FLOCCULATION PERFORMANCE OF FINE PARTICLES IN TRAVERTINE SLIME SUSPENSION

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Abstract. The flocculation performance of new generation of flocculants (Magnafloc 5250 and 6250) possessing unique molecular architecture (UMA) and conventional polyacrylamide based SB 1836 was investigated for the solid-liquid separation of travertine processing wastewater. The settling rate and turbidity values were considered as the performance criteria. Based on the settling rate and turbidity values the anionic UMA flocculant 6260 showed better performance compared to the other anionic flocculants, SB 1836, which is currently used in the travertine processing plant, and the UMA flocculant 5250. The results obtained from this study clearly indicated that the type of the flocculants showed no significant effect on the adsorption of the polymers on the travertine particles at natural pH. The settling rates of the travertine particles and the turbidity of the suspensions were greatly affected by the surface charge of the flocculants at high and low pH regimes. The flocculation tests results with the medium charge flocculants (Magnafloc 5250 and SB 1836) were slightly affected by pH, and resulted in poor performance in terms of turbidity.

keywords: travertine processing, wastewater, flocculation, settling rate, turbidity

1. Introduction

The use of natural stones such as marble and travertine in construction industry has been growing rapidly during the last few years. Particularly, there is a significant increase in production level for both domestic consumption and export markets in Turkey. However, processing of marble and travertine for the end use generates fine dust. In addition, a significant amount of water is used for cutting, shaping, and polishing operations. For this reason recovery and reuse of water from these processes has become an important topic of interest from both environmental and a dust suppression point of view.

Although thickeners may be utilized to settle and remove particles less than 75 μm, some colloidal particles (<1 μm) may still remain in water which adversely affects surface polishing and cause plugging in pipes (Acar, 2001; Önenç, 2001). Sedimentation, another method used to dewater travertine processing wastes is often applied with addition of water soluble polymers which accelerate the settling of

particles. An effective solid–liquid separation of tailings is crucial for producing good quality circulating water and also for obtaining an underflow with high percentage of solids which in turns enhances the performance of mineral processing equipment in plant and tailing dam.

Developments of future flocculants including polyacrylamide-based ones is likely to be based on the "molecular architecture" concept. That will enable to produce the flocculants of required performance to meet the increasing and changing demands of solid–liquid separation processes in mineral industry. The UMA[TM] approach is an unconventional way of thinking in polymer design and presents multiple pictures (Pearse et al., 2001). For example, highly branched and reactive polymer chains produce flocculant solutions containing a proportion of semi-particulate entities and polymer chains reticulated in three dimensions which produce flocs of different characteristics than those formed by conventional flocculants. Another aspect of UMA technology is manipulation of the molecular mass distribution to produce fractions that have greater activity in efficient flocculation. Benefits to be seen from this approach are better overall dosage efficiency, better clarification at a given settling rate and better rheological properties of settled solids than shown with conventional flocculants in terms of higher solids concentrations for a given yield stress (Pearse, 2003).

The aim of this study was to investigate the type and concentration of flocculants for solid-liquid separation of travertine processing wastewater. The new generation flocculants (Unique Molecular Architecture) were used to obtain a high settling velocity, hence a solid waste at high solid ratio, and finally circulation water with low turbidity. The settling rate and turbidity values were considered as the performance criteria. The characterization of the particles and the process water were also performed.

2. Experimental

2.1. Materials

The travertine processing wastewater used for the flocculation tests was obtained from a local travertine company in Afyonkarahisar region in Turkey. Figure 1 shows the sample port on the plant schematic diagram. The representative samples were taken according to TSE 5667-10. Three high molecular weight polyacrylamide based polymers were used for the flocculation tests. The detailed characteristics of the polymers used for the tests are presented in Table 1. HCl and NaOH (analytical grade) solutions were used to adjust the suspension pH.

Table 1. Basic characteristics of polymers

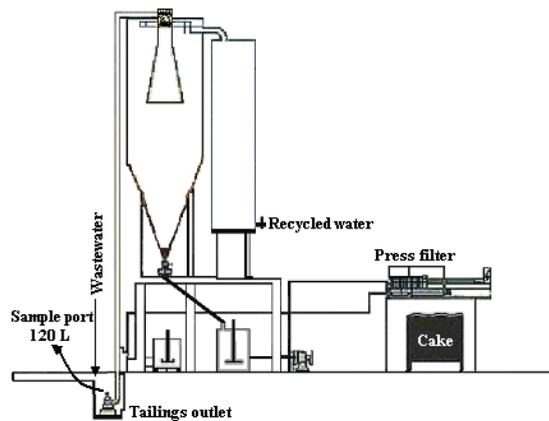| Commercial name	Type	Molecular Weight	Charge density (%)	Supplier	Effective pH range
SB 1836	anionic	high	40[*] (medium)	Snf Floerger	4-12[*]
Magnafloc 5250	anionic	high	30[*] (medium)	Ciba	4-10[*]
Magnafloc 6260	anionic	high	49.4[*] (high)	Ciba	4-10[*]

* According to the manufacturer description

Fig.1. A schematic illustration of travertine processing plant

2.2. Methods

The hardness and cation (Mg^{2+} and Ca^{2+}) concentrations in water were determined by volumetric methods. The chemical composition of the particles was analyzed by X-ray fluorescence. The size distribution of the sample was determined using Malvern Mastersizer Particle Size Analyzer. The mineral composition of the travertine particles was determined by X-ray diffraction (XRD), using Rigaku-Giger Flex diffractometer. The zeta potential measurements for the travertine fines were conducted by Zeta-Meter 3.0, which is equipped with a microprocessor unit capable of directly measuring the average zeta potential and its standard deviation. The pH measurements were conducted with a WTW 526 pH Meter. The zeta potential experiments were carried out at 0.1% solid ratio.

A stock solution (0.1% w/v) of polymer was prepared using distilled water for the flocculation tests. A diluted solution (100 mg/dm^3) was prepared from this stock solution, and used throughout the flocculation tests. The sedimentation experiment was initiated by taking the representative suspension from the slurry. Then, the suspension was placed in a 500 cm^3 mixing cylinder with a glass stopper, and continuously agitated using a mixer at 350 rpm (DIN 12217, 2003). A specified amount of flocculant was then added to the suspension. The suspension was vigorously shaken three times. The height of the sediment bed was measured at selected time intervals after the agitation was completed (DIN 23007, 1985). After 15 min of settling of the suspension, an aliquot of the supernatant was taken for turbidity measurements using a WTW Turb 550 turbidimeter.

The operating conditions were adjusted at the required levels according to the Box-Behnken experimental design and the results have been interpreted by SPSS 15.0 software package to evaluate optimum parameter values.

3. Results and discussion

3.1. Characterization of travertine samples

3.1.1. Mineralogical and chemical analyses

The X-ray diffraction (XRD) and chemical analysis (Table 2) revealed that the travertine sample is predominately composed of calcite.

Table 2. Chemical compositions of travertine fines

CaO	MgO	Fe$_2$O$_3$	SiO$_2$	Al$_2$O$_3$	Na$_2$O	K$_2$O	LOI
%	%	%	%	%	%	%	%
55.27	0.42	0.06	0.32	0.05	0.27	0.06	43.55

3.1.2. Particle size distribution

As shown in Fig. 2 more than 90% of the sample is composed of particle with the diameter less than 38 µm. The average particle size was found to be 10.3 µm.
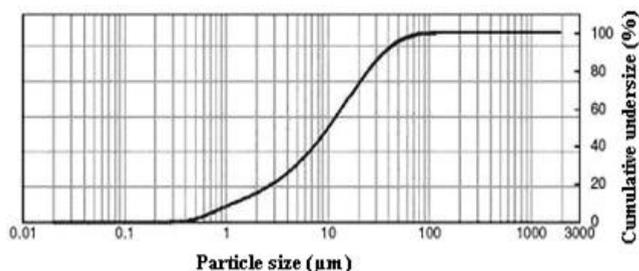

Fig. 2. Particle size analysis of travertine fines

3.1.3. Zeta potential

Zeta potential is a measure of surface charge acquired on particles in a liquid. Zeta potential provides important information about the behavior of particles in dispersing medium and stability of the dispersion. Figure 3 shows the zeta potential of the sample as a function of pH. In these experiments, NaOH and slaked lime (Ca(OH)$_2$) were used to adjust the pH of the suspension. The zeta potential value of the particles at natural pH (8.23) was found to be -13.7 mV. As shown in Fig. 3, the tailings exhibit negative charge at all pH values with no apparent point of zero charge (pzc) when NaOH was used to adjust the pH. However, the negative charge of the particles reversed and became positive at high pH values (11-12) when Ca(OH)$_2$ was used to adjust the suspension pH. As shown in the speciation diagram for Ca^{2+}, in aqueous solution Ca^{2+} concentration is higher at the pHs 11-12. In addition, CaOH$^+$ concentration increases with pH increasing from 10 to 12. The concentration of Ca^{2+} and CaOH$^+$ has a profound effect on the zeta potential of travertine fines acquiring

negative charge in water. The increasing concentration of Ca^{2+} and $CaOH^+$ ions in the suspension caused the zeta potential values to shift toward more positive values due to Ca^{2+} and $CaOH^+$ adsorption on negatives sites of the travertine surfaces. Generally, polyvalent ions (e.g. CO_3^{2-}, Mg^{2+}, Ca^{2+}) tend to change the surface charge by adsorption onto oppositely charged surface sites on travertine fines. On the other hand, the zeta potential of travertine fines in the presence of monovalent cations such as Na^+ did not show similar trend. The increase in the concentration of OH^- ions with the increasing pH also increases the negative charge of the travertine particles, hence the zeta potential values shift toward more negative values.
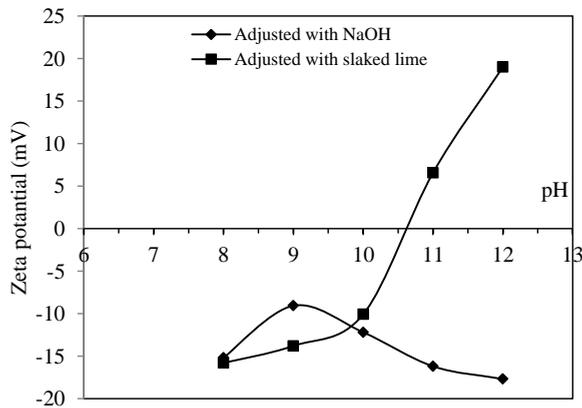

Fig. 3. Zeta potential of the travertine fines as a function of pH

3.2. Characterization of travertine suspensions

The ionic composition of water is important in flocculation of fine and colloidal particles. When hardness of water is less than 9^0F, interaction between polymer molecules and colloidal particles weakens due to relation between hardness of water and effectiveness of a flocculant. Therefore, not only an inferior settling rate but also low turbidity is observed (Sabah and Erkan, 2006).

The flocculation experiments were carried out with the travertine processing water. The hardness of the travertine processing water from which tailings are dewatered is 26ºF. This is well above the proposed limiting value and falls within the class of very hard waters because of high bivalent ion concentration (29.7 mg/dm^3 Mg^{2+} and 54.4 mg/dm^3 Ca^{2+}). These colloidal suspensions usually exhibit relatively high conductivity.

Figure 4 shows the effect of pH on settling behavior of the particles in the travertine processing wastewater at 1.1% (w/w) solid ratio without any flocculants.

According to ASTM D-4187 Standard Test Method (1990), if zeta-potential of colloids in water or waste slurry is above -60 mV, the stability of the system is

classified as 'perfect'. The maximum zeta potential values for the travertine slurry for this work was reported to be –17.7 mV and +19 mV at pH 7 and 12 respectively. Therefore, the stability of the travertine processing slurry is considered to be weak and could be improved by using coagulation or flocculation. The settling rate and the turbidity results shown in Fig. 6 also confirm this behavior.
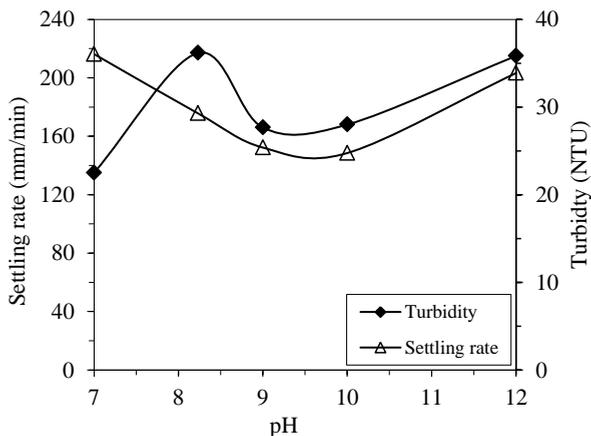

Fig. 4. Influence of pH on settling rate and turbidity for original travertine processing wastewater without flocculants

3.3. Flocculation tests

Figures 5a and b show the effect of flocculant dosage on the settling rate and the turbidity using two new generation flocculants (Magnafloc 5250 and 6260) along with a conventional flocculant SB 1836. As seen in Fig. 5a, the settling rate of the particles gradually increases with an increase in flocculant dosage for all flocculants. On the other hand, it was observed that the travertine suspensions can have similar clarity of supernatant with lower flocculant addition as shown in Fig. 5b. Based on these results, an optimum flocculant dosage at 900 mm/min setting rate occurs at 37.5 g/Mg of solids. This settling rate is higher compared to the settling rates for the same size coal settling speeds and wastes from ceramic processing plants (Cengiz et al., 2004).

These results indicate that the best settling performance for the fine particles was obtained with Magnafloc 6260 flocculant in terms of both settling rate and supernatant turbidity. An optimum flocculant dosage for Magnafloc 6260 appears to be about 12.5 g/Mg-solids. This concentration resulted in a turbidity of 6.25 NTU and a settling rate of about 558.6 mm/min. It is interesting to note that although the flocculant and the travertine fine particles are negatively charged, a higher sedimentation performance was achieved. The possible mechanism for polymer adsorption on the fine particles may be listed as follows: (i) the presence of the polymer COO^- pendant group,

although leads to a more expanded polymer chain conformation at natural pH, apparently mitigates the adsorption onto the negatively charged travertine particles. (ii) at low concentrations of Magnafloc 6260 (12.5 g/Mg of solids), the high settling rates and low turbidities were achieved due to chemical bonding between metal sites on the travertine surfaces and the flocculants' high charge density anionic groups.
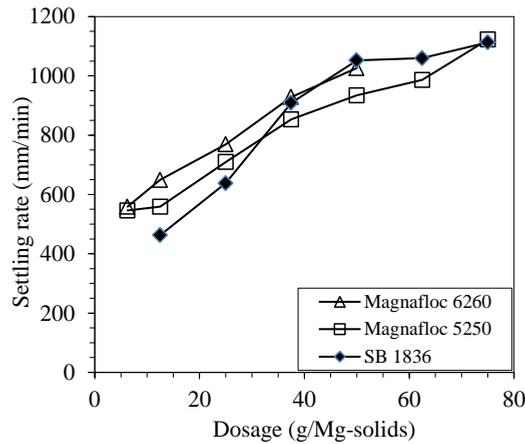
(a)
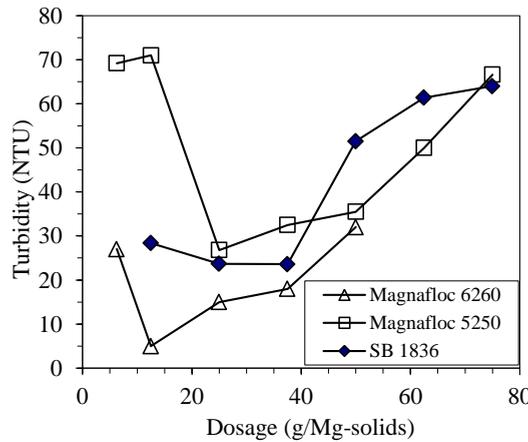
(b)

Fig. 5. Effects of polymer type and dosage on the settling rate (a) and turbidity (b) (solid concentration: 4%, pH 8.23)

Figure 3 clearly shows that the surface charge of travertine fines is low at natural pH of 8.23. Under these circumstances, the acceleration of particle aggregations should be expected. As a result, the bigger aggregates will settle faster due to gravity. Therefore, all flocculants showed good performance with regard to settling rate and turbidity. On the other hand, Magnafloc 5250 which has a relatively low charge density compared to other flocculants showed a dispersive effect at low dosages. In

such systems, with negatively charged particles, this is an expected behavior with polymers of high molecular weight and low to high charge density. At low concentrations of Magnafloc 6260 (12.5 g/Mg of solids), the high settling rates and low turbidities were achieved due to chemical bonding between metal sites on the surface of the travertine fines and the flocculants' high charge density anionic groups.

The type of the flocculant showed significant effect on the adsorption of the flocculants on the travertine particles at natural pH, as seen in Fig. 6a and b. However at pH values lower or higher than the natural pH these flocculants show different performance in terms of settling rates and turbidity. This behavior is understandable since each polymer has different chemical structure and different affinity for a given particle surface.

The settling rate and the turbidity of the travertine fine particles was significantly affected by the charge density of the flocculants at high and low pH values. The suspensions with low turbidities were obtained at low and high pH values with the use of high surface charge density Magnafloc 6260 floculant. The flocculation tests with Magnafloc 5250 (medium charge density) were slightly affected by pH, and hence exhibited a poor sedimentation performance in terms of turbidity. However, the flocculation tests with the conventional flocculant SB 1836 (medium charge density) showed an unstable behavior with a pH dependent flocculation of colloidal particles.

The high charge density Magnafloc 6260 formed small and compact flocs in the travertine process water at natural pH. This caused a decrease in the settling rate of the travertine fine particles with a clear supernatant. The decrease in the settling rate is due to the decrease in the number of carboxyl groups of the anionic polymer which can be hydrolyzed in the acidic pH. It is plausible that the intra molecular bonds between carboxyl groups may cause the polymer molecule to form a ring shape and thus weakening the bridge formation. The suspension pH can change charge characteristics of polymer chain and their conformation in solution and thus may directly affect the flocculation power of polymer (Foshee et al., 1982; Reuter and Hartan, 1986). The flocculation power of anionic polymers by bridging decreases as the polymer molecules are in a random coil conformation in sections, whereas at relatively high pH the configurations of the polymer extends due to electrostatic repulsion between the charged groups on the polymer chain. Taylor et al. (2002) and Sworska et al. (2000) reported that the addition of Ca^{2+} and Mg^{2+} ions prior to the addition of the flocculant improves the clarity of the supernatant in alkaline environment in the presence of stable clay suspensions.

Obtaining a fairly clear supernatant (with low turbidity) is important since water used in cutting and polishing operation is generally recycled. In order to achieve a suspension with a lower turbidity, the suspension pH was adjusted using slaked lime. The tests results with Magnafloc 6260 indicated that the best flocculant performance can be achieved by utilizing lime for the adjustment of the suspension pH. The lime resulted in much lower turbidity (0.33 NTU) and also reduced the required flocculant dosage (25 g/ton-solids). However, the settling rate decreased to 371 mm/min which is

tolerable level. These results indicate that Ca^{2+} adsorption at the travertine-H_2O interface involves the transfer of Ca^{2+} ions into Stern plane without the release of an equivalent number of protons into the diffuse layer and bulk solution. The subsequent decrease in the zeta-potential due to adsorption of Ca^{2+} ions may be related to unstable colloidal suspension and very small, dispersed floc particles in the presence of Ca^{2+} solutions when lime was used as pH modifier. This may imply that if lime solutions were to be added to the travertine slime suspension prior to Magnafloc 6260 addition, there is a good probability that the flocculation would be "activated" because of the presence of Ca^{2+} ions in the system. In addition, Ca^{2+} ions may also act as bridges between the anionic sites on the ionized polymer chain and travertine fines at pH 9 as shown in Fig. 7
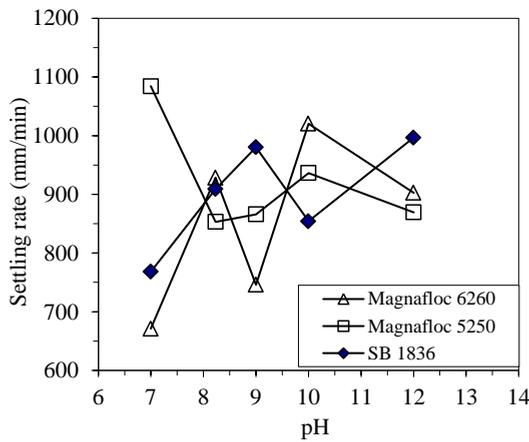
(a)
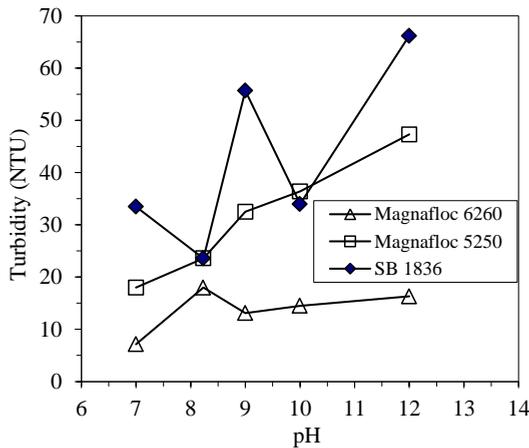
(b)

Fig. 6. Effect of suspension pH on settling rate (a) and turbidity (b) at optimum polymer dosages (solids concentration: 4%, pH 8.23, dosage 37.5 g/Mg of solids)
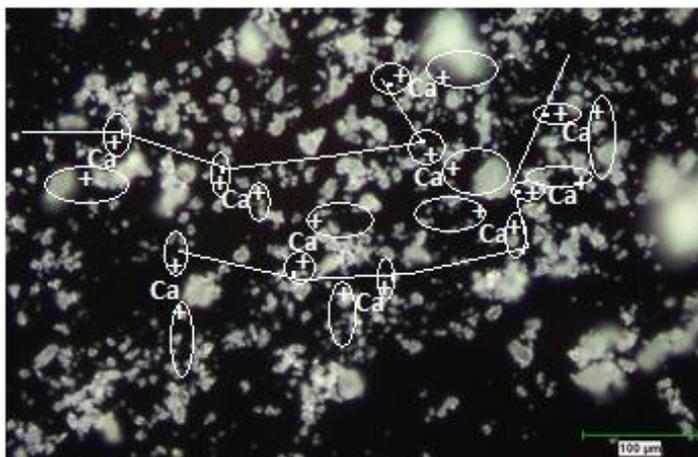
Fig. 7. Schematic illustration of Ca^{2+} activation on adsorption of high molecular weight anionic
flocculant onto a negatively charged suspended travertine fines

3.4. Modeling of settling rate and turbidity

The regression analysis was chosen to determine the relationship between the
response functions (settling rate and the turbidity) and the operating conditions
(dosage and pH). A two factor matrix three level Box-Behnken design was used to
determine the response (settling rate and turbidity). Two significant variables of
flocculation performance are flocculant dosage and pH. When the number of tests at
the central points is three, the total number of tests required for the two variables
comes out to be $3^2+2+2=13$ for the Box-Behnken design (Souzaa et al., 2005). The
variables and their levels used in this study are shown in Table 3.

Table 3. The level of variables chosen for the Box-Behnken design.

Variable		Variable level		
		Low	Center	High
		-1	0	+1
Dosage, g/Mg of solids	x_1	6,25	37,5	75
pH	x_2	7	9	12

For the three-level two-factorial Box-Behnken experimental design, a total of 13
experimental runs are needed. Using the relationships in Table 3, the levels of the
variables for each of the experiments in the design matrix were calculated as given in
Table 4.

For the settling rate of travertine:

$SR_{SB\ 1836} = 77 + 10.3 \cdot D + 44.3 \cdot pH;\ R^2 = 0.832$
$SR_{MG\ 5250} = 579 + 8.41 \cdot D - 4.5 \cdot pH;\ R^2 = 0.778$
$SR_{MG\ 6260} = 182 + 8.35 \cdot D + 31.3 \cdot pH;\ R^2 = 0.702.$

For the turbidity of travertine:

$T_{SB\ 1836}$= - 43.3 + 0.738·D + 6.38·pH; R^2 = 0.681

$T_{MG\ 5250}$=30.9 + 0.087·D-1.72·pH; R^2 = 0.022

$T_{MG\ 6260}$=13 + 0.056·D + 0.13·pH; R^2 = 0.012.

Table 4. The level of variables x_1 and x_2

Run no.	Dosage (g/Mg of solid)	pH
1	0	1
2	0	-1
3	-1	0
4	1	-1
5	1	0
6	0	0
7	-1	1
8	0	0
9	-1	-1
10	0	0
11	0	0
12	0	0
13	1	1

$SR_{SB\ 1836}$ is the settling rate (mm/min) of the travertine suspension with SB 1836, $SR_{MG\ 5250}$ is settling rate (mm/min) of the travertine with Magnafloc 5250, $SR_{MG\ 6260}$ settling rate (mm/min) of the travertine with Magnafloc 6260, $T_{SB\ 1836}$ turbidity (NTU) of the travertine with SB 1836, $T_{MG\ 5250}$ turbidity (NTU) of the travertine with Magnafloc 5250, $T_{MG\ 6260}$ turbidity (NTU) of the travertine with Magnafloc 6260, D polymer dosage in flocculation tests (6.25-75 g/Mg) and pH (7-12) is pH solution in flocculation tests.

The match of predicted values with the actual data points indicates a good fit (R^2 value of 0.832, 0.778, and 0.702 with SB 1836, Magnafloc 5250, and Magnafloc 6260, respectively) of the equation for settling rate of travertine. For the turbidity of travertine, the predicted values and the observed data points, indicating a poor fit with SB 1836 (R^2 value of 0.681) and a very poor fit with Magnafloc 5250 and Magnafloc 6260 (R^2 value of 0.022 and 0.012, respectively) of the equations.

4. Conclusions

The results from the zeta potential experiments for the fine particles indicated that the particles are negatively charged at all pH values with no apparent point of zero charge. On the other hand, the zeta potential of the particles measured using slaked lime showed positive charge at high pH values. This can be attributed to the specific adsorption of the dissolved ions such as Ca^{2+} and $CaOH^+$ on the particles.

In terms of the settling rate and turbidity, the UMA Magnafloc 6260 anionic polymer showed a better flocculation performance compared to UMA Magnafloc 5250 and conventional SB 1816 at natural pH of travertine suspension.

The polymer charge density at high and low pH regimes played a crucial role in the flocculation of the travertine particles. On the other hand, the medium charge density polymers (Magnafloc 5250 and SB 1836) were slightly affected by pH, and exhibited a very bad performance in terms of the turbidity. In the case of the pH dependant flocculation of colloidal particles, conventional flocculant SB 1836 presented an unstable behavior.

The decrease in the polymer dosage and turbidity (0.33 NTU) can be achieved by Magnafloc 6260 when slaked lime is used to adjust the suspension pH due to the presence of Ca^{2+} ions in the system.

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