Evaluation of the flocculation and de-flocculation performance and mechanism of polymer flocculants
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ABSTRACT
Understanding the interaction mechanism between polymeric flocculants and solid particles in two oppositely charged solutions: bentonite and calcium fluoride, is of great practical and fundamental importance. In this work, inorganic flocculants based on aluminum(III) or iron(III); cationic, anionic and non-ionic organic flocculants were used. The solution pH, which highly influenced the flocculation performance of the system, has been used as a function of turbidity removal, sediment volume and velocity. Results show that the flocculation of inorganic polymers does not depend on the zeta potential but on the solution pH, contrary for cationic and anionic polymers. Non-ionic polymer was independent on both. By varying the final pH of the heterogeneous solution formed of flocs/liquid, it was found for inorganic polymers, the optimum condition of pH < 3 to separate inorganic flocculant particles from flocs. Inductively coupled plasma atomic emission spectrometer and X-ray fluorescence analysis proved the reversibility of flocculation process by indicating the concentration of flocculant representative atom (Al or Fe) in the flocs and in the emerging solutions when the flocculation was optimized and the reversibility was effective. As results, weak forces were suggested as responsible for inorganic polymers flocculation where electrostatic interaction and hydrogen bonds may enroll the mechanism of organic flocculants.

Key words | bentonite, calcium fluoride, de-flocculation, flocculation, polymers flocculants

INTRODUCTION
Flocculation is an important industrial process for solid–liquid separation during the primary purification of wastewater and sludge (Yang et al. 2012). Depending on the chemical nature (zeta potential, solution pH, etc.) of the wastewater, various flocculants have been tested. Numerous polymer flocculants are currently available on the market (Swerin et al. 1993, 1997; Khiari et al. 2010; Yang et al. 2012, 2015; Ji et al. 2013; Liu et al. 2013; Wang et al. 2013).

Generally, flocculants can be classified into two main groups: organic and inorganic. Each group is divided into two sub-groups: monomer and polymer. Much work has been done to evaluate polymers performance according to a specific kind of wastewater. Indeed, our understanding of the particle flocculation process has progressed considerably in recent years.

Nevertheless, flocculation optimization practices in industries are still reliant, to a very large extent, on trial and error (Yan et al. 2004). This reflects the highly complex nature of the flocculation process which can involve the following stages (Elimelech et al. 1995; Yan et al. 2004): (a) particle-polymer mixing; (b) attachment of the polymer molecules onto the particle surface; (c) reconformation of the polymer molecules on the particle surface; (d) particle flocculation; and (e) flocs breakup due to shear mixing (Elimelech et al. 1995; Yan et al. 2004). Unfortunately, the common properties of inorganic or organic polymers have not been well studied, independently of the wastewater. Establishing the flocculation mechanism applicable to all kinds of wastewater has been a point of great interest.

Generally, different pH levels result in various changes in the densities and morphologies of the polymer chain (Yang et al. 2011). Hence, various Al(III) species of aluminum-containing flocculants and iron-containing flocculants at...
various pH levels lead to different flocculation mechanisms (Yang et al. 2011; Ji et al. 2013).

Traditionally, flocculation mechanism studies are based on evaluation of the change in turbidity, sedimentation rate, zeta potential, chemical oxygen demand and total organic carbon (Li et al. 2006; Zeng et al. 2008; Yang et al. 2011; Ji et al. 2013). This study focuses on the change in solution turbidity to evaluate the flocculation performance as well as the mechanism of organic and inorganic polymers. For this purpose, bentonite solution, mainly composed of an aluminum clay with negative zeta potential, and calcium fluoride, a contrarily charged solution have been selected as flocculate to better clarify the mechanism. For further understanding, the de-flocculation process has been also investigated to point out the possibility of recycling the flocculants used and the mechanism underlying the process.

MATERIALS AND METHODS

Equipment

Electrophoresis analysis was carried out to determine zeta potentials of the flocculates using Zetasizer Nano series (Malvern Instruments). The turbidity of the solutions was measured using HI93.703B microprocessor turbidimeter (Hanna Instruments). pH meter D-52 (Horiba, Ltd) was used for all the experiments. Inductive coupled-plasma optimal emission spectrometer (ICP-OES/SPS4000 Plasma Spectrometer-Seiko Instruments) was used to analyze the concentration of dominant atoms of the system flocculant-flocculate. X-ray fluorescence (XRF/SEA2210A Element Monitor-Hitachi High-Tech) was used to analyze the particle count rate of the dried solid obtained after flocculation and de-flocculation processes. Scan electromagnetic images were obtained using field emission scanning electron microscope (FE-SEM/JEOL/JSM 6330F).

Flocculants

Poly aluminum chloride (PAC) containing 10% of alumina was purchased from Sankei Chemical Co., Ltd. Poly silicate iron (PSI-025) containing 1.1 wt% of silica and 4.0 wt% of iron, poly ferric sulfate containing 11% of iron were purchased from Nankai Chemical Co., Ltd; and used as inorganic flocculants to remove suspended solids present in the flocculate solutions. The above flocculants were used as purchased without any modification.

As organic flocculants, cationic, anionic and non-ionic polymers are selected based on their molecular weight (MW). Each category was composed of strong, medium and weak flocculants. In this order, we have C-508UL (MW = 500); C-535L (MW = 700); C-510 (MW = 500) for cationic polymers, respectively, and A-150 (MW = 1,500); A-120 (MW = 1,800); A-97 (MW = 1,700) for anionic polymers, respectively. Non-ionic polymer used was N-100 (MW = 1,700). The chemical structures of organic polymers are shown below.

![Chemical structures of organic polymers](image)

The terms strong, medium and weak is related to the number of cationic or anionic functional groups present in the polymer macro-molecules compared to amide groups.

Organic polymers were prepared according to the instructions of the manufacturer (Wako Pure Chemical Industries, Ltd). Cationic and non-ionic flocculants were prepared at 0.2% of concentration and anionic at 0.1%.

To prepare 50 mL of flocculant, an appropriate amount of powder was added to 25 mL of deionized water under agitation and the volume made up to 50 mL by adding additional 25 mL of deionized water. Then mixing by stirring was performed for 1 h to obtain a high viscose fluid used in the whole experiment.
Flocculates

Solutions of bentonite and calcium fluoride were used as flocculate in the present study. 1 g/L of bentonite solution was prepared using commercialized bentonite clay powder. Bentonite was provided by Wako Pure Chemical Industries, Ltd. Bentonite is mainly composed of SiO$_2$, Al$_2$O$_3$ in the ratio SiO$_2$/Al$_2$O$_3$ = 4–6, Fe$_2$O$_3$ 2.99%, CaO 0.7%, MgO 1.28%, K$_2$O 0.7%, Na$_2$O 3.42% and the main material is Montmorillonite.

After a few minutes of stirring using the magnetic stirrer, the solution was removed from the paddle in order to study the sedimentation kinetic as a function of hold time.

Slow sedimentation of bentonite was observed by keeping the prepared solution for several hours until a change occurred in the turbidity of the emerging solution. The solution obtained after an hour of hold time had a turbidity range of 300–350 FTU and an initial pH = 10. Bentonite solution obtained after 1 h was used as flocculate in the present work. In addition, we evaluate the possibility of coagulation of bentonite by changing the solution pH in the range 2 to >12. A relatively rapid deposit of particles which can be assimilated to coagulation is observed at pH >12 (no change at pH = 12).

To further understand the flocculation performance of the selected flocculate, a solution of calcium fluoride was prepared by mixing 5 g of calcium chloride and 5 g of sodium fluoride in 1 L of water. This solution had a rapid deposit of CaF$_2$, resulting in a turbidity change from 370 to 70 FTU within 30 min. The solution used for experiments had a turbidity range of 70–80 FTU. Variation of calcium fluoride solution pH shows coagulation at pH <2 (normal behavior at pH = 2).

Then, all experiments were done in the pH range 2–12 where any coagulation should not occur.

Experimental procedure

Flocculation procedure

The experiments were done at pH 2, 5, 10 and 12. The pH of the solution was adjusted using 1 mol/L of NaOH or HCl solution. 100 mL of bentonite (or calcium fluoride) solution was placed in 100 mL of beaker and stirred in a paddle mixer for a few minutes. 0.1 mL of flocculant (1 mL for organic flocculants) was added to the mixer and the stirring process was conducted for 5 min. In order to measure the sediment volume, the mixture was removed from the beaker to a 100 mL graduated cylinder and then the sediment volume was recorded after 3, 6, 10, 20 and 30 min of hold time (Figure 1). The final pH and turbidity was measured at 30 min of hold time. The turbidity removal was evaluated by using the following equation:

\[
\text{Turbidity removal} \% = \left(\frac{T_{\text{treated}}}{T_{\text{raw}}}\right) \times 100
\]

where $T_{\text{treated}}$ and $T_{\text{raw}}$ are the turbidities of treated and raw solution, respectively.

In order to measure the flocs sediment volume, the reference point was taken at the bottom of the graduated cylinder. In the case of no deposit, the sediment volume was taken to be 100 mL. The evaluated parameters were the turbidity removal rate, the solution pH and the sediment volume as function of hold time.

De-floculation procedure

De-floculation process refer to the phenomenon that once suspended solids formed flocs by reacting with floculants, there is a possibility that the mixture return to the starting point, meaning that floculant and flocculate are in suspension. Once solid was separated from liquid by floculation process, 1 mol/L of HCl or NaOH was added to the mixture in order to disperse floculant particles from flocculate ones. This study was made in order to examine the possibility of recycling the floculant used.

Two coagulated solutions were prepared. To the first solution, 1 mol/L of HCl was added progressively and turbidity, sediment volume were measured every 6 min. A similar experiment was performed with the second solution by adding NaOH. In both cases, an increase in turbidity indicated a possibility of de-floculation occurring (Figure 2).

As shown in Figure 2, the emerging solution at the state where solid–liquid separation was visible (1) and that at the state where the reverse phenomena was maximum (3) were analyzed on ICP-OES in order to compare the concentration of aluminum or iron (aluminum and iron are the most reactive atoms for the selected floculants) at those points. In addition, the particle count rate for the solid obtained at (2, 4) was carried out using XRF to compare the concentration of (Ca, Al) or (Ca, Fe) using calcium chloride solution.

RESULTS AND DISCUSSION

Zeta potential of the flocculates

The floculation performance can be related to the electric potential of flocculate i.e. zeta potential at each pH. The experiment to determine zeta potential was carried out by dispersing fine particles of bentonite (or calcium fluoride) in deionized water loaded at a pH range of 2–10. Figure 3 shows the experimental results. In the pH range 2–10 bentonite is negatively charged whereas calcium fluoride is positively charged. High potential is observed in the pH range 3–5 for both, bentonite and calcium fluoride and a timid peak is observed around pH = 4. The peak observed at pH = 4 may be explained by the good stability of colloidal dispersion at this pH for both bentonite and calcium fluoride. At high alkali pH, the potential is relatively low.

Evaluation of floculation processes

One of the most important parameters affecting the floculation efficiency is the pH of the solution. The pH effect was evaluated in terms of turbidity removal rate. Floculation efficiency of the selected flocculants increases as more suspended solids are removed from solution as sediment reaches a maximum when turbidity removal rate is close to 100%. Experimental results are summarized in Figure 4.

Figure 2 | De-floculation processes and summary of the parameters evaluated during this process.
Based on inorganic polymers using bentonite solution, PAC shows no flocculation at pH 5 and 10 but has high turbidity removal rate at pH 2 and 12. There is slight variation in terms of turbidity removal depending on pH value for other inorganic flocculants. For instance, at pH 2, PAC, PSI-0.25 and poly ferric sulfate showed a high turbidity removal of 95, 99, and 99%, respectively. The emerging solution was very cloudy, low turbidity values indicated the efficiency of the flocculants used. With calcium fluoride, PSI-0.25 showed the worst performance at pH 2 but had the best efficiency at other pH values. The turbidity removal rate at pH 5 was 98, 97, and 93% for PAC, PSI-0.25, and poly ferric sulfate, respectively. Despite the fact that bentonite and calcium fluoride are contrarily charged the turbidity removal of inorganic polymers did not seem to depend on the zeta potential of the flocculates but mainly on the pH of the solution.

Many flocculants have been tested in the literature and their efficiency has been evaluated according to a particular flocculant-flocculate system, and depending on the nature of the flocculate (sewage, sludge, etc.), such as zeta potential.
and pH (Migo et al. 1993; Li et al. 2006; Rasteiro et al. 2008; Yang et al. 2012, 2013; Ji et al. 2013). The results obtained in the present work seem to relate floculation process with the nature of the system flocculant–floculate. Indeed, high turbidity removal rate have been observed using both bentonite and calcium fluoride (independently on their contrary zeta potential) for each flocculate but at different pH. The zeta potential of the solution plays the less important role. Overall, we conclude that the evaluation the best floculation conditions can be done only by varying the solution (flocculate) pH when working with inorganic flocculants.

As opposed to inorganic floculants, the effect of zeta potential appeared to be significant in the case of organic floculants, as expected. This is due to the tendency for cations to react with bentonite more than anions, and for anions to react with calcium fluoride more than cations. The strength of the floculant and the solution pH both play an important role in the floculation efficiency. Despite the fact that they carry the same charge with them, weak and medium cationic floculants react with calcium fluoride whereas anionic ones react with bentonite. Furthermore, non-ionic polymer floculation process was neither related to the zeta potential nor to the pH.

**Sedimentation velocity**

The floculation kinetics was measured in terms of sediment volume function of hold time. Results obtained at pH 12 are shown in Figure 5. The more the sediment deposited rapidly, the higher the floculation efficiency.

For inorganic floculants, the sediment volume decreases with hold time for all floculants, indicating a progressive formation of flocs with the release of emerging liquid from sediment. For both bentonite and calcium fluoride, a progressive sedimentation was observed for all floculants and the sediment volume decreased with time. A kind of rapid deposition was observed for calcium fluoride even when sediment volume still decreasing with bentonite.

![Figure 5](https://iwaponline.com/wst/article-pdf/69/6/1249/472319/1249.pdf)
After 30 min of experiment, more than 95% of the turbidity was removed, showing that the efficiency of the process was high. The initially light flocs coalesced together and fell down rapidly, explaining the rapid sedimentation velocity. The coagulation of PAC after 10 min may be the result of slow formation of flocs due to weak attractive forces between PAC and calcium fluoride.

For organic flocculants, rapid deposition was observed in the first 3 min (except A-120). Once deposited, no modification of the sediment volume was observed. The sediment volume was very low and hard flocs were observed.

**SEM**

The surface morphology of the flocs was studied using field emission scanning microscopy (FE-SEM). Figure 6 shows FE-SEM images of the flocs obtained with the selected inorganic flocculants using calcium fluoride solution. The flocculation performance was well observed for all samples. The floc size could not be measured accurately owing to the filtration made during sample preparation.

**Evaluation of the de-flocculation process**

The reverse phenomenon of flocculation was studied to evaluate the possibility of separating flocculant from sludge. Figure 7 shows the experimental results.

**Inorganic flocculants**

For both bentonite and calcium fluoride, the reversibility effect was observed when the final pH of the solution was less than 3. The turbidity of the final solution increased progressively when the pH was highly acidic, indicating the possibility that once flocs are formed, their dispersion can only occur by varying the solution pH. This further illustrates the effect of pH in the flocculation process. In other words, pH can improve the formation of flocs, improve the hardness of flocs and can also enhance their dispersion. Therefore, binding and releasing of suspended solids may be realized by choosing the right pH conditions.

In order to further understand the de-flocculation process, the flocs sediment at the optimum sedimentation pH and the slight deposit obtained after maximum reversibility were dried at 60 °C for 72 h and analyzed by XRF. The emerging solutions (addition of 1 mol/L of HCl solution to the heterogeneous solution obtained when the flocculation was done until the final pH reached pH < 3) was analyzed on ICP-OES in terms of the concentration of Al or Fe present in the solution. Both results are shown in Table 1.

Table 1 results indicate that the concentration of Al or Fe in the solution obtained after reversibility was much higher than the one obtained before, suggesting that flocculants released from the flocs, mixed with the emerging solution. Concurrently, the concentration of Al or Fe decreased in the sludge (solid), proving the occurrence of floc dispersion and mixing of flocculant with flocculate to form newly suspended solids. With ICP-OES analysis, it
was observed that 95, 100, and 100% of PAC, PSI-0.25 and poly ferric sulfate dosages were recovered, respectively. The possibility of floculants regeneration is high (Shin et al. 2012). Thus, our study not only resolved the water pollution problem, but also showed the recycle and reuse possibility for both floculant and flocculates.

Once the de-flocculation process was proved, further experiments needed to be improved in order to separate floculant from the sludge.

### Organic flocculants

A contrary phenomenon to the one outlined above was observed for organic flocculants. No variation of sediment volume was observed in the pH range considered (Figure 7). Variation in turbidity was insignificant, proving the absence of reversibility effect for both bentonite and calcium fluoride. Due to the hardness of the flocs, they were not dissolved by the potential of acid or alkali. Stronger forces may reinforce suspended solids with floculates polymers molecules.

### Possible mechanism

Based on the tests figured out flocculation and de-flocculation performance, it is evident that the different settling behaviors of bentonite and calcium fluoride solutions are mainly driven by the differences in the interactions among fine colloidal particles and polymers as well as the polymers functional groups and conformations under various solutions conditions (Ji et al. 2010, 2013). Thus, the mechanism varies from organic to inorganic polymers.
PAC, PSI-0.25 and poly sulfate iron are inorganic non-polar polymers characterized by their high relative molecular mass. Their reactivity during flocculation process and the separation of polymers flocculants from flocs during deflocculation process help to clarify the mechanism. The fact that flocculation process depended on solution pH but not zeta potential suggests that flocculation may occur due to the formation of inter-molecular forces between polymers and flocculate molecules (or atoms) in the solution. By varying the solution pH, charges may be created randomly around atoms, and then temporary forces (attractive forces during flocculation and repulsive forces during deflocculation process) or the so called Van der Waals forces may appear. Van der Waals forces may pull together polymer macro-molecules and suspended solids forming flocs, that sediment due to the scope of weight. Those forces may become stronger or weaker due to the charges formed around non-polar molecules, explaining the flocculation and deflocculation processes.

For organic polymers, the mechanism may differ for strong, medium or weak cationic or anionic flocculants, to non-ionic ones.

Non-ionic flocculant was characterized by lack of dependence on zeta potential and pH; as well as lack of reversibility once the flocs were formed. This suggests the formation of strong forces during the flocculation process. The presence of amide functional group may explain the phenomenon. Because of the greater electro negativity of oxygen, the carbonyl group (C = O) is known to have a stronger dipole than the N–C one. The presence of a C = O dipole and, to a lesser extent an N–C dipole, allows amides to act as H-bond acceptors. Thus amides can participate in hydrogen bonding with water; the oxygen atom can accept hydrogen bonds from water and the N–H hydrogen atoms can donate H-bonds.

Strong and medium cationic or anionic flocculants were characterized by their dependence on zeta potential. The anionic or cationic functional group is the most important in terms of number of molecules present in a polymer. Moreover, in addition to the hydrogen bonds, some interactive forces may be formed, making the bond between polymers and colloid particles present in the solution more powerful.

Weak cationic or anionic flocculants were characterized by the small number of anionic or cationic group and their dependence on the solution pH.

When the flocculant charge is opposite to the solution zeta potential, both hydrogen and interactive forces may be formed but these may be weaker than the ones obtained with strong and medium cationic or anionic flocculants.

In the case of the same charges, amide group can accept or donate protons depending on the solution pH, hence weak interactive forces may be formed.

CONCLUSION

The flocculation and deflocculation performance of PAC, poly silicate iron and poly sulfate iron as inorganic polymers and strong, medium and weak cationic or anionic polymers as well as non-ionic polymers have been studied using two flocculates: bentonite solution (negative zeta potential within pH range 2–12) and calcium fluoride solution (positive zeta potential within the same pH range). It was shown that the flocculation performance is almost independent on zeta potential for inorganic polymers unlike organic ones. Thus, the solution pH plays the most important role in the flocculation process using inorganic flocculants. De-flocculation process has been found to be optimum at pH less than 5 for all inorganic flocculants studied and no reversibility was observed for organic ones. Therefore, the possibility of recycling inorganic flocculants has been proved. Van der Waal forces between inorganic polymers and suspended solids may explain their flocculation mechanism. Formation of hydrogen bonds and interactive forces may characterize organic polymers flocculation process.

ACKNOWLEDGEMENTS

The present work was supported by Toshiba Research and Development Center. We thank the collaboration of the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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First received 8 October 2013; accepted in revised form 17 December 2013. Available online 2 January 2014