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Investigation of effective chemical flocculation conditions for the treatment of reverse osmosis reject water from coal power plant: a case study

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ABSTRACT

Power generation processes generate wastewater that is rich in scale-forming agents and which, therefore, requires suitable pre-treatment prior to further treatment with an RO system. In this study, Rheofloc5023 was used as a coagulant, while Rheofloc5414, ARFloc100, and Genefloc were the selected flocculants applied after the pH adjustment with lime and NaOH to alter the solubility of the ions in the water. The tests were conducted at 40°C and 60°C to observe the effect that temperature has on the treatment process. Four parameters were considered during the optimization process, namely, conductivity, turbidity, total hardness, and alkalinity. When lime was used, it was found that the treatment was superior at 60°C with ARfloc100 as flocculant. A coagulant dosage of 0.5 mg/L, a flocculant dosage of 0.2 mg/L, and a lime dosage of 220 mg/L were found to be optimal for a conductivity removal of 36%, a turbidity increase of 59%, a total hardness removal of 54%, and an alkalinity removal of 71%. When NaOH was used, Rheofloc5414 at 40°C was found to be optimal with coagulant and flocculant dosages of 5 and 0.5 mg/L, respectively. This yielded a conductivity removal of 1.26%, a turbidity removal of 58.75%, a total hardness removal of 20.3%, and an alkalinity removal of 50.6%. Thus, lime treatment was more efficient for the removal of scaling agents from the water. However, it was found that settling occurred faster at 60°C with both lime and NaOH and that the latter had a better settling velocity characterized by the formation of more stable crystals. This finding was confirmed with a scanning electron microscopy, as the treatment with NaOH and Rheofloc5414 at 60°C had larger and more densely packed crystals. From the above findings, it is suggested that lime should be used for treatment, as it removed more scaling agents and it is less expensive and more readily available than NaOH.

Keywords: Crystallization; Flocculation; RO-reject; Scalants removal; Temperature effect

1. Introduction

Coal power plants use large volumes of water to lower high temperatures, and to power turbines with steam to generate electricity. The power sector is among the largest industrial water users around the world, however, there is limited information in relation to water management by some power plants mostly in developing countries. In South Africa, wet cooling plants of the main power utility Eskom are reported to use on average 1.38 L of water per kWh of electricity. This is relatively high compared to China, where wet cooling power stations use on average 1.15 L of water to generate a kWh of electricity [1]. The relatively high amount of water required to generate a kWh unit sent out

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(USO) coupled with the strict national water regulations, have motivated Eskom to embark on a campaign to reduce its water usage to 1.34 L/kWh USO by 2020, hence, strengthening the existing zero liquid effluent discharge policy, which aims to recycle wastewater from cooling tower in order to reduce the volume of water extracted from rivers and to minimize Eskom's footprint [2–4].

Currently, the water treatment system used at Eskom includes RO, however, after a number of cycles of RO treatment, the concentration of total dissolved solids (TDSs) in the retentate is relatively high, making the RO no longer suitable for the treatment of such salted water (RO-reject), which will normally be discharged in a sump. However, the policy recently adopted by Eskom has resulted in consideration of pre-treatment processes, to significantly reduce the TDSs level in RO-reject prior to further treatment with the RO system [5,6]. The RO-reject water considered in this study was collected from the Grootvlei power station, which is situated near Balfour, Mpumalanga, South Africa. This water contains salty brine that consists of calcium and magnesium salts, which can scale downstream equipment and cause a reduction in equipment efficiency. It is, therefore, the necessity to remove such scaling agents from the water to prevent scale formation. These scaling agents can be removed through a crystallization process.

Crystallization can be achieved through super-saturation where the scaling agents in the water become insoluble as their concentrations significantly increase. Flocculation is then used to ensure that the crystals that form agglomerate, increasing the mass of the crystals, which in turn settle through the influence of the gravitational force [7].

Inorganic metal-based flocculants have been traditionally used for the treatment of wastewaters, however, some limitations related to increased concentration of metals in sludge and ineffective removal of particles in solutions, have led to investigations over the years by researchers resulting in the identification of polymers and nanomaterials based flocculants which have been continuously improved to address the complexity of wastewaters [8]. Natural polymers provide an additional advantage to be environmentally friendly and biodegradable [9–11]. Bioflocculants have particular macromolecular structures with a variety of functional groups that can interact with contaminants [12,13]. These properties give the bioflocculants the ability to destabilize particles that are resistant to aggregation through an increase of the ionic strength or specifically adsorbing counterions to neutralize the particle size.

Polyamines are cationic coagulants with a medium molecular weight, mostly linear, which are soluble in water and can be used over a wide pH range. Due to their length, these molecules wrap flocs together. In a study conducted by Lee et al. [14], it was found that polyamines reduced the turbidity of raw water from 9.4 to 1 NTU and the total organic carbon levels in the water from 3.3 to 1.97 mg/L. According to a study conducted by Choi et al. [15], polyamines, in conjunction with aluminum sulfate, led to a lower amount (50% less) of aluminum sulfate used to achieve the same results. This makes the treatment more cost-effective and minimizes sludge production. The turbidity also decreases from 145 to 2 NTU. The polyamines used in the study were Rheofloc and ARfloc 100.

Genefloc is a polyquaternary amine that can function over a large pH range and which is produced by Genesys International Limited (Amsterdam, The Netherlands). The positive charge of these molecules can be found in the backbone of the polymer chain. Thus, if there is an excess of flocculants in the water, it will adhere across the length of the membrane surface and not by its sub-branches.

Lime is used to increase the pH and reduce the solubility of metal ions in the water. Different grades of lime can be used to increase the pH. In this study, industrial-grade lime was used, which consists of more or less 50% lime. The calcium and magnesium ions react with carbonates and hydroxides, respectively, and precipitate at high pH values. Strontium, calcium, and magnesium removal is pH dependant, and lime is a relatively less expensive and highly effective substance to increase the pH [10]. According to Lim et al. [16], when lime is added to water, it dissociates into calcium cations and hydroxyl anions. At high pH values, these ions bind with other ions in water to form crystals. For example, calcium ions can either bind with sulfate ions or carbonate ions, which form calcium sulfate or calcite, respectively, and the hydroxyl ions can bind with magnesium ions in the water to form magnesium hydroxide.

Sodium hydroxide can also be used as an alkaline reagent for water softening. The calcium carbonate will precipitate and sodium carbonate will form as a by-product, which is stable [17]. According to the study done by Malanova et al. [17], sodium hydroxide is a good reagent to use in water softening, as $CaCO_3$ precipitates. Sodium hydroxide is, however, more expensive than lime and is less freely available than lime.

This study assessed the performance of the above coagulants, flocculants and, lime and sodium hydroxide in the removal of hardness, alkalinity, and conductivity from RO-reject water, the effect of temperature on the performance of the above chemical reagents was investigated simultaneously.

2. Experimental procedure

2.1. Sample collection

CRO-reject water samples were collected in 25 L drums from the RO system at the Power Station A. The water was collected at the taps releasing wastewater with too high TDS to be treated through the RO system, and which was then discharged to the sumps. Samples were transported to the Water Laboratory at the School of Chemical and Minerals Engineering at the North-West University (Potchefstroom), the water containers were covered with black plastic to prevent the penetration of light and stored in a refrigerator prior to use.

2.2. Water analysis

During the analysis of water, different parameters were considered, measured, and calculated. This included pH and conductivity, measured with a Lovibond 150 m at the sampling site, turbidity was measured using a Hach (Germany) 2100Q portable turbidity meter. Total hardness and alkalinity were measured through titrations as reported by van der Linde et al. [18].

2.3. Coagulants

Rheofloc5023 was used as a coagulant and dosages ranging from 0.2 to 7 mg/L were used in the optimization tests. The dosages used were 0.2, 0.5, 0.7, 2, 5, and 7 mg/L, and the effect of dosage was carried out in duplicate during the optimization procedure. This coagulant is often used to treat processed water at the power plant and was kindly offered by the company.

The flocculants used in the optimization process have been discussed in introduction and included Rheofloc5414 obtained from the plant, ARfloc100, obtained from the labs at the university, and Genefloc, obtained from Genesys. The dosages considered for each of these flocculants were 0.2, 0.7, 1, and 7 mg/L.

The pH should be increased to improve the crystallization process which will promote the removal of potential scale forming agents from the water, this was done with the addition of calcium hydroxide, lime ($Ca(OH)_2$). A dosage of 220 mg/L was used to increase the pH to 10.1, where magnesium and calcium ions are no longer soluble in the water, and, thus, likely to precipitate. At the optimal coagulant and flocculant dosages, lime was replaced with the same concentration of sodium hydroxide (NaOH), to establish treating comparison in their ability to remove salts from RO-reject water.

2.4. Jar test

A six-paddle jar test apparatus used to maximize interaction between chemical reagents and suspended particles was connected to a water bath connected used to ensure that the temperature of the samples remained constant. During the jar test runs, rapid mixing was carried out at 240 rpm for 5 min, at which point the coagulant and flocculant were added to the sample. Thereafter, slow mixing was carried out for 90 min at 80 rpm. At the start of the slow mixing period, the lime or NaOH was added to the samples in different containers. After the slow mixing period, settling occurred for 30 min, then the supernatants were analyzed to determine the levels of parameters mentioned above.

2.4.1. Optimization

The optimum dosage of the coagulant was determined by keeping constant the dosage of flocculant in the six beakers while altering the coagulant dosage in each beaker. Thereafter, the following tests were conducted to observe the optimal conditions for each flocculant: conductivity, turbidity, total hardness, and alkalinity. The percentage removal of chemicals related to each of these parameters was calculated by taking into account their initial values before treatment of the water. The optimal conditions determined using lime were then considered during treatment with NaOH.

2.5. Settling velocity tests

The optimal dosages were used to determine the settling velocity of the particles formed. This was done by using the same mixing method considered for the optimization process. Instead of 30 min settling time, the sample was added into a calibrated Imhoff cone directly after the mixing occurred. The Imhoff cone was calibrated by adding 1 mL of water at a time and marking the volume of the water up until 10 mL [6]. Thus, the volume of the sludge could be observed until it reached 10 mL and the time recorded.

2.6. Stability tests

The same optimal dosages were used to determine the stability of the sludge that formed. The mixing regime was followed and, after the mixing, a 30 min settling time was allowed. Thereafter the samples were mixed for 30 s at a speed of 100 rpm. Then, the sample's turbidity was measured at 3 min intervals to determine how rapidly the sludge settled after the disturbance. The same method was followed to determine the difference in disturbance as a factor of stirring the process was repeated at a mixing speed of 200 rpm.

2.7. Morphology analysis

After the settling tests had been conducted, the water was decanted and the crystals were collected and dried in an oven for 24 h at 50°C. These dried crystal samples were analyzed using the following methods.

The morphology of the crystals was determined using a scanning electron microscopy (SEM; TECSAN, model VEGA 3 XMU from Czech Republic, with 10-micron lens). The size of the particles, as well as the compounds in the particles, could be observed using this apparatus.

The dried crystal samples were also characterized using a Philips (The Netherlands) X'Pert pro MPD X-ray diffractometer to determine the crystallinity of the compounds. A higher crystallinity refers to more stable crystals.

2.8. Model prediction

After the measurement of the physico-chemical parameters, the information gathered was used to build a geochemical model using French Creek software. It was found that, when using lime, calcite, anhydrite, and gypsum were the leading scaling agents.

It was predicted that the calcite will precipitate at a pH of 10.1, this value was considered during the adjustment of pH using lime and NaOH. The concentration of lime used was also calculated with French Creek software.

The amounts of lime and NaOH used in this study were calculated from the values predicted by the French Creek software.

3. Results and discussion

3.1. Water characterization

The results for the physico-chemical parameters, such as conductivity, turbidity, total hardness, and alkalinity are given in Table 1.

Table 1 indicates that the conductivity and total hardness of the RO-reject water samples were considerably increased compared to the raw water and therefore likely to form scale, such water could not, therefore, be considered for further cycles of RO without pre-treatment.

3.2. Geochemical simulation with French Creek

The cations and anions concentrations in Table 2 were used in the French Creek model to simulate the scale formation potential of RO-reject water as shown in Table 3. According to Rahardianto et al. [19], higher concentrations of scale precursor ions, such as Ca^{2+}, Ba^{2+}, SO_4^{2-}, and CO_3^{2-} in the membrane retentate beyond solubility limits, are likely to form mineral scalants, such as barite, calcite, and gypsum, resulting in the scaling of membrane.

The various minerals with the potential to cause scale on the RO membrane were predicted with French Creek software and are shown in Table 3.

Ferric hydroxide and barite are most likely to form scale according to the French Creek model simulation. These compounds can be removed from water by stimulating crystallization at the superstation level, which can be achieved with the aid of coagulants and flocculants. A study conducted by Sun et al. [20] showed the potential of ferric hydroxide to scale in pipes, thereby affecting effective treatment of water. According to Martinez-Ruiz et al. [21], barite crystals form when barium reacts to an abundance of sulfates in the water, thus, the potential of barite forming is an indication that the crystallization mechanism is taking place during the tests. According to Yan et al. [22] inhibiting and reducing barite is important, as barite has a negative impact on laminar and turbulent flow.

Table 1
Results of water samples characterization

Conductivity (mS/cm)	1.92–7.38
Turbidity (NTU)	0.85–4.44
Total hardness (mg$CaCO_3$/L)	783.6–2,084
Alkalinity (mg$CaCO_3$/L)	58–60

Table 2
Cations and anions from French Creek

Cations (mg/L)	
Calcium (as Ca)	826
Magnesium (as Mg)	357
Barium (as Ba)	0.44
Strontium (as Sr)	5.71
Sodium (as Na)	883
Potassium (as K)	192
Lithium (as Li)	4.8
Iron (as Fe)	0.13
Ammonia (as NH_3)	0.00
Aluminum (as Al)	0.1
Anions (mg/L)	
Chloride (as Cl)	551
Sulfate (as SO_4)	4,611
Dissolved CO_2 (as CO_2)	3.34
Bicarbonate (as HCO_3)	173
Carbonate (as CO_3)	7.56
Silica (as SiO_2)	0.00
Phosphate (^{0}Fr)	0.3
H_2S (as H_2S)	0.00
Fluoride (as F)	6.9
Boron (as B)	2.07

3.3. Optimization of dosages and conditions

During the optimization of the dosages of coagulants and flocculants, Rheofloc5023 was used as coagulant with the following dosages (mg/L): 0.2, 0.5, 0.7, 2, 5, and 7. This was used in conjunction with 220 mg/L lime, as well as the different flocculants. These flocculants were Rheofloc5414, ARfloc100, and Genefloc. The parameters that were used to determine the optimal conditions included conductivity, turbidity, total hardness, and alkalinity. Two different temperatures were also used to determine the optimal conditions for operation, namely 40°C and 60°C.

3.3.1. Rheofloc5414 as flocculant

The first flocculant used with Rheofloc5023 was Rheofloc5414, which was used in conjunction with a lime dosage of 220 mg/L.

3.3.1.1. Conductivity removal

The reduction of conductivity at 40°C can be seen in Fig. 1a.

As can be seen in Fig. 1a, conductivity removal was the highest at 9.2% at a coagulant dosage of 2 mg/L and a Rheofloc5414 dosage of 1 mg/L at 40°C. Thus, at that dosage, 9.2% of the dissolved ions were removed from the solution. However, the optimal dosage was found to be a coagulant dosage of 0.2 mg/L with a flocculant dosage of 0.2 mg/L, as there was no significant difference observed compared to the maximum removal of conductivity.

The results obtained using the same coagulant and flocculant dosages at 60°C can be seen in Fig. 1b.

As can be seen in Fig. 1b, the optimal conditions at 60°C were a coagulant dosage of 0.2 mg/L with a

Table 3
Scaling potential generated with French Creek

Mineral scalants	Saturation levels
Calcite ($CaCO_3$)	9.03
Aragonite ($CaCO_3$)	8.4
Magnesite ($MgCO_3$)	3.23
Anhydrite ($CaSO_4$)	1.02
Gypsum ($CaSO_4 \cdot 2H_2O$)	1.7
Barite ($BaSO_4$)	111.4
Celestite ($SrSO_4$)	1.05
Ferric hydroxide ($Fe(OH)_3$)	147.8
Siderite ($FeCO_3$)	2

flocculant dosage of 0.2 mg/L. The efficiency of the reduction of the conductivity at these dosages is 46%. Thus, there was a reduction of 46% in the dissolved ions in the treated water. It can also be observed that the removal of conductivity at 60°C was relatively consistent compared to 40°C.

It can, therefore, be suggested that conductivity removal at 60°C is superior to conductivity removal at 40°C. This is due to super-saturation that improves at higher temperatures, more scaling agents are formed at these temperatures, partly due to evaporation. In a study conducted by Zhang et al. [1], scaling occurred more frequently at higher temperatures, thus, super-saturation occurred and fewer particles were soluble in the water. Elevated temperatures are likely to induce an increase in precipitation.

3.3.1.2. Turbidity removal

The turbidity removal of the coagulant and flocculant dosages at 40°C can be observed in Fig. 2a.

As shown in Fig. 2a, there was an increase in the turbidity (corresponding to the negative values) with all the dosages used, because of the relatively low initial values of the turbidity before treatment. At 40°C, the best conditions were a coagulant dosage of 0.5 mg/L and a flocculant dosage of 7 mg/L, under these conditions, the solution was less turbid. The turbidity removal at 60°C is given in Fig. 2b.

As can be seen in Fig. 2b, a decrease in the turbidity of water was achieved with only two flocculant dosages, 0.2 and 7 mg/L. The optimal dosage was, however, a coagulant dosage of 0.5 mg/L and a flocculant dosage of 7 mg/L, which yielded a turbidity removal of 26%.

Thus, at higher temperatures, turbidity removal was superior, due to the same reasons given for conductivity removal.

3.3.1.3. Total hardness removal

The total hardness reduction with the same coagulant and flocculant dosages at 40°C is given in Fig. 3a.

This is an important parameter, as it relates directly to the amount of scaling agents in the water. It can be seen in Fig. 3a that the highest removal at 40°C was achieved with a coagulant dosage of 7 mg/L and a flocculant dosage of 1 mg/L. These dosages yielded a total hardness reduction of 17.1%. The optimal dosages, however, were a coagulant and flocculant dosage of 0.2 mg/L, as fewer reagents were needed to obtain a total hardness removal of 12%. This relates to a 12% reduction of the scaling agents in the water.

The total hardness removal at 60°C is given in Fig. 6, using the same coagulant and flocculant dosages.

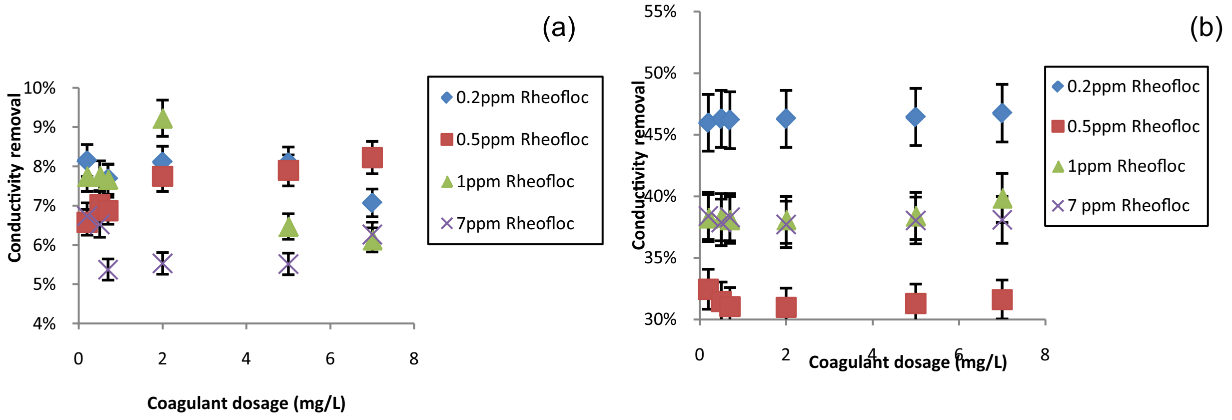

Fig. 1. Conductivity removal with Rheofloc5414 as flocculant at (a) 40°C and (b) 60°C.

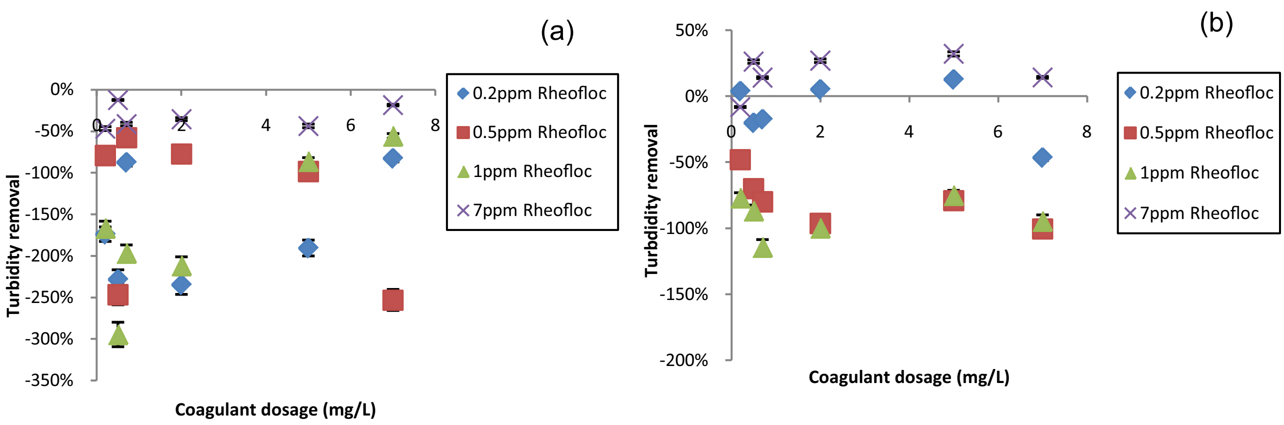

Fig. 2. Turbidity removal with Rheofloc5414 as flocculant at (a) 40°C and (b) 60°C.

As can be seen in Fig. 3b, the optimal dosage at 60°C is a coagulant and flocculant dosage of 0.2 mg/L, which yields a total hardness removal of 53%, implying that there are 53% less scaling agents in the water at these conditions. It can also be stated that any of these dosages can be used, but 0.2 mg/L dosage is optimal, as it will be the most cost-effective dosage to use.

The higher efficiency at higher temperatures is due to increased super-saturation and a decrease in the solubility of the scaling agents in the water, as stated by Zhang et al. [1]. Thus, crystallization is more effective and there is an increase in the precipitation, higher temperatures are likely to provide more energy which can then allow ions to react faster to form crystals [23].

3.3.1.4. Alkalinity removal

Removal of alkalinity with the same coagulant and flocculant dosages at 40°C is illustrated in Fig. 4a.

As can be seen from Fig. 4a, the optimal conditions for alkalinity removal at 40°C are a coagulant dosage of 5 mg/L and a flocculant dosage of 0.2 mg/L. These dosages yielded a 72% reduction of the alkalinity in the water, which relates to a 72% reduction of the carbonates in the water.

The alkalinity removal of the same dosages at 60°C is illustrated in Fig. 8.

As can be seen in Fig. 4b, optimal alkalinity removal, of 77%, was achieved with a coagulant dosage of 0.5 mg/L and a flocculant dosage of 0.2 mg/L at 60°C. This achievement relates to 77% fewer carbonates in the treated water at these conditions.

The efficiency of alkalinity removal is higher at increased temperatures because of the decrease in solubility accompanying an increase in super-saturation. This was also found in a study by Zhang et al. [1].

3.3.2. ARFloc100 as flocculant

The next flocculant used was ARFloc100 in conjunction with 220 mg/L lime. The dosages used for the ARFloc were 0.2, 0.5, 1, and 7 mg/L.

3.3.2.1. Conductivity removal

The results of conductivity removal obtained using ARFloc100 at 40°C in conjunction with the coagulant, Rheofloc5023, and lime can be seen in Fig. 5a.

It is clear from Fig. 5a that a higher flocculant dosage yielded a better conductivity removal. The highest conductivity removal at 40°C, 22%, was obtained when using dosages of 5 mg/L coagulant and 7 mg/L flocculant. The optimal dosage is, however, a coagulant dosage of 0.2 mg/L and a

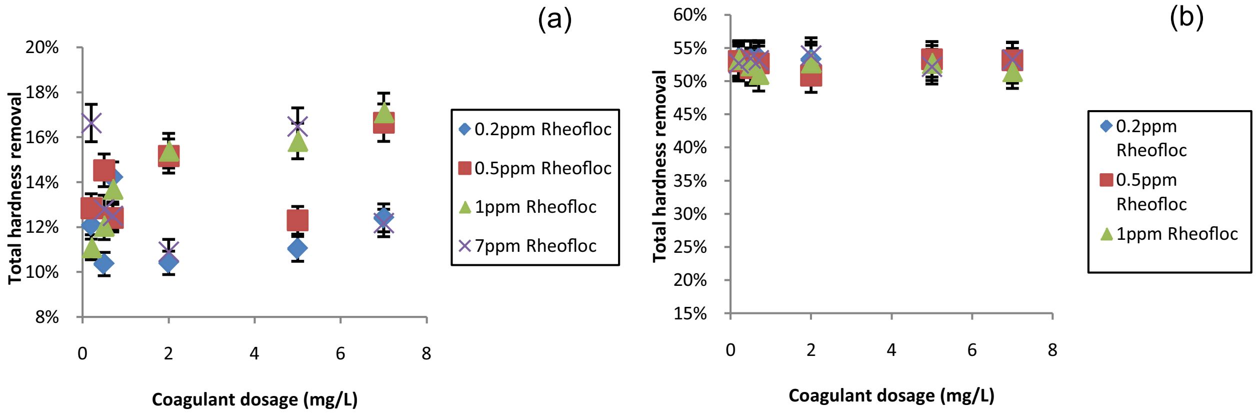

Fig. 3. Total hardness removal with Rheofloc5414 as flocculant at (a) 40°C and (b) 60°C.

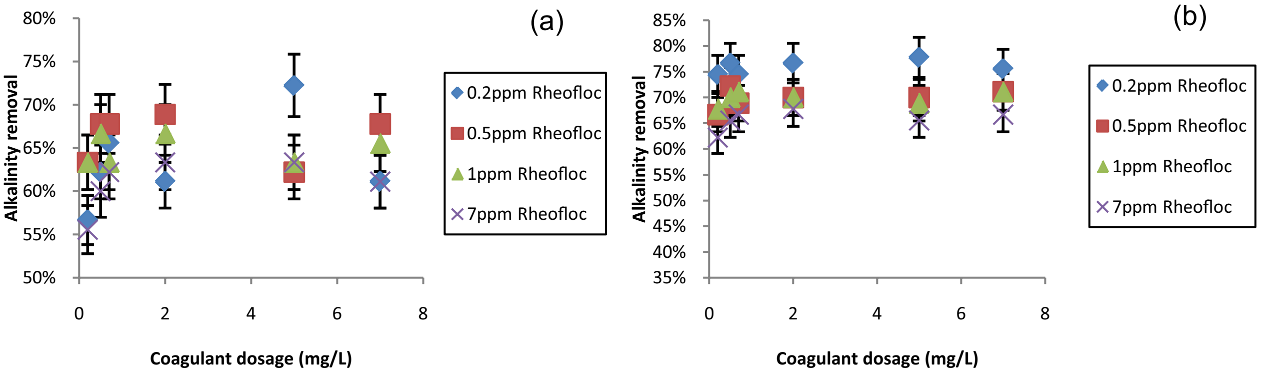

Fig. 4. Alkalinity removal with Rheofloc5414 as flocculant at (a) 40°C and (b) 60°C.

flocculant dosage of 7 mg/L, which yielded a conductivity removal of 20%. This indicates a 20% reduction of dissolved solids from the water after treatment.

With the same dosages, the conductivity removal at 60°C can be observed in Fig. 5b.

It can be seen from Fig. 5b that less coagulant and flocculant is needed to reach an improved conductivity removal at 60°C. The coagulant and flocculant dosages that yielded the highest conductivity removal at this temperature were 0.5 and 1 mg/L, respectively, resulting in a 39.4% reduction in conductivity. The optimal dosages were, however, a coagulant dosage of 0.2 mg/L and a flocculant dosage of 1 mg/L. This yielded a conductivity removal of 39.2%.

The conductivity removal was, once again, higher at 60°C. This finding is due to the increase in super-saturation and the decrease in the solubility of the dissolved solids, which then precipitate, thus, reducing the conductivity of the water after treatment.

3.3.2.2. Turbidity removal

The turbidity removal results obtained from the same coagulant and flocculant dosages at 40°C can be seen in Fig. 6a.

In general, there was an increase in turbidity when the coagulant and flocculant were added into the water sample, except at coagulant and flocculant dosages of 5 and 0.2 mg/L, as well as 7 and 0.5 mg/L, respectively. The optimal dosages regarding turbidity removal were 5 mg/L coagulant and 0.2 mg/L flocculant dosage, which yielded a 14% reduction in turbidity.

With the same dosages, the turbidity removal at 60°C can be seen in Fig. 6b.

The turbidity increased with almost every dosage used, except at coagulant and flocculant dosages of 5 and 0.2 mg/L, respectively, at 60°C. Therefore, these are the optimal dosages at these conditions, which reduced the turbidity by 8%.

Thus, in this case, turbidity removal at 40°C was more efficient than at 60°C, however, further investigation could be required to ascertain the reasons behind such an unexpected trend.

3.3.2.3. Total hardness removal

The same flocculant, coagulant, and dosages were used to test the reduction in the total hardness of the water and the results at 40°C are illustrated in Fig. 7a.

As can be seen in Fig. 7a, optimal total hardness removal at 40°C was obtained using a coagulant dosage of 0.7 mg/L and a flocculant dosage of 7 mg/L, yielding a removal of 25.8%, at which level there was 25.8% less scaling agents in the water after treatment.

The total hardness removal with the same dosages at 60°C can be seen in Fig. 7b.

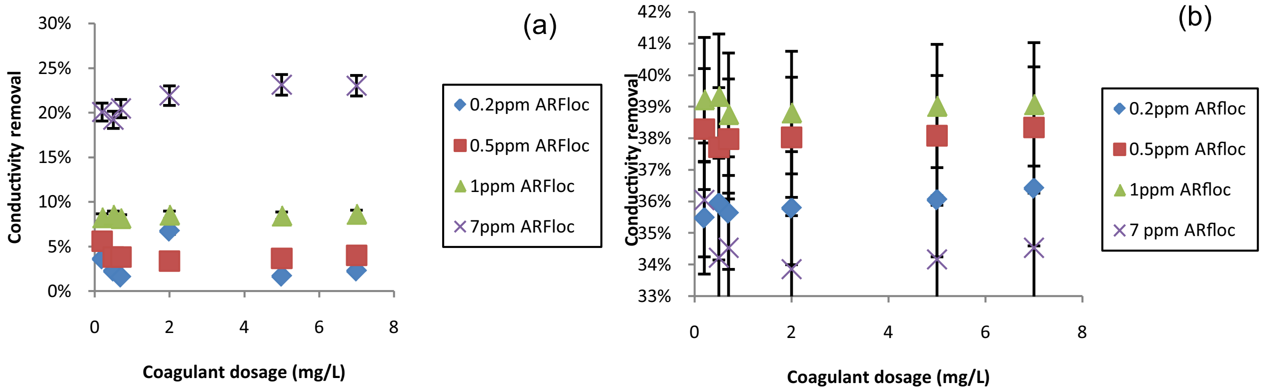

Fig. 5. Conductivity removal with ARFloc100 as flocculant at (a) 40°C and (b) 60°C.

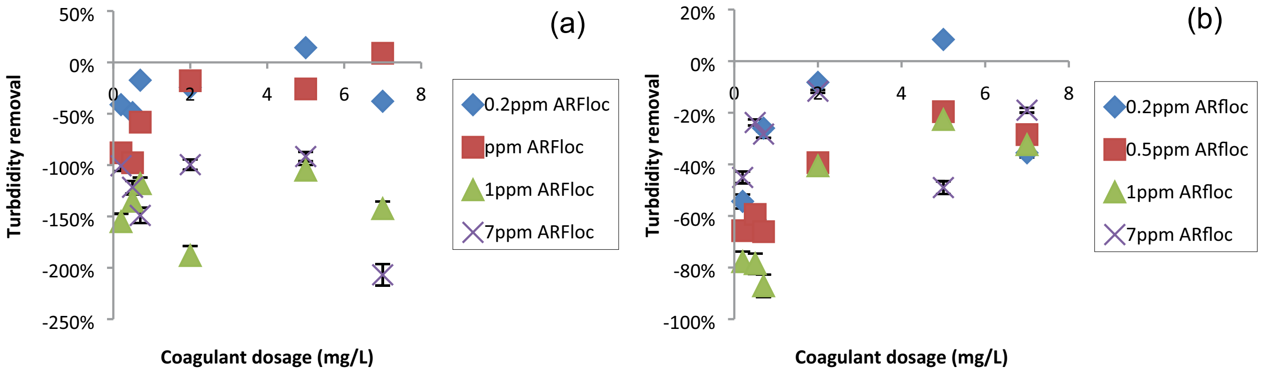

Fig. 6. Turbidity removal with ARFloc100 as flocculant at (a) 40°C and (b) 60°C.

The total hardness removal at 60°C was significantly higher than at 40°C and required fewer reagents. The optimal dosages at these conditions are 0.5 mg/L coagulant dosage and 0.2 mg/L flocculant dosage, yielding a 54.3% reduction in scaling agents in the water after treatment. A trend can also be seen in Fig. 14, where the coagulant dosage of 0.5 mg/L is at a peak, and as the coagulant dosage increases after this peak, the total hardness removal decreases, therefore, an excess of coagulant or flocculant is likely to destabilize the crystallization process.

Higher temperatures increase the total hardness removal as precipitation increases, as also observed with Rheofloc5414.

3.3.2.4. Alkalinity removal

Using the same dosages of flocculant and coagulant, the alkalinity removal at 40°C can be seen in Fig. 8a.

The optimal dosages regarding alkalinity removal at 40°C are 2 mg/L coagulant and 7 mg/L flocculant, resulting in an alkalinity removal of 72%. There are, thus, 72% fewer carbonates in the treated water.

The alkalinity removal with the same dosages at 60°C can be seen in Fig. 8b.

According to Fig. 8b, the highest alkalinity removal at 60°C occurred with a coagulant dosage of 0.5 mg/L and a flocculant dosage of 1 mg/L. These dosages yielded a 73% reduction in the alkalinity after treatment. However, the optimal dosages for alkalinity removal at 60°C were a coagulant dosage of 0.5 mg/L and a flocculant dosage of 0.2 mg/L, which yielded an alkalinity removal of 71%.

At 60°C, lower dosages are needed to achieve almost similar alkalinity removal rates at 40°C. It can also be said that, when ARFloc100 is used, the coagulant dosage should not exceed 0.5 mg/L, as the efficiency of treatment decreases with an increase in the dosage.

3.3.3. Genefloc as flocculant

The next flocculant used was Genefloc at dosages of 0.2, 0.5, 1, and 7 mg/L, used with the coagulant dosages discussed previously, and 220 mg/L lime.

3.3.3.1. Conductivity removal

The results obtained at 40°C with regards to conductivity removal with this flocculant, Genefloc, in conjunction with the coagulant, Rheofoc5023, and lime can be seen in Fig. 9a.

As can be seen from Fig. 9a, low Genefloc dosages yielded better conductivity removal, with an optimal dosage of 0.5 mg/L coagulant and a flocculant dosage of 0.2 mg/L. These dosages yielded a 22% reduction in conductivity. Higher flocculant dosages do not react well with regard to conductivity removal from the water.

The same dosages were used for the conductivity removal at 60°C, and the results can be seen in Fig. 9b.

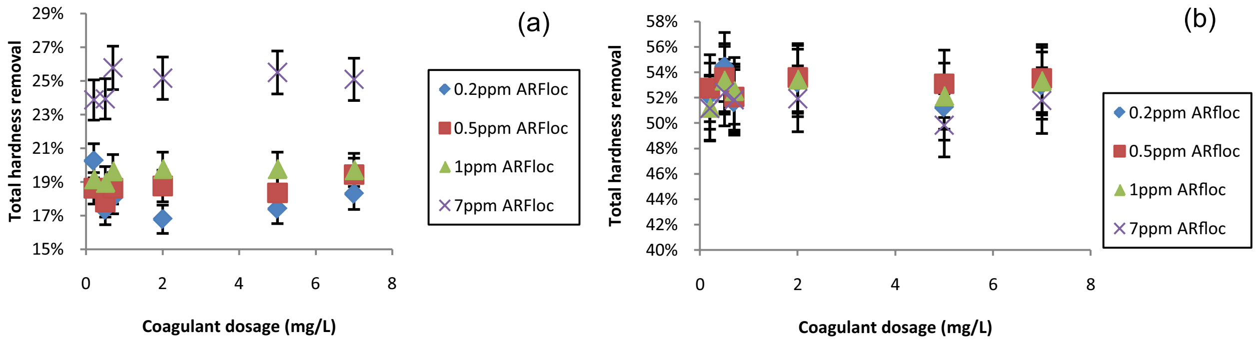

Fig. 7. Total hardness removal with ARFloc100 as flocculant at (a) 40°C and (b) 60°C.

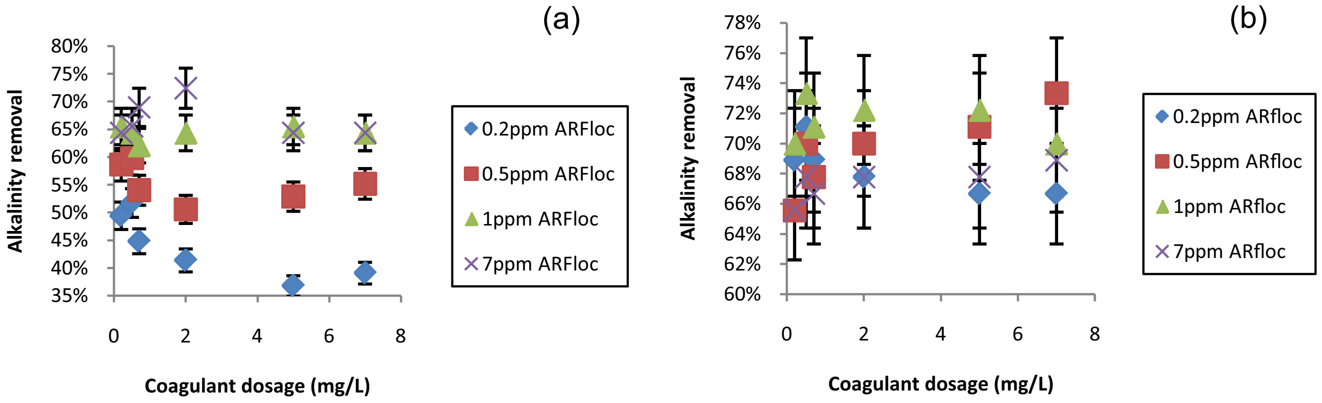

Fig. 8. Alkalinity removal with ARFloc100 as flocculant at (a) 40°C and (b) 60°C.

It can be seen in Fig. 9b that lower dosages yielded a better result at 60°C. The optimal dosages at 60°C for conductivity removal are a coagulant dosage of 0.2 mg/L and a flocculant dosage of 0.2 mg/L, which yielded 38% reduction in the conductivity of the treated water, which is significantly higher than the 22% removal achieved at 40°C. At a flocculant dosage above 0.2 mg/L, the efficiency of treatment decreases significantly with regard to conductivity removal.

An increase in the temperature increases the efficiency of the conductivity removal from the water. This trend is due to an increase in precipitation because of higher super-saturation.

3.3.3.2. Turbidity removal

The same dosages were used to determine the turbidity removal and the results at 40°C can be seen in Fig. 10a.

As can be seen from Fig. 10a, the optimal conditions for turbidity removal at 40°C were a coagulant dosage of 0.2 mg/L and a flocculant dosage of 0.2 mg/L. These dosages yielded 28% removal of the turbidity after treatment.

The same dosages were used to determine the turbidity removal at 60°C and the results can be seen in Fig. 10b.

The optimal turbidity removal at 60°C was 6.4% removal at a coagulant dosage of 2 mg/L and a flocculant dosage of 1 mg/L. There was an increase in the turbidity with the other dosages, due to the initial low turbidity of the water sample prior to the treatment.

The treatment at lower temperatures induced a higher turbidity removal.

3.3.3.3. Total hardness removal

The same dosages were used to determine the total hardness removal of the treated water at 40°C, and the results can be seen in Fig. 11a.

As can be seen from Fig. 11a, the highest total hardness removal at 40°C was achieved at a coagulant dosage and flocculant dosage of 7 mg/L, which yielded a 21% removal. The optimal dosages were, however, a coagulant dosage of 0.2 mg/L and a flocculant dosage of 0.5 mg/L, which yielded a total hardness removal of 19%. Thus, there were 19% less scaling agents present in the treated water.

The same dosages were used to determine the total hardness removal at 60°C, and the results are illustrated in Fig. 11b.

As can be seen from Fig. 11b, the optimal dosages for total hardness removal at 60°C were a coagulant dosage of 0.5 mg/L and a flocculant dosage of 0.2 mg/L. These dosages yielded a total hardness removal of 54%.

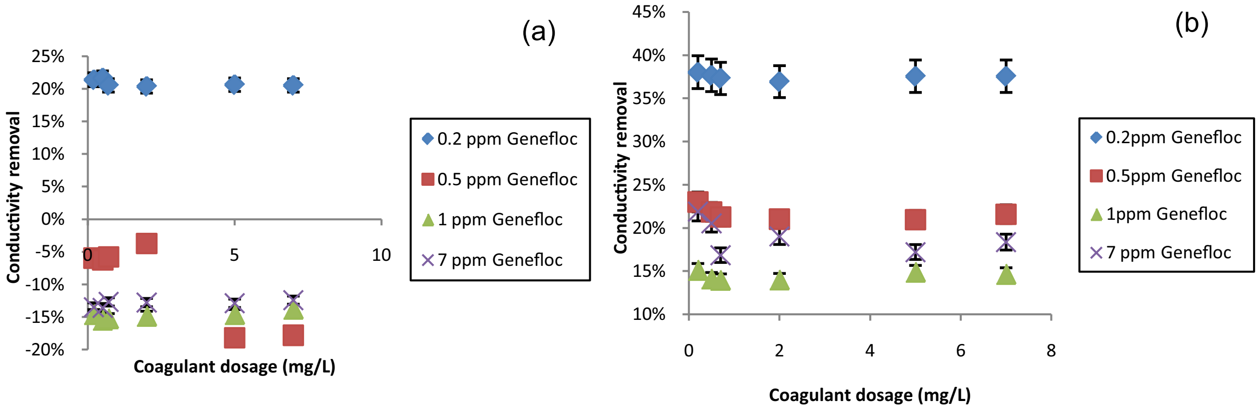

Fig. 9. Conductivity removal with Genefloc as flocculant at (a) 40°C and (b) 60°C.

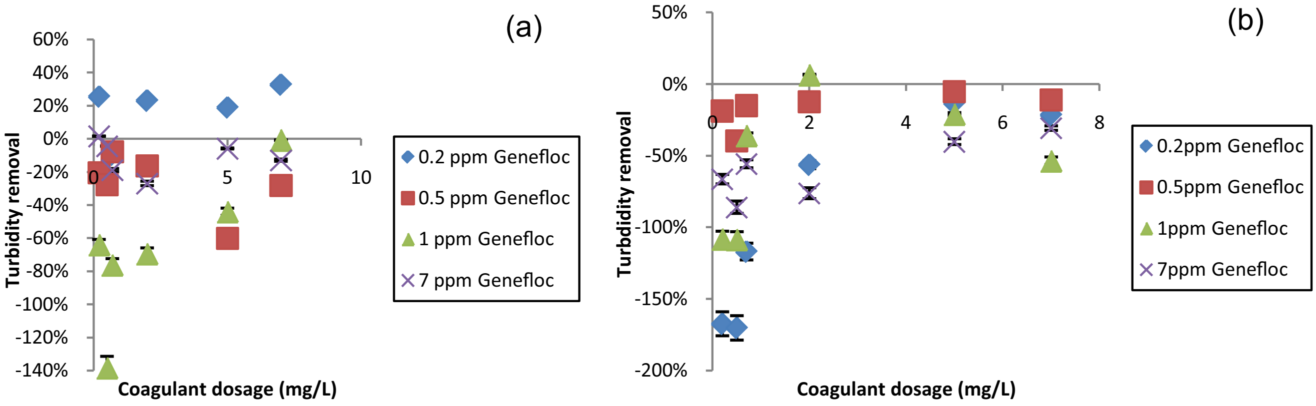

Fig. 10. Turbidity removal with Genefloc as flocculant at (a) 40°C and (b) 60°C.

At higher temperatures, the total hardness removal is elevated, because of the precipitation of the crystals that formed due to super-saturation.

3.3.3.4. Alkalinity removal

The same dosages were used to determine the alkalinity removal at 40°C and the results can be seen in Fig. 12a.

As can be seen from Fig. 12a, the highest alkalinity removal was achieved with a coagulant dosage of 7 mg/L in conjunction with a flocculant dosage of 0.2 mg/L, yielding alkalinity removal of 67%. The optimal dosages were, however, a coagulant dosage of 0.5 mg/L and a flocculant dosage of 0.2 mg/L, which yielded an alkalinity removal of 64%, which represents a 64% reduction of the carbonates in the treated water.

The same dosages were used to determine the alkalinity removal at 60°C and the results can be seen in Fig. 12b.

As can be seen from Fig. 12b, the optimal dosages for alkalinity removal at 60°C were a coagulant dosage of 0.5 mg/L and a flocculant dosage of 0.2 mg/L, which yielded an alkalinity removal of 73%.

Higher temperatures induce higher alkalinity removal as the carbonates precipitate as crystals due to an increased super-saturation at these higher temperatures.

3.3.4. Optimal dosages using lime

The optimal dosage for each flocculant and temperature can be seen in Table 4.

The parameters measured at these optimal conditions can be seen in Table 5.

From Table 5, it can be seen clearly that treatment with lime is more effective at 60°C than at 40°C. This finding is due to the increase in super-saturation when the temperature increases. The increased effectiveness at higher temperatures is partially due to the evaporation and increase

Table 4
Summary of optimal dosages

Flocculant and temperature	Coagulant dosage (mg/L)	Flocculant dosage (mg/L)
Rheofloc5414 at 40°C	5	0.5
Rheofloc5414 at 60°C	0.5	0.2
ARfloc100 at 40°C	0.7	7
ARfloc100 at 60°C	0.5	0.2
Genefloc at 40°C	0.7	0.5
Genefloc at 60°C	0.5	0.2

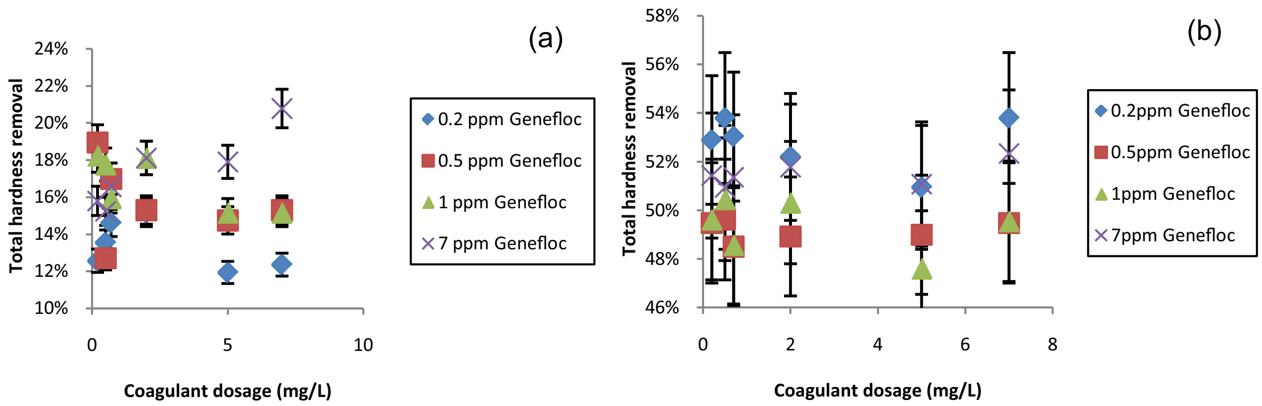

Fig. 11. Total hardness removal with Genefloc as flocculant at (a) 40°C and (b) 60°C.

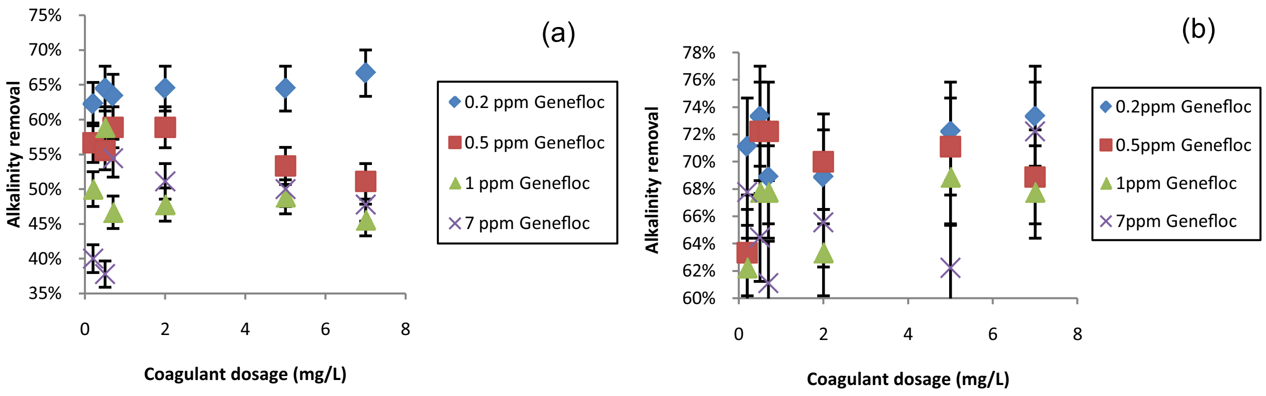

Fig. 12. Alkalinity removal with Genefloc as flocculant at (a) 40°C and (b) 60°C.

in ion energy at high temperatures, which promote crystal formation and settling. The data in Table 5 confirm the fact that the treatment is more effective at a higher temperature, thus, hot lime softening proven to be more effective.

Taking into account all the parameters, Genefloc was the least efficient flocculant used in conjunction with lime, thus, it should be disregarded for the settling velocity and stability tests.

3.3.5. Using NaOH instead of lime

The optimal conditions for the coagulants and flocculants were used to determine the effect of lime replacement by NaOH on the treatment of the water samples. The results for the conductivity removal, turbidity removal, total hardness removal, and alkalinity removal are given in Table 6.

From Table 6 it can be concluded that NaOH will be more efficient only if turbidity is the main parameter investigated. This observation further confirmed the impact of chemical reagents color on the turbidity after treatment. The lime was of white milky color when it was added to the samples, thus, increasing the turbidity of the sample. NaOH is transparent, with little to no effect on the turbidity, which will only depend on the presence of particles in suspension.

It was also found that NaOH is more efficient at lower temperatures, thus, reducing the running costs of the treatment process. However, NaOH is more expensive than lime and is not as freely available as lime. Lime is also more efficient in removing dissolved solids and scaling agents, thus, lime will be a better option for removing these substances.

Settling velocity tests, stability tests, and the morphology tests can be used to assess the potential of flocculants and the effect of temperature on the water treatment process further.

3.4. Settling velocity tests

Using the optimal conditions obtained during the removal of the conductivity, turbidity, total hardness, and alkalinity, settling velocities were tested with all the best flocculants, namely, Rheofloc5414 and ARFloc100. The tests were conducted at 40°C and 60°C with lime as well as NaOH. The results can be seen in Fig. 13 and Table 7.

When using lime, the fastest settling rate was observed with the flocculant ARfloc100 at 60°C. According to the settling prediction model in Fig. 13, the settling will be concluded in 874 s. It is also clear that, when using lime, settling will occur faster at higher temperatures.

When NaOH is used, the settling occurs faster at higher temperatures with Rheofloc5414. Using the prediction model in Fig. 13, it is estimated that complete settling will occur within 11 s.

It can be concluded that treatment with NaOH promotes faster settling than when the water is treated with lime.

3.5. Stability tests

Stability tests were conducted with Rheofloc5414 and ARfloc100 in conjunction with lime and NaOH at 40°C and 60°C. The coagulant and flocculant were added and rapid mixing was carried out for 5 min, then slow mixing was carried out for 90 min, at which point the lime or

Table 5
Parameters at optimal dosages using lime

Flocculant and temperature	Conductivity removal (%)	Turbidity removal (%)	Total hardness removal (%)	Alkalinity removal (%)
Rheofloc5414 at 40°C	8	–99	12	62
Rheofloc5414 at 60°C	46	–20	53	77
ARfloc100 at 40°C	4	–58	19	54
ARfloc100 at 60°C	36	–61	51	71
Genefloc at 40°C	–13	–19	17	54
Genefloc at 60°C	38	–170	54	73

Table 6
Parameters at optimal dosages using NaOH

Flocculant and temperature	Conductivity removal (%)	Turbidity removal (%)	Total hardness removal (%)	Alkalinity removal (%)
Rheofloc5414 at 40°C	1.26	58.75	20.31	50.57
Rheofloc5414 at 60°C	–4.66	5	21.87	64.37
ARfloc100 at 40°C	0.63	29.17	20.17	54.02
ARfloc100 at 60°C	–4.28	16.81	21.51	63.22
Genefloc at 40°C	0.19	73.33	20.74	58.62
Genefloc at 60°C	–5.23	16.39	20.38	63.22

NaOH was added. A 30 min settling time was allowed and the turbidity was measured the original turbidity. Thereafter disturbances at 100 and 200 rpm were applied. After the disturbance, the turbidity was measured at 3 min time intervals, until the original turbidity was reached. These results can be seen in Table 8.

When lime was used, the ARFloc100 at 60°C was the most stable crystals that formed, because it took the least amount of time for the turbidity to reach the same value as before the disturbance occurred. This is due to better bonds that formed with the addition of this polyamine as well as the availability of active surfaces after fragmentation of flocs, which allow for attachment of broken flocs and re-growth of flocs [24,25]. This finding coincides with the results of the settling velocity tests, thus, using lime with ARFloc100 will give the heaviest, most stable flocs, and remove a good amount of the impurities in the water.

Using NaOH, Rheofloc5414 gave the most stable crystals at 60°C even more stable than the crystals formed using lime. Smaller amounts of impurities are removed from the water when using NaOH compared to lime, thus, lime will still be the best option.

3.6. Morphology analysis

3.6.1. Scanning electron microscopy

The morphologies of the flocs were determined using an SEM. The flocs formed when using lime in conjunction with the optimal conditions of ARfloc100 at 60°C can be seen in Fig. 14.

In Fig. 14 it can be seen that small, dense flocs formed, that are smaller than 10 μm. It was also determined that CaO is the most predominant compound in the flocs, with a weight percentage of 33.37%, this is illustrated in Fig. 15.

The morphologies of the flocs were determined using an SEM. The flocs formed when using NaOH in conjunction with the optimal conditions of Rheofloc5414 at 60°C can be seen in Fig. 16.

In Fig. 16, it can be seen that larger flocs formed than the flocs formed when lime was used, and they are densely packed. This explains why the crystals formed in this case, are more stable and have a better settling velocity. Here, too, CaO was the dominant compound in the flocs, with a weight percentage of 60.1%. This is confirmed in Fig. 17.

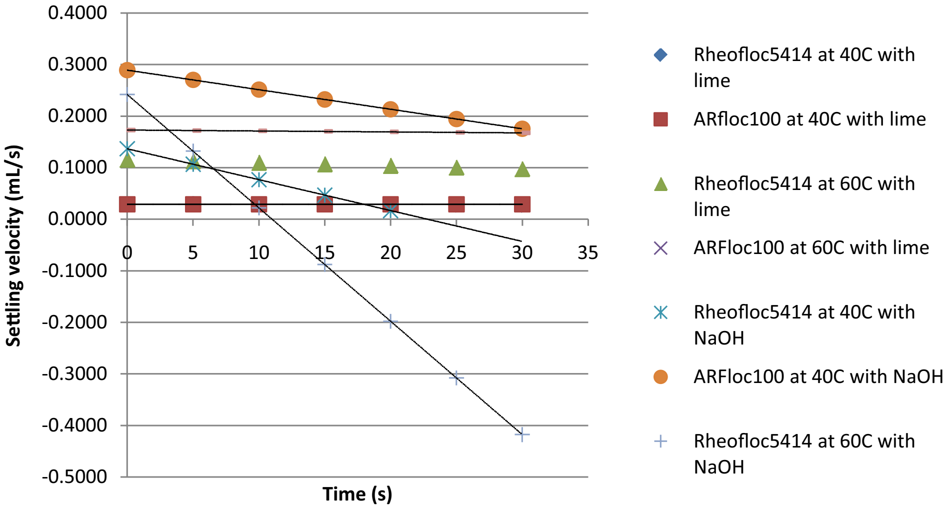

Fig. 13. The results of the settling velocity tests.

Table 7
Settling velocity at different time intervals

Time (s)	Settling velocity (mL/s)							
	Rheofloc5414 at 40°C with lime	ARFloc100 at 40°C With lime	Rheofloc5414 at 60°C with lime	ARFloc100 at 60°C with lime	Rheofloc5414 at 40°C with NaOH	ARFloc100 at 40°C with NaOH	Rheofloc5414 at 60°C with NaOH	ARFloc100 at 60°C with NaOH
0	0.0294	0.0289	0.1155	0.0874	0.1365	0.2892	0.242	0.1729
5	0.0291	0.0289	0.1125	0.0869	0.1065	0.2702	0.132	0.172
10	0.0288	0.0289	0.1095	0.0864	0.0765	0.2512	0.022	0.1711
15	0.0285	0.0289	0.1065	0.0859	0.0465	0.2322	–0.088	0.1702
20	0.0282	0.0289	0.1035	0.0854	0.0165	0.2132	–0.198	0.1693
25	0.0279	0.0289	0.1005	0.0849	–0.0135	0.1942	–0.308	0.1684
30	0.0276	0.0289	0.0975	0.0844	–0.0435	0.1752	–0.418	0.1675

Table 8
Stability test results

Reagents used	Time (min)	
	100 rpm disturbance	200 rpm disturbance
Rheofloc5414 at 40°C with lime	21	19
ARFloc100 at 40°C With lime	20	21
Rheofloc5414 at 60°C with lime	22	24
ARfloc100 at 60°C with lime	13	24
Rheofloc5414 at 40°C with NaOH	21	7
ARFloc100 at 40°C with NaOH	28	11
Rheofloc5414 at 60°C with NaOH	3	6
ARFloc100 at 60°C with NaOH	7	24

3.6.2. X-ray diffractometer results

X-ray diffractometer quantitative analytical results, showing crystallinity are represented in Fig. 18.

From Fig. 18, it can be observed that the best crystallization took place when ARFloc100 was used in conjunction with lime at 60°C. This finding reiterates that when lime softening is done, the crystallization mechanism takes place, however, improved crystallinity will also take place at higher temperatures due to super-saturation of the ions that form mineral scalants more likely to precipitate in the treated water.

4. Conclusion and recommendations

RO-reject water was tested and it was found that the levels of TDSs were abnormally high, which preclude the

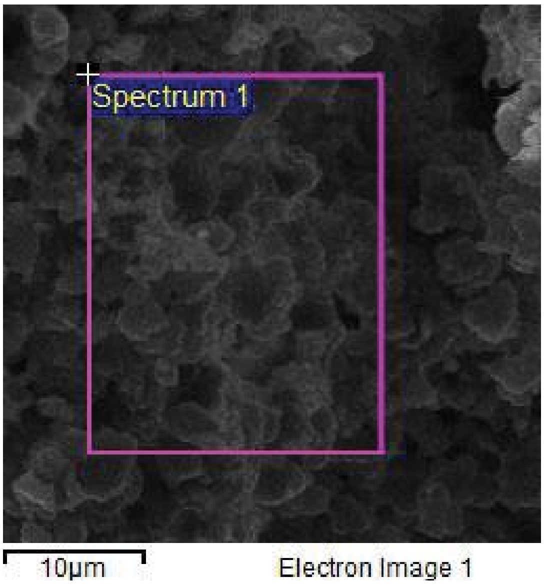

Fig. 14. Electron image of crystals formed using lime with ARFloc100 at 60°C.

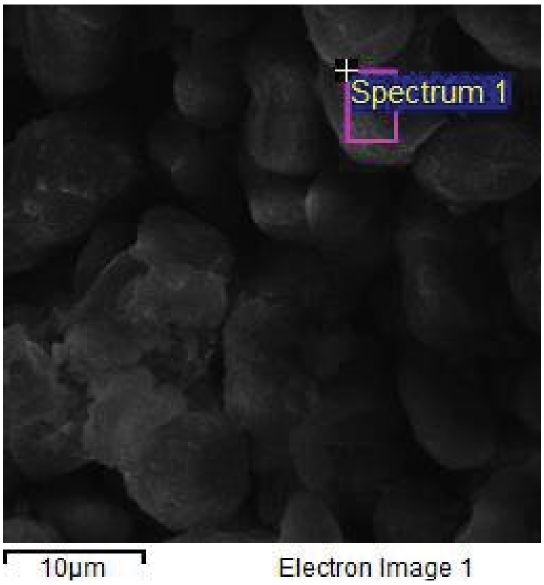

Fig. 16. Electron image of crystals formed using NaOH with Rheofloc5414 at 60°C.

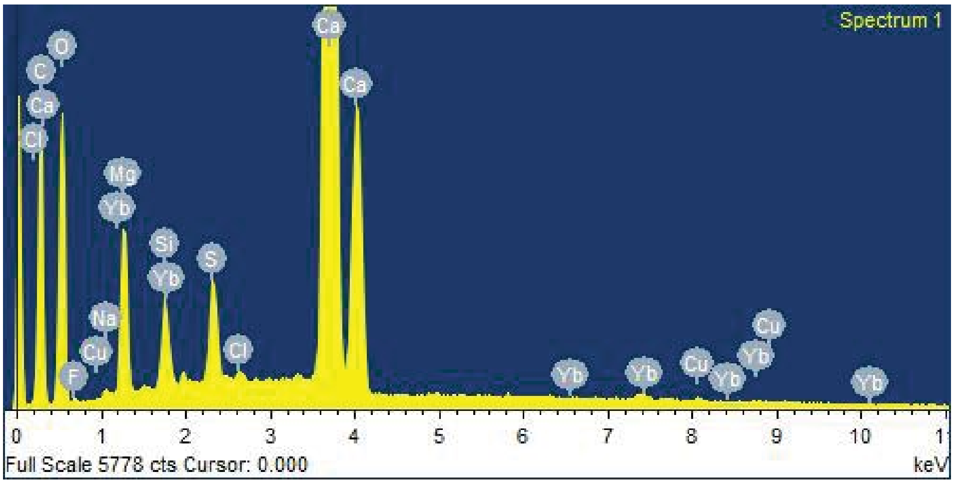

Fig. 15. Scanning electron microscopy showing compounds formed when lime was used with ARFloc100 at 60°C.

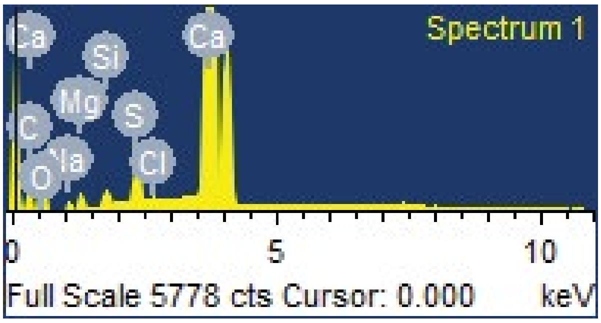

Fig. 17. EMS that illustrates compounds formed when NaOH was used with Rheofloc5414 at 60°C.

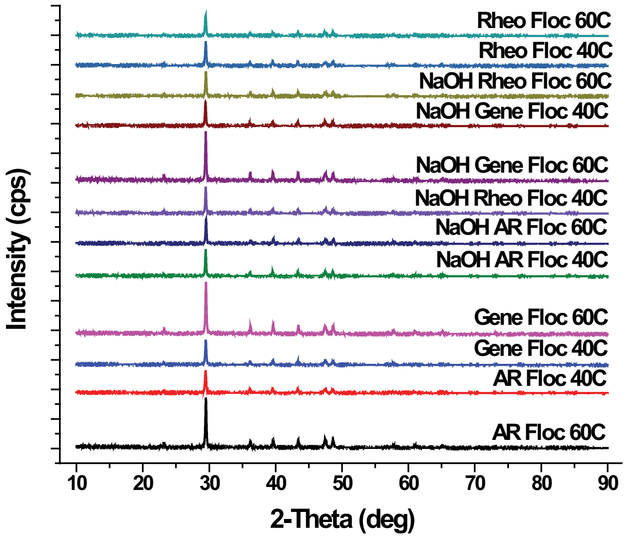

Fig. 18. X-ray diffractometer results showing crystallinity.

use of water directly for further cycles of RO. Pre-treatment was done to reduce the solubility of scale-forming agents, to stimulate the formation and growth of crystals that would lead to rapid settling. This aim was achieved using lime and NaOH to adjust the pH while flocculants, namely Rheofloc5414, ARFloc100, and Genefloc were used for agglomeration of crystals. The removal of scaling agents was assessed by monitoring the variation of conductivity, hardness, turbidity, and alkalinity. It was found that a dosage of 220 mg/L lime or NaOH was enough to increase the pH to a value of 10.1, which was suitable for reducing the solubility of calcium and magnesium in water. On the other hand, an increase in temperature to 60°C resulted in improved performance of flocculants. Optimal dosages of flocculants varied with the neutralizing agent considered. A coagulant dosage of 0.5 mg/L, a flocculant dosage of 0.2 mg/L, and a lime dosage of 220 mg/L were found to be optimal for a conductivity removal of 36%, a turbidity increase of 59%, a total hardness removal of 54%, and an alkalinity removal of 71%. When NaOH was used, Rheofloc5414 at a dosage of 0.5 mg/L and a coagulant dosage of 5 mg/L at 40°C was found to be optimal for a conductivity removal of 1.26%, a turbidity removal of 58.75%, a total hardness removal of 20.3%, and an alkalinity removal of 50.6%. The crystals resulting from the use of NaOH were found to settle faster and were found to be more stable. The diversified advantages in using either NaOH or lime suggest the need for further cost analysis to determine the combination of chemicals that will be of superior benefit to the industry.

References

[1] F. Zhang, Z. Dai, C. Yan, N. Bhandari, F. Yan, Y. Liu, Z. Zhang, G. Ruan, A.T. Kan, M.B. Tomson, Barite-scaling risk and inhibition at high temperature, Soc. Pet. Eng., 22 (2017) 69–79.
[2] E. Fosso-Kankeu, J. Redelinghuys, F. Waanders, D. Rogers, D. Bruinsma, G. Gericke, Determination of Water Evaporation Rate in an Assembled Bench Scale MED and Impact of Anti-Scaling Agents on the Morphology of Scale, International Conference on Advances in Science, Engineering, Technology and Natural Resources (ICASETNR-16) Nov. 24–25, 2016, Parys, South Africa, ISBN: 978-93-84468-79-8, 2016a.
[3] E. Fosso-Kankeu, F. Waanders, D. Van Niekerk, D. Rogers, D. Gericke, Treatment of Raw and Processed Waters from Coal Power Plant Using PACl Supplemented with Cationic Organic Polymer and Bentonite, International Conference on Advances in Science, Engineering, Technology and Natural Resources (ICASETNR-16) Nov. 24–25, 2016, Parys, South Africa, 2016b.
[4] J.G. Redelinghuys, E. Fosso-Kankeu, G. Gericke, F. Waanders, Coal Power Plant Wastewater Treatment by Thermal and Membrane Technologies, Elvis Fosso-Kankeu, Ed., Nano and Bio-Based Technologies for Wastewater Treatment: Prediction and Control Tools for the Dispersion of Pollutants in the Environment, Wiley Scrivener, USA, 2019, pp. 149–168.
[5] E. Fosso-Kankeu, F. Waanders, R. Swiegers, I.O. Ntwampe, D. Rogers, G. Gericke, Impact of the Physico-Chemical Properties of Water On the Flocculation Performance of Lime, Clay and Other Polymers, International Conference on Advances in Science, Engineering, Technology and Natural Resources (ICASETNR-16) Nov. 24–25, 2016, Parys, South Africa, 2016c.
[6] J.C. van der Linde, E. Fosso-Kankeu, G. Gericke, N. Lemmer, F. Waanders, Removal of Total Hardness and Alkalinity from RO – Reject Water, F. Waanders, E. Fosso-Kankeu, B. Topcuoglu, M. Plaisent, Y. Thaweesak, Eds., 9th International Conference on Advances in Science, Engineering, Technology and Waste Management (ASETWM-17), 27–28 November 2017, Parys, South Africa, 2017, pp. 147–151.
[7] I. Bremere, M.D. Kennedy, A. Johnson, R. van Emmerik, G.-J. Witkamp, J.C. Schippers, Increasing conversion in membrane filtration systems using a desupersaturation unit to prevent scaling, Desalination, 119 (1998) 199–204.
[8] E. Fosso-Kankeu, F. Waanders, A.F. Mulaba-Bafubiandi, A.K. Mishra, Flocculation Performances of Polymers and Nanomaterials for the Treatment of Industrial Wastewaters, A.K. Mishra, Ed., Smart Materials for Waste Water Applications, Wiley Scrivener, USA, 2016d, pp. 213–235.
[9] N. Maximova, O. Dahl, Environmental implications of aggregation phenomena: current understanding, Curr. Opin. Colloid Interface Sci., 11 (2006) 246–266.
[10] S. Deng, G. Yu, Y.P. Ting, Production of a bioflocculant by *Aspergillus parasiticus* and its application in dye removal, Colloids Surf., B, 44 (2005) 179–186.
[11] Y. Chen, B. Lian, Progress of microbial flocculant study and its application, Bull. Mineral. Petrol. Geochem., 23 (2004) 83–89.
[12] B.R. Sharma, N.C. Dhuldhoya, U.C. Merchant, Flocculants-an ecofriendly approach, J. Polym. Environ., 14 (2006) 195–202.
[13] G. Crini, Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment, Prog. Polym. Sci., 30 (2005) 38–70.
[14] S. Lee, W. Shin, M. Shin, S. Choi, L.S. Park, Improvement of water treatment performance by using polyamine flocculants, Environ. Technol., 22 (2001) 653–659.
[15] J.-H. Choi, W.S. Shin, S.-H. Lee, D.-J. Joo, J.-D. Lee, S.J. Choi, L.S. Park, Application of synthetic polyamine flocculants for dye wastewater treatment, Sep. Sci. Technol., 36 (2001) 2945–2958.

[16] S. Lim, W. Jeon, J. Lee, K. Lee, N. Kim, Engineering properties of water/wastewater-treatment sludge modified by hydrated lime, fly ash and loess, Water Res., 36 (2002) 4177–4184.

[17] N.V. Malanova, V.V. Korobochkin, V.I. Kosintsev, The application of ammonium hydroxide and sodium hydroxide for reagent softening of water, Procedia Chem., 10 (2014) 162–167.

[18] J.C. van der Linde, E. Fosso-Kankeu, G. Gericke, F. Waanders, L. Dreyer, N. Lemmer, Flocculant types and operating conditions influencing particles settling rates in feed water used at a coal power plant, Desal. Water Treat., 150 (2019) 293–300.

[19] A. Rahardianto, J. Gao, C.J. Gabelich, M.D. Williams, Y. Cohen, High recovery membrane desalting of low-salinity brackish water: integration of accelerated precipitation softening with membrane RO, J. Membr. Sci., 289 (2007) 123–137.

[20] H. Sun, B. Shi, F. Yang, D. Wang, Effects of sulfate on heavy metal release from iron corrosion scales in drinking water distribution system, Water Res., 114 (2017) 69–77.

[21] F. Martinez-Ruiz, A. Paytan, M.T. Gonzalez-Muñoz, F. Jroundi, M.M. Abad, P.J. Lam, J.K.B. Bishop, T.L. Horner, P.L. Morton, M. Kastner, Barite formation in the ocean: origin of amorphous and crystalline precipitates, Chem. Geol., 511 (2018) 441–451.

[22] F. Yan, Z. Dai, G. Ruan, H. Alsaiari, N. Bhandari, F. Zhang, J.K.B. Bishop, T.L. Horner, P.L. Morton, M. Kastner, Barite scale formation and inhibition in laminar and turbulent flow: a rotating cylinder approach, J. Pet. Sci. Eng., 149 (2017) 183–192.

[23] S. Muryanto, A. Bayuseno, H. Ma'Mun, M. Usamah, Calcium carbonate scale formation in pipes: effect of flow rates, temperature, and malic acid as additives on the mass and morphology of the scale, Procedia Chem., 9 (2014) 69–76.

[24] W. Yu, J. Gregory, L.C. Campos, Breakage and re-growth of flocs: effect of additional doses of coagulant species, Water Res., 45 (2011) 6718–6724.

[25] I. Solomentseva, S. Barany, J. Gregory, The effect of mixing on stability and break-up of aggregates formed from aluminium sulfate hydrolysis products, Colloids Surf., A, 298 (2007) 34–41.