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The effectiveness of polyaluminum ferric chloride (PAFCl) for turbidity and color removal from Isfahan raw water

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ABSTRACT

In this study the performance of polyaluminum ferric chloride, a composite inorganic polymer of aluminum and ferric salt, was investigated for the removal of turbidity and color from Isfahan raw water. Water samples were collected from the main resource of Isfahan raw water. For the evaluation of the coagulation procedure, conventional Jar test apparatus was used according to the standard methods. Experiments were conducted in the School of Public Health, Isfahan University of Medical Science. The findings showed that the optimum pH for the coagulation of Isfahan raw water at August 2013 was 7.5–8 and the optimum dosage of the coagulant was 5 mg/L. Without filtration, the removal of turbidity, color and total coliform achieved was 85, 100, and 86%, respectively, at the above-mentioned dosage and pH. Residual turbidity, color, and UV_{254} dropped below 0.33 NTU, zero Pt.Co Units, and 0.022 cm^{-1}, respectively. As, the residual concentration of aluminum and iron in treated water was 0.008 and 0.05 mg/L, respectively, this coagulant does not has any adverse health effect on consumers. The efficiency of this coagulant for the removal of turbidity, color, and organic matter in Isfahan raw water was very good and it has potential for selecting as a new coagulant for this city.

keywords: Coagulation; Inorganic pre-polymerized coagulants; Polyaluminum ferric chloride (PAFCl); Turbidity and water treatment

1. Introduction

Organic and inorganic impurities like suspended or colloidal particles and dissolved organic substances are major pollutants for water pollution. As the colloidal matter is stable in water mostly because of the electrostatic repulsive force; it is not removed by simple sedimentation. Conventional drinking water treatment processes include coagulation, flocculation, sedimentation, filtration, and disinfection [1–3]. One of the most important processes among the above-mentioned processes is coagulation; it is an effective process for the removal of fine particulate matter, colloidal particle, and natural organic matter in water [4–6].

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Inorganic salts of Al^{+3} or Fe^{+3} (conventional coagulants) is predominantly used for water and wastewater treatment. The weak points for the use of these materials include the inability to control the nature of the coagulant species formed rapidly during dilution under the prevailing raw water conditions, deterioration of their performance with changes in water temperature and in the nature of the raw water, and finally a possible need for changes in the coagulant dose and pH of water. Today, one of the attractive ways for improving the efficiency of coagulation is the use of pre-polymerized coagulants [7–11].

These coagulants contain pre-hydrolyzed forms of the metals and many of these products contain substantial proportions of the tridecamer Al_{13} [12]. The superiority of the pre-hydrolyzed coagulants as compared with the conventional coagulants are due to the different metal species distribution in the polymerized format, more efficiency in lower dosages range; lower sensitivity to water temperature variation, very low effect on alkalinity consumption in treated water or buffering effect of them in treated water, and control their degree of hydrolysis during manufacture so that the complicated reactions caused by the hydrolysis of the metal salt in coagulation can be reduced [13–18].

Recent studies on the application of pre-hydrolyzed coagulants such as polyaluminum chloride in water treatment have shown promising results. However, detailed information about the use of polyaluminum ferric chloride (PAFCl) as a coagulant is still scarce [19–25]. It is a composite inorganic polymer of aluminum and ferric salts [26] which has the characteristics of both aluminum and iron coagulants [27]. The aims of this study were to evaluate the performance of PAFCl coagulant and optimum coagulation conditions in it's application for the removal of turbidity, color, and organic materials in Isfahan water treatment plants.

2. Materials and methods

2.1. Water samples

Isfahan's water treatment plant has a capacity of $12\,m^3/s$. Raw water samples were collected before entering to this plant and transferred to the laboratory for jar test experiments, using PAFCl as a coagulant. About 200 L of water was collected as a grab sample and used for experiments.

2.2. Experimental procedure

The experiments were conducted according to the jar test principle including coagulation, flocculation, and settlement. Coagulation was carried out by the simultaneous use of six beakers with 1,000 ml in volume; each equipped with an rpm adjustable agitator. The adopted experimental condition includes coagulation with rapid mixing at 120 rpm for 2 min, flocculation with slow mixing at 40 rpm for 10 min, and settlement by a settling period of 20 min. Samples of the treated water were collected at a depth of 2.5 cm below the supernatant surface. To attain an optimal pH, a constant dose of PAFCl (5 mg/L) was used for the coagulation process at various pH (5–10). The pH which leads to gain the best results for turbidity and color removal was adopted as an optimal pH. The pH adjustment of the solutions was conducted with 0.1 M H_2SO_4 or 0.1 M NaOH solutions. An optimal dose of application was selected by applying the identical optimal pH with different doses of PAFCl . Thus, the coagulation procedure was conducted for Isfahan raw water according to the optimal pH and dose.

2.3. Analytical methods

All samples were analyzed for residual turbidity, true color, total coliforms, UV_{254} absorbance, residual aluminum (Al), iron (Fe), and heavy metals like arsenic, lead, nickel, and chromium. All experiments were conducted according to the standard method for the examination of water and wastewater [28]. Turbidity, color, TDS, EC, and pH of the samples were measured by TN-100 (EUTECH) Turbidimeter, DR 5000-HACH LANGE, EC meter SENSION5 (HACH LANGE), and pH-meter model CG 824, respectively. For true color analysis, the treated water was already filtered using a 0.45 μm filter.

2.4. Preparation of coagulant solution

The PAFCl coagulant was purchased from a Chinese company. It is a commercial grade product with a composition of 28% of Al_2O_3, 1.84% of Fe_2O_3, and basicity of about 81.22%. The molecular formula for this coagulant is: $[Al_2\ (OH)\ nCl_6\text{-}n]\ m\ [Fe_2\ (OH)\ nCl_6\text{-}n]\ m\ (SO_4)\ x$. For the preparation of the coagulant stock solution, 1 g of PAFCl was added as a solute into 1 L distilled water to achieve a concentration of 1 mg/L.

3. Results and discussion

The parameters of interest in raw water and treated water samples after coagulation at optimum PAFCl dose and pH were analyzed in duplicate. The averages of the results with standard deviations are reported in Table 1.

Table 1
Water quality before and after coagulation with PAFCl

Parameter	Raw water	After coagulation (at optimum dose and pH)
Turbidity (NTU)	2.2 (±0.14)	0.33 (±0.02)
Color (Pt.Co)	10 (±0.7)	0 (±0)
EC (μs/cm)	357 (±1.41)	357.8 (±1.97)
TDS (mg/L)	176 (±0.7)	176.3 (±0.7)
pH	7.8 (±0.14)	7.7 (±0.14)
Alkalinity (mg/L)	130 (±2.82)	120 (±1.13)
Total coliform (MPN/100 ml)	4,600 (±212)	644 (±69.2)
Fe (mg/L)	0.106 (±0.08)	0.05 (±0.01)
Al (mg/L)	0.002 (±0.007)	0.008 (±0.001)
Arsenic (μg/L)	1.18 (±0.08)	1.18 (±0.08)
Lead (μg/L)	7 (±0.56)	3 (±0.4)
Chromium (μg/L)	7 (±0.42)	4 (±0.28)
Nickel (μg/L)	0.286 (±0.02)	0.286 (±0.02)
Temperature (℃)	21	21
Sludgsludgee volume (ml/L)	Negligible	0.5 (±0.14)
UVA_{254} nm (/cm)	0.045 (±0.002)	0.026 (±0.002)
DOC (mg/L)	1.5 (±0.12)	0.62 (±0.04)

3.1. Optimum pH selection

Fig. 1 shows the effect of pH on the PAFCl performance at a constant dose of 5 mg/L for turbidity and color removal. It can be seen that in the pH value greater than 9, the performance of the coagulant was dramatically alleviated. This coagulant showed a good efficiency at a pH range from 6.5 to 9 to obtain residual turbidities ≤ 0.6 NTU. However, at pH 7.8 the efficiency reached to its optimum which was capable to reduce the turbidity down to 0.31 NTU.

Effective chemical coagulation of water occurs only within a specific pH range. As the pH value is in the range of 7.0–8.4, the low positive charge and high polymerized species of PAFCl could effectively make the particles to destabilize by charge-neutralization and adsorption-bridge functions, so that an excellent coagulation performance can be achieved. In contrast,

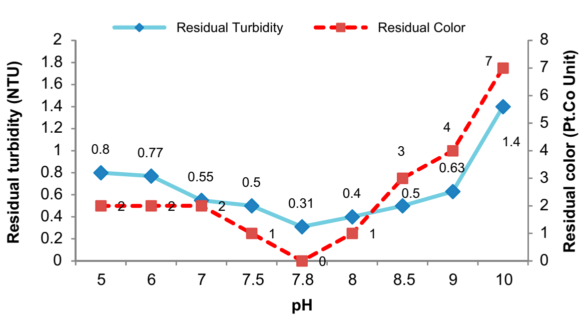

Fig. 1. Optimum pH for turbidity and color removal by 5 mg/L of PAFCl (initial turbidity and color were 2.2 NTU and 10 Pt.Co Unit, respectively).

PAFCl will be hydrolyzed into negatively charged precipitates when the pH value is higher than 8.4. Therefore, the removal efficiency of turbidity is decreased with the increase of the pH value [29]. Acidic water tends to keep minerals in solutions and decrease the color of water. Optimum removal of color was observed at pH 7.8 (or 7.5–8). At this pH, the color removal efficiency was 100%. It can be seen that when the pH is above 8.5 the color removal efficiency decreases and at pH range of 5–7 it has a constant effect for color removal (Fig. 1). In this study, the optimum pH value was selected as 7.5–8 (exact 7.8).

3.2. Optimum dose selection for the removal of turbidity, color, and UV_{254}

The effects of coagulant dose on turbidity, color removal, and UV_{254} absorbance can be seen in Figs. 2 and 3. By increasing the coagulant dose up to 5 mg/L, the removal efficiency for turbidity, color, and UV_{254} nm was increased. Dosage higher than that has worsened the removal efficiency due to re-stabilizing of the colloidal suspension. In this study, the optimum PAFCl dosage of 5 mg/L at pH 7.8 was applied for the set of experiments. The efficiency for turbidity removal was slightly decreased by increasing the coagulant concentration. This may be attributed to charge reversal and destabilization of colloidal particles due to coagulant overdosing [30]. Also, at low dose the flock did not formed because the coagulant was not adequate to compress the double layer of the colloid particles or to bind the colloid particles to form bridging.

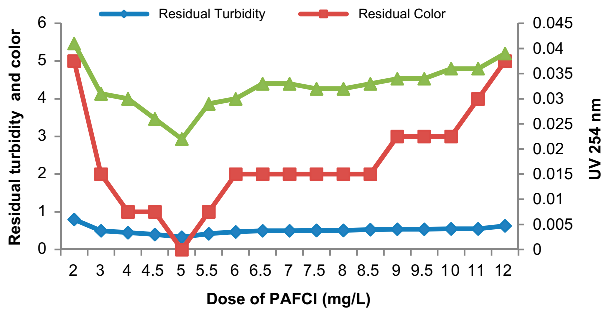

Fig. 2. Optimum PAFCl dose selection based on pH 7.8 with initial turbidity 2.2 NTU, color of 10 Pt.Co Unit, and UV_{254} absorbance 0.045 nm.

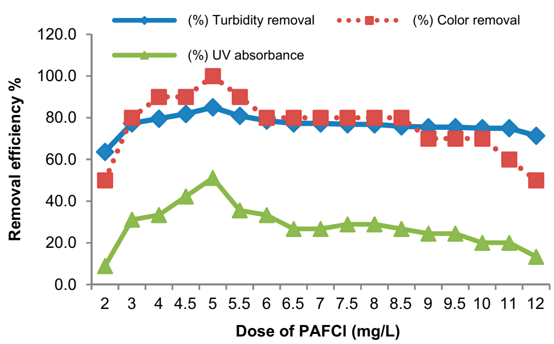

Fig. 3. The efficiency of PAFCl for turbidity, color, and UV_{254} removal in relation to its various dosages at an optimum pH of 7.8.

As the PAFCl is a positively charged coagulant, it can effectively remove negatively charged colors from waters by charge neutralization. On the other hand, PAFCl is an inorganic polymer and can aggregate the destabilized dyes together by adsorption-bridge function of the coagulant [29]. Results of this study showed that PAFCl has a very good efficiency for the removal of turbidity and color, producing water with residual turbidity about 0.33 NTU. This reduces the concerns related to turbidity ≥ 1 NTU, which affects the maintenance and operation of water filters. Although turbidity is not a direct indicator of health risk, but numerous studies show a strong relationship between removal of turbidity and reduction of protozoa in treated water [31,32].

In Isfahan water treatment plant, the application of 3 mg/L polyaluminum chloride as an optimum dose could reduce the water turbidity to 1 NTU whereas, using 3 mg/L of PAFCl at similar condition, reduced the residual turbidity down to 0.5 NTU (Fig. 2). This implies that for a desired residual turbidity of 1 NTU, the application of ≤2 mg/L PAFCl could be sufficient. Thus, in comparison with polyaluminum chloride (PACl), this new coagulant (PAFCl) can save coagulation consumption by about 1036.8 kg/d.

3.3. *Effect of coagulation on treated water alkalinity, EC, and TDS*

Inorganic coagulants will decrease the alkalinity of water; as a consequence the pH of the chemically dosed raw water will decrease. This often means that the supplemental alkalinity in the form of lime, soda ash, or caustic soda will have to be added to maintain an acceptable dosed-water pH. New age coagulants such as polyaluminium chloride have less impact than alum. Organic coagulants do not affect the raw water alkalinity and pH [33]. Pre-hydrolyzed materials are often found to be considerably more effective because they are already partially neutralized. As a result, they have a smaller effect on the pH of water and finally reduce the need for pH correction.

An important property of polymeric coagulants is their basicity, which is defined as the ratio of hydroxyl to aluminum ions in the hydrated complex. The low basicity will lead to the consumption of alkalinity in the treatment process and hence affects pH. In this study, our coagulant had 81% basicity. Initial pH and alkalinity of raw water were 7.8 and 130 mg/L, respectively. After coagulation at an optimum dose and pH, low change in pH and alkalinity occurred accounting to 7.7 and 120 mg/L, respectively (Table 1). However, by increasing the coagulant dosage, pH and alkalinity were slightly decreased but it was negligible. One reason for this phenomenon may be related with this matter that as PAFCI hydrolization takes place, the flock formed incorporates the chloride ion into the flock's structure so it is not available for producing acid.

Inorganic coagulants have the potential to increase the total dissolved solids concentration of the treated water. This action is not very good, especially when using conventional coagulant which increases the anions and cations levels in the finished water. Chemicals such as polyaluminum chloride and polyaluminum hydroxychloride could result in a smaller or even negligible increase in TDS and smaller (or none) need for neutralization [34]. Fig. 4 shows the effect of increasing coagulant dose vs. TDS and EC content of treated water. It can be seen that PAFCl has very low effect for increasing TDS and EC content of treated water. The removal efficiency of PAFCl for turbidity, color, and total coliform in Isfahan raw water at optimum dose and pH was 85, 100, and 86%, respectively.

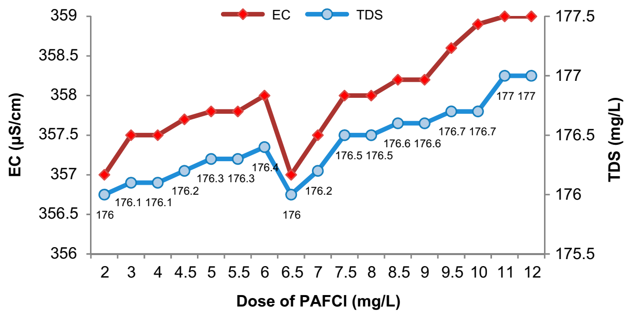

Fig. 4. The variation of TDS and EC value after coagulation by PAFCl with different doses (primary TDS and EC were 176 mg/L and 357 µs/cm, respectively).

3.4. Sludge production

All coagulants produce sludge in the form of the metal hydroxide with the colored and colloidal matter that is removed from the raw water; not all inorganic coagulants behave in the same way. Polyaluminum chloride produces less sludge than alum when dosed at equivalent levels. In our study, the sludge volume of raw and treated water was negligible as polymeric coagulants produce less sludge. The experiments on sludge volume were performed using Imhoff cones. After coagulation with PAFCl at optimum dose only, 0.5 ml/L sludge was produced. With increasing in coagulant dose, we had more production of sludge (Fig. 5). Visual observation revealed that flock forming was larger at higher pH value than those at optimum pH conditions. One reason may be related to the solubility of aluminum and ferric hydroxides in lower pH.

3.5. Residual metals

One of the most important subjects in the application of coagulant is the residual concentrations of Al and Fe in treated water. Analysis of heavy metals repellence after coagulation is very important because some coagulant increase heavy metals concentration in

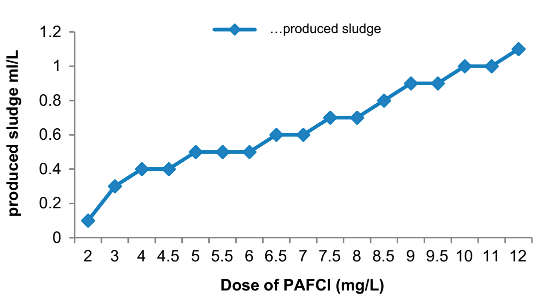

Fig. 5. The effect of PAFCl dosage increase on settled sludge volume.

treated water. Use of Al-based coagulants especially $Al_2(SO4)_3$ (alum) often leads to an increase Al concentrations in treated water. The maximum recommended range of aluminum in drinking water by WHO is 0.05–0.2 mg/L. Table 1 shows the specification of treated water quality. It can be observed that PAFCl has not released any heavy metals to treated water.

In this study the concentration of Fe in treated water was decreased, and only Al concentration was increased about 0.006 mg/L. A plausible explanation of this is that the residual aluminum is low in neutral pH due to the formation of $Al(OH)_3$ amorphous precipitates which is then removed by sedimentation, as a result, the residual aluminum concentration drops significantly around neutral pH. While in pH > 7.5, due to the formation of soluble $Al(OH)_4$, the residual aluminum content increases in the solution [35].

Fe concentration in raw water was 0.106 mg/L and after coagulation it reached to 0.05 mg/L which may be due to the presence of mineral-organic combined form of iron in raw water. Furthermore, our coagulant created insoluble aluminum hydroxides that produced flakes and absorbed iron compounds [36]. PAFCl similar to polyaluminum chloride and polyaluminum silicate chloride leaves low residual Al in treated water [37]. Fortunately, this coagulant has not repelled any heavy metals like nickel, arsenic, lead, and chromium to treated water (Table 1).

3.6. UV_{245} and specific UV absorbance

The conventional view of coagulation is that coagulant dosing is controlled by the raw water turbidity and/or color. It has been suggested that the raw water specific UV absorbance (SUVA) can be used to control coagulation. For water with SUVA of ≥4 or greater, the natural organic matters (NOM) composition is dominated by humic substance and NOM-control coagulant dosing. For water with SUVA between 2 and 4, the water contains a mixture of humic and non humic substances; in this case the NOM can control coagulant dosing. For water with SUVA ≤ 2, the NOM composition is dominated by non humic substance, therefore, the NOM does not control coagulant dosing [38]. According to SUVA equation (Eq. (1)), the amounts of SUVA in Isfahan raw water before and after coagulation were 3 and 4.19, respectively (Table 1). As Isfahan raw water contains a mixture of humic and non humic substances; NOM can control coagulant dosing.

$$\text{SUVA} = \frac{(\text{UV}_{254}\ \text{in}\ \frac{1}{\text{cm}})100}{\text{DOC in mg/L}} \quad (1)$$

Precipitation of metal–humic complexes and adsorption of humic substances onto metal hydroxide precipitates are the two important mechanisms for the removal of natural organic matter from the solution. These mechanisms are dependent on the pH of the system and the coagulant dose. Adsorption of humics onto metal hydroxide precipitates is dominant at higher coagulant doses and higher pH conditions, while the precipitation of metal–humic complexes is a dominant mechanism at lower coagulant doses and lower pH conditions [38].

4. Conclusions

- It is founded that the optimum pH and dose of PAFCl for the treatment of Isfahan's raw water at August 2013 was 7.5–8 and 5 mg/L, respectively.
- The removal efficiency of PAFCl was affected very little at pH range 5–9. At this pH range, the residual turbidity was below 1 NTU.
- PAFCl removes approximately 100, 85, and 86% of the Isfahan's raw water color, turbidity, and total coliform, respectively.
- As the coagulants' concentrations were increased, variation in the values of TDS and EC was negligible; there are no more changes in the values of TDS and EC of water after coagulation.
- Increasing dosages of PAFCl coagulant decreases the value of PH and alkalinity, but at an optimum dosage of 5 mg/L it is negligible.
- Coagulation with PAFCl does not release any Al and Fe in treated water.
- Turbidity of the produced water was 0.33 NTU which is a very good level for subsequent process such as filtration because of reducing the operation and maintenance cost of water treatment plant.
- PAFCl didn't show any effects for the release or addition of heavy metals like lead, chromium, nickel, and arsenic to treated water.

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