새롭게 기능화된 키토산 유도체에 의한 하수슬러지의 탈수에 관한 연구

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Dewatering of Sewage Sludge by Novel Functionalized Chitosan Derivatives

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INTRODUCTION

Sludges are dispersions of solid waste particles in water and constitute an important class of waste products. A characteristic feature of different types of sludges is the very high water content, with only 1- 5% solids on a mass basis. Conventional techniques for dewatering are based on application of mechanical forces. Sludge conditioning is a topic of considerable interest and provides timely focus around the world with increasing strict requirements for sludge application to land and the high costs of landfill. A number of references are known in the literature regarding the conditioning and dewatering of sewage sludges[1-5].

Both inorganic and organic reagents have been used for sludge conditioning. However, use of inorganic conditioning chemicals increase not only the sludge mass by 15-30% but also reduces the fuel value of the sludge for incineration[3]. As a result, high molecular-weight polymeric materials have been widely accepted in the flocculation of suspended particles in sludge dewatering and water treatment[6].

Sakohara and Nishikawa[7] have recently proposed the use of thermosensitive polymersfor effective flocculation of sludges. Thermosensitive polymers in aqueous solutions become soluble (hydrophilic) at low temperatures and insoluble (hydrophobic) at high temperatures. This hydrophilic/hydrophobic transition is reversible and occurs at the transition temperature, which is determined by a primary structure of polymer. Poly(*N*-isopropylacrylamide) (poly(NIPAM) is a representative nonionic thermosensitive polymer with a transition temperature of about 32 $^{\circ}$C.

Carbohydrate based polymers represent a versatile class of polymers that provide the scientists with a broad spectrum of raw materials that exhibit biodegradability, biocompatibility, and versatility. These polymers can be exploited in the dewatering of sludges that will biodegrade and pose no threat to the environment after their use. It is curious to note that chitosan, a non-toxic and environmentally friendly polymer obtained from the native polymer chitin, by fully or partially *N*-deacetylation, has not merited special attention of the scientific community as promising alternative. It is important to note that chitin is second to cellulose most abundant polysaccharide found in nature[8-16]. In continuation of the ongoing research activities at KIER using sludge-coal-oil co-agglomeration, we wish to report the preparation, characterization and evaluation of the novel and modified chitosan derivatives vis-a –vis cationic polyacrylamide polymers in achieving the titled goal.

EXPERIMENTAL

Commercially available chitosan was used for the preparation of water soluble precursors. Reagent grade succinic anhydride (Kanto Chemicals), pyridine(Samcuun Chemicals), acetic acid and hydrochloric acid (Daejung Chemicals), D_2O and CD_3COOD were purchased from Fluka-Aldrich and were used without further purification. The degree of deacetylation was determined by proton NMR spectrometry with a Jeol 400 MHz spectrometer in D_2O/d^4-CD_3COOD.

The oil-coal agglomeration (A) was carried out by vigorously stirring coal:oil (4:1) in 300ml of water at 7000rpm for 10 minutes. The amount of coal is four times the concentration of the suspended solid (SS) in the sewage sludge whereas the amount of oil is 25% of the coal amount. The

polymer solution was made by dissolving (0.1 - 0.5g) of the appropriate chitosan in 100ml of distilled water containing few drops of acetic acid/hydrochloric acid.100ml of the sludge with an equal amount of water was stirred with 18g of the polymer solution (B) initially at 800 rpm for 5 minutes followed by additional stirring at 300 rpm for 10minutes.

The oil-coal agglomerate (A) was mechanically stirred at 300 rpm for 5 minutes after mixing with the sludge-polymer solution (B) .The contents of the mixture were filtered in a sieve. The collected mass on the sieve was dried in the oven at 38^OC for 24 hours. A portion of the oven dried residue (1 mg) was heated to 850 ^{0}C for 2hours and 30 minutes. The ash contents were analyzed. The filtrate collected water was subjected to COD measurements.

Preparation of Chitosan Succinate

Chitosan (1.00 g, corresponding to approximately 6.20 mmols glucosamine) was dissolved in HCl aqueous solution (0.37%, 50 ml) at ambient temperature, and a solution of succinic anhydride (6.25 mmol; 0.63 g,) in pyridine (5 ml) was added dropwise with vigorous stirring. The reaction pH was maintained at 7.0 by the dropwise addition of NaOH solution (1.0 M). NaOH addition was continued till the pH was stabilized. After 40 min the reaction was terminated by the addition of NaCl aqueous solution (20%, 200 ml). The resulting precipitate was filtered, washed with acetone and diethyl ether, and desiccated to give chitosan succinate conjugates and was characterized through spectroscopic techniques.

RESULTS AND DISCUSSION

Dewatering reduces the water content in the sludge. A number of studies have shown that the ability of dewatering to reduce the water content is dependent on the specific dewatering process and the nature of the sludge. Removal of additional water by changing the properties of the sludge reduces substantially the cost and make the process economically viable.

It is well known that the flocculation of suspended solids using polymeric materials occurs by the bridging of the suspended solids through the polymer molecules. However, the resulting flocs are usually bulky and are associated with a large amount of water. This is primarily due to the hydrophilicity of the solid surface and the polymer molecules. It has proved difficult to remove this large amount of water effectively by conventional mechanical dewatering methods.

Kang and Shin[6] have attempted co-agglomeration of municipal sewage sludge with a mixture of oil and coal in order to remove heavy metals and ash from agglomerates and significantly lower water contents of agglomerates. Surface property of sewage sludge was controlled with surface control agents. Agglomerates of sewage sludge and oil-coal mixture of sludge-oil-coal-agglomerates (SOCA) possess less than 60% water. As a result, it can be processed mechanically for enlargement of the SOCA particles. It is expected that the relatively low water content in the SOCA could be achieved by removal of internal water in coal particles as well as water on the SOCA surface. The scheme for the process is as shown in Figure 1.

Coagulation has commonly been used to remove turbidity typically in drinking water and natural organic matter (NOM). Inorganic coagulants widely used are aluminium and iron salts. Since release of metals in the effluent concern is a matter of concern with particular regard to aluminium, which may induce Alzheimer disease as well as have other carcinogenic properties, the use of natural organic coagulants may be an interesting alternative.

Chitosan, a linear cationic polymer of high molecular weight, obtained by deacetylation of chitin has recently been proposed for applications in drinking water treatment. Although the polymer backbone consists of hydrophilic functional groups and is hydrophobic in nature, chitosan is normally insoluble in water and most common organic solvents (e.g. DMSO, DMF, NMP, organic alcohols, pyridine). The insolubility of chitosan in aqueous and organic solvents is a result of its crystalline structure, which is attributed to extensive intra-molecular and inter-molecular hydrogen bonding between the chains and sheets, respectively.
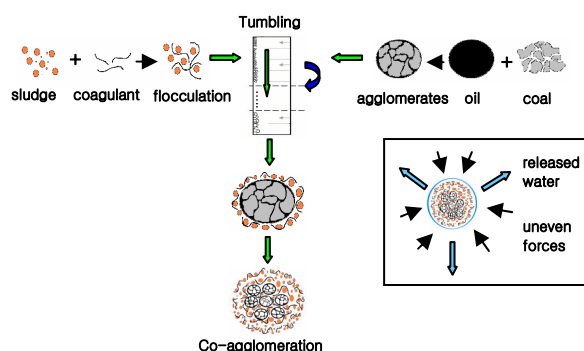
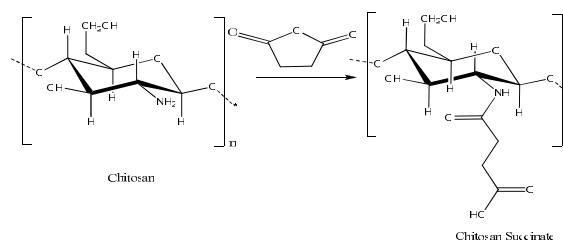Figure 1. The scheme for the SOCA production process.

Figure 2. The reaction of chitosan with succinic anhydride.

Chitosan is virtually insoluble in water under normal conditions but it can be dissolved in carboxylic acid solutions such as acetic acid (AA). However, this solvent can increase the organic content of the coagulated solution. Hydrochloric acid (HCl) was used as an alternative solvent to acetic acid in order to evaluate the coagulation capacity of HCl-prepared chitosan.

A very well known naturally occurring copolymer composed of monosaccharides that have amino groups in the non-anomeric position is chitosan. It is a widely investigated copolymer whose monomeric units are made of 2-amino-2-deoxy-D-glucopyranose and residual 2- acetamido-2-deoxy-D-glucopyranose units. Like cellulose, the monomeric units are linked by *β*-glycosidic linkages, and the configuration of the anomeric carbon atoms in chitosan makes the polymer chains essentially linear.

A few attempts have been made to enhance solubility of chitosan by modifying the molecular structure of chitosan by introduction of groups such as carboxymethyl, dihydroxyethyl, sulfuryl, or phosphoryl[12-14] that can serve as precursors or standard intermediates for useful further application of the polymer. Recently, chemical modification of chitosan with methyl acrylate or DAC-50 with ethyl acrylate by Michael reaction has been reported.

The amino acid of the naturally occurring polymer chitosan was made to react with succinic anhydride in an effort to prepare a precursor that should be soluble in water over a wide pH range (see Figure 2). It was found that the prepared chitosan derivatives were fairly soluble at different pH (3, 7 and 10) values. The results on solubilities are in agreement due to the increasing substitution of the amino groups of chitosan by carboxylic groups.

A representative ^{1}H NMR spectrum of chitosan is discussed. The internal standard used for assigning the chemical shifts of the protons was D_2O/d^4-CD_3COOD. The chemical shift of the internal standard appears at 4.65 ppm. Three peaks could be assigned unambiguously. The chemical shift of the acetal proton (-C**H**) of the glucosamine overlaps with the chemical shift of the internal standard and shows most downfied at 4.58 ppm. The -C**H**-NH_2 proton appears at 3.03 ppm. The -C**H**-OH, HOHC-C**H**-CHCH$_2$-, and -C**H$_2$**-OH protons overlap and are assigned to the chemical shift at 3.76 ppm. The chemical shifts of -C**H**-CH$_2$ and - C**H$_2$**-OH appear at 3.58 ppm. The proton, -NHCO-C**H$_3$** appearing at 1.93 ppm is that of the carbon bearing the acetamido group. Succinic anhydride derivative of chitosan displayed additional four protons corresponding to –CH$_2$-CH$_2$- group at 2.46 ppm as a multiplet attached to the –NH group of glucosamine.

The infrared spectrum of chitosan shows the C=O absorption at 1647 cm^{-1} whereas the N-H bend of the amide occurs at 1585 cm^{-1}. The N-H stretch of the amide at 3100 cm^{-1}, overlaps with the amino N-H absorption. Carbonyl absorptions generally appear at higher frequencies around 1700 cm^{-1}. However, this lowering of frequency of the C=O absorption can be explained in terms of the "back donating" effect of the unpaired electrons on the nitrogen, which conjugates with the carbonyl group. This results in an increased single bond character between the carbon and the oxygen and a lowering of the C=O absorption frequency. The aliphatic C-H stretch occurs at 2870 cm^{-1}. The absorption appearing at the frequency of 1025 cm^{-1} corresponds to the C-O group. Infrared spectrum of the

succinic anhydride derivative showedintense absorption band at 1642 cm^{-1} overlapping with the C=O of the acid. The NH bending was observed at 1554 cm^{-1} and the shifting of the NH bend to a lower frequency indicates the formation of *N*-acyl bond .The appearance of a new band at 2880 cm^{-1} corresponds to the aliphatic methylene CH stretch.

Several formulations of the sludge (*p*H 7.5-7.7 and conc.1.5-1.7 %). with varying degree of deacetylated chitosan dissolved in acetic/hydrochloric acid, in different concentrations (0.1-0.5%) were studied. The surface-conditioned sludge is mixed with coal- oil agglomerates that act as a bridging agent to form co-agglomerates of hydrocarbon in the form of small spheres, thereby dewatering the sludge. The sludge-coal-oil agglomerates are formed when the fine oil particles cover the surface of the lipophilic and hydrophobic sludge. This formation of small and hard sludge-oil agglomerates reduces the amount of water bound to the surface of sludge, and facilitates selective separation of the agglomerates from un-agglomerated materials, such as metals and ash components.

Three types of oils viz., Bunker A, Bunker B and Chicken oil were used for the agglomeration studies. The results obtained with chitosan derivatives were comparable with the use of cationic polyacrylamide polymers used in the studies for dewatering the sludges. However, improved results with the modified chitosan derivatives are anticipated. Detailed studies are in the pipeline and will be communicated at a later stage.

CONCLUSION

Modified water soluble chitosan derivatives are being searched as effective flocculants for municipal sewage sludges that will co-agglomerate with a mixture of oil and coal to lower the water content of agglomerates significantly. The improved agglomeration and dewatering will ensure the usefulness of the dewatered sludge as a clean fuel.

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