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REVIEW

Advances on Sludge Properties and Dewaterability with Chemical Conditioning

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Chemical conditioning of sludge dewatering has the advantages of simple operation, low investment cost and stable conditioning effect. It is the most commonly used pretreatment method. The components of sludge play an important role on sludge dewaterability and the choice of appropriate coagulants. The adoption of the coagulants contributes to the alteration of sludge characteristics and sludge dewaterability. The relationship between sludge components and chemical conditioning effects should be understood better to give lights to more appropriate selection of coagulants and the research of new coagulants. In this paper sludge properties including water distribution, sludge particle size distribution, the types and contents of metal ions and the fractions and structures of extracellular polymeric substances which would mostly affect sludge dewatering were reviewed as well as the chemical conditioning technologies and the methods' conditioning effects. Finally, the perspective of sludge properties research and chemical conditioning methods were discussed.

Keywords: Sludge dewatering, Sludge components, Chemical conditioning.

INTRODUCTION

In recent years industrialization and urbanization of the world were developed rapidly and the quality of people's life was improved fast. As a result, municipal and industrial sewage was discharged more than ever before. So the amount of sludge was becoming larger and larger. The improvement of the wastewater treatment degree would produce even more sludge. The volume of sludge accounts about 1-2 % of treated water but contains 50-80 % of pollutants including organic debris, bacterial cells, inorganic particles and colloidal. The operating cost of sludge treatment can be as much as 50 % of the whole wastewater treatment plant^{1,2}. The typically treating technology of sludge is gravitationally thickened and stabilized by anaerobic and aerobic digesters and then dewatering³. Dewatering is an unavoidable part of any kinds of sludge disposal methods as it can reduce the volume of sludge greatly, consequently, the cost of transporting and disposal⁴. The most commonly used method is mechanical dewatering which remove the moisture from sludge by pressure or centrifugal force. Mechanical dewatering efficiency isn't always desirable if it was disposed directly since wastewater sludge is a type of non-newtonian fluid because its shear rate changes with shear stress and there is no linear relation observed between shear rate and shear

stress⁵. The pretreatment or conditioning can enhance sludge dehydration and disinfection and promote the hydrolysis of the organic substances.

The methods involved in pretreatment of sludge include physical and chemical means. During which physical method is to change the structures and properties of sludge by energy or stress such as thermal pretreatment⁶, ultrasound conditioning⁴, microwave irradiation⁷ and electric field-assisted dewatering⁸⁻¹⁰. The utilization of these methods may lead to high dewatering potentials, but the limit factors such as increased sludge volume and high energy needed and high cost requirement for operation as well as the complexity of implementation imposed restrictions to the applications. Chemical conditioning methods aim to enlarge the floc size and to compress the floc interior to facilitate solid-liquid separation³ by the addition of inorganic flocculants or high molecular weight organic flocculants¹¹⁻¹³. The application of chemical conditioning has the advantages of simple operation, low investment cost and stable conditioning effect so it is commonly used in sludge mechanical dewatering pretreatment. The adoption of the coagulants contributes to the alteration of sludge characteristics and consequently, sludge dewaterability. The relationship between sludge components and chemical conditioning effects should be understood systematically to give lights to more appropriate selection of

coagulants and the research of new coagulants. In this paper sludge structural characteristics such as water distribution, the content of metal ions and the extracellular polymeric substances which would affect dewatering effect of sludge were reviewed as well as the chemical conditioning technologies.

Properties of sludge and chemical conditioning methods:

The moisture and particle size distribution are two important parameters of sludge. Sludge flocs are composed of microorganisms, debris, extracellular polymeric substances and inorganic cations¹⁴. These characteristics play a significant role in sludge dewaterability. However, it is not advised to separate them up when it is considering the optimum chemical conditioners and types. The dewatering performances of sludge are measured by capillary suction time and specific resistance to filtration.

Moisture distribution: There are four different types of water in sludge according to the different intensity and bonding force between sludge particles and water. These are the free water which is not bound to the particles, the interstitial water which is bound by capillary forces between the sludge flocs, the surface (or vicinal) water which is bound by adhesive forces and intracellular (or bound, hydration) water^{15,16}. The content of these four types of water varies for different types of sludge. The methods such as drying test, differential thermal analysis, differential scanning calorimetry, mechanical strain test and sorption isotherms¹⁷ involved in measuring the amount of sludge water may result in different water content¹⁸ and there is still no best-adapted method which could get a clear picture of the distribution of water within activated sludge. Results indicated chemical conditioning could increase the amount of free water when cationic polyelectrolytes or inorganic coagulants were added to the sludge^{19,20}. It was supposed due to the replacement of water molecules by the adsorbed coagulant and the reduction of water binding capacity to particle. The addition of chemical conditioner could accelerate the dewatering rate leading to a lower filter moisture content cake. Mechanical dewatering can only remove the free water of the sludge so a given kind of sludge should have the theoretical largest dewatering efficiency. And it is reasonable to assume that a model could be built to calculate the amount of chemical conditioners or the energy that would be needed for sludge dewatering if an effective measuring method was utilized¹⁶.

Sludge particle size distribution: Sludge particle size distribution especially the fine particles proportion is an important factors that affect sludge dewatering performance²¹. The additives of Fe salts, Al salts, acid or alkaline and polyelectrolytes were to overcome resistance between fine particles to form larger flocs. The strength of flocs formed by chemical conditioners is very important²². Because shear force increases turbidity and viscosity of sludge suspensions which means the ratio of fine particles is higher. The increase of fine particles ratio leads to the increase (in an exponential way)²³ of specific surface area of sludge particles and so as the resistance of sludge dewatering and filtration^{24,25}. As a result more chemical conditioners would be needed to decrease the proportion of sludge colloid particles and to improve sludge dewatering and filtration performance²⁶. In addition, higher solid content of sludge also leads to higher ratio of fine particles. So it is beneficial to decrease the degree of sludge thickening to

lower sludge solid content before sludge conditioning and dewatering.

Sludge cations and dewaterability: Cations play an important role in the formation or the deterioration of cation bridges with microorganisms²⁷. According to the divalent cation bridging theory the goal of chemical selection is to reduce the ratio of monovalent-to-divalent cations to improve sludge dewaterability has been developed for years²⁸. Excess monovalent cations led to the deterioration of both settling and dewatering ability of sludge. It was found that the concentration of potassium affected the concentration of readily extractable (slime) proteins in the floc and the proteins in the surrounding solution. An increase of potassium with low equivalent monovalent to divalent cation ratio improved the settling performances of sludge while the concentration of potassium beyond nutrient requirements deteriorated sludge dewatering properties²⁹. Similarly, the increase of sodium or ammonium led to the deterioration of activated-sludge settling performances³⁰. The floc structure was significantly weakened even the increase of the concentration of sodium and potassium ions was general correlated to the total extracellular polymeric substances concentration since monovalent cations were unable to bind the floc components together^{14,31}. The monovalent-to-divalent ratio should be lower than 2 for the record.

Divalent cations tended to retain the biopolymers in the floc and relative studies found that an increase in divalent cations concentration in the feed to the reactors was associated with an increase of the concentration of the bound biopolymers^{27,31}. Furthermore, divalent cations contributed to the floc formation of cation-polymer complexes which promoted sludge dewaterability and this was the most important mechanisms for sludge coagulation-flocculation^{27,32}. With the experiment results mentioned above it could safely come to the conclusion that the monovalent-to-divalent ratio was positively correlated to sludge dewatering properties and the ratio of two was about to reach an equivalent basis. When the monovalent-to-divalent was over 2 the deterioration of sludge occurred and it could be offset by the addition of divalent or trivalent cations³³. Higgins *et al.*³⁴ checked the divalent cation bridging theory on the pilot and full-scale activated sludge systems and the results fitted well with the divalent cation bridging theory.

Extracellular polymeric substances and sludge dewaterability: Extracellular polymeric substances are macromolecular organic polymers which attach to the microbial cell wall. The main sources of extracellular polymeric substances are microorganisms, the products of cellular lysis and hydrolysis of macromolecules and the adsorption of organic matters from wastewater³⁵. The major components of extracellular polymeric substances are carbohydrates and proteins which account about 70-80 % of total extracellular polymeric substances. Other components of extracellular polymeric substances whose content are relative lower are humic substances, lipids, nucleic acids and some inorganic components³⁶⁻³⁹. The contents or types of influent carbon sources, dissolved oxygen, pH, hydraulic retention time (HRT) and sludge loading influence the components percent of extracellular polymeric substances greatly and so as extraction methods^{36,40,41}.

The components of extracellular polymeric substances influence sludge dewaterability but according to different literatures the same component may have various effects. This may be due to the complex mechanisms of the process of dewatering. For instance, the hydrophilicity of extracellular polymeric substances depends on the content of proteins and carbohydrates since most amino acids are hydrophilic and carbohydrates contain a large percent of hydrophobic groups^{37,42}. Hydrophilicity is the driving force of microbe aggregation and it enhances the affinity between cells. Therefore, the higher percent of proteins leads to better dewaterability. But it was reported that proteins had high water-holding capacity, the reduced protein contents improved the sludge dewatering ability^{43,44}. And it was reported that the increasing polysaccharide in extracellular polymeric substances would enhance the sludge dewatering^{44,45}. Almost all sludge surfaces are negative charged because of protein, sulfate radicals, phosphate radicals and carboxyl group⁴⁶. As a result, cationic polyelectrolytes are widely applied in the pretreatment of sludge dewatering through neutralization and bridging mechanism⁴⁷⁻⁴⁹. More extracellular polymeric substances would increase the viscosity of the surrounding solution which would make sludge dewatering more difficult.

The study of the structure of extracellular polymeric substances is relative less important since it was pointed out that the fractions of extracellular polymeric substances in sludge was the more important parameter with respect to sludge structure⁵⁰. The forms of extracellular polymeric substances can be divided into bound extracellular polymeric substances and soluble extracellular polymeric substances which affect the microbial activity and surface characteristics of sludge⁵¹. Commonly, a two-layer model is used to illustrate the structure of bound extracellular polymeric substances. The tightly bound extracellular polymeric substances are the inner layer part and clearly have a certain shape and are stably and tightly bound with the cell surface. The loosely bound extracellular polymeric substances are the outer layer and are loose and dispersible slime layer without an obvious edge^{52,53}. The total concentration of extracellular polymeric substances has no obvious correlation with sludge dewatering performance⁵⁴⁻⁵⁶. The content of tightly bound extracellular polymeric substances is higher than loosely bound extracellular polymeric substances but the later influence sludge dewaterability more remarkably⁵⁷. Because the loosely bound extracellular polymeric substances are rheological and can increase the volume of sludge flocs thereby weakening sludge compression and dewatering performance⁵⁵. It was analyzed that the increase of loosely bound extracellular polymeric substances made a contribution to the increase of interstitial water content, the enlargement of

sludge floc size and the risen of surface zeta potential which increased electrostatic repulsion between sludge flocs^{58,59}.

On this discussion, it is concluded that lower extracellular polymeric substances cannot enhance agglomeration of flocs while excessive extracellular polymeric substances lead to the deterioration of sludge dewaterability. There is an optimum concentration of extracellular polymeric substances where sludge exhibit maximum dewaterability. Houghton *et al.*⁶⁰ examined that raw sludge was 20 mg extracellular polymeric substances/g suspended substance; activated sludge was 35 mg extracellular polymeric substances/g suspended substance; digested sludge was 10 mg extracellular polymeric substances/g suspended substance.

Chemical conditioning methods: The addition of coagulants leads to the alteration of suspended colloids chemical components and physical structure of sludge. As a result, the colloidal structure is destructed and the resistance between particles is lowered. With the help of stir cations, some extracellular polymeric substances of sludge and coagulants aggregate together to form flocs and settled down⁶¹⁻⁶³. At the same time, the surface area of colloids and sludge water distribution is changed thereby enhancing sludge dewaterability. The mechanism theories of chemical conditioning are compressing electrical doubles layers, sweeping, charge neutralization and bridging^{64,65}. The former two is often for inorganic coagulant while the other two is for organic coagulant. The metal salts hydrolyze rapidly to form various positive species, these ions swarm into the adsorbed and even diffusion layer. The diffusion layer becomes thinner which means the resistance between colloids is smaller and flocculation is easily to occur. At low coagulant dosages, compressing electrical doubles layers is a possible mechanism. And when a metal salt is added to water at a concentration sufficiently high enough to cause precipitation of amorphous metal hydroxide, particles can be enmeshed in these precipitates. This is called sweep flocculation. The charge neutralization is that cationic polyelectrolytes neutralize negative colloids particles to form large flocs. Destabilization by bridging occurs when segments of a polymer chain absorb lots of particles, thereby linking these particles together. One obvious advantage of bridging is that the flocs produced can be stronger than those formed when particles are destabilized by simple salts⁶⁶.

The flocculants applied in sludge conditioning include inorganic, organic (natural and synthesized flocculants) and microbial flocculants. The characteristics and references of them are shown in Table-1.

The single flocculant alone may not produce strong flocs or ideal dewatering effect. As a result dual or even ternary flocculants system was researched. It was reported that

TABLE-1
TYPES AND CHARACTERISTICS OF FLOCCULANTS FOR DEWATERING

Types	Characteristics	References
Inorganic flocculants	Rarely used, high dosage, limited application conditions	67-70
Natural organic-based flocculants	Potential widely applications, biodegradable, low dosage, undeveloped manufacture technology	47, 71-73
Synthesized organic flocculants	Widely used, low cost, low dosage, controllable molecular weight, good dewatering performance, potential health risks	11, 12, 48, 49, 74
Microbial flocculants	Not used, complex synthesize process, high cost, biodegradable	75-77

surfactant and cationic flocculant could result in stronger flocs. The mechanism was that the addition of surfactant altered the hydrophobicity of colloids to hydrophilicity. Then particles were more easily to aggregate together and the cationic polymers can enhance dewatering by charge neutralization and bridging more effectively⁹. The other methods include: cationic polymer followed non-ionic polymer⁷⁸, inorganic flocculant or cationic polymer followed by anionic polymer⁷⁹. It was found dual polymer conditioning generated flocs with enhanced strength. Because cationic polymer or inorganic flocculant aggregated fine particles through charge neutralization or compressing electrical double layers and then non-ionic or anionic polymers bridged flocs generated with long molecule chains. Physical conditioners such as minerals, carbonaceous materials have been used with chemical conditioners. These materials, acting as skeleton builders, are able to enhance sludge dewaterability and cake properties by adding more rigid and incompressible structures to the sludge solids providing water passages^{80,81}.

Perspectives: Future work should be focus on the quantitative relationship between the chemical fractions and physical characteristics, sludge dewatering performance and physical properties, conditioning treatment and physical characteristic of sludge. As mentioned above, a model could be established to obtain the optimum flocculants dosage and even mechanical operating parameters with the known sludge indicators.

The standard test methods of the indicators of sludge properties should be established. We still cannot test the exact content of the four types of moisture distribution of sludge. And the extraction and identification methods of extracellular polymeric substances also have different methods and results.

Chemical conditioners biological and environmental hazardous effects should be more studied as the influences may be long-term insidious. Therefore, natural organic-based and microbial flocculants need to research more. And the manufacturing technologies need to develop as they are biodegradable and eco-friendly. The research directions of cationic polyacrylamide should be focused on lowering residual monomers, increasing molecular weight and researching micro-block cationic structures which can enhance charge neutralization.

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