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On the necessity of sludge conditioning with non-organic polymer: AOP approach

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Abstract Organic polymers have long been used as sludge conditioners to improve its dewaterability in sludge management practice. Although polymers can bring about a great dewatering performance of the sludge, their potential health related risk remains unknown regarding their residual in dewatered sludge cakes in the environment when the sludge is finally disposed as landfill especially in long term point of view. For this regard, as an initiative action, Fenton (Fe^{2+}/H_2O_2) and its related reagents were tested in this study as potential alternative an alum sludge conditioners for the purpose of eliminating the perceived long term risk associated with polymer residual in the environment.

Keywords: Advanced oxidation process (AOP); alum sludge; conditioning; Fenton reaction; organic polymer

1. Introduction

The global use of chemicals in wide range of types plays important role in water purification and wastewater treatment engineering. The use of synthetic organic polymers or polyelectrolytes (with molecular weights varied normally from 10^4 to 10^6 Daltons) in drinking water treatment as flocculent aid and mainly in conditioning of water treatment sludge has been a worldwide practice for a long time. Great performance of sludge dewatering devices was obtained when various types of polymers were adopted as sludge conditioners. In recent year, however, such use of polymers has raised increased concerns of their residuals in the surrounding environment, which was associated with the cycling/reuse and even the landfilling of the treated or dewatered sludge. Although organic polymers are specifically manufactured for water industry, the monomers used in the manufacture of many polyelectrolytes are toxic (Bolto and Gregory, 2007). Long-term effects of polymer residual on aquatic organisms, human health and the biota related to the disposal of such sludge are still remaining unknown. Therefore, as an initiative action, research work to seek the alternative chemicals in water treatment processes especially in sludge conditioning is desirable in terms of sustainable development.

In this paper, the necessity of the sludge conditioning to avoid using organic polymers was discussed based on the updated information from the literature. Thereafter, a new approach of using Fenton (Fe^{2+}/H_2O_2) and its related reagents as one of the advanced oxidation processes (AOPs) (Neyens and Baeyens, 2002) for conditioning of an aluminum salt-flocculated drinking water treatment sludge was summarily presented.

2. The Necessity of Non-polymer Approach: Mini Review

2.1. Concerns of organic polymers

A recently critical review of the polymers used in water industry was given by Bolto and Gregory (2007). As is known the polymers are mainly made of acryl amide and acrylate, they can be one of possible toxic chemicals to aquatic animals and human bodies at certain concentration even though they are sometimes biodegradable. Unfortunately, techniques of appropriate monitoring of the polymer residual are shortage (Zhao et al., 2008), this makes it unknown of the polymer residual in water treatment and sludge conditioning process although the amount of the polymer addition is accurately known. Furthermore, information on the fate of the added polymers in water and sludge treatment is extremely lack. As a result, it is unclear regarding the risk of the polymers used from the long-term point of view. It has been noted that the use of polyelectrolytes in Japan and Switzerland are not permitted in the drinking water treatment, while Germany and France located a strict limit for such use (Bolto and Gregory, 2007). Accordingly, a stringent limit for the polymer use to prevent the environmental damage has been proposed (Majam and Thompson, 2006). Therefore, new concepts and principles for sludge conditioning/treatment in line with sustainable development remain a great challenge to engineers and scientists who are called upon to develop solutions that are technically, economically, and socially sound.

Due to a lack of research and information as to the toxicological effects of the polymer residual that could possibly leach out from landfills when the dewatered sludge cake is deposited, much of the information on the toxicity of polymers is in relation to the effects on aquatic organisms. The presence of residual polymer is a cause of concern around the world but no research has been undertaken to determine if it is actually in attendance. It is generally found that the cationic polymers are more toxic especially to aquatic organisms. Anionic and non-ionic polymers are usually of low toxicity. Some countries have taken drastic measures with regard to the use of polymers in water treatment due to concerns about contaminants. Examples of these include Japan and Switzerland disallowing their use in water treatment and France and Germany setting severe limits on their usage. Criddle (1990) indicated that the monomers are more toxic than the polymers. Where limits have been placed on the level of monomer these are strictly controlled. In particular the level of arylamide is scrutinised where the maximum allowable content of free acrylamide is 0.025%, and the residue for drinking water is limited to 0.05ug/l. In Europe the level of monomer for PDADMAC is 0.5% and 2% in USA (BSI, 1998; NSF International, 2001). Recommended limits have also been set for regularly used commercial polymers in drinking water production by the National Sanitation Foundation. They are as follows: <20mg/l for ECH/DMA polymers, <1mg/l for PAM's, and <50mg/l for PADMAC.

Hamilton et al, (1994) maintained that aquatic organisms are not inclined to readily absorb the synthetic polymer and alterations to their toxicity may take place by key aquatic components. They also found that cationic polymers are noticeably more toxic to aquatic organisms than anionic and non-ionic polymers. Cationic polymers are also regarded as moderate to high toxicity. Cationic polymers are detrimental to fish because of mechanical gill blockage that causes suffocation (Biesinger and Stokes, 1986; Cary et al, 1987). If however solids such as clays are added to the receiving water this problem is greatly reduced as the sediments in the water absorb the cationic polyelectrolytes. Humic acids also affect the toxicity (Goodrick et al, 1991).

Timofeeva et al, (1994) found during their study that the toxicity of polymers is greatest for polymers of high charge density. This was observed during the study of the toxicity of CPAM's of various molecular weight and charge density towards daphnia and minnows. A greater toxicity was found in daphnia that were exposed to higher molecular weight polymers at low charge density, however concentrations of 0.2mg/l, which greatly exceeded the likely polymer concentration in the final product water, were found. Toxic level for minnows was found to be ten times higher. Narita et al, (2001) found in another study that cationic polymers drastically disturbed yeast cells at a dose of ca.70mg/l while non-ionic and anionic were not found to disturb them.

In a study undertaken by Takigami and Taniguchi (1998) looking into toxicity assays and their evaluation on organic flocculants, two different toxicity assays were identified *Closterium ehrenbergii* algal toxicity test and the *Bacillus subtilis* rec-assay. Investigations were made with and without the addition of a flocculant into the algal toxicity of the effluents from a pilot scale sewage treatment plant. Lethal effects in this study were mainly contributed by a polymer fraction of molecular weight greater than 100,000. However it is thought that the genotoxicity of the flocculants could be perhaps caused by a combination of effects of various components such as monomer, oligomers, and additives.

2.2. Non-polymer approaches

In recent years, considerable efforts have been made to explore the non-polymer approaches for sludge conditioning/treatment. These approaches may be studied for thriving the sludge conditioning research, rather than dealing with the concern of the potential polymer threat. From the literature, the non-polymer approaches include: (1) non-reagent approaches of freeze-thaw conditioning (Vesilind and Martel, 1990; Parker et al., 1998; Ormeci and Vesilind, 2001); microwave heating (Jones et al., 2002; Wojciechowska, 2005); ultra-sound conditioning (Yin et al., 2004), and (2) non-organic polymer approaches of sludge ozonation (Park et al., 2003) and Fenton's reagent conditioning (Fe^{2+}/H_2O_2) of wastewater treatment sludge

(Neyens et al., 2003; Buyukkamaci, 2004; Dewil et al., 2005).

Fenton's reaction (using reagent of Fe^{2+}/H_2O_2) as one of the advanced oxidation processes (AOPs) (Neyens and Baeyens, 2002) has long been employed in many areas. However, little has been found in conditioning of aluminum salt-flocculated drinking water treatment sludge (termed as alum sludge thereafter). In our previous study, the effectiveness and optimization of Fenton's reagent for an alum sludge conditioning was preliminarily investigated (Tony et al., 2008). The addition of Fe^{2+}/H_2O_2 led to a considerable improvement in the alum sludge dewaterability as evaluated by the CST (capillary suction time).

3. Alum Sludge Conditioning Using Fenton's and its Related Reagents

3.1. Alum sludge and Fenton & Fenton-like reagents

The alum sludge samples used in this study were taken from a water treatment plant in Southwest Dublin, Ireland where raw water from a local reservoir was coagulated with aluminum sulphate. The sludge had a suspended solids concentration of 2,850 mg/L. The capillary suction time (CST), specific resistance to filtration (SRF), pH, and Al content of the alum sludge were 67.5 s, 6.3×10^{11} m/kg, 5.7-6.0 and 194 mgAl/g sludge, respectively. Six dibasic salts ($FeCl_2 \cdot 4H_2O$, $FeSO_4 \cdot 7H_2O$, $ZnCl_2$, $CuSO_4 \cdot 5H_2O$, $MnCl_2 \cdot 4H_2O$ and $CoCl_2 \cdot 6H_2O$) and two ferric salts ($FeCl_3 \cdot 6H_2O$ and $Fe_2(SO_4)_3$) were used individually to make different metal solution in Fenton and Fenton-like reagents. Hydrogen peroxide in liquid form (30% by wt.) was obtained from a commercial supplier.

3.2. Experimental methods

The experimental investigation of the alum sludge conditioning was conducted in a standard jar-test apparatus. Initially metal solution was added to a series of 250 ml sludge samples, Fenton or Fenton-like reagent reaction was then initiated after adding hydrogen peroxide. Thereafter, the sludge was subjected to rapid mixing (for 30 second) and slow mixing (for 30 second) to generate reaction. This conditioning procedure, especially the reaction time, has been investigated previously for the time of reaction from 1 min to 4 hrs (Tony et al., 2008). The optimum doses of hydrogen peroxide and metal salt were also optimized previously on the response surface methodology (RSM), which is a collection of mathematical and statistical techniques for optimising purpose. According the previous study (Tony et al., 2008), the dosage of metal ions in Fenton and Fenton-like reagents of 20 mg/g DS (dry solids) and the dosage of H_2O_2 of 125 mg/g DS are applied in this study.

The CST of the sludge samples before and after various conditioning was measured by CST apparatus (Trition-WPRL, Type 130 CST). Dewaterability of the sludge under Fenton and Fenton-like conditioning is evaluated by the percentage reduction (*E*%) of CST via the following equation:

$$E(\%) = \frac{C_0 - C}{C_0} \times 100$$

where C_0 and C are, respectively, the CST of alum sludge before and after conditioning.

3.3. Results and discussion

Table 1 presents the results (in a manner of average data) of the alum sludge conditioned with Fenton and Fenton-like reagents. As can been seen in Table 1, a clear advantage of conditioning efficiency with Fenton reagent ($FeCl_2/H_2O_2$) was identified among all the Fenton and Fenton related reagents tested. $FeCl_3$ and $FeSO_4$ used with H_2O_2 also showed considerable improvement of sludge dewaterability. This may be due to the fact that they are useful coagulants in water purification. Testing of $FeCl_3$ and $FeSO_4$ alone without H_2O_2 for alum sludge conditioning showed that $FeCl_3$ do have the same function of combined use of it with H_2O_2 for CST reduction, but $FeSO_4$ did not.

Table 1 Results of an alum sludge conditioning with Fenton and Fenton related reagents

Reagent	Mean CST reduction (%)	Note
$FeCl_2$	47	Doses of Fe^{2+}, Co^{2+}, Cu^{2+}, Mn^{2+}, Zn^{2+}, Fe^{3+} are all at 20 mg/g-DS (dry solids). Dose of H_2O_2 is 125 mg/g-DS. Experiments were conducted at pH=6.0.
$FeCl_3$	38	
$FeSO_4$	37	
$CuSO_4$	11	
$CoCl_2$	7	
$MnCl_2$	7	
$Fe_2(SO_4)_3$	3	
$ZnCl_2$	1	

Also seen from table 1, the Cu, Co, and Mn salts can only bring about a quite similar CST reduction rate in a range of 7% to 11% when they are used as Fenton-like reagents, reflecting a marginal effect regarding sludge dewaterability improvement. However, the CST reduction rate obtained using Zn salt was 1%, indicating its ineffectiveness.

The reason of the difference in the abilities of the various transition metal salts in Fenton and Fenton-like reagents conditioning of alum sludge may be related to the different abilities of transition metals to react with oxygen in a variety of ways, due to the unpaired oxygen electrons (Mustranta and Viikari, 1993). The hydroxyl radicals formed is not enough to attack the sludge particles to form the new intermediates which is able to treat the sludge in order to enhance its filtration properties. However, for the iron ions, the produced hydroxyl radicals are much more sufficient than for the other transition metals. More significantly, our previous investigation (Tony et al., 2008) has demonstrated (by the molecular size distribution measurement of sludge samples before and after Fenton reagent conditioning) that the Fenton reaction degraded/broke the organics from large molecular sizes into smaller ones via highly reactive hydroxyl radicals. Thus improving sludge dewaterability through the release of both interstitial waters, which were trapped among organics, and adsorbed and chemically bound water by the degradation of organics.

It should be pointed out that the Fenton's reagent ($FeCl_2/H_2O_2$) cannot achieve the same level of CST reduction as that achieved by the polymers (data not shown), Thus, the application of the Fenton reagent for alum sludge conditioning as alternative conditioner lies in its advantage over polymer on environmental safety, rather than the efficiency regarding the CTS reduction. The study of using Fenton reagent/reaction for alum sludge conditioning as an alternative options to overcome unknown potential health related risk of polymer conditioning may provide a showcase of proactive treatment engineering. However, further investigation is obviously desirable, which includes the cost-effective analysis of the cost increase of equipment installation, operation and control process.

4. Conclusions

Fenton reagent (Fe^{2+}/H_2O_2) can be considered as an alternative option for alum sludge conditioning for the purpose of eliminating the perceived long term risk associated with polymer residual in the environment. From the results of this study, CST reduction of 47% can be achieved when Fenton reagent was used for an alum sludge conditioning. Obviously, it is not the same level regarding the CST reduction of using polymers. In addition, it should be noted that there may be some increase of cost associated with the Fenton's reagent due to its dual-reagent addition. Such costs may be related to cost increase of equipment installation, operation and control process. Full consideration and review should be conducted before any large application of such conditioning approach.

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