Acidic and hydrogen peroxide treatment of polyaluminum chloride (PACL) sludge from water treatment

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Abstract The water treatment sludge including coagulants cannot be easily removed by conventional dewatering methods. The possibility of hydrogen peroxide (H_2O_2) oxidation as a pretreatment to enhance the dewaterability of polyaluminum chloride (PACl) sludge from water works was investigated. H_2O_2 treatment alone was not effective but H_2O_2 treatment under acidic condition significantly reduced both the cake water content and specific resistance to filtration (SRF), indicating the enhancement of dewaterability and filterability. The filterability after acid/H_2O_2 treatment was comparable to polymer conditioning and even more dewatered cake than polymer conditioning was produced. By H_2O_2 combined with sulfuric acid (H_2SO_4), leached iron caused Fenton's reaction, which showed a potential to significantly reduce the amount of solids mass and to produce more compact cake with higher filterability.
Keywords Acid treatment; dewatering; Fenton reaction; H_2O_2; PACl sludge

Introduction

Water purification plants produce 16 million m^3/d of tap water in Korea. It implies 672 m^3/d of sludge cake. However, the treatment and disposal of water residuals is becoming even more difficult not only because of cost, but also because of new regulations that limit the disposal of waste in ocean and landfill. Therefore, technology for sludge reduction and resource recovery is urgently needed.

The major part of water treatment sludge is contributed by coagulation process that generates up to 70% of the total waste produced in the water industry. Aluminum containing coagulants such as PACl, alum and polyaluminum silicate-sulfate are mostly used in Korea. In case of alum coagulant, aluminum hydroxide occupied up to 30 to 50% in sludge (Sengupta and Shi, 1992). Aluminum hydroxide content is dependent on turbidity of raw water. Turbidity to aluminum addition ratio is generally controlled in range from 0.05 to 0.2. Thus, raw water of low turbidity is favorable in sludge dewatering and reduction.

A considerable amount of water contained in PACl sludge cannot be easily removed by conventional dewatering methods. Generally, polymer was added as conditioner to aid water removal and to increase dewatering rate. However, it is difficult to remove the water contained in sludge mixture to a level desirable for safe disposal even in polymer-aided dewatering processes (Kelkar and Schafran, 1994). Reducing both organic and aluminum content in sludge by pre-treatment could be an alternative to promote dewatering performance. A few studies have been reported on sludge pretreatment to enhance its dewaterability and to overcome the limit of polymer conditioning (Pere *et al*., 1993; Mustranta and Viikari, 1993; Kelkar and Schafran, 1994; Waite *et al*., 1997). Acid or alkali treatment was suggested to reduce and recover aluminum (Sengupta and Shi, 1992). H_2O_2 treatment was effective to oxidize organic matters in sludge (Kelkar and Schafran, 1995). However, peroxidation alone is not effective due to low reaction rate. H_2O_2 could be activated by iron salt, known as Fenton's agent (Neyens and Baeyens, 2003).

In this study, the possibility of combined acidic treatment and peroxidation (H_2O_2 oxidation) as a pretreatment to enhance the dewaterability of polyaluminum chloride (PACl) sludge from water works was investigated. The effects of pretreatment on the water content of the final cake and the filterability of residuals were determined at different pH, various H_2O_2 doses. The efficiency of solids reduction by both acid and peroxidation was also evaluated.

Material and methods

Thickened waste sludge (TS 3.0% to 3.5%) was taken from a water treatment plant. This sludge was produced by water coagulation with about 30 mg/L dose of PACl. After pouring one-litre aliquots of each sludge sample into a two-litre coagulation jar, H_2O_2 (30% by wt) was added to sludge aliquots at different doses from 0.5 to 10 mL/L-sludge. And then the residual aliquots were rapidly mixed at 150 rpm for reaction time varied from 2 to 60 minutes. Acidic treatment was also conducted by using H_2SO_4 (97% by wt) without the addition of H_2O_2. In order to investigate the synergistic effect of pH and peroxidation, H_2SO_4 was added and allowed to react for 15 minutes and then H_2O_2 was added. Cationic polymer (FO4550SH, Nalco Korea, LTD) was compared as a common conditioner.

Solids properties including particle size distribution, bound water, and zeta potential were investigated before and after pretreatment to address how the treatment affects the dewatering characteristics of solids. Laser diffraction spectrometer (Coulter, LS100Q) was used to analyze the particle size distribution of sludge floc. Bound water content was determined using dilatometric method at –20°C (Smith and Vesilind, 1995; Wu *et al.*, 1998) and zeta potential was measured via zeta potential analyzer (Zetasizer 3000HS, Malvern). The efficiency of sludge dewatering is generally expressed by two ways, which are firstly the amount of water removed (dewaterability) and secondly dewatering rate (filterability). Moisture content of dewatered cake is a common parameter used in the evaluation of dewatering performance, while sludge filterability is generally evaluated by parameters such as specific resistance to filtration (SRF). The SRF and moisture content of cake (W_c) were measured by using a pressure filter operated at a pressure of 300 kPa.

Results

H_2O_2 treatment

In the experiment of H_2O_2 treatment, PACl sludge was dewatered using a pressure filter at 3 atm. Figure 1 a) and b) represented the effect of H_2O_2 dose at pH 7.0 without pH adjustment. It was observed that H_2O_2 treatment did not significantly reduce both the cake water content and SRF, indicating the enhancement of dewaterability and filterability, respectively. The SRF of raw sludge was 60×10^{12} m/kg. SRF did not change in the course of H_2O_2 addition to 10 mL/L-sludge. Floc size and zeta potential also showed almost constant at that time. Bound also did not decrease much. In sequence dewatering performance expressed as cake water content showed up to 75%.

Acidic treatment

The effects of sludge pH on dewatering characteristics are shown in Figure 2. As shown in Figure 2 a), the rapid decrease of SRF was followed by increase at pH lower than about 3. Improvement of filterability at pH higher than 3 can be explained by the increase of floc size as illustrated in Figure 2 a). Mean size of particle diameter increased with pH drop, reaching a maximum at a pH around 3.5, and then decreased with further increase of H_2SO_4

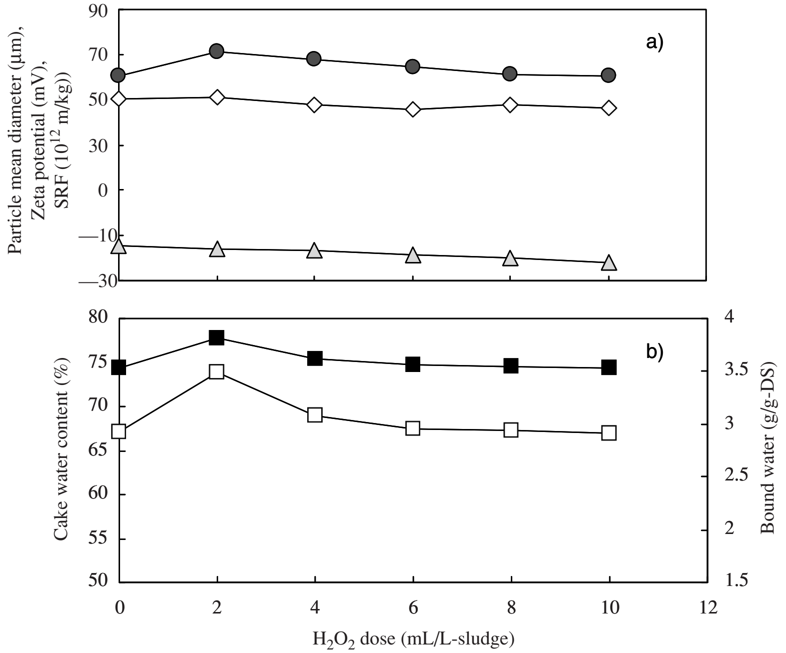

Figure 1 Effect of H_2O_2 addition on dewaterability and filterability: ●, SRF; ◇, particle size; △, zeta potential; ■, cake water content; and □, bound water

dose. It seems that flocculation of sludge particles occurs due to release of metal ions with decreasing pH. But decrease of particle size at pH lower than 3 might result from increase of organics released in the sludge floc as well as variation of ions form. Converting particle surface charges in a positive direction from –12 mV at pH 7 to around –5 mV at pH 3.5 probably can enable sludge particles to be coagulated. As shown in Figure 2 b), water content of cake significantly increased at pH lower than 5, for example, to 60% at pH of 3.5 from initial 71% for a raw sludge. It seems that the reduction of bound water content is directly related to the enhancement of sludge dewaterability.

Synergistic effect of H_2O_2 and acid

To figure out the synergistic effect of acidic and peroxidation treatment, adjustment of sludge pH was conducted before H_2O_2 addition. As shown in Figure 2, SRF rapidly decreased with pH drop to 3.5, and then bounced up with further decrease of pH, so pH was adjusted to 3.5. Figure 3 a) shows that addition of peroxide into acidified sludge caused further sharp decrease of SRF to 2 mL-H_2O_2/L-sludge. At a dose of 2 mL-H_2O_2/L-sludge, the SRF represented 8×10^{12} m/kg. Further increase of peroxide dose did not result in meaningful reduction. On the other hand, peroxidation of sludge at pH 3.5 did not show the meaningful reduction of water content of cake compared with acidic treatment, even though slight reduction was observed at relatively high doses of H_2O_2.

Figure 3 a) and b) also demonstrate the variations of sludge properties affecting dewatering. It should be noted that zeta-potential increased with H_2O_2 doses, reaching a zero value around a dose of 2 mL-H_2O_2/L-sludge. Bound water content has a key effect on the dewaterability of sludge. As shown in Figure 2 b) and 3 b), the bound water content decreases rapidly by only acidic treatment without H_2O_2 and reduces slowly with increasing doses of H_2O_2 under acidic condition. Pere *et al.* (1993) reported the decrease of surface charge of flocs and the increase of hydrophobicity by oxidative treatment using Fenton's reagent. The decrease of the bound water content by acidic treatment following by oxida-

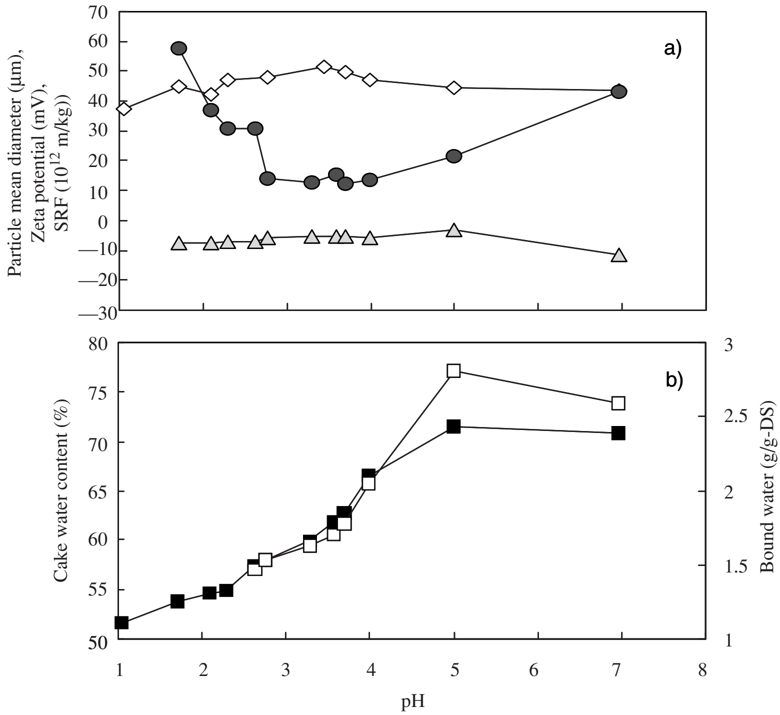

Figure 2 Effect of acidic treatment on dewaterability and filterability: ●, SRF; ◇, particle size; △, zeta potential; ■, cake water content; and □, bound water

tion of H_2O_2 may be explained by the increase of hydrophobicity and the release of interstitial water trapped inside floc.

Discussion

Effects of Fenton's reagent

The acidic treatment of waterworks sludge released organic materials as well as inorganic such as Al and Fe resulting in increased dewaterability of sludge. However, over dosing of H_2SO_4 made dewaterability deteriorate. It showed that the optimal condition of acidic treatment appeared around pH 3 as mentioned before, even though organic and metals were continuously leached under such a condition as shown in Figure 4 a). Leached Al and total organic carbon (TOC) could affect dewaterability as well as mass reduction in dewatered cake. Iron salts and ions could contribute more effectively to dewatering and filtration systems, since Fe can activate H_2O_2 to form hydroxyl radicals as in the following equation (Neyens and Baeyend, 2003):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^-$$

Oxidation processes generally are based on radical reactions. Lu *et al*. (2003) reported that sludge dewatering efficiency expressed as the specific resistance and moisture increased in filtration when applying the Fenton system, Fe^{2+}/H_2O_2 and Fe^{3+}/H_2O_2. Figure 4 b) shows that solubilized Fe was consumed according to dose of H_2O_2, indicating occurrence of Fenton's reaction. On the other side, the concentration of Al and TOC was not changed. The interval of Fe decrease in Figure 4 b) corresponds to the interval of SRF decrease in Figure 3 a).

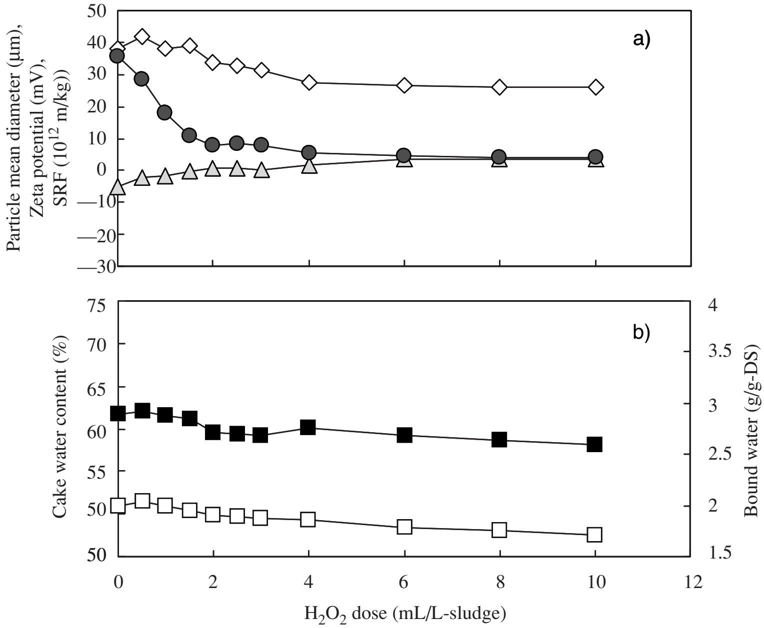

Figure 3 Synergistic effect of acid and H_2O_2 on dewaterability and filterability: ●, SRF; ◇, particle size; △, zeta potential; ■, cake water content; and □, bound

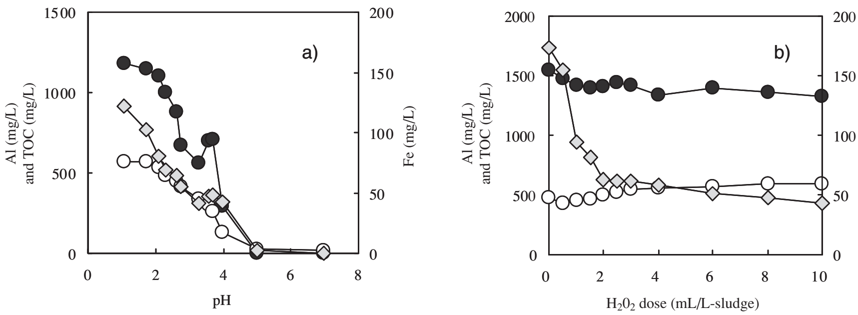

Figure 4 Organic and metals leaching and consumption, a) according to pH and b) according to H_2O_2 dose under acidic condition: ●, Aluminium; ◇, Iron; ○, TOC

Comparison of sludge reduction

Results on acidic and peroxidation as pretreatment were summarized in Table 1 and compared with no pretreatment sludge and conventional polymer conditioning. Table 1 illustrates that the mass of filter cake produced by acidic treatment is significantly reduced when compared with polymer conditioning and untreated sludge, indicating a better dewaterability when pH decreases. The mass of wet cake represents 66% of untreated value, especially 48% of polymer conditioning. Water content of cake also decreases to 58% from 68% of untreated sludge. Therefore, 34% of reduction efficiency results from both 22% of water reduction and 12% of solid reduction. It notes that polymer conditioning increases the water content of cake adversely and produces larger amount of cake although improves the filterability. However, the SRF for acidic sludge is even higher compared with sludge conditioned by polymer. This means that filtration rate is too low to operate the dewatering facility actually.

Addition of H_2O_2 under the acidic condition decreases SRF value to a level of polymer conditioning, keeping the same amount of filter cake compared with acidic treatment. As a

Table 1 Comparison of filterability, dewaterability and mass reduction at different pretreatments

	Wet cake mass change (–)*	SRF (10^{12} m/kg)	Water content of cake (%)
No pretreatment	1.00	65.63	68.29
Polymer 0.005 g/gTS	1.38	5.29	76.56
Acidic pH 3.5	0.66	35.68	58.22
H_2O_2 0.02 g/gTS, pH 3.5	0.66	7.99	57.64

* Ratio of g-cake mass to g-cake mass of no pre-treatment sludge

result of the experimental investigations, it can be concluded that peroxidation using H_2O_2 is efficient in reducing the residual sludge amount through enhancement of filterability as well as dewaterability. The mechanism is not fully understood, but the release of bound water due to disintegration of flocs by acidic treatment and subsequent increase of hydrophobicity may result in reducing the moisture content of dewatered cake. H_2O_2 treatment at low pH affects sludge filterability in positive direction, which promotes flocculation by means of particle charge reduction. The oxidation rate of H_2O_2 highly increases in presence of ferrous ion, producing hydroxyl radicals with powerful oxidizing ability to degrade organic matters. Organic matters released from sludge solids by acidic treatment can be oxidized through following H_2O_2 treatment using Fe^{2+} released along with organics. The reduction of organic matters in water phase may improve the filterability of sludge suspension.

Conclusions

The effects of acidic and H_2O_2 treatment on the dewaterability and filterability of waterworks sludge were determined by measuring the cake water content and SRF respectively at various conditions. It was observed that H_2O_2 treatment at pH 3.5 significantly reduces both the cake water content and SRF, indicating the enhancement of dewaterability and filterability. The reduction of sludge mass at pH 3.5 represented 34% and 52% when compared with untreated sludge and polymer conditioning respectively. It is suggested that the selective oxidation of viscous organic matters released from sludge floc at low pH by the hydroxyl radicals formed by H_2O_2 reacted with iron, results in the reduction of the surface charge of sludge particles and promotion of the flocculation. The decrease of bound water after H_2O_2 treatment at low pH indicates that the release of the interstitial water trapped inside floc is responsible for the observed decrease of water content of the dewatered cake. From the experimental observations, it was concluded that H_2O_2 treatment combined with H_2SO_4 has a potential to significantly reduce the amount of sludge and to produce more compact cake even with good filterability.

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References

Lu, M.-C., Lin, C.-J., Liao, C.-H., Huang, R.-Y. and Ting, W.-P. (2003). Dewatering of activated sludge by Fenton's reagent. *Advances in Environmental Research*, **7**(3), 667–670.

Kelkar, U.G. and Schafran, G.C. (1994). Hydrogen peroxide amendments to alum sludge; Effects on sludge characteristics and dewaterability. *Proceedings of AWWA Annual Conference, New York, NY, June 19–23*.

Kelkar, U.G. and Schafran, G.C. (1995). Enhanced Coagulation: Effects on Particle Size and Dewaterability. *Proceedings of the American Water Works Association Nation Conference, Anaheim, CA, June 20–24*.

Mustranta, A. and Viikari, L. (1993). Dewatering of activated sludge by an oxidative treatment. *Wat. Sci. Tech.*, **28**(1), 213–221.
Neyens, E. and Baeyens, J. (2003). A review of classic Fenton's peroxidation as an advanced oxidation technique. *J. Hazardous Materials*, **B98**, 33–50.
Pere, J., Alen, R., Viikari, L. and Eriksson, L. (1993). Characterization and dewatering of activated sludge from the pulp and paper industry. *Wat. Sci. Tech.*, **28**(1), 193–201.
Schafran, G.C., Kelkar, U.G., Bokka, U.L. and Marasco, D.F. (1995). Influence of natural organic matter on enhanced coagulation and residual dewaterability. *Proceedings of the American Water Works Association Nation Conference, Anaheim, CA, June 20–24*.
Sengupta, A.K. and Shi, B. (1992). Selective aluminum recovery from clarifier sludge. *J. AWWA*, **84**(1), 96–103.
Smith, J.K. and Vesilind, P.A. (1995). Dilatometric measurement of bound water in wastewater sludge. *Wat. Res.*, **29**(12), 2621–2626.
Waite, T.D., Wang, T., Kurucz, C.N. and Cooper, W.J. (1997). Parameters affecting conditioning enhancement of biosolids by electron beam treatment. *Journal of Environmental Engineering*, **123**(4), 335–344.
Wu, C.C., Huang, C. and Lee, D.J. (1998). Bound water content and water binding strength on sludge flocs. *Wat. Res.*, **32**(3), 900–904.