An Investigation on the Turbidity Removal from Natural Stone Processing Plant Wastewater by Flocculation

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Abstract

This study aimed to determine the effects of three different high molecular weight (HMW) flocculants (anionic, cationic and non-ionic flocculants) on the fine particles removal from natural stone (foid-bearing rock) processing plant wastewater at alkaline pH conditions. The test results were investigated in terms of turbidity values depending on pH of the medium, flocculant concentration and time (0–60 min). According to the results obtained, the turbidity values of the wastewater in the absence of the flocculants were pH dependent and decreased as the pH increased, resulted in the minimum turbidity values at pH 12. In the presence of the flocculants, the pH depended turbidity removal efficiencies varied with flocculant type, flocculant concentration and time. The best results were obtained at highly alkaline pH values (pH 12) with the turbidity removal efficiency of ≤99% in the presence of non-ionic flocculant. In the case of anionic and cationic flocculants, the minimum turbidity values were also obtained at pH 12 with turbidity removal efficiencies over 90%.

Keywords: natural stone processing plant wastewater, turbidity removal, flocculant addition, flocculant concentration, pH, time

Introduction

Water has vital importance in almost every step of the mining industry, starting from the pre-mining operations to an obtaining salable concentrate after the ore preparation/mineral processing operations.

In general, it is used for machine cooling (cutting parts), removing the ore bodies from the surface of the excavation/cutting processes in open pit mining, underground mining and natural stone processing (sizing of natural stones such as marble and granite) and applied as water sprays for suppressing dust (Ediz vd. 2001; Mavis, 2003; Ağirtmıs, 2017). The wastewater can have 2–10% solid content (by Wt) which approximately contain 25–40% (by Wt) of the products formed during mining operations (Wright et al., 1976; Ashton et al., 2001; Thomashausen et al., 2018). Thus, the water used in the mining/processing plants for different purposes contains solid (mostly mineral particles) having with a wide size distribution, from millimeter to microns, depending on the method applied.

In the case of the wastewater is recirculated to the system without solid/liquid separation, it will negatively affect the life and cutting performance of the cutting units as well as causing clogging of water transfer pumps and pipes etc. (Acar, 2001; Celik et al., 2008). As there is a high density difference between mineral particles and water in the wastewater of the natural stone processing plants, the solid/liquid separation processes are usually applied by sedimentation method (Ipekoglu, 1997; Svarovsky, 2000). In the sedimentation process, the settling rate of the mineral particles is mostly affected by the density and size of the particles. The bigger the size and the higher the density of the mineral particles the faster the settling velocity (Bradby, 1993; Table 1). The solid particles in the size range of 1 nm–0.1 nm, which are called colloids, cannot be removed by classical physical treatment methods because they cannot settle easily by themselves (Öztürk et al. 2005). The other factors affecting the settling velocity are the shape, the charge of the particles and pH of the medium etc. (Leschonski, 1993; Ersoy, 2005; Tripathy et al., 2006; Tasdemir et al., 2012; Watanabe, 2017) and can be increased by the use of natural/synthetic flocculants. In addition, the hardness of the process and recycle water, the presence of high-valence cations like Ca” and Mg”, may aid coagulation by reducing the magnitude of potential and/or neutralizing the surface charge of the mineral particles. Therefore, their presence may promote flocculation efficiency with the use of lower flocculant concentrations (Hosten et al., 2013; Wang et al., 2009).

The most of the researches on the removal of fines in natural stone processing plant wastewaters have been done on the effluents of processing plants which only contain marble or travertine fines (Ersoy, 2005; Tasdemir et al., 2012; Bayraktar et al., 1996; Sabah et al., 2012; Arslan et al., 2005). In this regard, this study aimed to determine the effect of the presence and the concentration of three different flocculants with different charging mechanisms (anionic, cationic and non-ionic flocculants) depending on pH and time on flocculation behavior of foid-bearing rock fines; containing silicates, clays and iron-bearing minerals etc., in processing plant wastewater.

Materials and methods

The wastewater sample was obtained and collected in sealed pet bottles from a wastewater pond of a foid-bearing rock processing plant (FRPP) located near Isparta, Turkey. The schematic presentation of the processing plant and the particle size distribution of the sample are given in Fig. 1.
According to the results given in Figure 1(b), the wastewater contains mineral particles having sizes -3 mm (d80: -0.04 mm) with a pulp density of 1.25 ± 0.15% (by Wt).

According to the results of the mineralogical analysis, the sample contains approximately 45% nepheline, 25% or-thoclase, 15% oligoclase, 8% amphibole, 2% pyroxene, 5% opaque minerals mostly composed of magnetite and ilmenite. The rock also has illite and kaolin clay formations, which are formed by the alteration of nepheline and orthoclase. The chemical analysis of the minerals in wastewater is given in Table 2.

The HMW-flocculants having high bridging ability; an-ionic (Cyfloc A-150) and non-ionic (N-100) flocculants were obtained from Cytec Inc., and cationic flocculant (425Ca) was obtained from ECS Chemicals. The stock solutions (0.1 g/100 ml) of each flocculant were diluted to desired flocculant concentrations with appropriate amounts of distilled water before the experimental analysis. After the dilute flocculant addition, the pulp (wastewater) was conditioned in previously determined optimum parameters: 5 min at a stirring speed of 500 rpm. Then the sample was transferred in the 500-ml graduated cylinder, shaken 10 times gently to prevent breaking of the flocs, and then left to stand still. The turbidity measurements of the wastewater were carried out by Hanna HI 93703 portable turbidity meter with a sensitivity of ±0.5 FTU between 0.00 and 1000 NTU (Nephelometric Turbidity Unit).

Results and discussion

Turbidity of foid-bearing rock processing plant wastewater

In this research study it was aimed to determine the effect of different flocculants on turbidity removal from FRPP wastewater at three different alkaline pH conditions. Even so, the turbidity values of wastewater were also determined depending on pH (pH 8–12) and time (0–120 min) in order to make the results more comparable and the results are given in Figure 2.

In Figure 2, the results show that the initial turbidity value of as-received wastewater at natural pH value (pH 8.5 ± 0.5) was about 760 NTU after the mixing process. However, as the high settling velocity of the coarse particles in the wastewater a turbulent flow conditions created leading higher turbidity value of 1000 NTU a min after mixing process. The turbidity values remained constant at 1000 NTU between 1 and 20 min due to slow settling rate of very fine particles and then gradually decreased to 445 NTU after 60 min and 120 NTU with a turbidity removal efficiency of 88% after 120 min. The turbidity values at pH 8 displayed similarities with the results of the as-received wastewater sample at the original pH condition.

| Particle size (mm) | Classification                      | Examples                                                                 | Time required to settle 100 mm* |
|--------------------|-------------------------------------|--------------------------------------------------------------------------|---------------------------------|
| 10^1               | Coarse dispersion (visible to naked eye) | Gravel, coarse sand, mineral substances, precipitated and flocculated particles, silt, macroplankton | 0.1 s                            |
| 10^2               | Fine particulate dispersion (visible under microscope) | Mineral substances, precipitated and flocculated particles, silt, bacteria, plankton and other organisms | 11 min                           |
| 10^3               | Colloidal dispersion (submicroscopic) | Mineral substances, hydrolysis and precipitated products, macromolecules, biopolymers, | 1 years                          |
| 1                  |                                     |                                                                          | 20 years                         |
As the pH increased to higher alkaline pH conditions, at pH 10, the turbidity values decreased rapidly from initial turbidity of over 900 NTU to below 250 NTU after 10 min and decreased gradually to about 60 NTU at the end of 40 min.

When the zeta potential values of the minerals in wastewater are taken into account, as they have been reported to have highly negative values at alkaline pH conditions (Kolarik and Priestly, 1995; Nduwa-Mushidi et al., 2017; Ozun et al., 2019, 2019a), it is expected that the mineral particles will repel each other, leading higher turbidity values. However, the mineral particles aggregated and settled rapidly over pH 9 due to the increasing effectiveness of the polyvalent ions (Ca$^{2+}$ and Mg$^{2+}$) in wastewater on turbidity removal (Clark et al., 1968; Ozkan et al., 2009).

**Turbidity of foid-bearing rock processing plant wastewater with flocculants**

In Figure 3-5, the effects of HMW flocculants (anionic, cationic, non-ionic) on turbidity removal from the FRPP wastewater were given as graphical presentation depending on the pH conditions.
on the flocculant concentration (0.25–1.50 mg/L) and time (0–60 min) at three alkaline pH values (pH 8–12). According to the results obtained in the presence of each flocculant, the turbidity values varied depending on concentration, pH value and time.

In Figure 3, the results show that the effectiveness of anionic flocculant on turbidity removal from wastewater increased with increasing flocculant concentration up to 0.50 mg/L. In the presence of 0.25 mg/L flocculant concentration, compared to those without flocculant, the turbidity values at pH 8 decreased rapidly from initial turbidity value of 1000 NTU to about 550 NTU with a turbidity removal efficiency of 45% after 5 min, and decreased to 50 NTU after 60 min. With increasing flocculant concentration (0.50 mg/L), the turbidity of the supernatant decreased more resulting in lower turbidity values of <150 NTU with a turbidity removal efficiency of >85% after 5 min and about 50 NTU after 10 min.

The similar trend with pH 8 was obtained at pH 10 with each flocculant concentration. The test results with 1.50 mg/L flocculant concentration exhibited much higher turbidity values than those with lower flocculant concentrations (0.25-0.50 mg/L). In the case of turbidity removal at pH 12, as the mineral particles in wastewater displayed a stable behavior in the pulp because of they had highly negative (−) zeta potential values at alkaline pH values, a strong electrostatic repulsion between the anionic flocculant and the mineral particles was expected. However, a rapid settlement of the mineral particles was observed resulting in the minimum turbidity values <100 NTU after 5 min of flocculation. The reason might be interaction of the oppositely charged high-valence ions (Ca$^{2+}$ and Mg$^{2+}$) with mineral particles in the plant wastewater causing charge neutralization on their surfaces (Ozun et al., 2019a).

In the presence of cationic flocculant (Figure 4), considering that all mineral particles had negative zeta potential values for the given pH value, the turbidity values at pH 8 decreased because of an electrostatic attraction occurred between mineral particles and oppositely charged flocculant species.

The results also show that the turbidity values in the presence of 0.25 mg/L and 0.50 exhibited higher turbidity values compared to those in the presence of 1.50 mg/L flocculant concentration having 92% turbidity removal efficiency after 5 min. However, with increasing pH, the turbidity removal efficiencies at pH 10 and pH 12 were much lower contrary to expectations even though mineral particles and flocculant had oppositely charged. Because of the charge neutralization effect of mono and polyvalent ions present in the wastewater, the mineral particles exhibited unstable behavior leading insufficient interaction with the oppositely charged flocculant species.

In the case of turbidity removal with non-ionic flocculant, the results given in Figure 5 show that the effect of non-ionic flocculant on turbidity removal from wastewater especially at pH 8, which is the closest pH value to the natural pH of the wastewater, was superior compared to those with ionic flocculants. The results also showed that at any pH values tested, the turbidity values obtained with 0.25 mg/L and 0.50 mg/L of non-ionic flocculant concentrations displayed similarities with each other. The turbidity values for the given flocculant concentrations decreased from the initial turbidity of 1000 NTU to >180 NTU after 20 min of flocculation. However, the best turbidity removal efficiencies were obtained with 1.50 mg/L non-ionic flocculant concentration at any pH conditions tested. After 1 min of flocculation, the initial turbidity value of <400 NTU decreased down to <100 NTU at pH 8 and decreased down to 40 NTU at pH 10. The turbidity values then decreased less than to 25 NTU after 5 min of flocculation for both pH conditions. In the case of flocculation at pH 12, the turbidity values obtained with each flocculant concentration were lower than the turbidity values of the original sample.

The turbidity values started to decrease from the initial turbidity value of about 1000 NTU to ≤ 100 NTU after 1 min, decreased to <5 NTU with a turbidity removal efficiency of ≤99% after 60 min.

Conclusion

According to the results obtained with experimental analyses, the settling velocities of mineral particles in FRPP wastewater varied depending on pH conditions, flocculant type, flocculant concentration and time. The settling velocities increased with increasing flocculant concentration, resulting in the minimum turbidity values at certain circumstances.

The turbidity values obtained with non-ionic flocculants at any pH values tested were found to be superior compared to those with anionic and cationic flocculants. The best results with each flocculant were obtained at highly alkaline pH conditions (pH 12) due to the effect of the polyvalent Ca$^{2+}$ and Mg$^{2+}$ ions present in wastewater and the high concentration of sodium hydroxide used to adjust pH conditions. Their presence might be one of the reasons which promoted the flocculation behaviour of mineral particles at certain pH values (>pH 9) by reducing the magnitude of potential and/or neutralizing the surface charge of the mineral particles, resulted in ≤99% turbidity removal efficiency at pH 12.

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Badanie usuwania zmętnienia ze ścieków z zakładu przeróbki kamienia naturalnego w procesie flokulacji

Badania miały na celu określenie wpływu trzech różnych flokulantów o wysokiej masie cząsteczkowej (HMW) (flokulanty anionowe, kationowe i niejonowe) na usuwanie drobnych cząstek (pyłu kamiennego) ze ścieków z zakładów przeróbki kamienia naturalnego w alkalicznym pH.

Zbadano zmętnienie w zależności od pH, stężenia flokulantu i czasu (0–6 min). Zgodnie z uzyskanymi wynikami, wartości zmętnienia ścieków przy braku flokulantów zależy od pH i zmniejszały się wraz ze wzrostem pH, co skutkowało minimalnymi wartościami zmętnienia przy pH 12. W obecności flokulantów wydajność klarowania zależy od rodzaju flokulantu, stężenia flokulantu i czasu. Najlepsze wyniki uzyskano przy wysokich alkalicznych wartościach pH (pH 12) ze skutecznością usuwania zmętnienia ≤99% w obecności flokulanta niejonowego. W przypadku anionów i flokulantów kationowych minimalne wartości zmętnienia uzyskano również przy pH 12 przy skuteczności usuwania zmętnienia powyżej 90%.

Słowa kluczowe: ścieki z zakładów przeróbki kamienia naturalnego, usuwanie zmętnienia, dodawanie flokulantu, stężenie flokulantu, pH, czas