Flocculation of Fine Particles in Ceramic Wastewater Using New Types of Polymeric Flocculants

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ABSTRACT: It appears to be quite a few national and international studies were reported regarding flocculation and settling properties of ceramic industry wastewater containing various mineral matters. Cleaning of ceramic industry wastewaters with ever increasing environmental standards needs effective and economical solid–liquid separation processes. In this study, quantity and type of optimum flocculant concentration were investigated for solid–liquid separation of Umpac ceramic plant (located at Usak, Turkey) wastewaters. A new generation of flocculants namely unique molecular architecture (UMA) are used to obtain high settling velocity along with high solid content waste and circulation water with low turbidity values. Zeta potential of the tailings including quartz, feldspar, clorite, and mica was also measured at different pH values. The flocculation tests were performed in the presence of different types of polymers at different polymer dosages. It seems that Magnafloc 5250 shows higher performance than the anionic flocculant SPK 508 and other anionic UMA flocculants Magnafloc 6260 and Magnafloc 3230. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 1258–1264, 2009

Key words: ceramic wastewater; flocculation; settling rate; turbidity

INTRODUCTION

The clarification of municipal and industrial wastewaters by solid–liquid separation techniques and the removal of suspended particles are the problems of growing environmental consciousness.[1] However, there appears to be very limited number of studies reported in the literature to investigate the flocculation and settling properties of ceramic industry wastewaters, which known to contain rich mineral matters.

Solid–liquid separation or dewatering processes generally involve unique set of challenges because of the presence of colloidal particles of varying sizes, shapes, and specific gravities as well as solution chemistry of their environments. The objective of dewatering processes is often to obtain clear water containing low percentage of solids as well as high percentage of solids after separation. Most ceramic factories generate considerable amount of wastewater with finer tailings composed of rich inorganic matters, which may be reused/recycled.

There are two output parameters to evaluate the flocculation performance of the industrial thickeners. First is the clarity of water taken from the upper flow of a thickener. Ceramic plants because of the magnitude of usage are often recycled water. Therefore, the suspended colloidal particles in recycled water should be eliminated because of their possible negative effects in ceramic processing. The second parameter is the settling rate of flocculated particles, which directly affects the thickener capacity. However, controlling the speed of settling rates highly desired because high settling rates often translates into lower turbidity or undesired water clarity issues, whereas low settling rates require the design of bigger thickeners.[2–4]

The desired settling rates and the water clarity are possible by optimizing the polymer type, polymer dosage, and suspension pH. In addition, accurate determination of physical, chemical, and electrokinetic properties of solid matters in pulp plays a crucial role for the successful destabilizing of fine-particle suspensions.

For dewatering of ceramic wastewater, sedimentation method is applied by using polymers, which accelerate the settling rate of particles. An effective solid–liquid separation of tailings is important for both producing a good quality circulating water and also obtaining an underflow with high percentage of solids; this in turn enhances the performance of mineral processing equipment in the plant and shrinks the size of tailing dams as well.

In recent years, a new generation of flocculants namely unique molecular architecture (UMA) were introduced in addition to conventional flocculants

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used in the last half century. The UMA technology introduced by Ciba Specialty Chemicals has adopted a new approach to molecule design, or the UMA approach. The conventionally polymeric flocculants technology uses a concept of the molecular chain is almost two-dimensional, whereas the UMA approach relies on a more three-dimensional model with chain interaction playing apart. This, in turn, is coupled to more emphasis being placed, during manufacturing, on the much active parts of the molecular mass distribution.[5] As a result, these products offer true multifunctionality and aid greater operational efficiency across a broad range of mineral processing environments and can be used for sedimentation, filtration, and centrifugation.[6] Pearse et al.[5] reported that Magnafloc 4240 produced with UMA technology gave low turbidity and high precipitate volume for optimum settling rate in suspensions including chine clay and it is stable toward changing in mixing rate and flocculant dosages.

In an other study, using Magnafloc 4240 for the dewatering of coal preparation plant wastewater, a 20% benefit is reported to obtained with the use of Magnafloc 1011.[7] Cengiz et al.[8] investigated the performance of Magnafloc 4240, again produced with UMA technology. It is reported that with the use of Hydrofloc 7170, required flocculant quantity was reduced by 25% by approximately the same settling rate and turbidity for Tuncbilek Coal Preparation Plant wastewater. Kaytaz and Dinçer[9] made sedimentation tests with Kartal Eczacıbaşı ceramic wastewater. They had satisfactory results particularly in settling rate and turbidity by adding first aluminum sulfate, then lime and flocculant (Superfloc C110), and finally sodium hydroxide.

In this study, type and optimum concentrations are investigated using new generation UMA flocculants. The results are also elucidated with the zeta potential of solids and suspension pH measurement of which known to affect colloidal stability of fine particles significantly.

EXPERIMENTAL

Materials

A schematic illustration of Umpac ceramic plant waste water treatment process flow is shown in Figure 1. The ceramic wastewater for this work was collected from tailings outlet of the Umpas Ceramic Plant shown in Figure 1. Polyacrylamid-based polymers with high molecular weight (14×10^6) and various charge densities were provided by the Umpas and Ciba Chemicals. These include Magnafloc 3230 (low charge density), Magnafloc 5250 (medium charge density), Magnafloc 6260 (high charge density), and SPK 508 (medium charge density). Prior to flocculation tests, a homogeneous stock solution (0.1% w/v) of polymer was prepared using distilled water. This stock solution was further diluted to 100 mg/L and used in flocculation tests. Both hydrochloric acid and sodium hydroxide solutions were used to adjust the suspension pH.

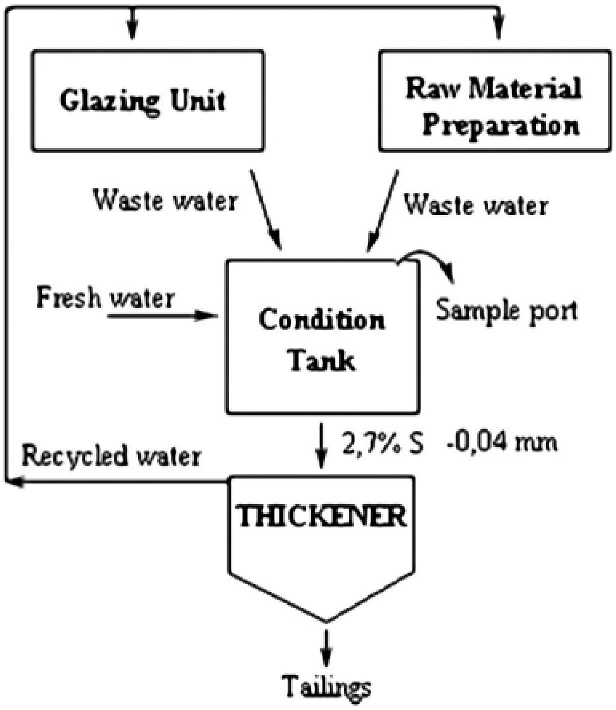


Figure 1 A schematic illustration of ceramic producing plant.

Methods

The concentration of Mg^{2+} and Ca^{2+} for the measurement of water hardness was determined by volumetric methods. The chemical composition of tailings solid was analyzed by X-ray fluorescence, and the particle size distribution was determined using Malvern Mastersizer Particle Size Analyzer. The mineral composition was determined by X-ray diffraction (XRD), using Rigaku-Giger Flex diffractometer. Electrokinetic (zeta potential) measurements were obtained using a Zeta-Meter 3.0 device. This device was equipped with a microprocessor unit capable of directly measuring the average zeta potential and its standard deviation. The pH was measured with a lab pH Meter (WTW pH 720).

The flocculation experiments were carried out using a mechanical mixer (IKA RW20) with a speed control. For each test, 500 mL of original ceramic wastewater containing 2.7% w/w solids was placed in a 600 cm^3 glass jar and stirred for 2 min at a rotational speed of 200 rpm to ensure homogeneous dispersion. The required amount of polymer solution was added continuously into the suspension during

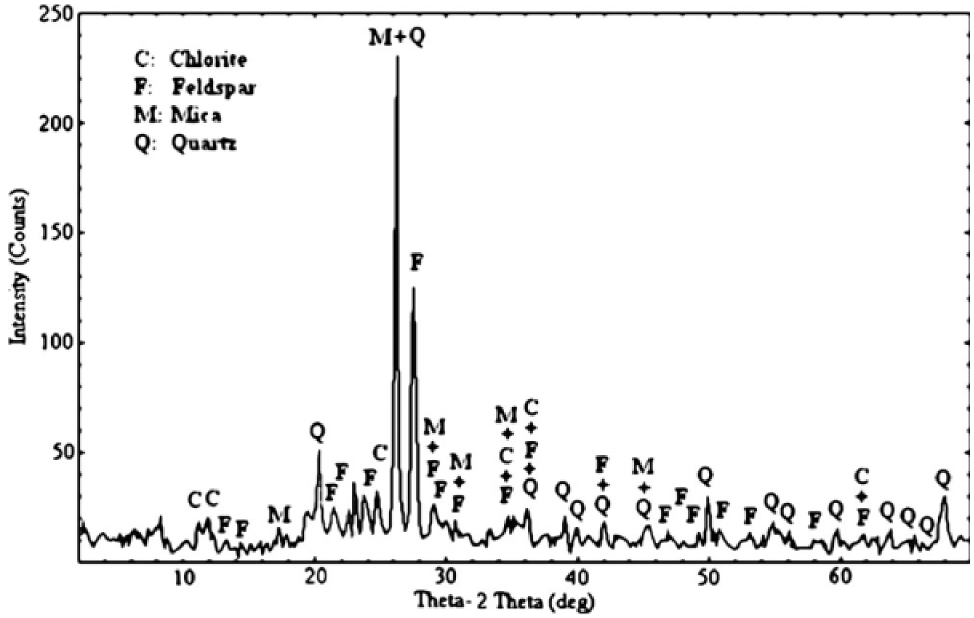


Figure 2 XRD peaks of particles from ceramic wastewater.

the stirring, which was stopped after optimum mixing time (15 s.). The height of the slurry and water interface was recorded as a function of time and used to calculate the settling rate of the flocculated suspension. After 15 min settling time, an aliquot of the supernatant was taken for turbidity measurement using a WTW Turb 550 turbidimeter.

RESULTS AND DISCUSSIONS

Characterization of inorganic suspended particles in ceramic wastewater

Mineralogical analysis

XRD analysis of the ceramic tailings was indicated that the main minerals are mica, feldspar, chlorite, and quartz (Fig. 2).

Chemical analysis

The chemical compositions of the associated minerals in ceramic tailings were determined by XRF method as shown in Table I. As expected, the tailings are mainly composed of SiO_2 and Al_2O_3.

Particle size distribution

The average particle size determined from the Gaudin-Schuhman type of plot was 9.47 μm, and the percentage of slime size (<20 μm) was constituted 74% of the overall material. Based on the Wentworth classification,[10] although the percent of particles in clay size accounts for 28% (<4 μm), the percentage of particles in silt size is 68% (4–63 μm). Those particles in sand size were 4% (>63 μm).

Zeta potential

Because of the high ionic strength (or high conductivity) of ceramic wastewaters, zeta potential of particles from the wastewater was not measured directly. Instead, original wastewater was dried at first, and then test solution was prepared with distilled water and the solid particles of 100 μm in size. Zeta potential of this solution was then measured at different pH values. Figure 3 presents the effect of pH on the zeta potential of ceramic tailings. As apparent, the tailings exhibit negative charge at all practical pH values with no apparent zero point of charge. The highest zeta potential (−32.2 mV) was measured in the neutral pH (8.71) indicates that the suspension is quite stable. A suspension which has zeta potential of 40 mV is quite stable. pH of the

TABLE I
Chemical Compositions of Particles in Ceramic Wastewater

Component	Wt %
SiO_2	62.49
Al_2O_3	17.54
Fe_2O_3	1.420
MgO	0.710
Cao	3.890
Na_2O	3.420
K_2O	1.420
TiO_2	0.500
P_2O_5	1.000
MnO	0.010
Cr_2O_3	0.042
LOI	7.558
Total	99.948

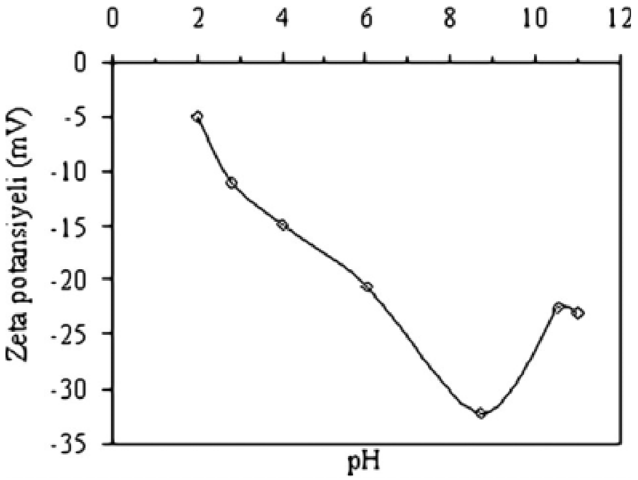


Figure 3 Zeta potential–pH profile for the particles from ceramic wastewater.

solution was adjusted by adding HCl and NaOH inside test solution.

Qualitative and quantitative analysis results were used to identify the properties of the particles in ceramic wastewater.

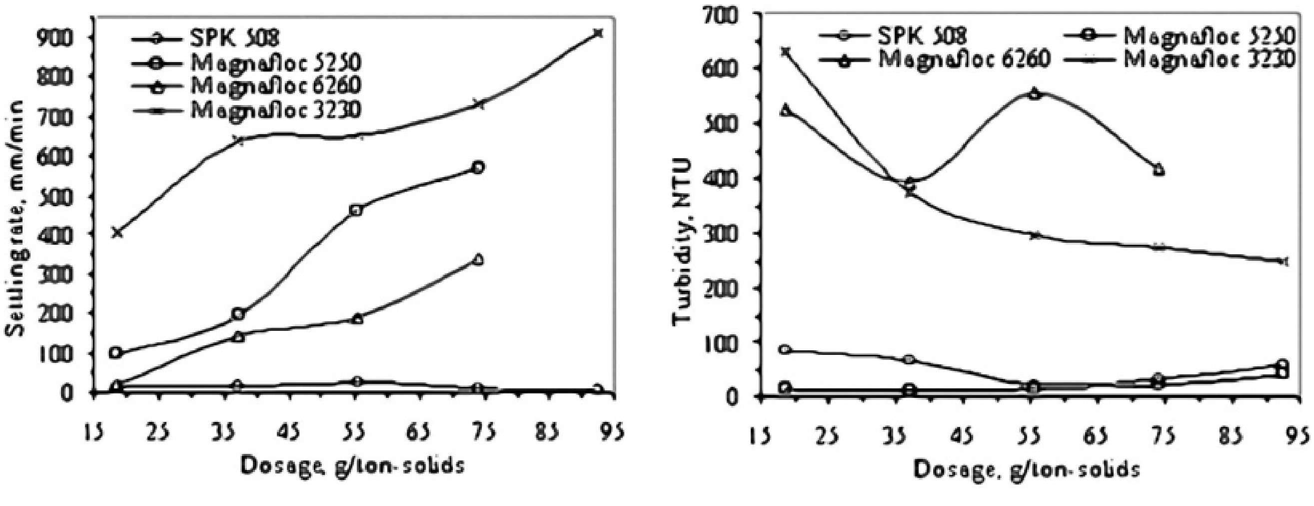
Characterization of ceramic suspensions

The ionic composition of water and the colloidal behavior of solid particles in water are important parameters that affect the flocculation of fines. When the hardness of water is less than 9°F, the interaction between polymer molecules and colloidal particles deteriorates. Hence, a good settling may not always be achieved with an acceptable turbidity.[11] The hardness of the Umpac plant water was measured to be 26.4°F, which is higher than the proposed limit value of 9°F. Therefore, the Umpas ceramic wastewater is classified as hard water because of its high bivalent ion concentration (43.2 mg/L $Mg^{2+}$and 33.6 mg/L Ca^{2+}). These colloidal suspensions usually exhibit relatively low resistance and high conductivity. In this study, the conductivity value of water containing ceramic tailings was measured to be high (2200 μS/cm) at natural pH.

Flocculation tests

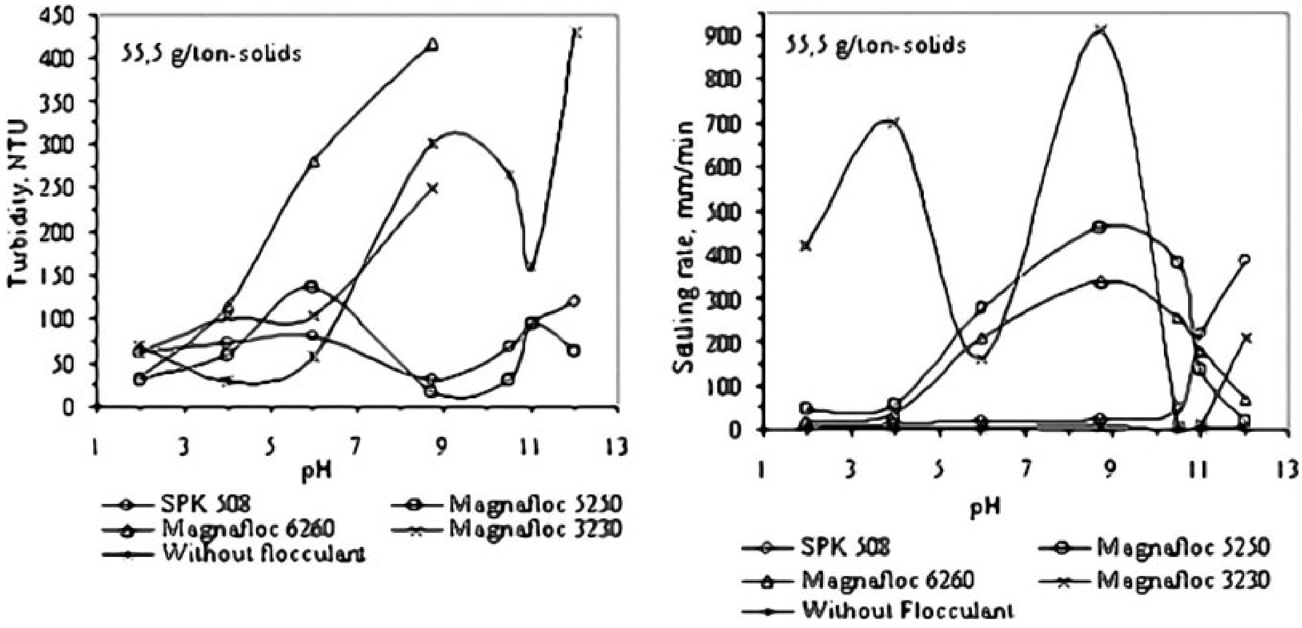
The flocculation tests were performed in the presence of different types of polymers at different polymer dosages [Fig. 4(a,b)]. Figure 4(a) shows the effect of polymer type and its dosage on the settling rate of ceramic tailings. The settling rate increased with increasing polymer dosage for all polymer types except SPK 508. As for SPK 508, settling rate reached a maximum at around 55.5 g/ton-solids polymer dosage and then began to decrease with increasing polymer dosage.

At low dosages, the floc size is expected to be very small because of insufficient amount of polymer adsorption on particles. The increase in the amount of adsorbed polymer results in the incorporation of more suspended particles in the floc and in turn enlargement of the floc size, leading to the enhanced settling rate. Figure 4(a) clearly shows that in most polymer dosages, Magnafloc 3230's settling rates are higher than that of others. Therefore, Magnafloc 3230 shows quite better performance than other UMA flocculants and SPK 508. For instance, at 74 g/ton-solids polymer dosages, Magnafloc 3230 has 731.7 mm/min settling rate, whereas SPK 508 has only 12.5 mm/min. Magnafloc 5250, on the other hand, has 572.5 mm/min and Magnafloc 6260 has



(a) (b)

Figure 4 Effects of polymer type and dosage on the settling rate (a) and turbidity (b) (solids concentration: 2.71%; pH: 8.71).



(a) (b)

Figure 5 Effect of suspension pH on settling rate (a) and turbidity (b) (solids concentration: 2.71%; pH: 8.71). Note: Tests were performed at the optimum polymer dosages.

340.9 mm/min settling rates. In other words, at the same polymer dosage (74 g/ton-solids), Magnafloc 3230 was produced larger flocs.

Figure 4(b) shows the variation of turbidity of suspension for various polymers and the optimum polymer dosage corresponding to the settling rates from Figure 4(a). Magnafloc 6260 and magnafloc 3230 show high turbidity values at all polymer dosages, whereas magnafloc 5250 and SPK 508 show lower turbidity values at 37 g/ton-solids for magnafloc 5250 (12.8 NTU) and 55.5 g/ton-solids for SPK 508 (22.8 NTU). Turbidity may be influenced from the suspended fine particles especially clay-sized (−4 μm) particles, which was existed as much as 28% in the present Umpac tailings. Hogg[23] has suggested that particle destabilization by polymer adsorption occurs preferentially on coarser particles. Consequently, the larger particles are effectively destabilized by the added polymer and tend to associate into larger flocs, whereas the finer material remains in the dispersed state.

The suspension pH plays a significant role in polymer adsorption at the particle/water interface[13–15] and can determine the extent of floc size.[16] Because H^+ and OH^- ions are the potential determining for most mineral particles, i.e., coal, clay minerals, quartz,[17,18] and the concentration of these ions in a suspension determines the sign and magnitude of surface charge of the particles. Figure 5(a,b) demonstrates that both settling rate and turbidity are pH dependent. It should be noted that optimum dosage values obtained from previous tests were used in pH optimization tests.

Settling rate of UMA flocculants (Magnafloc 5250, Magnafloc 6260, and Magnafloc 3230) was reached a maximum at natural pH (8.71), whereas above pH 10, settling rate of UMA flocculants began to decrease. The effective pH range for these polymers is reported to be between pH 4 and 10. However, settling rate of conventional SPK 508 was reached the maximum at pH 12. The results clearly indicate that the flocculation made by UMA flocculants, the natural pH of ceramic slurry may be the most appropriate pH for an optimum settling rate. However, Magnafloc 6260 and Magnafloc 3230 were showed the highest turbidity values (417 and 250 NTU) at natural pH, whereas Magnafloc 5250 was reached the minimum turbidity value (15.5 NTU) like SPK 508 (30 NTU).

At low pHs remarkably a decrease in the settling rate occurred in the presence of Magnafloc 5250, Magnafloc 6260, and SPK 508. But Magnafloc 3230 shows higher pH values than other flocculants at low pHs. At high pHs, Magnafloc 5250 and Magnafloc 6260 show low settling rates, whereas Magnafloc 3230 and SPK 508 show high settling rates relatively.

Figure 5(b) shows that low pHs have positive effects on the supernatant clarity for all flocculants used. Low turbidity is possibly generated from the colloidal feldspar and quartz minerals at low pHs because of adsorption of H^+ ions onto negative charge centers of colloids leading to their destabilization. This enhances the flocculation of colloidal particles in the presence of polymer, even though the H^+ ions lead to the decrease of effectiveness.

Effective pH range of UMA flocculants used in this study is reported to be between 4 and 10. High settling rates obtained in the pH range (4–10) support this thought. In other words, except this pH range, active groups of the flocculants are not functional.

The suspension pH can change charge characteristics of polymer chain and their conformation in solution and thus may directly affect the flocculatin power of polymer.[19,20] First, the flocculation power of anionic polymers by bridging decreases as the polymer molecules are in a random coil conformation in solution, whereas at relatively high pH configuration of the polymer extends because of electrostatic repulsion between the charged groups on the polymer chain.[21] The relatively low settling rate at low pH may be attributed to the weakened electrostatic attraction of the negative particle surface, because the zeta potential of original wastewater was about −5 mV at pH 2, whereas at natural pH (8.71) the zeta potential was about −32 mV. Second, the covalent bond and/or electrostatic bond formation between the ($=C-O^-$) groups of anionic polymers and metal cations on the external surfaces of mineral particles may be inhibited.[22] At low pHs, low turbidity was resulted from formation of small and more compact flocs by means of low zeta potential of wastewater. During the flocculation process performed at a natural pHs for a medium and low molecular weight of anionic flocculants, the interparticle bridge formation was the dominant mechanism for floc formation. The hydrocarbon chain of flocculant, at pH 7.0, becomes more stretched because of the electrostatic repulsion among negatively charged groups. The association of more particles in large volumes of flocs leads to an increase in a poor turbidity, which was observed at low pHs [Fig. 5(b)]. However, high turbidity values for Magnafloc 3230 and Magnafloc 6260 at the pH of maximum zeta potential obtained (pH = 8.71) were the result from the formation of large and less compact flocs by means of relatively high zeta potential of wastewater. But on the contrary, Magnafloc 5250 and SPK 508 show minimum turbidity at pH 8.71.

CONCLUSIONS

Characterization of ceramic tailings using a XRD technique reveals that the tailings are mineralogically composed of mica, feldspar, chlorite, and quartz. The tailings exhibit negative charge at all pH values with no apparent zero point of charge. The highest zeta potential (−32.2 mV) was observed at neutral pH (8.71). The average particle size determined from the Gaudin-Schuhman type of plot was 9.47 μm, and the percentage of slime size (<20 μm) constitutes 74% of the overall material. Hardness of the ceramic wastewater is 26.4°F, which falls within the class of hard water because of its high bivalent ion concentration (43.2 mg/L $Mg^{2+}$and 33.6 mg/L Ca^{2+}).

The flocculation tests were performed in the presence of different types of polymers at different polymer dosages and pHs. The settling rate increased with increasing polymer dosage and reached a maximum at highest polymer dosage for all polymer type except SPK 508. In SPK 508, settling rate reached maximum at 55.5 g/ton-solids polymer dosage then began to decrease with increasing polymer dosage.

In most polymer dosages, Magnafloc 3230's settling rates were higher than others. It is clear from the results that Magnafloc 3230 shows quite better performance than other UMA flocculants and SPK 508.

Magnafloc 6260 and magnafloc 3230, on the other hand, were showed high turbidity values at all polymer dosages relatively, whereas magnafloc 5250 and SPK 508 were showed lower turbidity values at 37 g/ton-solids for magnafloc 5250 (12.8 NTU) and 55.5 g/ton-solids for SPK 508 (22.8 NTU).

Reported values demonstrate that both settling rate and turbidity are pH dependent. Settling rate of UMA flocculants (Magnafloc 5250, Magnafloc 6260, and Magnafloc 3230) reached the maximum at natural pH (8.71), whereas settling rate of SPK 508 reached the maximum at pH 12. In other words, flocculation made by UMA flocculants, the natural pH of ceramic slurry might be the most appropriate pH for an optimum settling rate. But Magnafloc 6260 and Magnafloc 3230 were showed the highest turbidity values (417 and 250 NTU) at natural pH, whereas Magnafloc 5250 was reached the minimum turbidity value (15.5 NTU) like SPK 508 (30 NTU).

In conclusion, high settling rate (461.54 mm/min) and low turbidity (15.5 NTU) values obtained by Magnafloc 5250 at 55.5 g/ton-solids flocculant dosage, 250 D/D mixing rate, 30 s mixing time, and at natural pH (8.71) were found to be optimum conditions.

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