: 44–45 NTU, and rapid mixing rate: 120 rpm).



Fig. 5. Trend of changes in output UV_{254} in relation to the dose of poly-aluminum chloride (pH = 8, temperature: 23.9, initial turbidity: 44–45 NTU, and rapid mixing rate: 120 rpm).

in monomer form. Through neutralization of all negative charges of colloidal particles by poly-aluminum chloride, the probability of the presence of aluminum in monomer form is lower, given the turbidity of water and degree of charge neutralization. Therefore, it emerges less in the form of residual aluminum in water treatment. This phenomenon is the reason for the superiority of poly-aluminum chloride in flocculation. Mehdinejad et al. [30] showed that the amounts of residual aluminum in the application of poly-aluminum chloride in waters with low, medium, and high turbidity were 0.006, 0.05, and 0.07 mg/L, respectively. Hassani et al. [31] compared the performance of coagulants in removing turbidity, aluminum, and organic compounds. This investigation showed the effects of the elevation of the dose of poly-aluminum chloride in removing turbidity, aluminum, TOC, and $\mathrm{UV}_{\mathrm{254}}$ when compared with other coagulants to a better extent. Deng et al. [32] reported the efficiency of removal of turbidity under optimal conditions for surface waters by poly-aluminum chloride as 73.3%-83.3%.

Under optimal conditions obtained from the previous stage, different concentrations of chitosan were applied to determine the maximum turbidity removal, where the optimal concentration of chitosan was obtained as 0.02 mg/L. The highest mean of the percentage of turbidity removal - with a confidence interval of 95% for the coagulant dose of 0.02 mg/L – is as much as 99.2%. In addition, the flocs formed by chitosan were larger when compared with the control sample (10 mg/L poly-aluminum chloride) and had a greater sedimentation rate. The mean input turbidity lay within the range of 62.7-132.6 NTU, while the mean output turbidity at the 10 mg/L dose of poly-aluminum chloride with the coagulant aid of chitosan within the doses of 0-10 mg/L lay within the range of 0.53-2.5 NTU. The results obtained (Fig. 6) indicate that the addition of chitosan as the coagulant aid has enhanced the process efficiency. In the best scenario, that is, when the concentrations of poly-aluminum chloride and chitosan are 10 and 0.02 mg/L, respectively, the percentage of turbidity removal was obtained at 99.2%. Overall, with the increase in the concentration of the chitosan as coagulant aid, the removal of turbidity has increased. When compared with the control sample, the final turbidity of the sample was lower in



Fig. 6. Trend of changes in output turbidity and TOC in relation to the dose of chitosan (initial concentration of poly-aluminum chloride: 10 mg/L, pH = 8, temperature: 24.7, and rapid mixing rate: 120 rpm).

conditions where the dose of the coagulant aid chitosan lay within the range of 0.02 and 0.8 mg/L. At higher doses of chitosan, within the range of 1–10 mg/L, the final turbidity was greater than that of the control sample, but it was lower than the input turbidity. The reason of this behaviour can be attributed to the fact that until 1 mg/L, chitosan has a positive charge, and has neutralized the negative charge of the existing colloid particles, that is, the electrical charge of the solution has reached zero.

The extra injected chitosan itself caused the development of extra positive charge. This means that the potential has been reversed and has resulted in secondary turbidity. Therefore, 0.02 mg/L of chitosan was chosen as the optimal dose. Moreover, the flocs developed by chitosan were larger and had a greater sedimentation rate than the control sample (10 mg/L poly-aluminum chloride). Fig. 6 represents the trend of changes in output TOC in accordance with the dose of chitosan. The mean input TOC has been calculated as 1.5 mg/L. During this period, the mean output TOC lay within the range of 0.8-5.7 mg/L. Based on the Fig. 6, with the increase in the dose of chitosan up to 0.6 mg/L the degree of TOC removal grew, but from 0.6 mg/L onwards, it diminished. The output TOC was lower than the control sample's (0.91 mg/L) up to the dose of 0.1 mg/L. Fig. 7 illustrates the trend of changes in the output organic compounds, based on the dose of chitosan. The mean input and output levels of organic compounds during this stage of sampling lay within 0.03 and 0.006–0.089 cm⁻¹, respectively. Based on the Fig. 7, with the increase in the dose of chitosan up to 0.08 mg/L, the degree of removal of organic compounds increased, but from 0.08 mg/L onwards, it declined. The amount of the output organic compounds up to 0.1 mg/L was lower than that of the control sample (0.011 cm⁻¹). Lower doses of chitosan caused a further removal of organic compounds, because of the high density resulting from amine groups in chitosan. Renault indicated that chitosan develops larger flocs through the mechanism of bridging between particles and charge neutralization, resulting in further removal of organic compounds [33]. At this stage, with the increase in the dose of chitosan, the level of aluminum did not change when compared with the control sample (poly-aluminum chloride). The mean input and output levels of aluminum have been calculated at 0.004 and 0.04 mg/L (the output state: poly-aluminum chloride alone and poly-aluminum chloride with chitosan). According to



Fig. 7. Trend of changes in output UV_{254} in relation to the dose of chitosan (initial concentration of poly-aluminum chloride: 10 mg/L, pH = 8, temperature: 24.7, and rapid mixing rate: 120 rpm).

the analysis of variance with p > 0.05, there is no significant difference between the dose of chitosan and the level of output aluminum. In other words, the factor of the dose of chitosan has no effect on the level of aluminum. The results obtained in this study have been congruent with those obtained by Yarahmadi et al. [34] on chitosan as a coagulant aid. In a study, Ganjidoust et al. [35] reported TOC removal by chitosan as 70%. Wang et al. [36] investigated the effect of chitosan as coagulant aid in the shape and strength of flocs. Under optimal conditions for the removal of turbidity, chromium, and TOC, the optimal dose of chloride ferric and chitosan were obtained as 29 and 0.1 mg/L, respectively [36]. The size and dimensions of flocs, when chloride ferric was used alone, increased from 1.1855 to 1.3028, compared with when chloride ferric and chitosan were used concurrently.

Fig. 8 represents the trend of changes in the output turbidity in terms of the doses of poly-aluminum chloride added in the rapid mixing stage. The mean input and output (within the doses of 1-20 mg/L) turbidity lay within the ranges of 46.8-70 and 0.64-7.98 NTU, respectively. The degree of removal of turbidity in this period for 0.02 mg/L chitosan plus poly-aluminum chloride, within the doses of 1–20 mg/L, varied between 83.54% and 98.63%. The maximum efficiency of turbidity removal has been observed at the chitosan dose of 0.02 mg/L at the injection dose of 10 mg/L, but since there was no significant difference between the efficiency of turbidity removal at doses below 10 mg/L, hence, 5 mg/L was chosen as the optimal dose. As can be inferred from the figure, with the increase in the dose of poly-aluminum chloride at this stage, the turbidity of the samples diminishes from the dose of 1–5 mg/L, but from 5 mg/L onwards, it declines with a very slight rate of reduction. The results obtained showed that the combination of poly-aluminum chloride and chitosan is able to remove turbidity up to the standard level (5 NTU). Huang et al. [37] showed that the maximum removal of turbidity occurred at an optimal dose of poly-aluminum chloride at 4 mg/L and of chitosan at 1 mg/L. Furthermore, experimental observations indicated that the flocs obtained from the application of chitosan as coagulant aid were very much larger, and required less time for sedimentation when compared with the mere use of poly-aluminum chloride [37]. Roussy et al. [38] showed that the predominant mechanism



of turbidity removal by chitosan (because of the high number of amine groups and the generation of large amounts of positive charge under neutral and slightly acidic conditions) is charge neutralization. Furthermore, the application of these compounds has no effect on the alkalinity and pH of the sample's water before- and after-jar test.

Fig. 9 shows the trend of changes of output TOC in terms of the coagulant dose of poly-aluminum chloride. The mean input and output TOC has been 1.04 and 0.54– 0.77 mg/L, respectively. The TOC removal efficiency in this period varied between 25.96% and 48.08%. The mean output TOC for the control sample (10 mg/L for poly-aluminum chloride) has been calculated at 0.78 mg/L. At this stage, with the increase in the dose of poly-aluminum chloride up to 10 mg/L, TOC has declined, but from 10 mg/L onwards, the output TOC has increased. Fig. 10 indicates the trend of changes in the output aluminum and organic compounds in terms of the dose of the poly-aluminum chloride. The mean input aluminum and organic compounds have been calculated as 0.006 and 0.028 mg/L, respectively. During this period, the mean output aluminum and organic compounds lay within the ranges of 0.006–0.057 and 0.007–0.023 cm⁻¹, respectively. The removal efficiency of organic compounds in this period varied between 17.86 and 0.75. The mean output aluminum and organic compounds for the control sample (10 mg/L poly-aluminum chloride) has been calculated as 0.051 mg/L and 0.015 cm⁻¹, respectively. At this stage, with the increase in the dose of poly-aluminum chloride up to 5 mg/L, the removal rate of organic compounds has increased, but from this level onwards, it has an almost constant trend. Fig. 10 demonstrates that the aluminum level up to 5 mg/L has an ascending trend with a minor slope, but from 5 mg/L onwards, it shows an ascending trend with a sharp slope. The experiments indicated that when poly-aluminum chloride was alone used to remove turbidity, the amount of aluminum that remained in treated waters was 0.008-1.4 mg/L, which was larger than the secondary standard limit of drinking water (USEPA). Based on this standard, the maximum level of aluminum in drinking water is 0.05-0.2 mg/L. On the other hand, using chitosan as a coagulant aid, the amount of aluminum remaining in treated waters was obtained at 0.006-0.057 mg/L. The results of the studies conducted showed that higher concentrations



Fig. 8. Trend of changes in the output turbidity in relation to the dose of poly-aluminum chloride (initial concentration of chitosan: 0.02 mg/L, pH = 8, temperature: 26.2, and rapid mixing rate: 120 rpm).

Fig. 9. Trend of changes in the output TOC in relation to the dose of poly-aluminum chloride (initial concentration of chitosan: 0.02 mg/L, pH = 8, temperature: 26.2, and rapid mixing rate: 120 rpm).



Fig. 10. Trend of changes in the output aluminum and output UV_{254} in relation to the dose of poly-aluminum chloride (initial concentration of chitosan: 0.02 mg/L, pH = 8, temperature: 26.2, and rapid mixing rate: 120 rpm).

of aluminum remained in treated water because of the improper control of pH and a lack of optimal conditions, where the best way to reduce residual aluminum in treated water is achieving optimal conditions at the concentration of the coagulant and pH [39]. The use of chitosan as a coagulant aid resulted in both reduced residual turbidities up to below 5 NTU and decreased consumption of poly-aluminum chloride by 50% under optimal conditions. This reduction in the consumption of poly-aluminum chloride in the process of water treatment reduced both the purchase costs of this coagulant and the residual aluminum up to below the standard level (0.2 mg/L). The results of the application of chitosan as a coagulant aid in the coagulation process showed that under optimal conditions, the amount of TOC liberated from it was 0.56 mg/L. Considering the values of TOC obtained by chitosan, it was observed that with the increase in the concentration of these compounds, the degree of TOC changes in the treated water is trivial, and under optimal conditions, the amount of the TOC obtained from the control sample was lower (0.78 mg/L).

Based on the results obtained, the water of Ahvaz belongs to waters with low values of organic compounds. Studies have shown that waters with greater content of hydrophobic organic compounds (humic components with a high molecular weight) contain high levels of UV_{254} ; in contrast, waters with larger amounts of hydrophilic organic compounds (non-humic components with a low molecular weight) contain lower values of UV₂₅₄. These hydrophilic components are not removed during conventional water treatment processes and enter the distribution system, since they have a lower molecular weight in comparison with hydrophobic components. Hassani et al. [31] and Bing-tao et al. [40] investigated the effect and mechanism of chitosan coagulant aid for removing turbidity and organic compounds in drinking water. The optimal concentration of poly-aluminum chloride and chitosan obtained were 35 and 0.15 mg/L, respectively, with optimal pH = 7.5. Machenbach [41] showed that the application of a combination of coagulation based on metal and polymer leads to further removal of turbidity and organic compounds. Roussy et al. [38] reported the degree of removal of turbidity by UV₂₅₄ and the solution's organic compounds by chitosan as 76.1%-93.1%, 68.4%-87%, and 55.6%-82.6%, respectively.

4. Conclusion

The findings indicated that chitosan, as a coagulant aid, can significantly reduce the dose of poly-aluminum chloride coagulant and, in turn, the aluminum remaining in treated water. The efficiency of the removal of turbidity, TOC, aluminum, and $UV_{\rm 254}$ under optimal conditions of chitosan performance was found to be 96.59%, 46.15%, 80.49%, and 67.86%, respectively. As the indices of TOC and UV_{254} were studied as indices of the substitutes of natural organic compounds, it can be concluded that the water of Karoon River can be considered to be water with a low content of organic compounds. Further, biodegradation of the sludge resulting from chitosan can lead to decreased costs in the purchase of chemicals and disposal of its sludge. In addition, the flocs that developed out of chitosan were larger and required less time for sedimentation, thanks to their high molecular weight. With the increase in the concentration of poly-aluminum chloride, the degree of turbidity removal also increased, while at higher concentrations of chitosan, rest ability of particles was observed. The governing mechanism for destabilization of colloid particles and the removal of natural organic compounds can be justified by bridging between polymer particles, neutralization of the charge of natural colloid organic compounds, and the common sedimentation mechanism by adsorption on metal hydroxides. Chitosan can be extracted from the skin of marine crustaceans, especially shrimp, and as the wastes of shrimp skin are available abundantly as by products in the production of fisheries, production of this compound is possible at low cost. Based on the achievements of this study, the application of biopolymers, especially chitosan, can be recommended for water treatment.

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