Mechanism and Process of Flocculation by Polymeric Flocculant

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Abstract

This paper shows the techniques for assessing the flocculation-sedimentation performances with polymeric flocculants addition to wastewater. The batch flocculation test was carried out using a large scale reactor (the capacity of 10 liters) instead of the conventional jar tester. The tecqniques described permits close control of the optimum flocculant dosage and makes it possible to determine the magnitude of mixing.

1. Introduction

As production scale in chemical and allied industries become larger, the amount of wastewater and a variety of constituents to be treated have been increasing rapidly. Thus the separation and removal of the suspended materials become a very important problem in the industrial and municipal wastewater treatment fields. This study is intended to provide experimental procedures for making reliable estimate of the influence of operating conditions on the degree of flocculation using a large scale reactor instead of the conventional jar tester with polymeric flocculant addition to a turbid water.

The efficiency of the coagulation-flocculation process is a function of numerous facters, including the chemical characteristics of wastewater, the types and concentrations of flocculants and the suspended materials, the duration and intensity of mixing at rapid mix stage and during flocculation step.

To adequately assess the optimum conditions for the overall process it is necessary to use a batch testing procedure which sequentially maintains each parameter constant while the optimum value of a particular parameter is determined. A difficulty in applying the conventional jar test to a full scale plant, however, arises from the fact that such a plant has not only a large scale structure, but also different type stirring mechanisms.

2. Experimental apparatus and procedure

The apparatus used for experiments is shown in Fig. 1 . It consists of a reactor that is made by acrvlic resin and has a capacity of 10 liters and is fitted with baffles in 24 mm width. The mixing intensity is characterized by determining the power in-

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put to the vessl using direct measurements of the torque on the shaft at various rotational speeds. The velocity gradient, G value is calculated using the net torque T_q (Nm), the impeller rotational speed N (s^{-1}) and the following expression

$$G=(2\pi NT_q/\mu)^{1/2} \tag{1}$$

Where V (m^3) is the vessel capacity and μ (Pa. s) is the viscoisty of liquid.

Measured valus of G with respect to paddle rotational speed are shown in Fig. 2. The slope of the calibration line in Fig. 2 is 1. 5. The thoretical value, obtained by dimensional analysis for the condition of fully developed turbulence, is the same value.

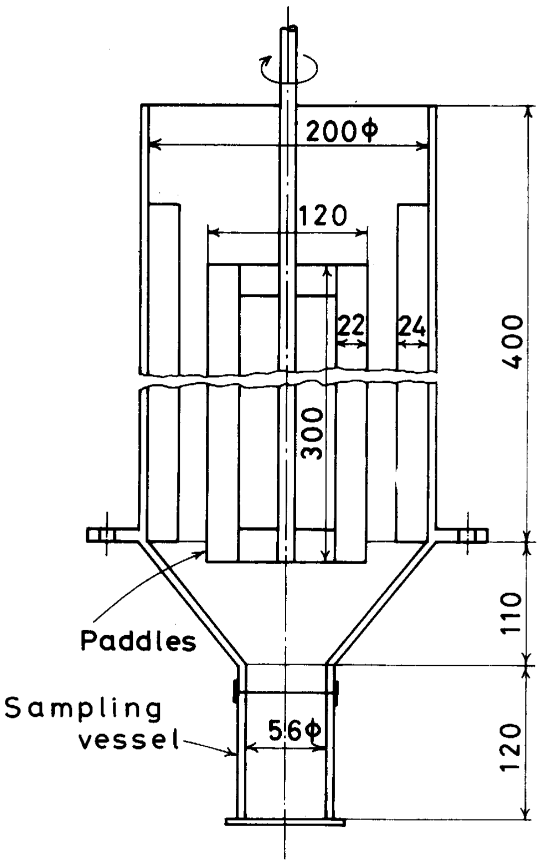


Fig. 1 Reactor for evaluating flocculation performances

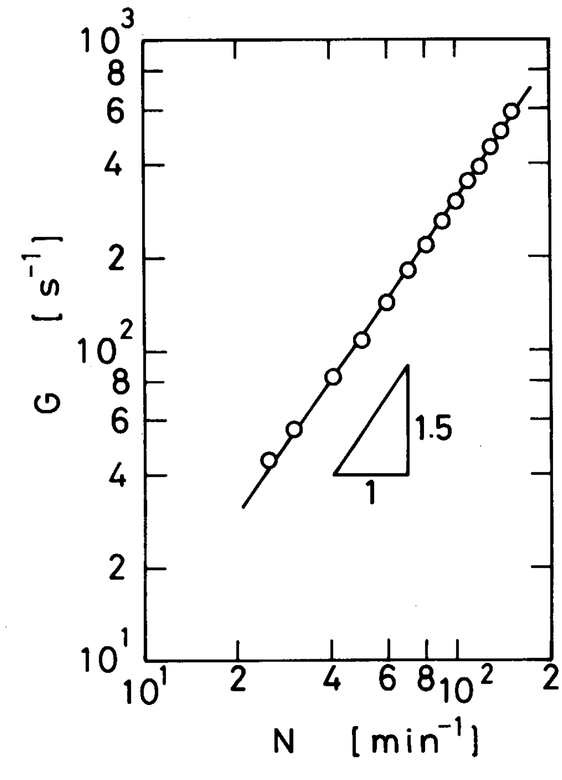


Fig. 2 G values produced for a range of paddle rotational speeds

The turbidities used were kaolin and the sludge from water works. As polymeric flocculants, cationic (medium molecular weight and medium charge density) and nonionic (high molecular weight) polyacrylamides were used.

With the use of apparatus showing Fig. 1, the experimental procedure is as follows : The required volume of flocculant working solution is added to the 10liters suspension of the desired initial solids concentration. After the rapid-max and sequent slow-mix periods, a 30min sedimentation period were used without exception. Samples for residual turbidity measurements were obtained with 10ml pipette immersed 100mm below the liquid surface. Residual turbidity measurements in percentage transmittance were made with a UV spectrophotomener. After 30min, the cylinder fitted with the bottom of the vessel was removed and the filterability of a sediment sludge was measured using the Capillary Suction Time apparatus. The traditional procedure for measuring sludge filterability is to determine specific resistance. The CST can, however, be directly correlated with specific resistance for a particular bulk of sludge. The effect of shear on a sludge was found by measuring the change in the CST of the sludge on being stirred for varying periods of time with the standard stirrer. A sludge with strong flocs of constant filterability when stirred, will exhibit little increase in CST after each stirring period, while a sludge with weak flocs will show a large increase.

3. Experimental results and discussion

3.1 *Flocculation in the Presence of Added Polymers*

Fig. 3 shows the effects of the ratio C_f/C_s on the efficiency of solids removal η and the CST for the system kaolin/cationic polymer. The behaviour of solids removal efficiency in connection with variation in flocculant concentration is observed to exhibit two peaks at C_f/C_s of about 2×10^{-3} and 9×10^{-3}. For the solids removal efficency after 3min, the efficiency at the first peak is smaller than that at the second peak but the inverse relation is obtained at the efficiency after 30min. It is found that flocs formed in lower concentration are compact and rigid, while flocs formed in higher concentretion were large and fragile, futhermore the redispersion by the excess dosage occurs. The value of CST is inversely proportional to the efficency after 3min as shown in Fig. 4. The CST decreases with increasing the ratio C_f/C_s and is

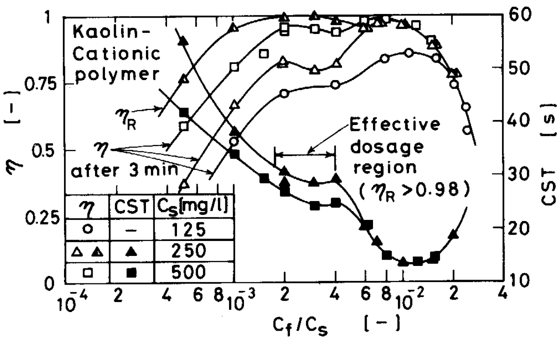


Fig. 3 Flocculation performances for kaolin-cationic polymer system

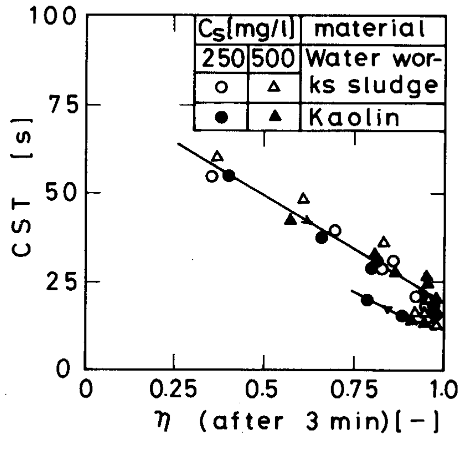


Fig. 4 Correlation between capillary suction time and solids removal efficiency after 3 min

nearly constant in the effective dosage region mentioned after and reaches a minimum value at $1\times10^{-2}C_f/C_s$. This finding implies that the filterability of a sediment is strongly affected by the amount of the larger flocs.

The effects of increasing nonionic polymer concentration on η and the CST for the sludge from water works are shown in Fig. 5. It is clear that the maximum flocculation is reached at about 1×10^{-2} of C_f/C_s alone and beyond this concentration the degree of redispersion is weak in comparison to that of the system kaolin/cationic polymer. The CST is in inverse proportion to η after 3min similar to the case of the system kaolin/cationic polymer.

In Fig. 3, the final solids removal efficiency is sufficiently high, say, over 98% in the range of 2×10^{-3} to 4×10^{-3} of C_f/C_s and this region can be defined as the effective dosage region[5]. Fig. 6 shows the effect of the solids concentration on the effective dosage region. In the system kaolin/cationic polymer, this region becomes wider with increasing the solids concentration at higher values of η_R but is nearly constant for the system sludge from water works/nonionic polymer.

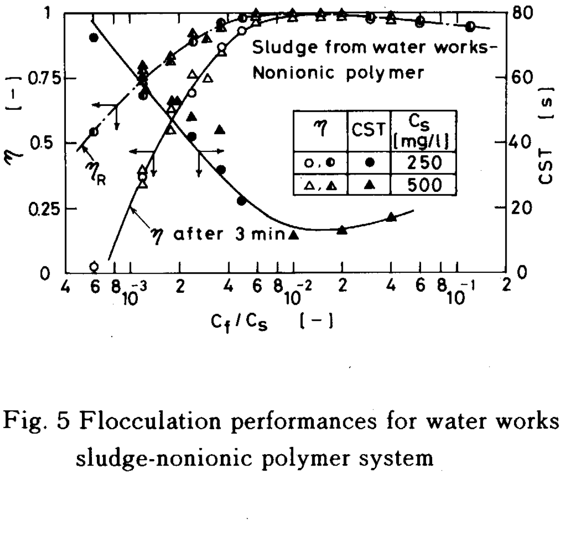


Fig. 5 Flocculation performances for water works sludge-nonionic polymer system

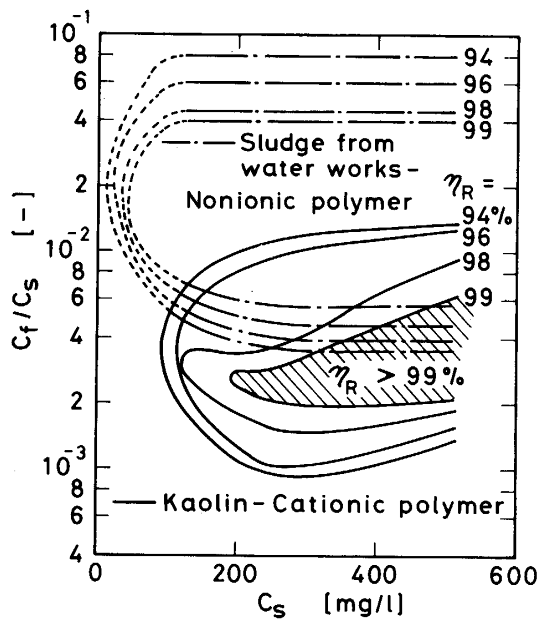


Fig. 6 Effect of polymer concentration on effective dosage region

Fig. 7 demonstrates the response of the floc mechanical strength with flocculant dosage ; a well defined minimum value is evident at 3×10^{-3} of C_f/C_s for the system kaolin/cationic polymer. With nonionic polymer applied to the sludge from water works, however, such a minimum value can not be noticeable and the floc strength decreases as the polymer concentration increases.

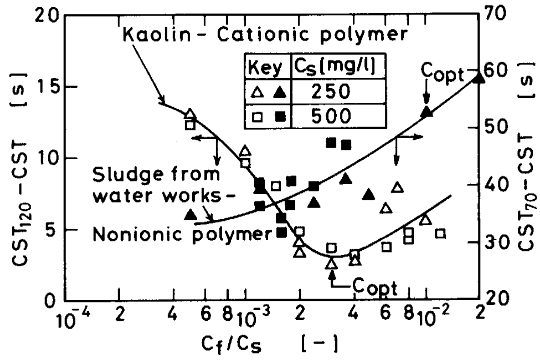


Fig. 7 Effect of polymer concentration on floc mechanical strength

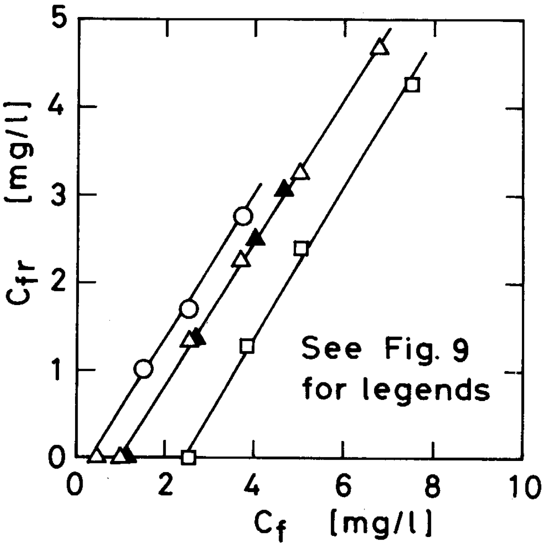


Fig. 8 Residual polymer concentration with cationic polymer

The measurement of residual polymer concentration in supernatant is important from the view of water polution by the monomer contained and the optimum dosage in terms of economics. Fig. 8 shows the comparison between C_f and the residual polymer concentration C_{fr}. The value of C_{fr} is determined with the spectrophotomeric method using bromophenol blue as an indicator, after fine particles in supernatant are removed by the centrifugal method. C_{fr} is nearly zero in the lower C_f region and finally increases proportinally to C_f. Fig. 9 shows the effect of the ratio C_f/C_s on the efficiency of polymer comsumption C_{fa}/C_f ($C_{fa}=C_f-C_{fr}$). It shows that the efficiency is nearly 100% until $4\times10^{-3}\,C_f/C_s$, but in higher concentration regions it decreases with polymer concentration and gradually approaches the asymptote, 30%.

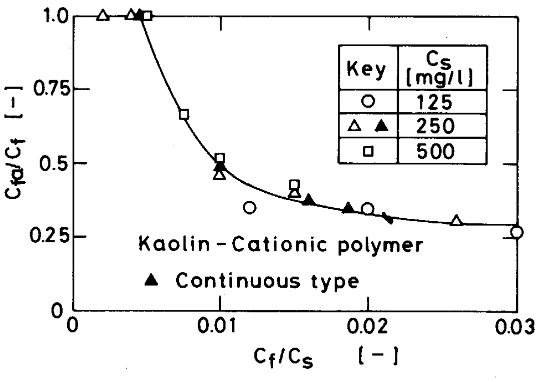


Fig. 9 Effect of polymer concentration on its consumption efficiency

The machanism of flocculation by polymer is considered to involve the two processes ; a bridging process, where polymer segments are absorbed on the surface of adjacent particles thereby binding them together and a charge neutralization process whereby inoic polymer, bearing a charge of opposive sign to the suspended material, are adsorbed and thereby reduce the potential energy of repulsion between adjacent particles.

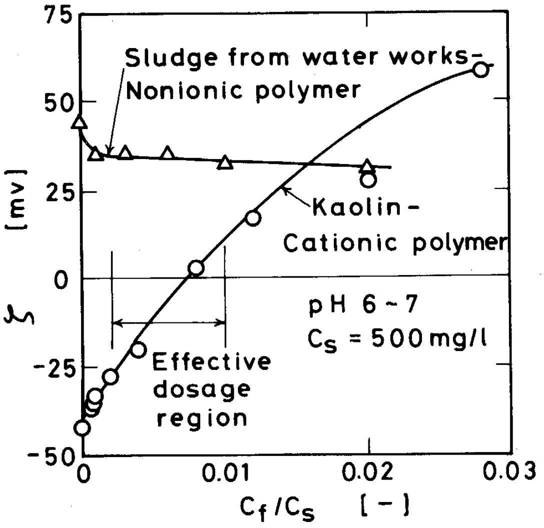


Fig. 10 Changes in zeta potential when polymers are added

The predominant factor in the system is determined by the measurement of electrophoretic mobilities of particles. In Fig. 10, zeta potential is plotted as a function of the ratio C_f/C_s with cationic polymer. Zeta potential can be reversed from net negative to net positive with increasing the polymer concentration and the point of zero charge is C_f/C_s of about 5×10^{-3}.

It is found that zeta potential is within about $\mp$ 25mv in the range of C_f/C_s from 2×10^{-3} to 1×10^{-2} and this region corresponds approximately to the effective dosage region ($\eta_R>98\%$) in Fig. 6. Therefor, it is concluded that charge neutralization is the predominant factor for the system kaolin/cationic polyemer. As can be seen in Fig. 10, in case of adsorption of nonionic polymer on the sludge from water works, however, zeta potential is constant about + 35mv. Therefor, in such a system the flocculation is caused principally by bridging.

The DLVO theory[6)] suggests that the stability of lyphobic paricles is treated in terms of the energy changes which take place when particles approach one another. The total energy of interaction, V [J] is obtained by summation of the electric double layer and Van der Waals energies for two spheres (radius a, shortest distance between the sphere surfaces H, $x=H/2a$), as given by the following equation.

$$V=\frac{32\pi\,\varepsilon\,ak^2T^2\gamma^2}{e^2z^2}\exp\left(-\kappa H\right)$$

$$-\frac{A}{12}\left[\frac{1}{x(x+1)}+\frac{1}{(x+1)}+2\ln\left\{\frac{x(x+2)}{(x+1)^2}\right\}\right] \tag{2}$$

$$\gamma=\frac{\exp(ze\psi_0/2kT)-1}{\exp(ze\psi_0/2kT)+1} \tag{3}$$

Where ε the permittivity, k the Boltzmann constant, T the absolute temprature, z the valency of electrolyte, κ the Debye–Huckel parameter, ψ_0 the surface potential. A is the effective Hammaker constant and about 2×10^{-19} J for kaolin (maybe for clays)[7]. Fig. 11 shows potential energy curves as functions of H and ψ_0. For the dispersion to be stable the potential energy maximum in the resultant curve, *Vmax* must be considerably greater than the thermal energy kT of the particles ; values of $5kT$ of more is normally recommended. The height of this energy barrier depends on the magnitude ψ_0 as shown in Fig. 11. From the above criterion it would appear that the surface potential for the dispersion to be stable shoud be greater than the absolute value of 25mv. It is indicated that the effective dosage region shown in Fig. 6 coresponds to the region which zeta potential is smaller than about | 25 | mv in Fig. 10. Therefor, applicability of the DLVO theory to the system using polymeric coagulant was confirmed experimentally.

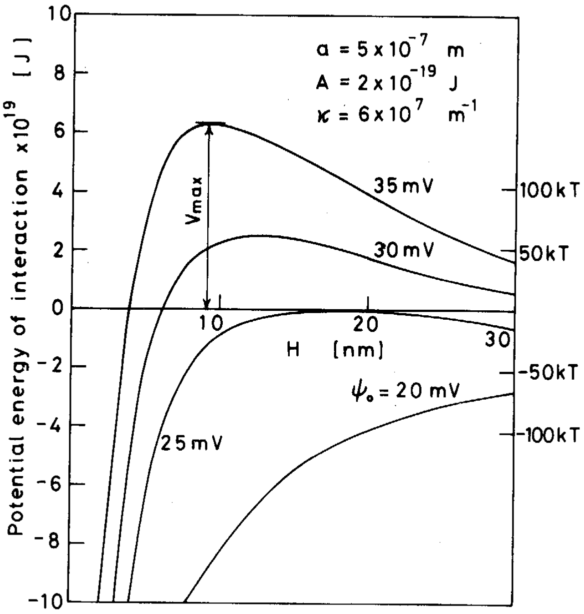


Fig. 11 Total potential energy between two particles

3. 2 *Flocculation process*

The degree or extent of flocculation is governed by both applied velocity gradients and the period of flocculation. These parameters influence the rate and extent of particle aggregation and the rate and extent of breakup of these aggregates. The rate of change in concentration of primary particles for a batch or a plug flow type reactor is thus given by the following equation[1,2,4]

$$\mathrm{d}n/\mathrm{d}t = -K_A nG + K_B n_0 G \tag{4}$$

in which n_0 is the initial number concentration of primary particles, n is the concentration of unflocculated primary particles at flocculation time t. The first term of right hand side of above equation shows the rate of flocculation and the second term indicates the rate of breakup. K_A and K_B are the coefficients of flocculation and breakup, respectively. If the residual turbidity, C, is assumed to proportional to n, Eq. (4) can be rewritten as

$$\mathrm{d}C/\mathrm{d}t = -K_A CG + K_B C_0 G \tag{5}$$

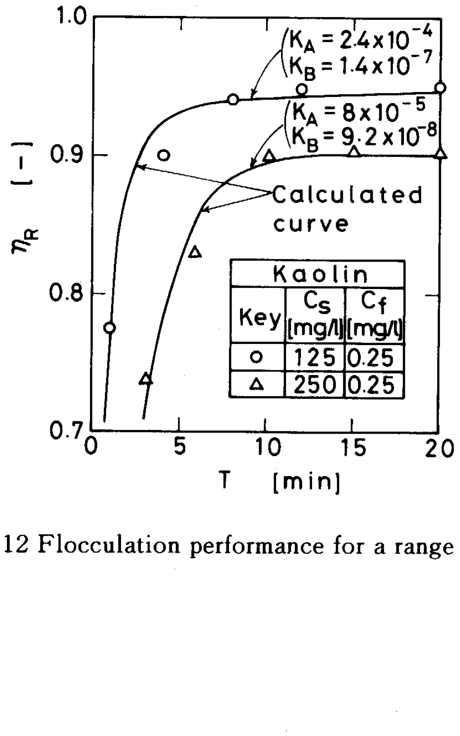
and integrated from $t = 0$, residual-turbidity $= C_0$ to $t = t$ and residual turbidity $= C$ to yield

$$\frac{C}{C_0} = \frac{K_B}{K_A}G + \left(1-\frac{K_B}{K_A}G\right)\exp\left(-K_A GT\right) \tag{6}$$

Rearranging

$$\eta_R = \frac{C_0-C}{C_0} = \left(1-\frac{K_B}{K_A}G\right)\{1-\exp\left(-K_A \mathrm{GT}\right)\} \tag{7}$$

Fig. 12 demonstrates the response of the final solids removal efficiency with the length of the flocculation period. The efficiency increases with increasing T and is



Kaolin		
Key	C_s [mg/l]	C_f [mg/l]
○	125	0.25
△	250	0.25

Fig. 12 Flocculation performance for a range of flocculation times

nearly constant at the long period. From curves such as those shown in Fig. 12, the constants K_A, K_B are determined by successive approximation, as the values for which the sum of the squares of the calculated values of as given by Eq. (7) and the experimental values of the efficiency is at a minimum. The solid lines in Fig. 12 are calculated from Eq. (7) using the previously determined values of K_A and K_B. There are fairly good agreements between the two sets of values, thus indicating that the model of flocculation expressed by Eq. (7) is satisfactory for a batch type flocculator.

4. Conclusions

1) Batch flocculation experiments were carried out, using the reactor of large capacity. The optimun dosages for the systems of kaolin-cationic polymer and water works sludge-nonionic polymer were determined on the base of the solids emoval efficiency, capillary suction time, floc mechanical strength, polymer consumption efficiency and zeta potential.

2) The flocculation mechanisms of both systems were as described mainly by the surface charge neutralization and the bridge models, respectively. The DLVO theory could be applied to the case using polymeric flocculants as primary coagulants.

3) The flocculation process for a batch type reactor was well explained by the concepts of aggregation and breakup of flocs used by Argaman and Kaufman.

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