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Optimization of flocculation process for cut-stone wastewater: effect of rapid mix parameters

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ABSTRACT

Wastewater produced from stone industry of Iran causes serious environmental problems associated with slurry disposal. In traditional method, many ponds are required for clarifying. The use of filtration and addition of chemicals enhance the efficiency of operation as well as saving laborer cost. The polymer bridging mechanism is responsible for flocculation of suspended particles. It was found that the increase of rapid mix velocity reduced the residual turbidity substantially except for the dosage of 0.2 mg of polymer. The addition of polymer was able to enhance flocs strength. For higher dosages of polymer, a direct relationship between increasing rapid mix velocity and reduction of turbidity was observed. The values of aggregation rate constant K_{app} were calculated to evaluate the effects of rapid mix velocity and dosage of polymer on residual turbidity. The maximum value of $K_{app} = 7.2 \times 10^{-3}$ was obtained for the rapid mix velocity 200 rpm and dosage of polymer 1 mg/l.

Keywords: Cut-stone wastewater; Flocculation; Rapid mix; Velocity gradient; Optimization

1. Introduction

Cut stone (CS) are specially cut or shaped stone for use in buildings, monuments, memorial stones, grave stones, curbing, and other construction or special uses. In the CS factories, during cutting and polishing, a large amount of wastewater is produced. This effluent is a stable suspension with very fine particles. For instance, in the cutting of a marble block, approximately 30–40% (in weight) fine powder is produced [1]. Large particles will settle by gravitational forces whereas small particles (<100 μm) move with water. This kind of wastewater can cause problems in receiving waters if it is not properly treated, e.g., increase turbidity in the receiving water and making lake bottom muddier when the slurry finally settles down. In addition, the presence of suspended particles, particularly larger than 50 μm in the recycling water may cause polishing problems and pipe clogging during processing [2]. The wastewater is to be treated by methods such as settling channel, coagulation/flocculation and filtration. Some studies on coagulation/flocculation of CS wastewater are summarized in Table 1.

As the settling properties of the particles are poor, one possible method for the separation could be addition of coagulant/flocculant. This is due to the fact that there are a large variety of polymers prepared with a broad range of MW's functional surface groups which cause a multiple attachment points to be created on different types of surfaces. In principle, a flocculant is able to treat fine colloidal particles to create larger units or flocs, which settle rapidly. When a polymer with high molecular weight is

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Table 1
A summary of some research work performed on coagulation/flocculation of CS wastewate

Objectives	Reference
Effect of agitation regime (stirring time and polymer addition method) on selective flocculation of minerals (quartz, calcite and galena).	[3]
Flocculation of marble suspensions.	[4]
Effect of pH and polymer type on the flocculation conditions of marble.	[5]
Influence of suspension pH and the anionicity degree of flocculant on flocculation of CS powder.	[6]
Effect of anionic polymer on settling rate on Bulgarian marble suspension.	[7]
Reduce the discharges of the liquid and solid wastes of the stone cutting industry to the environment; selection of the optimal coagulant type and addition methods.	[8]

added at an optimum dosage, it can bridge between particles and adsorb on particles through several segments with the other parts of the molecule extending into the solution [9]. Factors affecting the kinetics of flocculation are (a) intensity and time of shear, (b) rate of addition and concentration of polymer, (c) nature of charge, charge density, (d) molecular weight of the polymer and (e) pH of the suspension and solution species.

In this study, the effects of major physical parameters of rapid mix such as velocity gradient, time of mixing and dosage of polymer were investigated to optimize the wastewater treatment of stone cutting industries.

2. Theory

Coagulation is the growth of particles into larger flocs by collisions and bonding of smaller particles in solution. If destabilization and consequently coagulation is due to gentle stirring, it is called orthokinetic and if it is caused by Brownian motion, it is called perikinetic. Considering constant velocity gradient (e.g., uniform shear field), simple theory of flocculation kinetics can be derived. Such constant velocity gradients are difficult to be obtained in practice, but, the theory can be extended to velocity gradients created in turbulent flow conditions (e.g., paddle stirrers, baffled channels, oscillating paddles, fluidized beds, etc.). The classical coagulation theory, first developed by Smoluchowski, is expressed by the following equation [10,11]:

$$\frac{dN_{ij}}{dt} = N_i N_j \left(\frac{dv}{dt}\right) = \frac{4}{3} N_i N_j \left(\frac{du}{dz}\right) R_{ij}^3 \tag{1}$$

where N_i and N_j ($\mathrm{m^{-3}}$) are number concentration of *i*- and *j*-particles, respectively, R (m) is hydraulic radius, u and v ($\mathrm{m\ s^{-1}}$) are velocity of liquid motion in the x-direction and velocity of liquid being stirred, respectively.

Eq. (1) is the simple Smoluchowski equation of orthokinetic flocculation. It can be observed that the rate of flocculation is second order with respect to concentration, depends linearly on the velocity gradient and is proportional to the third power of the collision radius. Consequently, it can be inferred that the rate of flocculation increases with [12]:

1. Increasing the collision radius of the particles. Flocculation improves as larger flocs are produced, on the other hand, the presence of existing large particles will improve flocculation.
2. Increasing the concentrations of particles present.
3. Increasing the velocity gradient. However, the shear stress which flocs can endure limits the value of velocity gradient. Excessive gradients may cause floc break-up, particularly as the flocs grow in size. This occurrence can be overcome by decreasing the velocity gradient from an initially high value, when flocs are small, to lower values as the flocs grow.

The velocity gradient is represented by an average value G (du/dz). Assuming that the liquid is Newtonian, the mean velocity gradient is expressed below:

$$G = \sqrt{\frac{C_\mathrm{D} A_\mathrm{P} \rho (v_P - v)^3}{2V\mu}} \tag{2}$$

where C_D is drag coefficient, A_P ($\mathrm{m^2}$) is projected area of stirrer blade normal to motion, ρ ($\mathrm{kg\ m^{-3}}$) is density of liquid, v_P is velocity of stirrer blade, V ($\mathrm{m^3}$) is volume of tank and μ ($\mathrm{kgm^{-1}\,s^{-1}}$) is dynamic viscosity of liquid.

The magnitude of velocity gradient G is limited due to the possibility of large flocs being broken by the shear stress. Both the characteristic of flocs and the conditions of flocs formation affect flocs shear strength, i.e. flocs formed with polymers are usually stronger than those with hydroxide flocs and also flocs formed rapidly in intense velocity gradients are usually stronger than those formed in lower velocity gradients. As flocs become larger, they become less dense and more susceptible to shear. Fig. 1 represents the zones of aggregation and break-up. To obtain the maximum rate of flocculation without break-up, mixing should start at a high value of G when flocs are small and value of G should decrease as the flocs grow in size and approach the break-up zone.

The best flocculation conditions are when flocs form rapidly and leave no residual primary particles or small aggregates. However, due to the floc break-up, high rates of flocculation cannot be achieved if the velocity

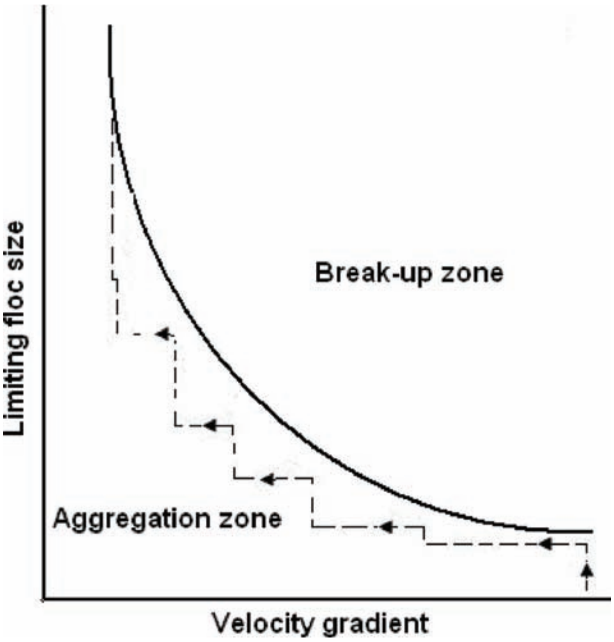

Fig. 1. Aggregation/break-up diagram [13].

gradients are too high. So a balance between the velocity gradient *G* and the time of flocculation *t*. It is therefore more convenient to study *Gt* rather than *G* and *t* separately. The optimum value of *Gt* is set between the limits of 10^4 and 10^5 [14,15].

To obtain the optimum values of velocity gradient and time of rapid mixing Vrale and Jorden [16] proposed the procedure based on the concept below:

$$-\frac{dN}{dt} = K_{app}N^n \tag{3}$$

They observed that turbidity as a function of slow mix time can be fit well to an equation in the form:

$$\frac{1}{N_t} = \frac{1}{N_0} + K_{app}t \tag{4}$$

where N_0 and N_t are the turbidity at initial and slow mixing time t, K_{app} is the aggregation rate constant and n is the order of dependence which is equal to unity.

The values of K_{app} can be obtained from the slope of best fit line of Eq. (4). These values represent the net result of all the interactions between the variables affecting aggregation rates. The maximum values of K_{app} show that flocs will be most rapidly produced in optimum velocity gradients and times of rapid mixing [17].

3. Experimental

The marble slurry was supplied from Ali Rabei Co. The sample was taken in its original slurry state from discharging canal, dried and brought to laboratory. Solid ratio of the suspension was selected as 4% (w/w), simulated of cut-stone wastewater. The pH of marble slurry was 8.3. Cationic flocculants, Aquisol C-4407, in powder form used in this study was supplied from Ionic Solutions Ltd. (UK).

A consequence of light scattering by particles is a reduction in the intensity of light transmitted through the suspension. Turbidity is a function of particle size, refractive index and particle concentration. Settling is assessed in a beaker, by stopping the stirring and following the final settling step and measuring the turbidity of the supernatant liquid. For measurement by sampling at a known depth, after a known time, it is assumed that all flocs with settling velocity greater than the depth/time are removed from the supernatant liquid. By taking samples at a given depth at sequential times, a settling velocity frequency distribution can be determined for the flocculated particles [18].

Flocculation tests were carried out in a 1000 ml graduated mixing beaker using distilled water. The investigation was designed as batch experiments involving rapid mixing, slow mixing and sedimentation. The turbidity of settled water was used to show the efficiency of flocculation. In this work, all parameters that influence the process of flocculation were held constant except for the parameters of rapid mix and dosage of flocculant. The initial turbidity of all samples is 750 NTU. A series of experiments was conducted using dosage of flocculant, 0.2, 0.4, 1, 1.5 and 2 mg/l to investigate the effects of velocity gradient. The slow mix and sedimentation operations were held constant throughout the experimental investigations irrespective of variation in the rapid mix parameters. Throughout the experiments, turbidity measurements were carried out using turbidity meter (Hach Model 2100 N).

4. Results and discussion

4.1. Effect of rapid mix velocity and dosage of polymer on residual turbidity

The effect of rapid mix velocity gradient for different polymer dosages during the initial fast mixing period (20 s) on the flocculation process is shown in Figs. 2 and 3. It can be observed that the residual turbidity decreased from an average of 250 to 100 NTU with the increase of rapid mix velocity from 50 to 300 rpm for all dosage of polymer except for dosage of polymer 0.2 mg/l. Figs. 2 and 3 show that the dosage of polymer has positive effect on decreasing turbidity except for dosage of 0.2 mg/l.

It can be observed from Figs. 2 and 3 that the value of turbidity decreased as the rapid mix velocity increased. When mixing in flocculator is too mild, the flocs hardly grow in the tank and an extremely long flocculation time

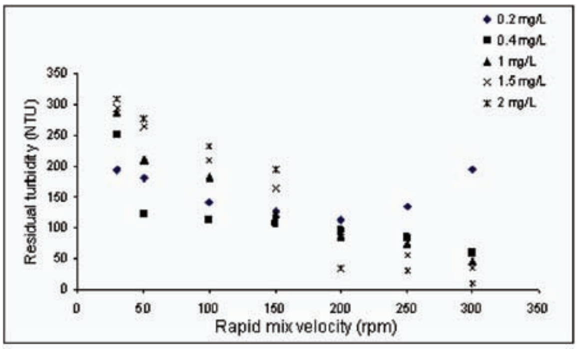

Fig. 2. Effect of rapid mix velocity on residual turbidity at rapid mix time of 20 s.

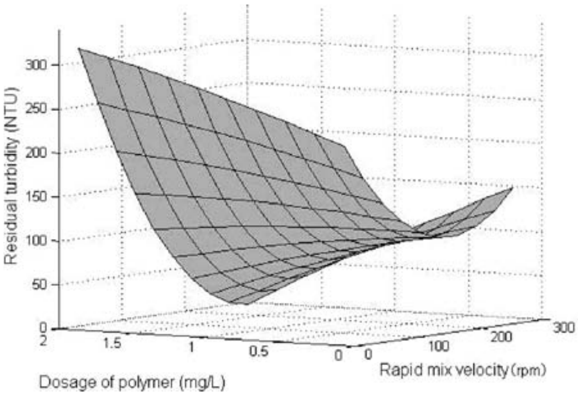

Fig. 3. Effect of rapid mix velocity and dosage of polymer on residual turbidity at rapid mix time of 20 s.

is required [19]. A high degree of turbulence at the point of addition of polymer solution enhances the flocculation process. It can be even more effective when suspensions are highly concentrated, where adsorption and particle collision rate are rapid [20]. In addition, it was found that when the dosage of polymer was 0.2 mg/l turbidity decreases to a minimum and then it increased. This can be attributed to the fact that floc formation and break-up may take place in different velocity, implying that flocs reaches to a maximum size and then breaks at higher shear rate [21]. On the contrary, for other dosages of polymer optimum points were not observed. This may be due to the increase of floc stability with increased polymer dosage. The maximum floc size depends on the applied shear or energy dissipation and on the floc strength. The strength of floc is dependent on the attractive forces between component particles and the number of particle-particle contacts. Thus, long-chain polymers make stronger bridge between flocs than simple salts [22].

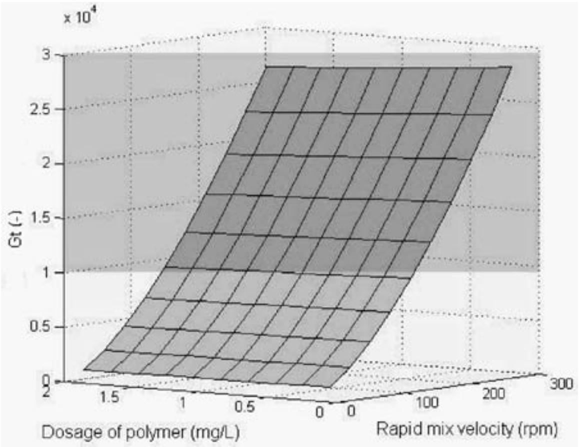

Fig. 4. Values of Gt as a function of rapid mix velocity and dosage of polymer.

4.2. Effect of rapid mix velocity and dosage of polymer on Gt

The values of Gt for different rapid mix velocities and dosages of polymer are shown in Fig. 4. The highlighted area represents the values of Gt more than 10^4. It can be observed that the values of Gt increased from 863 to 27,292 when rapid mix velocity increased from 30 to 300 rpm. The value of Gt decreased slightly from 9928 to 9331 when the dosage of polymer increased from 0.2 to 2 mg/l.

It can be observed from Eq. (2) that the value of G depends on drag coefficient (C_D), area of stirrer blade (A_P), density of liquid (ρ), velocity of liquid being stirred (v), volume of tank (V) and dynamic viscosity of liquid (μ). Parameters C_D, A_P and V are constant and density of liquid does not change much in the flocculation process. So, the parameters of v and μ have the main effect on Gt. Fig. 4 represents boundaries in which the values of Gt are more than 10^4. Except for dosage of 0.2 mg/l, the value of G had positive relationship with residual turbidity. If the fraction of particle surface with adsorbed polymer is θ, and it is assumed that the only successful collisions are those between coated and uncoated surfaces, then it can be concluded that the flocculation rate depends on the product θ and $(1 - \theta)$. For dosages of polymer used in this work, the surfaces of particles were not fully covered by polymer. Thus, rapid mix velocity gradient effectively increased the collision efficiency. The magnitude of the mean velocity gradient G is limited by the possibility of large flocs being broken by the shear stress. Both the nature of the material constituting the flocs and the conditions under which they were formed affect their shear strength. Thus, for dosage of 0.2 mg/l, in the higher value of mean velocity gradient floc-breakage overcame the effect of collision rate. Consequently, an optimum flocculation condition was required [9,19].

4.3. Optimum velocity gradient and time of mixing

The results of the experiments and the plots of residual turbidity ($1/N_t$) as a function of slow mixing time (t_s)

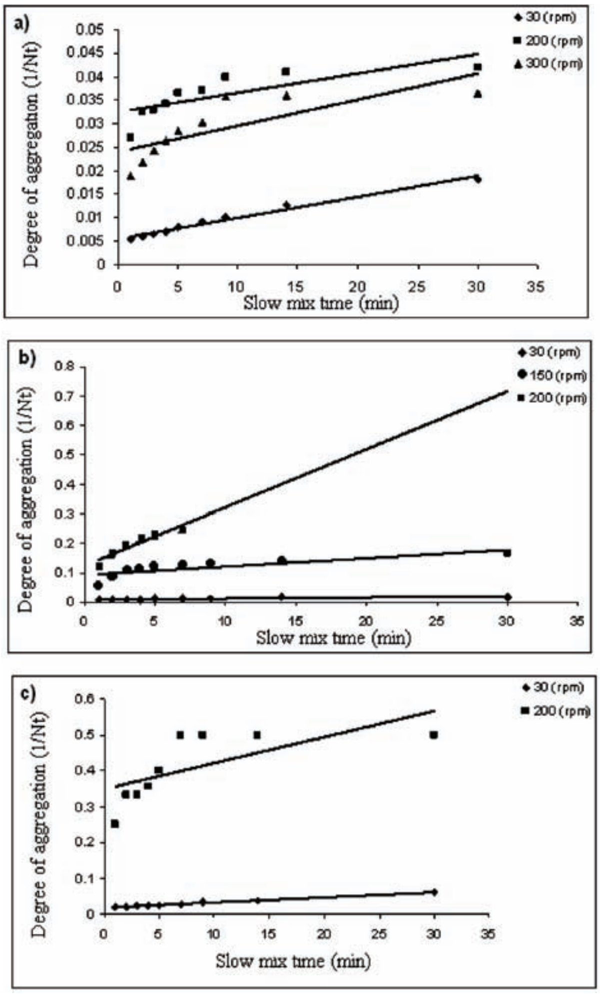

Fig. 5. Residual turbidity as a function of slow mix time for different rapid mix velocity and different dosages of polymer (a) 0.2; (b) 0.4; and (c) 1.0 mg/l.

Table 2
Values of K_{app} and R^2 for different dosages of polymer and different rapid mix velocity

Rapid mix velocity (rpm)	K_{app}	R^2
Dosage of polymer (0.2 mg/l)		
30	4×10^{-4}	0.98
200	4×10^{-4}	0.60
300	6×10^{-4}	0.64
Dosage of polymer (0.4 mg/l)		
30	4×10^{-4}	0.89
150	2.8×10^{-3}	0.66
200	1.9×10^{-2}	0.80
Dosage of polymer (1.0 mg/l)		
30	1.5×10^{-3}	0.99
200	7.2×10^{-3}	0.46

for raw cut-stone wastewater turbidity of 750 NTU are shown in Fig. 5 and Table 2. The apparent aggregation rate constant K_{app} is obtained from the slope of best fitted line. The values of K_{app} and R^2 for different dosages of polymer are summarized in Table 2. It can observed from Fig. 5 and Table 2 that the value of K_{app} for dosages 0.2, 0.4 and 1.0 mg/l increased from 4×10^{-4} to 6×10^{-4} , 4×10^{-4} to 1.9×10^{-2} and 1.5×10^{-3} to 7.2×10^{-3}, respectively, as the rapid mix velocity increased. While the value of R^2 decreased as the rapid mix velocity increased from 0.98 to 0.60, 0.89 to 0.66 and 0.99 to 0.46, respectively.

As it can be observed from Table 2 the value of R^2 decreased as the value of G increased. The optimum value of G was not observed for dosage of 0.2 mg/l polymer. Elimelech et al. [20] reported that several steps are initiated after addition of polymer to solution: (a) mixing of polymer among the particles; (b) adsorption of polymer; (c) achieving equilibrium. In equilibrium no significant difference in size of the flocs and residual turbidity is observed.

It can be concluded that the low values of R^2 were due to the equilibrium condition. In other words, the plots of residual turbidity ($1/N_t$) versus slow mixing time (t_s) had diversion from linearity after equilibrium point. The increase of rapid mix velocity caused solution to reach equilibrium faster [23].

5. Conclusion

Flocculation with polymer is an efficient method to remove the very fine solids from the wastewater of stone cutting. The study showed that the rapid mix velocity and polymer dosage had a great influence on the flocculation process. For dosage of 0.2 mg/l polymer, there existed an optimum velocity gradient. The apparent aggregation rate constant K_{app} proposed by Vrale and Jorden was used for evaluation of the process of rapid mix. The results showed that the plots of residual turbidity versus slow mixing time had diversion from linearity after equilibrium point. The increase of rapid mix velocity caused solution to reach equilibrium faster.

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References

[1] D.I. Önenç, Marble, 30 (2001) 66–68.
[2] H. Acar, The Third Marble Symposium, Kozan Ofset, Ankara, 2001, pp 289–296.

[3] B. Yarar and J.A. Kitchener, Trans. Institut. Mining Metall., 79 (1970) 23–33.
[4] M. Bayraktar, N. Öner, N. Karapinar, and S. Saklar, Changing Scopes in Mineral Processing. Balkema, Rotterdam, 1996.
[5] A. Seyrankaya, U. Malayoglu and A. Akar, Mineral Processing on the Verge of the 21st Century. Balkema, Rotterdam, 2000.
[6] B. Ersoy, Int. J. Mineral Process., 75 (2001) 207–216.
[7] I. Nishkov and M. Marinov, Mineral Processing in the 21st Century. Djiev Trade, Sofia, 2003.
[8] K. Nasserdine, Z. Mimi, B. Bevan and B. Elian, J. Environ. Mgmt., 90 (2009) 466–470.
[9] S. Lu, R.J. Pugh and E. Forssberg, Studies in Interface Science, D. Mobius and R. Miller, eds., Elsevier, 2004.
[10] O. Atteia, Coll. Surf. A: Phys. Eng. Aspects, 139 (1998) 171–188.
[11] J.W. Kim and T.A. Kramer, Coll. Surf. A: Phys. Eng. Aspects, 253 (2005) 33–49.
[12] M.R. Wiesner, Water Res., 26 (1992) 379–387.
[13] K.J. Ives, Nitrocellulose Particle Stability: Coagulation Thermodynamics, Oxford University Press, 1987, pp. 130–165.
[14] C.S. Fitzpatrick and J. Gregory, Handbook of Water and Wastewater Microbiology, Academic Press, 2003.
[15] N. Tambo and H. Hozumi, Water Res. 13 (1979) 441–448.
[16] L. Vrale, R.M. Jorden and J. Amer. Water Works Associat., 63 (1971) 52–58.
[17] V.A. Mhaisalkar, R. Paramasivam and A.G. Bhole, Water Res., 25 (1991) 43–52.
[18] M. Elimelech, J. Gregory, X. Jia and R.A. Williams, Particle Deposition and Aggregation, Butterworth-Heinemann, 1995.
[19] K. Miyanami, K. Tojo, M. Yokota, Y Fujiwara and T, Aratani, Indust. Eng. Chem. Fundament., 21 (1982) 132–135.
[20] M. Elimelech, J. Gregory, X. Jia and R.A. Williams, Modelling of Aggregation Processes, Butterworth-Heinemann, 1995, pp. 157–202.
[21] A. Yeung, A. Gibbs and R. Pelton, J. Coll. Interface Sci., 196 (1997) 113–115.
[22] A. Records and K. Sutherland, Decanter Centrifuge Handbook, Elsevier, 2001.
[23] J.R. Pan, C. Huang, S. Chen and Y.C. Chung, Coll. Surf. A: Physicochem. Eng. Aspects, 147 (1999) 359–364.