

Bahri Ersoy¹
 Ismail Tosun²
 Ahmet Günay³
 Sedef Dikmen⁴

¹Afyon Kocatepe University, Engineering Faculty, Material Science & Engineering Department, Afyonkarahisar, Turkey.

²Süleyman Demirel University, Engineering & Architecture Faculty, Environmental Engineering Department, Isparta, Turkey.

³Balikesir University, Engineering & Architecture Faculty, Environmental Engineering Department, Balikesir, Turkey.

⁴Anadolu University, Faculty of Science, Department of Physics, Eskisehir, Turkey.

Research Article

Turbidity Removal from Wastewaters of Natural Stone Processing by Coagulation/Flocculation Methods

The effectiveness of coagulation (at pH values of 6, 7.5, and 9), flocculation (at pH 9), and coagulation plus flocculation (at pH 9) on turbidity removal from natural stone (travertine) processing wastewaters (NSPW) were examined by applying classical sedimentation tests. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, AlCl_3 , and $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ were used as coagulants and a polyacrylamide based anionic polymer was used as the flocculant. In this way, it was found that the coagulation method alone was not sufficient to purify NSPW, whereas flocculation and coagulation plus flocculation methods provided superior purification. Among the coagulants used, AlCl_3 gave the best result in terms of turbidity removal by coagulation from NSPW at pH 6 and 9, whereas the turbidity removal performances of the three coagulants were almost identical at pH 7.5. In addition, relatively low pH (i.e., pH 6) improved the purification performance of all coagulants. During coagulation of NSPW at pH 6, a charge neutralization mechanism played a decisive role in turbidity removal. However, in neutral (pH 7.5) and slightly basic (pH 9) media, a sweep coagulation mechanism was predominant. For flocculation of NSPW, the basic mechanism comprised of polymer bridging.

Keywords: Coagulation; Flocculation; Natural stone processing wastewater; Turbidity removal

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1 Introduction

Processing plants for natural stone (e.g., marble, travertine, limestone etc.) are present in many countries of the world, especially Italy, China, Spain, Turkey, Greece, Portugal, South America, and South Korea. In these natural stone processing plants, large amounts of water are used during the cutting and polishing of stones such as marble, travertine, and granite. Wastewater that includes between approximately 2–10 wt% of stone powders are generated after these treatments [1]. After clarifying these waters in the wastewater treatment unit in a factory, generally through the flocculation method in sedimentation tanks, the relatively clean water with low turbidity is reused in the plant. If the turbidity of the reused water is higher than acceptable values, the stone powders in the water may cause polishing problems during the processing of natural stone and may lead to clogging of pipes [2]. Consequently, the maximum (residual) turbidity of the clean water should be less than 15 Nephelometric Turbidity Units (NTU) [1].

Aluminum and ferric compounds, such as alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$), aluminum chloride (AlCl_3), and ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), are the most common and traditionally used coagulants in water/wastewater treatments to remove turbidity. This turbidity may result from different sources such as organic colloids like humic substances [3–6], textile dyes [7], and colloidal sized solid

particles in the wastewaters of various chemical plants [8, 9]. In addition, these types of coagulants are used for the aggregation of fine clay [10–12] and other mineral [13] particles in the respective water suspensions.

Both the terms coagulation and flocculation convey the same connotation, implying the aggregation of suspended colloidal or fine particles in a liquid. Nevertheless, in coagulation, this aggregation process is aided by the addition of multivalent inorganic electrolytes, such as AlCl_3 , FeCl_3 , alum or CaCl_2 into the medium, whereas in the process of flocculation, the inducing agents are organic electrolytes such as polymers (or flocculants). For the removal of turbidity from water or wastewater, these are the most commonly used methods [14]. The two main aims of the aggregation (coagulation or flocculation) process are:

- (i) to settle the suspended colloidal particles in water/wastewater rapidly, which settle very slowly, or perhaps do not settle at all under normal conditions, hence leading to residual turbidity, and
- (ii) to remove residual turbidity from the water/wastewater and consequently to obtain clearer water/wastewater, which is a natural outcome of the former.

In practice, however, the two objectives mentioned above are incompatible with each other. In other words, in a turbid water (or suspension), the optimum conditions for the rapid sedimentation of suspended particles, i.e., flocculant/coagulant type, dosage, and pH of medium, may not be the optimum conditions for removal of residual turbidity from the water. This shows that coagulation or flocculation mechanisms may be more complex than supposed.

Correspondence: Dr. B. Ersoy, Afyon Kocatepe University, Engineering Faculty, Material Science & Engineering Department, Afyonkarahisar 03200, Turkey.

E-mail: bersoy@aku.edu.tr

Many studies support this assumption [14, 15]. Because both parameters, i.e., the settling rate of suspended particles and the residual turbidity of the supernatant water, are generally not at their optimum simultaneously, the most important of the two parameters is generally taken into consideration and both parameters are accordingly optimized for evaluation of the clarification performance of the method(s) used.

In the coagulation process it is very important to control the medium pH and the coagulant dosage which determines the efficiency of turbidity removal (in other words, coagulating power) of the coagulation mechanisms, the charge neutralization, and the sweep coagulation (or sweep flocculation) [14, 16–18]. Charge neutralization which occurs mostly at particularly low and neutral pHs, involves the following mechanisms:

- (i) specific adsorption of positively charged metal (M: Fe^{3+} , Al^{3+} , etc.) or metal-hydroxyl ions on the surface of the negatively charged colloids.
- (ii) double-layer compression of the negatively charged colloids in a medium of relatively high ionic strength without specific adsorption of these positive ions, which causes a reduction in the zeta potential of the colloids.
- (iii) deposition of positively charged amorphous $\text{M}(\text{OH})_3$ precipitates, such as $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$, on the surface of the colloid or the surface precipitation of $\text{M}(\text{OH})_3$ at pHs below the isoelectric points (ieps) of the precipitates.

Charge neutralization can be monitored and controlled using the zeta potential. This is important because overdosing can reverse the charge on the colloid and redisperse it as a positive colloid [14]. When a trivalent metal (Al or Fe) compound is added to a sample of water at approximately neutral pH the hydroxide, $\text{M}(\text{OH})_3$, forms fairly rapidly, initially as a colloidal precipitate with subsequent swift growth to form quite large flocs. During this precipitation and growth, many of the particles originally present in the water are coated with the hydrolyzed species or colloidal hydroxide particles and become enmeshed in the growing precipitate. The original particles may be said to be 'swept' out of suspension by the hydroxide precipitate, and for this reason the mechanism is often called 'sweep flocculation' or 'sweep coagulation' [14]. According to Duan and Gregory [18], with coagulation using simple Al and Fe salts, only monomeric hydrolysis products such as $\text{M}(\text{OH})_2^+$, $\text{M}(\text{OH})_3^0$ and the amorphous hydroxide precipitates $\text{Al}(\text{OH})_3$ or $\text{Fe}(\text{OH})_3$ occurring at intermediate pH values need to be considered. Moreover, the surface-charge characteristics of the precipitated metal hydroxides, which are of great importance in coagulation, depend on the pH of the suspension and the coagulant type. Precipitation from aluminum chloride solutions yields a precipitate with an iep around pH 9, whereas the value is closer to pH 8 for precipitation from aluminum sulfate. For amorphous ferric hydroxide, the iep is somewhat lower (\approx pH 7.8) [18, 19]. However, it should be noted that the iep of these solids may change depending on the methods and conditions used for measuring the zeta potential [20, 21]. On the contrary, the solubility of $\text{Fe}(\text{OH})_3$ is lower than that of $\text{Al}(\text{OH})_3$, and hence the former is precipitated over a much broader pH range, which makes the sweep coagulation of $\text{Fe}(\text{OH})_3$ less sensitive to pH [14]. The coagulant dosage, similarly to pH, determines the type of coagulation. At low doses charge neutralization is mostly predominant, whereas at relatively high doses, the sweep-flocculation mechanism becomes predominant. However, excess dosage can adversely affect coagulation by producing charge reversal and restabilization of colloidal particles [14]. Apart from these two parameters (pH and dosage or con-

centration), other parameters such as temperature, presence of specific anions (such as bicarbonate or sulfate) and mixing conditions can affect the performance of the metal coagulants [14, 18, 22]. Their coagulating performance is lower at low temperatures due to the kinetic basis of coagulation. In addition, the presence of sulfate ions in solution can markedly enhance the precipitation process and can significantly reduce the positive charge of the products of aluminum hydrolysis. On the contrary, at higher particle concentrations (as in the case of this study), the charge-neutralization mechanism becomes more important than sweep flocculation, principally due to the kinetic behavior of the particles [14].

A few studies have been previously conducted on the removal of turbidity from natural stone processing wastewaters (NSPW), but these reports are mostly related only to the flocculation process [1, 23]. In this work, the different aggregation methods; largely coagulation, flocculation, and their combined application, 'coagulation plus flocculation', to clarify NSPW have been investigated. In addition, the effect of pH of the medium and both type and concentration of the coagulant on the removal of residual turbidity from NSPW have been examined.

2 Experimental

2.1 Materials

The travertine powder obtained from NSPW was used in this study. Travertine is a kind of natural stone used commonly in Turkey and all over the world (its commercial name as mined in Turkey is Denizli Travertine). Firstly, the original travertine wastewater sample, in suspension form, was obtained from the wastewater collecting pool, positioned before the sedimentation tank in Tureks Travertine Inc., Afyon, Turkey, and was brought to the laboratory. Subsequently, it was passed through a 0.1 mm sieve and dried at room temperature. Mineralogical, chemical, and particle-size analyses of the natural stone powder were carried out using X-ray diffraction (Shimadzu XRD-6000), X-ray fluorescence spectroscopy (Spectro X-Lab 2000), and Laser particle sizing (Fritsch Particle Sizer Analysette-22) instruments, respectively. Figure 1 showed that the suspended powders of the NSPW consisted entirely of calcite mineral, and its chemical composition (in wt %) was: CaO 54.35, MgO 0.42, Fe_2O_3 0.20, SiO_2 0.17, Al_2O_3 0.85, Na_2O 0.03, K_2O 0.02, and loss on ignition 43.75% which resulted from the thermal decomposition of CaCO_3 (calcite). According to particle-size analysis, 90, 50 and 10 wt% of the natural stone powder were less than 38, 10 and 1.5 μm (average particle size) in size, respectively. The values for the zeta potential of the natural stone powders at pH 6, 7.5, and 9 were -12 , -16 , and -15 mV, respectively, measured using a Zeta-Meter 3.0 (Zeta Meter Inc.), using a procedure described in detail by Ersoy [1]. Although natural stone powders, such as travertine and marble, had almost the same mineralogical analysis with respect to the calcite content (see Fig. 1), surprisingly their surface electrokinetic properties (zeta potential versus pH of suspension) were considerably different with respect to the same, and this contradictory situation was discussed in detail in the previous publication by the authors [1].

Iron chloride or ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Fluka), aluminum chloride (AlCl_3 , Merck), and alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$, Merck) were used as coagulants, and a polyacrylamide based anionic polymer, sodiumpolyacrylate (Na-PA), with a high molecular weight and 28% anionicity degree (Ciba Specialty Chemicals) was used as a floccu-

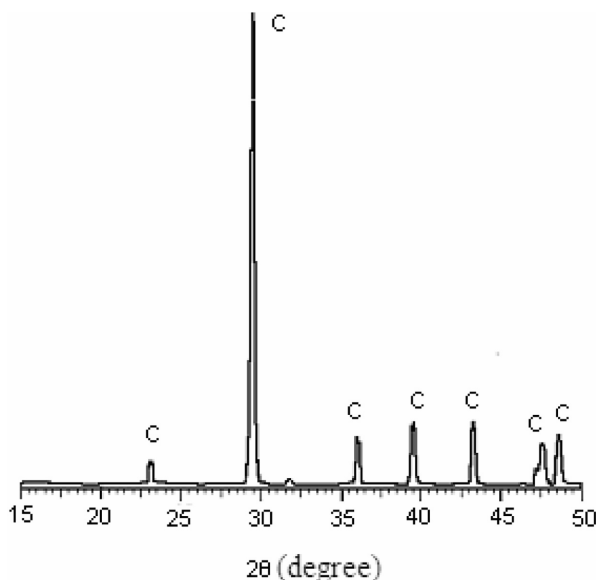


Figure 1. X-ray diffraction pattern of natural stone (travertine) (C: Calcite)

lant. 1 M NaOH and 1 M HNO₃ solutions were used for pH adjustments and pH was measured using an Inco-Lab pH meter, with a sensitivity of ± 0.001 . The pH and specific conductivity of the distilled water used for the preparation of stock solutions of the coagulant and flocculant were 6.2 and 10 $\mu\text{mhos/cm}$, respectively. The properties of the tap water used in the sedimentation tests were pH 6.2, specific conductivity 1330–1450 $\mu\text{mhos/cm}$, turbidity 0.3 NTU, and included anions and cations (in mg/L) HCO₃⁻ 439, SO₄²⁻ 144, Cl⁻ 114, F⁻ 0.4, NO₂⁻ < 0.1, PO₄³⁻ < 0.1, Ca²⁺ 112, Na⁺ 93.6, Mg²⁺ 33.5, K⁺ 9.6.

2.2 Sedimentation Tests

2.2.1 Coagulation

Sedimentation tests by the coagulation method as a function of coagulant concentration were carried out at different pH values (6, 7.5, and 9) on the travertine suspension prepared as to be representative of NSPW. First, the required amount of tap water was added into a 500 mL graduated mixing cylinder 355 mm in height and 21 g of natural stone powder was added. The cylinder was then sealed and inverted twice. The pH of the suspension was adjusted and it was again inverted four times to mix.

In the next step, the required amount of coagulant was taken from a stock solution of 0.1 g/L by an adjustable automatic pipette added to the cylinder, which was again sealed and inverted four times to obtain good mixing and left on a smooth surface for 15 min to facilitate sedimentation of the aggregated powders. After the appropriate time elapsed, an aliquot from the supernatant water was obtained at a depth of 12 cm, and its residual turbidity as NTU was measured using a Scientifica Velp-115 turbidimeter. The measurements of residual turbidity were based on nephelometry, in which a beam of light is passed through the water sample, causing scattering by particles in the water. The turbidimeter measures the intensity of scattered light, usually at an angle of 45 or 90° to the direction of the light beam, and the intensity is expressed in standard turbidity units. The range of measurement used for the turbidimeter was between 0–200 NTU.

All the sedimentation tests and the residual turbidity measurements in this study were conducted at room temperature. After the sedimentation tests were carried out at different pH, the residual turbidity curves were plotted as functions of the respective coagulant (or flocculant) concentrations.

2.2.2 Flocculation

Before the flocculation and ‘coagulation plus flocculation’ tests at pH 9 (which was close to natural pH of 8.4 for NSPW), a stock solution of 1 g/L of the flocculant (Na-PA) was prepared, and it was diluted to 0.1 g/L. This flocculant solution was used for the tests. The steps in the sedimentation tests and residual turbidity measurements were identical to those in Section 2.2.1 above.

2.2.3 Coagulation plus Flocculation

The experiments for the measurement of residual turbidity in this method, carried out at pH 9, were the same as those in the sedimentation tests outlined above in Section 2.2.1. However, these sedimentation tests were carried out at a constant flocculant concentration of 1.3 mg/L (the optimum dosage obtained from the flocculation tests for turbidity removal). During the sedimentation tests, the required coagulant dosage was first added into the cylinder containing the natural stone suspension and it was mixed as detailed in Section 2.2.1. Subsequently, the required flocculant solution was added into the suspension according to its optimum dosage.

3 Results and Discussion

3.1 Coagulation

The residual turbidities of the travertine suspension at different pH values (pH 6, 7.5, and 9) depending on the AlCl₃, FeCl₃, and alum concentrations, measured after the sedimentation tests of the suspensions as described above, are provided in Figs. 2, 3, and 4, respectively. It must be noted that due to the dissolution of natural stone powders in acidic media, the sedimentation tests were not carried out at pH values lower than 6. As observed from Fig. 2, the residual turbidity of the supernatant water in coagulant free medium was about 85 NTU at pH 9, whereas it decreased gradually with the addition of AlCl₃ and reached 65 NTU at a concentration of 100 mg/L. It remained nearly constant as concentrations were further increased. A similar trend was observed in the residual turbidity curve at pH 7.5. The residual turbidity was 80 NTU without AlCl₃, whereas it decreased with the addition of coagulant and reached 60 NTU at a concentration of 100 mg/L. It remained almost constant until 400 mg/L; however, only a small decrease was observed in the residual turbidity at 500 mg/L. Moreover, significant decreases in the residual turbidity, both without and with AlCl₃ addition, were clearly observed in slightly acidic medium (pH 6). The residual turbidity at zero concentration was 67 NTU, although it reached approximately 20 NTU at 300 mg/L and did not change beyond this concentration. As in Fig. 3, the decrease in the residual turbidity with the concentration of alum was insignificant at pH 9. The residual turbidity with no coagulant was 86 NTU, whereas it was 83 NTU at 20 mg/L and 75 NTU at 400 mg/L. Any further increase in the concentration did not change the residual turbidity. However, the decrease in residual turbidity with the increase in concentration at pH 7.5 and 6 were more than the decrease at pH 9. At pH 7.5, the residual turbidity was 80 NTU without coagulant; when a concentration of 20 mg/L of alum was used, it decreased to 70 NTU; and beyond this con-

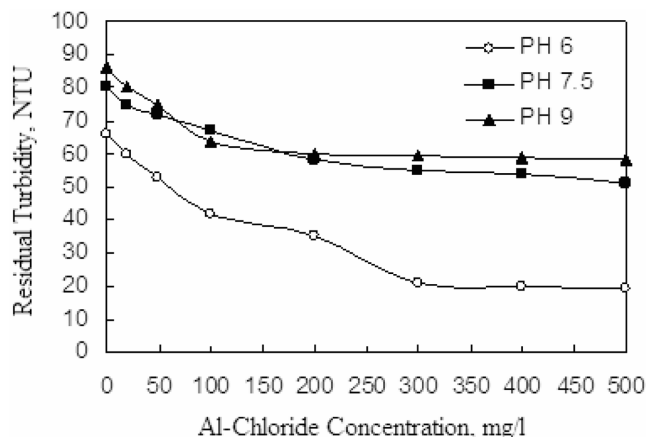


Figure 2. Residual turbidity of travertine suspension plotted as a function of AlCl_3 concentration at different pH values.

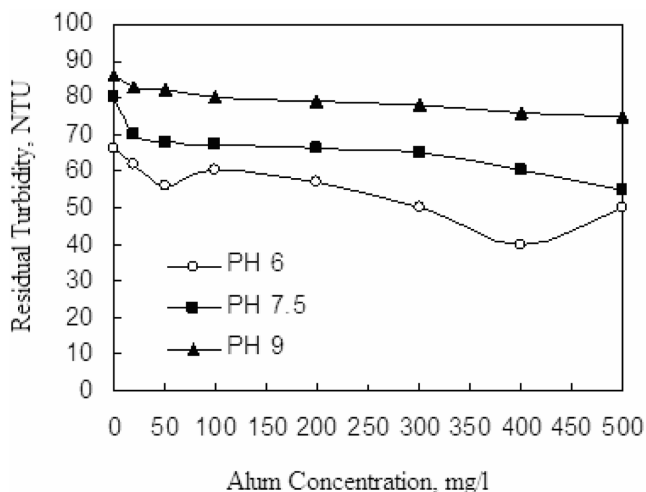


Figure 3. Residual turbidity of travertine suspension plotted as a function of alum concentration at different pH values.

centration it decreased gradually to reach 55 NTU at 500 mg/L. At pH 6, residual turbidity was 66 NTU at zero concentration, whereas it was 62 and 56 NTU at 20 and 50 mg/L alum dose, respectively. It remained almost constant until 300 mg/L. Beyond this concentration, residual turbidity decreased to 40 NTU at 400 mg/L; further increase in concentration led to an increase up to 50 NTU at 500 mg/L. Figure 4 indicates that the residual turbidity decreased from 86 NTU to 76 NTU when ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$; 50 mg/L) was used, and it did not change until a concentration of 300 mg/L. After this concentration, unlike the other coagulant curves, it began to reduce and was lowered to 42 NTU at 500 mg/L. At pH 7.5, it reduced from 80 NTU to 69 NTU when a concentration of 20 mg/L of ferric chloride was used and remained constant until 300 mg/L. Subsequently, it began to lower again to 38 NTU at 500 mg/L. However, the decrease in the residual turbidity versus the ferric dosage at pH 6 was lower but continuous compared to the decreases at pH 7.5 and 9. It lowered from 66 NTU to 54 NTU with the addition of 300 mg/L of ferric chloride and was 36 NTU at 500 mg/L.

When the residual turbidity curves in Figs. 2, 3, and 4 were compared, the best results in terms of lowering the residual turbidity of NSPW for all three metal coagulants were obtained at pH 6, as the

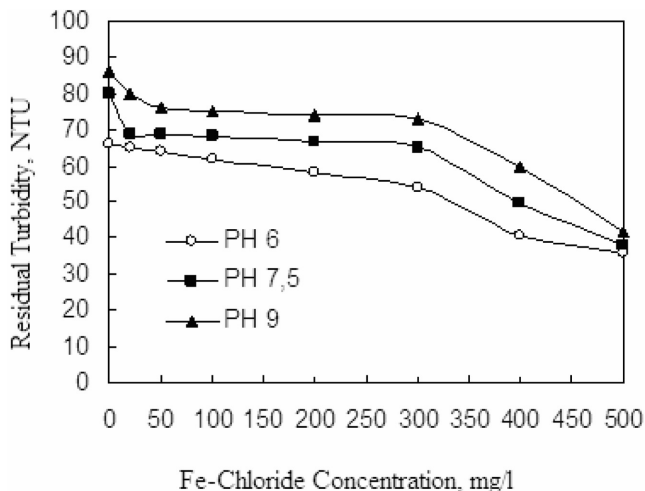


Figure 4. Residual turbidity of travertine suspension plotted as a function of FeCl_3 concentration at different pH values.

Table 1. Hydroxo-complex formation constants for iron (III) used to plot the solubility diagrams for amorphous ferric hydroxide precipitates, $T = 25^\circ\text{C}$ [31].

| Reaction | Log K |
|--|-------|
| $\text{Fe}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{FeOH}^{2+} + \text{H}^+$ | -2.2 |
| $\text{Fe}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_2^+ + 2\text{H}^+$ | -5.7 |
| $2\text{Fe}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Fe}_2(\text{OH})_4^{2+} + 2\text{H}^+$ | -2.9 |
| $\text{Fe}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_3^{\text{aq}} + 3\text{H}^+$ | -12.0 |
| $\text{Fe}^{3+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_4^- + 4\text{H}^+$ | -22.0 |
| $*3\text{Fe}^{3+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Fe}_3(\text{OH})_4^{5+} + 4\text{H}^+$ | -6.3 |

* $\text{Fe}_3(\text{OH})_4^{5+}$ complex formation does not occur when the total Fe(III) concentration is less than 10^{-3} M.

Table 2. Hydroxo-complex formation constants for Al(III) used to plot the solubility diagrams for amorphous alum hydroxide precipitates, $T = 25^\circ\text{C}$ [32].

| Reaction | Log K |
|--|--------|
| $\text{Al}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})^{2+} + \text{H}^+$ | 4.97 |
| $\text{Al}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})_2^+ + 2\text{H}^+$ | 9.30 |
| $\text{Al}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})_3^{\text{aq}} + 3\text{H}^+$ | -15.00 |
| $\text{Al}^{3+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})_4^- + 4\text{H}^+$ | -23.00 |

pH of the suspension increased, their coagulating power (or turbidity removal performance) was decreased. This indicated that a charge-neutralization mechanism played a more significant role in turbidity removal from NSPW (or in other words, in the coagulation of the natural stone powders present in a suspension) than sweep coagulation. Coagulation of the travertine powders by charge neutralization may occur by adsorption of the cationic products of hydrolysis, such as $\text{M}(\text{OH})_2^+$ and $\text{M}(\text{OH})_3^+$, and/or deposition of positively charged colloidal precipitates, such as $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$, onto the negatively charged travertine powders, which leads to elimination of the repulsive forces between the powders. Considering Figs. 5a and b, which were plotted based on calculations using the data in Tabs. 1 and 2 and the corresponding pH values, the effective charge-neutralizing species can be concluded to be colloidal metal-hydroxide particles (precipitates) at pH 6. This is because at

around neutral pH (pH 6–8), cationic hydrolysis products may represent only a very small fraction of the total soluble Al or Fe. At pH values of 9 and 7.5, the sweep coagulation mechanism was assumed to be the predominant force in the system because there are no other cationic metal-hydroxyl compounds in the medium. Moreover, the surface charges of the metal-hydroxide precipitates $M(OH)_3$ (M: Al or Fe) formed in the medium are very close to their iep values (for the precipitates resulting from addition of aluminum chloride) or even negatively charged (for the precipitates resulting from addition of alum and ferric chloride) at these pH values. In addition, anionic metal hydroxyl ions such as $M(OH)_4^-$ obtained from the dissolution of aluminum and ferric hydroxide precipitates have the effect of increasing the stability of the suspension. On the contrary, in suspensions with relatively large particle concentrations as in the case of natural stone suspensions (or NSPW) usual orthokinetic coagulation conditions are operative in the system, in which the charge-neutralization mechanism is more effective compared with the sweep coagulation mechanism [1]. This also supports the comments of the authors provided above. The results obtained from previous studies [10, 24] on the coagulation of kaolin suspension in the presence of alum and ferric chloride support the results of this study; that is the residual turbidity of the kaolin suspension decreases with decrease in the pH of the suspension. Unlike the results of this study, another study [13] on the coagulation of selestite ($SrSO_4$) mineral suspension with $AlCl_3$, found that higher pH values from 10–11 led to an increase in the coagulating power of the coagulant, and that a sweep-coagulation mechanism becomes predominant in the suspension. It was therefore considered that the differences in the results between the two studies (Özkan and Yekeler [13] and this study) resulted from the difference in suspension properties, especially particle concentration and particle size. Although both the powders (selestite and travertine) show similar surface charges in water (they are negatively charged between pH 6–11), the ratio of solids in the selestite suspension (0.6 g in 300 mL water) was lower and the particle size finer than the corresponding parameters of the travertine suspension used in this study. Consequently, the efficacy of the sweep coagulation mechanism was increased, as expected. Similarly, unlike this study, Al-Malack et al. [8] have studied the coagulation of wastewaters from a chemical factory using alum, ferric chloride, and ferric sulfate between pH 6–9.5 and determined that the efficiency of turbidity removal increased with increasing pH. Moreover, the efficiency reaches its maximum at pH 9, beyond which it decreases again. The reason for this occurrence was explained by the 'adsorption of organics onto preformed ferric hydroxide flocs, followed by precipitation, which is the most dominant removal mechanism at higher pH values and increased addition of coagulant'.

When the residual turbidity curves in Figs. 2, 3, and 4 are compared, among the three coagulants, $AlCl_3$ showed the best performance with regard to turbidity removal from NSPW at pH 6 and 9; however, the performance of all three was nearly the same at pH 7.5. This phenomenon may be attributed to the differences in surface properties of the precipitates formed. Additionally, these precipitates may affect the ionic strength of the medium depending on their different solubilities. As mentioned before, the iep of the precipitate obtained from $AlCl_3$ is pH 9, whereas the iep values of the precipitates obtained from alum and $Fe(OH)_3$ are about pH 8 and pH 7.8, respectively [19,21]. Therefore, it is expected that the positive surface charge or the zeta potential of the $M(OH)_3$ precipitate obtained from $AlCl_3$ should be more than that of the other precipi-

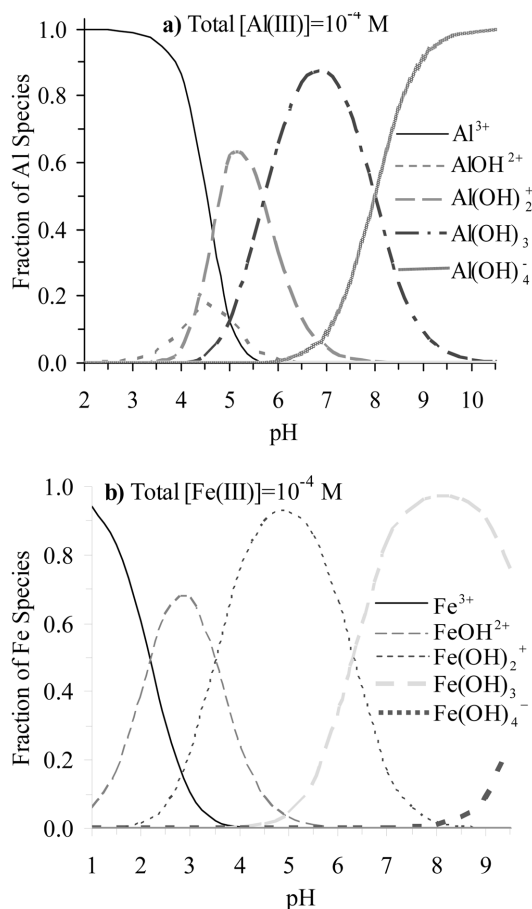


Figure 5. Equilibrium diagram showing the mole fractions of monomeric hydrolyzed (a) aluminum and (b) ferric species as functions of pH for 10^{-4} M total Al^{3+} (equals 2.70 mg Al/L or 31.50 mg alum ($Al_2(SO_4)_3 \cdot 16H_2O$)/L) and 10^{-4} M total Fe^{3+} (equals 5.59 mg Fe(III)/L or 27.02 mg $FeCl_3 \cdot 6H_2O$ /L).

tates, and thus the removal of turbidity by using the charge-neutralization mechanism is more effective. On the contrary, sulfate (SO_4^{2-}) anions, produced during the dissociation of alum, may reduce the positive surface charge of $Al(OH)_3$ precipitates and thus they may weaken the coagulating power of alum by charge neutralization. As reported in the literature, sulfate ions lower the surface charge of metal-hydroxide precipitates [14].

The coagulation occurring at pH 7.5 was largely assumed to be due to the sweep-coagulation mechanism for all the coagulants used. This is because the iep of the $M(OH)_3$ precipitates obtained from alum or ferric chloride are very close to this pH. In addition, cationic species with two valencies, $M(OH)^{2+}$, are nonexistent at this pH, whereas monovalent $M(OH)_2^+$ ions that are able to enhance coagulation through the charge-neutralization mechanism are present in only very small amounts in the medium (see Fig. 5). However, the iep of the $Al(OH)_3$ precipitate obtained from $AlCl_3$ is about pH 9, and although they still carry a small amount of positive charge at this pH, this does not provide significant levels of additive for the charge-neutralization mechanism. As a result, all the coagulants showed similar performance in terms of turbidity removal at around neutral pH (pH 7.5). However, at pH 9, alum and ferric chloride yielded higher residual turbidity values compared to aluminum

Table 3. Coagulant/flocculant dosage and pH values for optimum removal of turbidity.

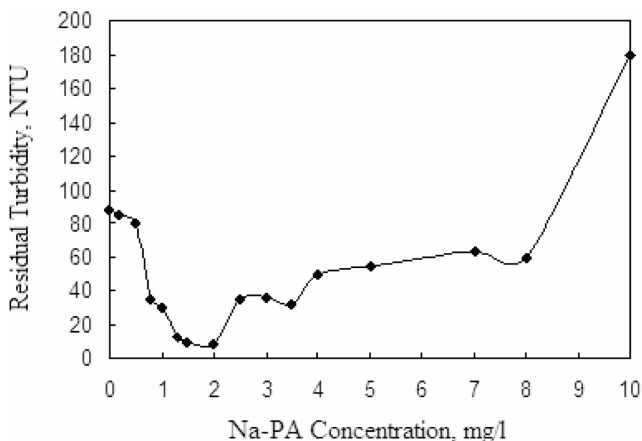
| Coagulant/Flocculant | pH | Optimal Dosage (mg/L) | Residual Turbidity (NTU) |
|---|----|-----------------------|--------------------------|
| Al ₂ (SO ₄) ₃ · 16 H ₂ O | 6 | 400 | 40 |
| AlCl ₃ | 6 | 300 | 21 |
| FeCl ₃ · 6 H ₂ O | 6 | 500 | 36 |
| Na – PA (Polymer) | 9 | 1.3 | 12 |
| FeCl ₃ + Na-PA | 9 | 20 + 1.3 | 5 |

chloride. This effect was observed because both the types of precipitates obtained from alum and ferric chloride are negatively charged, resulting in an enhancement of the stability of the natural stone suspension, thus, an increase in its residual turbidity.

The residual turbidity curves at all pHs for the treatments using AlCl₃ (see Fig. 2) and alum (see Fig. 3) showed similar trends, namely, the residual turbidities reduced with the addition of coagulant and they reached their minimum at specific dosages. They remained almost constant beyond this coagulant concentration. However, this trend in the curves was different for FeCl₃ (see Fig. 4) where the residual turbidity further reduced at higher dosages. This variable behavior in the curves of FeCl₃ cannot be explained exactly. This might be related to the difference in the solubilities of the metal-hydroxide precipitates. In other words, the solubility of the Fe(OH)₃ precipitate is lower than that of Al(OH)₃ [18], which leads to an increase in the concentration of solids in the medium. This further produces higher coagulation rates through an increase in the possibility of particle-particle collision during mixing. Coagulant dosage plays an important role, similar to pH, in the efficiency of coagulation mechanisms. In general, at low concentrations (approximately 1–20 mg/L or a few μM, depending on the conditions), the predominant coagulation mechanism is charge neutralization; when the concentration increases, sweep coagulation becomes more significant in the system [14]. Indeed, this general statement is also valid for the coagulation of NSPW. However, previous studies have indicated that excess dosage may cause charge reversal and restabilization of colloids, leading to increase in residual turbidity [4, 18], whereas, in other reports [10, 25], this negative effect of excess dosage has not been reported, as in the case of this study. When all the curves in Figs. 2, 3, and 4 are compared with each other, the lowest residual turbidity (≈20 NTU) was obtained by the addition of 300 mg/L AlCl₃ at pH 6. To obtain a residual turbidity of 40 NTU at pH 6, the required dosages are 400, 400 and 100 mg/L for alum, FeCl₃, and AlCl₃, respectively. The curves in Figs. 2, 3, and 4 indicate that the most suitable coagulant for clarifying NSPW was AlCl₃ at suspension pH values of 6, 7.5, and 9 throughout the entire dosage range studied (between 0 and 500 mg/L AlCl₃). Table 3 also shows the optimum coagulant dosage and suspension pH for optimum turbidity removal from NSPW, which shows the difference between the coagulating performances of the coagulants. As discussed above, this may be attributed to the difference in surface electrical properties, such as zeta potential and the iep, of the metal-hydroxide precipitates obtained from different sources, i. e., FeCl₃, alum, and AlCl₃.

3.2 Flocculation

In a previous study by the current authors [1], the effects of polymer-charge density and suspension pH on the settling rate and turbidity of the natural stone (travertine and marble) suspensions were inves-

**Figure 6.** Residual turbidity of travertine suspension plotted as a function of the anionic flocculant (Sodiumpolyacrylate or Na–PA) concentration at pH 9.

tigated. Consequently, it was determined that the most suitable polymer (or flocculant) for flocculation of the travertine suspension was sodium polyacrylate (Na-PA) of high molecular weight, with 28% anionicity degree at pH 6, 7.5, and 11. Therefore, the flocculation tests in this study at pH 9 were carried out using this polymer. Figure 6 shows the variations in residual turbidity of NSPW (or travertine suspension) as a function of the Na-PA concentration. The residual turbidity was reduced from 85 to 78 NTU with 0.5 mg/L Na-PA additive. Beyond this concentration, there was a sharp decrease in the turbidity till 1.3 mg/L and thereafter, the residual turbidity remained constant until 2 mg/L, after which an increase was again observed. Hence, the minimum residual turbidity value (12 NTU) was obtained with 1.3 mg/L of Na-PA. Even though the polymer and the travertine carry the same charge (negative), flocculation of the travertine suspension occurs, which implies that the sum of the attractive forces between the negatively charged travertine powder and the anionic polymer outweighs the electrostatic or electrical double-layer repulsive forces between them. A polymer-bridging mechanism was responsible for the flocculation of travertine powders, as determined before [1]. This type of flocculation mechanism is encountered commonly in the flocculation of different colloidal suspensions [26, 27] and water/wastewater [15, 28]. The most typical property of the polymer-bridging mechanism is that flocculation can occur in spite of the polymer and the colloidal particles carrying the same surface charge. Additionally, the large flocs thus obtained lead to high sedimentation rates of the particles in suspension [29] because high molecular-weight polymers can adsorb onto numerous particles at many points along the long polymer chain [14], providing high settling rates and relatively low turbidities. Similarly, this type of floc formation and high settling rates were observed in travertine suspensions (data not shown here). As observed in Fig. 6, in the presence of excess polymer (or flocculant), at concentrations >2 mg/L, the residual turbidity begins to increase due to redispersion, as generally shown in the literature on flocculation of different colloidal suspensions [14, 28, 30].

3.3 Coagulation plus Flocculation

The residual turbidities of the NSPW after ‘coagulation plus flocculation’ tests conducted at pH 9 and at an optimum flocculant

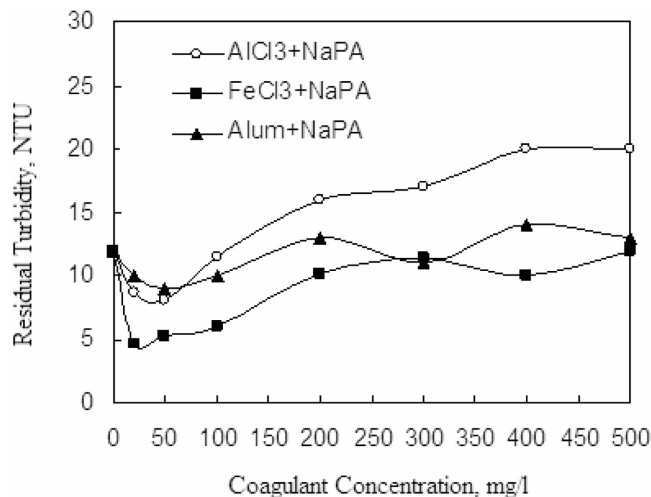


Figure 7. Residual turbidity of travertine suspension in the presence of coagulant plus flocculant (sodium polyacrylate) plotted versus coagulant concentration at a constant flocculant dosage of 1.3 mg/L at pH 9.

(sodium polyacrylate) dosage (1.3 mg/L) were plotted versus coagulant concentration (see Fig. 7). The figure clearly shows that the 'coagulation plus flocculation' method had a marginal effect on the turbidity removal when compared with the flocculation only method (see Fig. 6). The residual turbidity was 12 NTU in the presence of the 1.3 mg/L of flocculant alone, whereas it reduced to a lower NTU value, approximately 5–10 NTU, with an addition of 20 mg/L of coagulant, depending on the coagulant type; subsequently, it began to increase again. This indicated that addition of a small amount of coagulant is sufficient to increase the flocculation performance at pH 9. Indeed, flocculation might have been better if a lower pH value was chosen instead of pH 9 for increasing the performance of the 'coagulation plus flocculation' test because, at this pH, there are no cationic species such as $M(OH)_2^+$ in the medium, which adversely affect the charge-neutralization process. These cationic species cause destabilization of the suspension, in addition to being a part of the colloidal precipitates, whether they are negatively charged or without any charge. However, pH 9 was preferred because it was nearly equal to the original pH value (pH 8.4) of NSPW. Although these negative aspects in the improvement of the flocculation performance at pH 9 are to be considered, a minor positive effect of the addition of coagulant was noted. The reason for this is not clear at present. However, the negative effects of the coagulant addition were obvious at high coagulant dosages due to the reasons explained in the coagulation section above. Similar results were obtained in a study related to the aggregation of chemical wastewater using ferric chloride plus anionic polymer [9].

4 Conclusions

The following conclusions can be drawn from this study:

- (i) The most efficient methods for the removal of turbidity from the NSPW were flocculation and 'coagulation plus flocculation' methods. The lowest residual turbidity values were obtained with 1.3 mg/L polymer dosage (optimum dosage) and 20 mg/L $FeCl_3 \cdot 6H_2O$ + 1.3 mg/L polymer dosages, which gave a residual turbidity of 12 and 5 NTU, respectively. It must be noted the

value of 12 NTU, although relatively high, is within the acceptable turbidity range for reusing clarified water from NSPW.

- (ii) Chloride based aluminum coagulant ($AlCl_3$) gave the best results in terms of turbidity removal at pH 6 and 9, whereas at neutral pH (7.5), all the coagulants showed almost similar performances with respect to clarifying NSPW. However, even the best result (21 NTU), obtained by the addition of $AlCl_3$ at pH 6, was higher than the maximum allowable turbidity value (≈ 15 NTU). Moreover, it was higher than those obtained in the flocculation and 'coagulation plus flocculation' methods.

- (iii) The pH of the suspension directly affected the coagulation conditions of NSPW. The coagulating powers of all the coagulants (aluminum chloride, alum, and ferric chloride) increased with decreasing pH. As a result, the lowest residual turbidities were obtained at pH 6 for all the coagulants. This indicated that the charge-neutralization mechanism plays a more decisive role in comparison to the sweep coagulation mechanism on turbidity removal from NSPW. In addition, it was assumed that the effective charge-neutralizing species may be colloidal metal-hydroxide particles (precipitates), which can be deposited on the negative travertine powders, rather than cationic metal-hydroxyl compounds, such as $M(OH)_2^+$ and $M(OH)_2^+$. On the contrary, under neutral and slightly alkaline conditions, i.e., pH 7.5 and 9, the coagulation of the NSPW occurred through the sweep-coagulation mechanism. The polymer-bridging mechanism was responsible for the flocculation process in the NSPW.

The authors have declared no conflict of interest.

References

- [1] B. Ersoy, Effect of pH and polymer charge density on settling rate and turbidity of natural stone suspensions, *Int. J. Miner. Process.* **2005**, 75, 207–216.
- [2] H. Acar, Must be paid attention matters during the establishment and the running of a wastewater clarify unit for a marble processing plant (in Turkish), in *Proc. of the Third Marble Symp.*, Kozan Ofset, Ankara **2001**, 289–296.
- [3] J. E. Gregor, C. J. Nokes, E. Fenton, Optimizing natural organic matter removal from low turbidity waters by controlled pH adjustment of aluminum coagulation, *Water Res.* **1997**, 31, 2949–2958.
- [4] M. Franceschi et al., Optimization of the coagulation-flocculation process of raw water by optimal design method, *Water Res.* **2002**, 36, 3561–3572.
- [5] C. J. Gabelich, T. I. Yun, B. M. Coffey, I. H. Suffet, Effects of aluminum sulfate and ferric chloride coagulant residuals on polyamide membrane performance, *Desalination* **2002**, 150, 15–30.
- [6] W. P. Cheng, Comparison of hydrolysis/coagulation behavior of polymeric and monomeric iron coagulants in humic acid solution, *Chemosphere* **2002**, 47, 963–969.
- [7] T. A. Özbelge, Ö. H. Özbelge, S. Z. Baskaya, Removal of phenolic compounds from rubber-textile wastewaters by physico-chemical methods, *Chem. Eng. Process.* **2002**, 41, 719–730.
- [8] M. H. Al-Malack, N. S. Abuzaid, A. H. El-Mubarak, Coagulation of polymeric wastewater discharged by a chemical factory, *Water Res.* **1999**, 33, 521–529.
- [9] C. S. Poon, C. W. Chu, The use of ferric chloride and anionic polymer in the chemically assisted primary sedimentation process, *Chemosphere* **1999**, 39, 1573–1582.
- [10] H. W. Ching, T. S. Tanaka, M. Elimelech, Dynamics of coagulation of kaolin particles with ferric chloride, *Water Res.* **1994**, 3, 559–569.

- [11] A. C. Pierre, K. Ma, Sedimentation behavior of kaolinite and montmorillonite mixed with iron additives, as a function of their zeta potential, *J. Mater. Sci.* **1997**, 32, 2937–2947.
- [12] A. C. Pierre, K. Ma, DLVO theory and clay aggregate architectures formed with AlCl_3 , *Journal of the European Ceramic Society* **1999**, 19, 1615–1622.
- [13] A. Özkan, M. Yekeler, Coagulation and flocculation characteristics of celestite with different inorganic salts and polymers, *Chem. Eng. Process.* **2004**, 43, 873–879.
- [14] J. Gregory, Fundamentals of flocculation, *Crit. Rev. Environ. Contr.* **1989**, 19, 185–230.
- [15] M. C. Werneke, Application of synthetic polymers in coal preparation, *Soc. Min. Eng. AIME* **1979**, 76, 1–11.
- [16] B. Yarar, *Evaluation of Flocculation and Filtration Procedures Applied to WSRC Sludge. Report no: WSRC-TR-2001-00213*, Colorado School of Mines, USA **2001**, 1–34.
- [17] D. H. Bache, E. N. Papavasiliopoulos, Dewatering of alumino-humic sludge: impact of hydroxide, *Water Res.* **2003**, 37, 3289–3298.
- [18] J. Duan and J. Gregory, Coagulation by hydrolyzing metal salts, *Adv. Colloid Interface Sci.* **2003**, 100–102, 475–502.
- [19] D. A. Dzombak, F. M. M. Morel, *Surface complexation Modeling: Hydrous Ferric Oxide*, John Wiley and Sons, New York **1990**.
- [20] G. A. Parks, P. L. De Bruyn, The zero point of charge of oxides, *J. Phys. Chem.* **1962**, 66, 967–972.
- [21] G. A. Parks, The isoelectric points of solid oxides, solid hydroxides, and aqueous hydroxo complex systems, *Chem. Rev.* **1965**, 65, 177–198.
- [22] H. Hek, R. J. Stol, P. L. Bruyn, Hydrolysis-precipitation studies of aluminum (III) solutions. 3. The role of the sulfate ion, *J. Colloid Interface Sci.* **1978**, 64, 72–82.
- [23] A. Seyrankaya, U. Mayaloglu, A. Akar, Flocculation conditions of marble from industrial wastewater and environmental consideration, in *Proc. of the 8th International Mineral Processing Symp: Mineral Processing on the Verge of the 21st Century* (Ed: G. Özbayoglu), Balkema, Rotterdam **2000**, 645–652.
- [24] M. Rossini, J. G. Garrido, M. Galluzzo, Optimization of the coagulation-flocculation treatment influence of rapid mix parameters, *Water Res.* **1999**, 33, 1817–1826.
- [25] M. I. Aguilar et al., Improvement of coagulation-flocculation process using anionic polyacrylamide as coagulant aid, *Chemosphere* **2005**, 58, 47–56.
- [26] M. Özer, Y. E. Bentli, G. Önal, H. Dinçer, Settling of coal slimes by flocculation, in *Proc. of IXth International Mineral Processing Symposium*, Capodocia, Turkey September **2002**.
- [27] M. L. Taylor, G. E. Morris, P. G. Self, R. S. C. Smart, Kinetics of adsorption of high molecular weight anionic polyacrylamide onto kaolinite: The Flocculation Process, *J. Colloid Interface Sci.* **2002**, 250, 28–36.
- [28] R. Divakaran, P. V. N. Sivasankara, Flocculation of river silt using chitosan, *Water Res.* **2002**, 36, 2414–2418.
- [29] R. Hogg, Flocculation and dewatering, *Int. J. Miner. Process.* **2000**, 58, 223–236.
- [30] P. Somasundaran, K. K. Das, Flocculation and selective flocculation—An overview, in *Proc. of the 7th Int. Mineral Processing Symp.: Innovations in Mineral and Coal Processing* (Eds: S. Atak, G. Önal and M. S. Çelik), A.A. Balkema, Rotterdam **1998**.
- [31] W. Stumm, and J. J. Morgan, *Aquatic Chemistry*, 2nd ed., John Wiley and Sons, New York **1981**.
- [32] F. Ge, H. Shu, Y. Dai, Removal of bromide by aluminum chloride coagulant in the presence of humic acid, *J. Hazard. Mater.* **2007**, 147, 457–462.