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Speciation and effectiveness of aluminum formate as a coagulant: promising for water treatment

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ABSTRACT

In the current study, aluminum formate was synthesized in various molar ratios (formic acid to aluminum) from 1 to 2.5 using aluminum hydroxide and formic acid. The coagulation ability of synthesized compounds was evaluated and compared with alum. All the aluminum formates synthesized with various molar ratios (i.e., 1–2.5) were performed similar to alum except molar ratio 1. The influence of coagulant dose, pH, and alkalinity–turbidity combinations on coagulation behavior of aluminum formates was determined using jar test. The optimum coagulant dose for aluminum formate was found as 80 mg/L. The optimum pH for lower residual turbidity was achieved at pH 6 using aluminum formate. The residual aluminum concentration of aluminum formate synthesized with molar ratio 2.5 was within the limits. In addition to that for higher OH^-, CO_3^{2-}, and HCO_3^- alkalinity and turbidity combination relatively small quantity of coagulant was sufficient to remove turbidity effectively than with low OH^-, CO_3^{2-}, and HCO_3^- alkalinity and turbidity combination.

Keywords: Surface water treatment; Coagulation; Aluminum formate; Turbidity removal

1. Introduction

Water is a ubiquitous chemical substance, vital for all living beings. In nature, water exists in three different forms namely solid, liquid, and gaseous state. An incredible amount of water is present on the earth. About three-quarters of the earth surface is covered with water (about 1.4 billion km^3) occupying ~97% as saltwater and ~3% as clean water. Availability of clean water for daily life, industries, etc., is very less [1]. However, to fulfil the needs of growing population, more than 60 billion m^3 of clean water is required per year.

Rapid industrialization together with the growing population is responsible for water scarcity throughout the world [2]. In addition to that sudden swift in climate change, agriculture, improved quality of life, and urbanization leads to the deterioration of existing water resources [3]. Hence, the quality of water needs to be enhanced before it is supplying to the public [4,5]. Various methods are available to treat the deteriorated water. But the choice of method depends on characteristics of raw water [6]. Conventional water treatment method includes physico-chemical and biological treatment [7]. Among physico-chemical processes, coagulation–flocculation is the best simple, reliable, and relatively cost-effective option [8,9] and most widely used technique for producing portable water.

Turbidity is one of significant parameter that needs to be regulated before supplying water to the community [10]. Turbidity is mainly due to colloidal and suspended particles present in water [3]. High turbidity considerably diminishes the aesthetic appearance of water bodies, having an impact on recreation and tourism. The high-level turbidity

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removal in surface water resources could be attained effectively using coagulation–flocculation technique [11,12]. During coagulation all the small sized particles present in water are aggregated together and forms a floc and then it can be removed easily. Moreover, this technique is also utilized to remove color and natural organic matter from water in order to produce clean potable water [13,14].

Coagulants are most widely employed for removing turbidity, impurities, and other pathogenic bacteria from water [15]. Various coagulants used in water treatment processes are mainly categorised into inorganic salts (e.g., aluminum and ferric salts) [16], polymeric coagulants (e.g., poly aluminum chloride) [17,18], and natural coagulants (e.g., *Moringa oleifera*) [19]. In general coagulants are aluminum or iron-based salts, because these metals has a capacity to form high charged species and as well as hydroxide precipitates in water [20,21]. The major drawback with iron-based coagulants is imparting yellowish color to water during the process. Thus, aluminum based coagulants are most commonly preferred in industrial applications. The most frequently used aluminum-based coagulants are alum ($Al_2(SO_4)_3$) and aluminum chloride ($AlCl_3$) [22]. Furthermore, all the coagulants used for water treatment mainly contains chlorides and sulphates as anions. Being corrosive in nature, chloride might cause severe damage to process equipment. Sulfate reacts with calcium and forms calcium sulfate, which is responsible for the hardness of water. On the other hand, formate anion possess advantages like less corrosive [23] and easy decomposable over frequently used chlorides and sulfate anions [24,25].

The main aim of this article is to use formate as an anion rather than chloride and sulfate. Aluminum formate is synthesized with different formic acid (HCOOH) to aluminum (Al) concentrations. The turbidity removal performance of synthesized aluminum formate as a coagulant is investigated. The influence of various parameters such as pH, dose, and alkalinity–turbidity combinations on the coagulation potential of aluminum formate for treating turbid water is evaluated. In addition to that the residual aluminum concentration present the water after the studies is determined.

2. Materials and methods

2.1. Preparation of aluminum formate

Aluminum hydroxide ($Al(OH)_3$) and formic acid (HCOOH) were used for synthesizing aluminum formate. The synthesis was carried out by changing the HCOOH quantity on molarity basis from 1 to 2.5 by adding HCOOH to $Al(OH)_3$ powder and was mixed thoroughly. Then the product was dried at 105°C using hot air oven. This was used as a coagulant for treating turbid water. All the chemicals used in the study were obtained from Merck (Bengaluru) and utilized without further purification.

2.2. Preparation of synthetic turbid wastewater

The preparation of synthetic turbid solution was carried out by adding 10 g of dried, powdered, and sieved (75 μ sieve) kaolin particles in 1 L of tap water. In order to achieve complete mixing of particles, the solution was mixed for 30 min using magnetic stirrer and it was allowed to rest for 24 h. This was used as a stock solution for preparing samples of required turbidity.

2.3. Coagulation tests

Jar test is most commonly used to evaluate the coagulation performance of coagulant. Present study also used jar test to assess the performance of aluminum formate as coagulant for the turbidity removal. To determine the optimum quantity of aluminum formate required, predetermined quantity of it was added to 1 L glass beakers containing 500 mL of synthetic turbid solution. The tests involved rapid mix, slow mix, and settling. Rapid mixing was carried out at 150 rpm for 1 min and slow mixing was conducted at 40 rpm for 30 min. After slow mixing, settling was done for 30 min. Then, turbidity of supernatant was found using nephelometric turbidity meter. The initial turbidity was maintained as 350 NTU, to identify optimum conditions of coagulant dose and pH. All the experiments were performed in triplicates and the average value was reported.

2.4. Analytical techniques

All the parameters of the synthetic turbid solution were determined according to standards methods for water and wastewater [26]. The pH of the solution was computed using pH meter (Metrohm, 827 pH lab). Turbidity of the solution was measured using nephelometric turbidity meter (HF scientific, micro 100 IR). Aluminum concentration in the supernatant solution was estimated using atomic absorption spectrometer (PerkinElmer, pinaacle 900T). Turbidity removal in terms of percentage from the solution was estimated using below equation:

$$\text{Turbidity removal}(\%) = \frac{T_i - T_f}{T_i} \times 100 \tag{1}$$

where T_i is the initial turbidity; T_f is the final turbidity.

The composition of synthesized coagulant was analysed using X-ray diffracto meter (XRD; Rigaku, Ultima III).

3. Results and discussion

3.1. Preliminary characteristics of water

The primary characteristics such as pH, electrical conductivity, hardness, alkalinity, and chlorides of tap water used for preparing synthetic turbid solution were determined using standard methods for water and wastewater [26]. Table 1 presents the preliminary characteristics of water. The tap water has pH 8 and total alkalinity 165 mg/L as $CaCO_3$.

3.2. Characterization

Coagulants synthesized according to different molar ratio are characterized using XRD for composition analysis (Fig. 1). The aluminum formate exhibited a strong and sharp peak at 18.27° and 31.58°. Peak at 18.27° and 31.58° corresponds to formate and aluminum, respectively [27], which

Table 1
Preliminary characteristics of water

Parameter	Value
pH	8
Electrical conductivity	651.23 μs/cm
Total hardness	230 mg/L as $CaCO_3$
Total alkalinity	165 mg/L as $CaCO_3$
Chlorides	60 mg/L

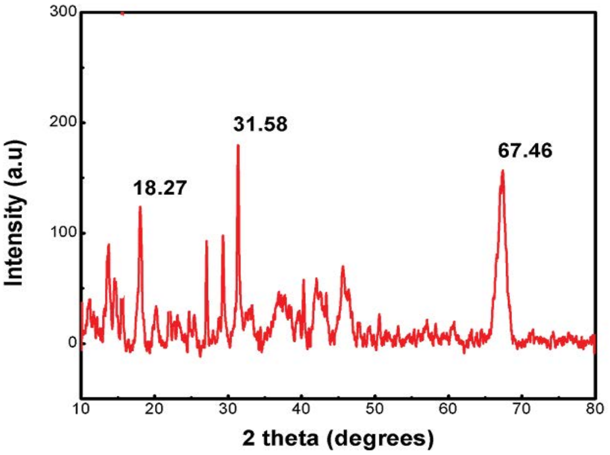

Fig. 1. X-ray diffraction of aluminum formate.

confirmed that the synthesized compound consist of both aluminum and formate ions.

3.3. Effect of coagulant dose

A series of experiments were performed with aluminum formate synthesized using different HCOOH to Al molar ratio range from 1 to 2.5 to find the optimum dose required to remove turbidity from water. The coagulant dose is varied from 0 to 100 mg/L and the corresponding residual turbidity values were noted (Fig. 2). The initial turbidity of the solution was maintained as 350 NTU. Furthermore, the performance of aluminum formate was compared with alum.

From Fig. 2, it was depicted that for coagulant synthesized according to HCOOH to Al molar ratio 1, the residual turbidity remains same up to a coagulant dose of 60 mg/L. Further increase in dose beyond 60 mg/L significantly reduced residual turbidity. Whereas for aluminum formate prepared with molar ratio 1.5, the residual turbidity decreased gradually with an increase in coagulant dose. Similarly, for coagulants synthesized using HCOOH to Al molar ratio 2 and 2.5, the residual turbidity diminished instantaneously with rise in dose. For molar ratio of 2.5, the residual turbidity for 80 and 100 mg/L was 17.9 and 25.8 NTU, respectively. However, for alum, the residual turbidity at 80 mg/L dose was 12.4 mg/L. The residual turbidity values for aluminum formate prepared with 2.5 molar ratio and alum were almost similar to each other at 80 mg/L coagulant dose.

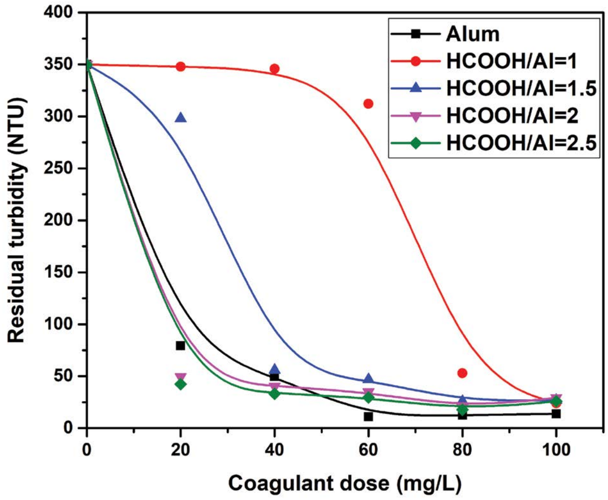

Fig. 2. Effect of coagulant dose (experimental condition: initial turbidity = 350 NTU and pH = 8).

Among all the synthesized coagulants, aluminum formate prepared with molar ratio 1 removed turbidity only at higher doses than other aluminum formates. The major reason for poor performance of aluminum formate with molar ratio 1 at low dose was due to the fact that amount of formic acid added for synthesis of coagulant was less. Therefore, most of the aluminum hydroxide remained unreacted and insoluble in water, which does not work as a coagulant. Furthermore, during the experiments it was observed that the solution remained turbid. Similarly, aluminum formate with 1.5 molar ratio also has less turbidity removal when compared with other aluminum formates of molar ratio 2 and 2.5. This represents that at lower molar ratios, aluminum hydroxide was not actively reacted with formic acid to form aluminum formate. Hence coagulants prepared with molar ratio of 1 and 1.5 are not suitable for turbidity removal.

3.4. Effect of pH

To study the influence of pH on residual turbidity using aluminum formates, experiments were conducted at different pH ranging from 4 to 9. The variation of residual turbidity with pH is shown in Fig. 3. In addition to that the variation of residual Al concentration with pH was also investigated (Fig. 4). Before performing the experiments turbidity of the solution was maintained at 350 NTU and coagulant dose added to the solution was 80 mg/L. The coagulation performance of different aluminum formate prepared with different molar ratios at different pH was compared with each other and with alum.

Fig. 3 illustrates that for aluminum formate prepared with molar ratio 1, the residual turbidity increases with pH up to 6 and then decreased slightly with further rise in pH. Hence, aluminum formate synthesized with molar ratio 1 was not effective for removing turbidity from water. However, for other aluminum formates (molar ratio 1.5, 2, and 2.5), the residual turbidity increased from pH 4 to 5, and reached lower residual turbidity at 6 but further increase in pH greater than 6 resulted in slight increment in residual turbidity when compared to residual turbidity at pH 6. Hence, the optimum pH for high turbidity removal using aluminum formate was 6. However, for alum the residual turbidity decreased with increase in pH and reached lowest residual turbidity at pH 6; further pH increase led to rise in residual turbidity. These results were similar to the studies reported by Mikola and Tanskanen [28].

The mechanism of coagulation for aluminum salts is majorly influenced by hydrolysis reaction [29]. When aluminum formate is added to the solution it dissociates into aluminum and formate ions. Hence, the aluminum present in the solution undergoes hydrolysis reaction and forms aluminum hydroxide. Therefore, sweep coagulation occurs and made all the colloidal particles that cause turbidity in the solution to trap in the aluminum hydroxide precipitate. Subsequently, residual turbidity is minimum at pH 6. In addition to that aluminum forms positively charged species at pH 6. These positively charged species would destabilize the negatively charged colloidal particles present in the solution and ultimately led to charge neutralization. Thus, sweep coagulation together with charge neutralization contributed for the lower residual turbidity at pH 6. As the pH increased (i.e., >6) major part of the aluminum would form negatively charged species. Hence, repulsion occur between negatively charged colloidal particles and aluminum ions and ultimately led to greater residual turbidity than residual turbidity at pH 6.

Furthermore, the residual Al concentration of synthesized aluminum formates and as well as alum with pH is shown in Fig. 4. These results illustrated that synthesized aluminum formate coagulants and alum showed similar tendency. As the pH increases, residual Al concentration reduced up to pH 6 and further rise in pH increased the Al concentration. For the aluminum formate synthesized with molar ratio 1, the Al concentration in the solution after the experiments was relatively high when compared with other aluminum formates. Since, the quantity of formic acid added for synthesis of coagulant according to molar ratio 1 was very low. Therefore, most of the aluminum hydroxide was remained in the solution. However, as the molar ratio of formic acid to aluminum increases, the residual concentration of Al also reduced, which represents that formation of aluminum formate might reduce further hydrolysis. Furthermore, the remaining Al concentration in the solution after the studies was low for aluminum formate synthesized with molar ratio 2.5 than alum.

3.5. Combined effect of turbidity and alkalinity

The combined impact of turbidity and alkalinity on residual turbidity was investigated (Fig. 5). This study was conducted by considering four different conditions: high turbidity – high alkalinity, high turbidity – low alkalinity, low turbidity – high alkalinity, and low turbidity – low alkalinity. NaOH was added to the solution to induce OH^- alkalinity to water. Presence of OH^- alkalinity in the solution significantly impact the coagulation mechanism [30]. In this study, high alkalinity was considered as 295 mg/L and low alkalinity as 65 mg/L as $CaCO_3$; high turbidity was considered as 350 NTU and low turbidity as 55 NTU. All the studies were carried out using aluminum formate synthesized using molar ratio 2.5.

For high OH^- alkalinity of 295 mg/L as $CaCO_3$, the results attained were:

- With high turbidity of 350 NTU, the minimum residual turbidity was achieved at a coagulant dose of 40 mg/L.
- With low turbidity of 50 NTU, the minimum residual turbidity was achieved at a coagulant dose of 60 mg/L.

For low OH^- alkalinity of 65 mg/L as $CaCO_3$, the results attained were:

- With high turbidity of 350 NTU, the minimum residual turbidity was achieved at a coagulant dose of 60 mg/L.
- With low turbidity of 50 NTU, the minimum residual turbidity was achieved at a coagulant dose of 80 mg/L.

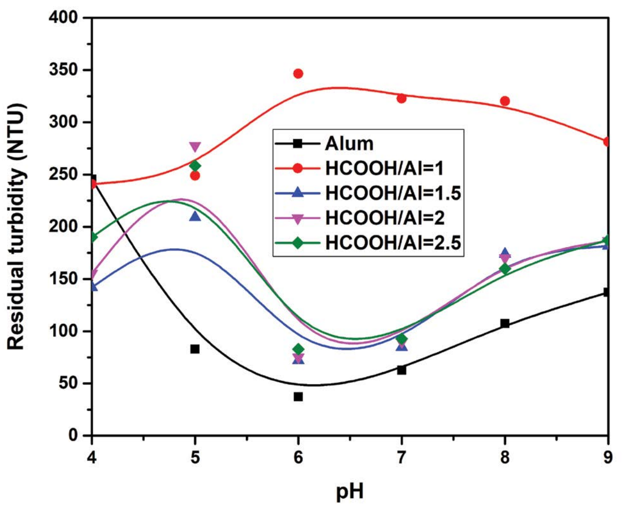

Fig. 3. Effect of pH (experimental condition: initial turbidity = 350 NTU and coagulant dose = 80 mg/L).

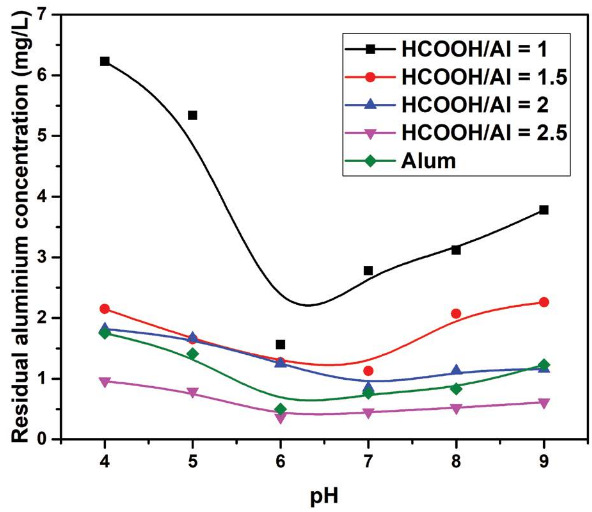

Fig. 4. Variation of residual aluminum concentration of different coagulants with pH.

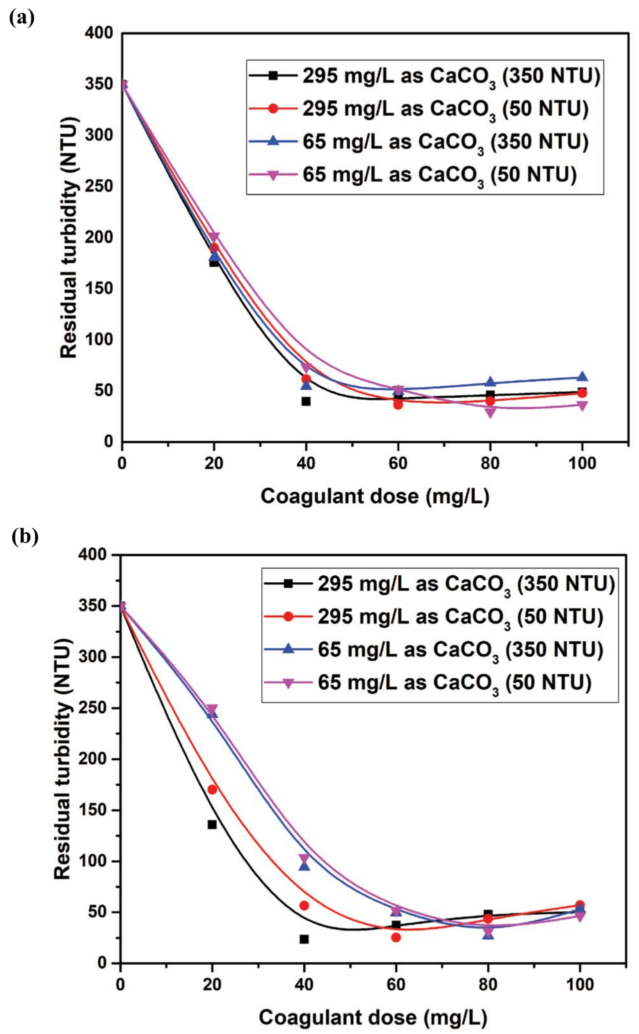

Fig. 5. Influence of (a) OH^- alkalinity and turbidity and (b) CO_3^{2-} and HCO_3^- alkalinity and turbidity on residual turbidity.

Fig. 5a illustrates that for low OH^- alkalinity water, the quantity of coagulant required was high to remove turbidity from the water. However, for high OH^- alkalinity water, the amount of coagulant essential to remove turbidity was minimum. In case of high OH^- alkalinity, lower quantity of coagulant dose was sufficient to remove turbidity from water. Therefore, the dominant mechanism for turbidity removal would be adsorption and charge neutralization. Whereas for low OH^- alkalinity water, greater quantity of coagulant dose is required to remove turbidity from water; thus, the turbidity removal was majorly by sweep coagulation rather than charge neutralization.

Similarly, to study the combined influence of carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) alkalinity on turbidity removal sodium carbonate and sodium bicarbonate was added to the solution in equal quantities (Fig. 5b).

For combined CO_3^{2-} and HCO_3^- alkalinity of 295 mg/L as $CaCO_3$, the results attained were:

- With high turbidity of 350 NTU, the minimum residual turbidity was achieved at a coagulant dose of 40 mg/L.
- With low turbidity of 50 NTU, the minimum residual turbidity was achieved at a coagulant dose of 60 mg/L.

For combined CO_3^{2-} and HCO_3^- alkalinity of 65 mg/L as $CaCO_3$, the results attained were:

- With high turbidity of 350 NTU, the minimum residual turbidity was achieved at a coagulant dose of 80 mg/L.
- With low turbidity of 50 NTU, the minimum residual turbidity was achieved at a coagulant dose of 80 mg/L.

From Fig. 5b, it is clearly observed that for higher CO_3^{2-} and HCO_3^- alkalinities the coagulant dose required was minimum when compared to solution with low CO_3^{2-} and HCO_3^- alkalinity. This represents that for water contains high CO_3^{2-} and HCO_3^- alkalinity small amount of coagulant was necessary to remove turbidity; hence, adsorption and charge neutralization might be the dominant mechanism responsible for turbidity removal. However, for low CO_3^{2-} and HCO_3^- alkalinity water, the quantity of coagulant required was greater, which indicates sweep coagulation would be the dominant mechanism for turbidity removal.

4. Conclusions

Synthesis of aluminum formate was carried out using aluminum hydroxide and formic acid in different molar ratios. The coagulation behavior of aluminum formates were compared with alum. The performance of aluminum formate synthesized with molar ratio 2.5 was similar to that of alum. The minimum residual turbidity was achieved at a coagulant dose of 80 mg/L using aluminum formate prepared with 2.5 molar ratio. Similarly, the optimum pH for high turbidity removal using aluminum formate was obtained at pH 6. The residual aluminum concentration of aluminum formate synthesized with molar ratio 2.5 was lower than the residual aluminum concentration of alum. For water possessing greater OH^- alkalinity relatively less coagulant dose was enough to attain low residual turbidity, when compared with water contains low OH^- alkalinity. Similarly, low CO_3^{2-} and HCO_3^- alkalinity water need high coagulant dose to achieve minimum residual turbidity. Thus, aluminum formate have a promising potential for turbidity removal especially for corrosion sensitive applications.

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