Conference paper

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An environmental application of functionalized chitosan: enhancement of the separation of the solid and liquid fractions of digestate from anaerobic digestion

DOI 10.1515/pac-2016-0705

Abstract: A high molecular weight chitosan was chemically modified to quantitatively incorporate quaternary ammonium groups. Its efficiency was evaluated in the liquid-solid separation for various liquors, and compared with the one of a polyelectrolyte usually used for this utilization. The performance of the liquid-solid separation was estimated through the determination of two parameters measured after the screening- settling of the mixture liquor/flocculating agent: the separation efficiency (EV) and the TS removal efficiency (ETS). Apart for liquor 6, TS removal was always better after an addition of functionalized chitosan. Furthermore, whatever the type of liquor, the distribution was modified by an increased presence of high-size particles when functionalized chitosan was added. Moreover, chitosan addition tended to homogenize the size of the particles, which could facilitate the choice of the liquid-solid separation process. This homogenization was particularly observed for the liquor initially highly dispersed in size, i.e. liquors 1, 4, 6 and 8.

Keywords: chitosan; digestate; flocculent; methanisation; POC-16.

Introduction

Chitosan is the fully or partially deacetylated form of chitin [1] the second most abundant natural polysaccharide derived from exoskeletons of crustaceans and also cell walls of fungi and insects [2]. With the poly(lysine), chitosan is one of the very few polymer from a natural origin which has primary amino groups along its backbone. This low-cost biopolymer possesses very interesting properties, for instance it is known to be biocompatible [3], biodegradable in the human body [4], non-toxic [5] and antibacterial [6]. Interest in chitosan materials is quite recent compared to cellulose, which has an age-long exploita-

Article note: A collection of invited papers based on presentations at the 16th International Conference on Polymers and Organic Chemistry (POC-16), Hersonissos (near Heraklion), Crete, Greece, 13 – 16 June 2016.

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tion history. Therefore, chitosan is one of the most promising materials derived from renewable resources and is currently explored very intensively [7]. In the last decades unmodified chitosan has been widely used in a variety of applications: for example as wound dressing [8], in tissue engineering [9], cosmetics [10], food [11] or textile industry [12]. Chemical modification of chitosan is also of primary interest in order to design new properties. Thus, chitosan functionalization is currently being explored intensively and could lead to new high-potential materials with advanced and high value-added applications [13, 14]. Specific groups can also be introduced to achieve original chitosan derivatives with new physicochemical properties and improved performances for selected applications. For instance, we have recently reported [15] the phosphorylation of chitosan oligomers by the Kabachnik-Fields reaction in order to chemically graft phosphonate moieties onto the chitosan primary amines. Such functionalized chitosan could be further used as flame retardant additive or even as anti-corrosive coating for metallic substrates. Another example is a new versatile functionalization method of chitosan through a two-step reaction [16]. In the first step, chitosan was partially functionalized with allyl glycidyl ether. In the second step, allylated oligochitosan was modified using thiol-ene radical coupling with 4,4'-Azobis(4-cyanovaleric acid) (ACVA) as a free radical initiator. Interestingly, the thiol-ene addition of water-soluble ω -functional mercaptans resulted in a library of novel functional chitosans, which could be particularly promising for the synthesis of zwitterions, polyelectrolytes, or amphiphilic block copolymers. Noteworthy, the first functionalizing step is based on the epoxy-amine reaction occurring in water at room temperature. In this paper, we have investigated this reaction onto chitosan by using glycidyl trimethylammonium chloride. The resulting functionalized chitosan (CHF), bearing quaternary ammonium salt, was used for an environmental application, i.e. for the enhancement of the separation of the solid and liquid fractions of digestate from anaerobic digestion (AD). Anaerobic digestion is a well-established biological process for the treatment of various types of organic feedstocks, as food waste, municipal solid waste, sewage sludge, fats, oils and grease. This treatment process is expected to grow significantly in the near future because it presents several economic and environmental advantages [17]; actually, anaerobic digestion guarantees efficient waste treatment, leading to production of methane-rich biogas, a renewable energy source that can be turned into electricity and heat, and solid and liquid nutrient-rich fertilizers, coming from the digestate. The digestate, produced by usual wet anaerobic digestion systems, is in a slurry form that is separated to produce liquid and solid fractions. This separation is usually based on mechanical dewatering (screw press, belt press, centrifugation, filtration, settling...) in one or several steps, and reduces the volume of digestate for subsequent storage, transport off site, and improves the feasibility of land application. Liquid fraction of the digestate, commonly referred to as liquor, contains a diverse range of nutrients (ammonium, potassium...) and can be used as a liquid fertilizer; for such applications, liquor needs to be fine-filtered to prevent blockage of feeder pipes or irrigation systems. The liquor generated by the dewatering process can be also discharged to the public sewer or recycled for feed processing, with the objective to dilute the feedstock; however, to be discharged or reused, the liquor requires also complementary treatment, involving the removal of solids and nutrients.

Therefore, in order to achieve an efficient solids capture during the dewatering stages to allow a relevant liquor valorization, flocculating agents are commonly used to improve the solid and liquid separation [18–20]. These agents are typically synthesized from organic, macromolecular, water-soluble polyelectrolytes; they are generally positively charged to promote bonds with liquid digestate macroscopic and colloidal particles, negatively charged.

In this study, we investigated the possibility of using functionalised chitosan (CHF) as flocculating agent for the enhancement of the solid-liquid separation of AD digestate. The efficiency of CHF addition was estimated through the modification of the digestate particle size distribution, as well as the facilitation of the phase separation. Different liquors from different full-scale anaerobic digester plants were investigated with the objective to test the effect of CHF addition on a broad spectrum of AD digestates. The efficiency of the functionalized chitosan addition was compared to that of a commercial polyelectrolyte commonly employed for this type of application.

Experimental part

Reagents

Chitosan (“652”, shrimp shell origin, degree of deacetylation: 90 %) was purchased from France Chitine. Glycidyltrimethylammonium chloride (GTMAC) was purchased from Sigma-Aldrich.

The polyelectrolyte (P) used for comparison was a cationic organic polyelectrolyte, based on polyacrylamide. This high molecular weight polymer was a water-soluble flocculating agent obtained from copolymerization of acrylamide with various cationic monomers (confidential data). This polymer was available in liquid emulsion.

Synthesis of chitosan carrying ammonium chloride groups

Chitosan (10.2 g–0.063 mol) was dispersed in 250 mL of distilled water. GTMAC (28.2 g–0.184 mol) was added in three portions, and the mixture was stirred for 24 h at 85 °C. Functionalized chitosan was precipitated in isopropanol and dry under vacuum at 40 °C overnight.

¹H-NMR (400 MHz, δ , ppm): 2.1 (H11), 2.4 (H7), 2.7 (H2), 2.8 (H9), 3.1 (H10), 3.3–4.2 (H3, 4, 5, 6), 4.4 (H8) and 4.6 (H1).

Characterizations

Chemical structures of the prepared compounds were determined by ¹H-NMR spectroscopy in a Bruker Avance 400 MHz spectrometer at room temperature in D₂O solutions. External reference was tetramethylsilane (TMS) for ¹H-NMR. Shifts are given in ppm. The molecular weights of chitosan were analyzed by size exclusion chromatography GPC 50 (Varian) with Shodex SB 804 SBHQ column at 25 °C in an aqueous acetic acid eluent ([CH₃COOH] = 0.5 mol/L; [CH₃COONa] = 0.2 mol/L; [LiBr] = 0.1 %w; 200 ppm of NaN₃). Molecular weights were obtained using a pullulan calibration.

Liquor origin

8 digestate liquors (named 1–8) were sampled from 8 different full-scale anaerobic digestors operated in mesophilic condition with different types of feedstocks (Table 1); the liquors were issued from screw presses, except for the digestate liquors 2 and 3, extracted from a drum filter and a centrifuge, respectively.

Table 1: Digestate liquor origin.

Digestate liquor	Feedstock nature	Digestate post-treatment technology	TS g·L ⁻¹	TSS g·L ⁻¹	TSS/TS %
1	Manure	Screw press	72 ± 1	42 ± 2	58
2	Manure + food waste	Drum filter	52 ± 1	30 ± 1	58
3	Manure + crops	Centrifuge	13 ± 1	3 ± 1	23
4	Livestock manure	Screw press	73 ± 1	56 ± 2	77
5	Household waste	Screw press	21 ± 1	3 ± 1	14
6	Food waste + cereal residues	Screw press	40 ± 1	18 ± 1	45
7	Food waste + crops + sewage sludge	Screw press	60 ± 1	56 ± 2	93
8	Agricultural residues	Screw press	95 ± 1	16 ± 2	17

Liquor characterization

Particle size distribution

The particle size distribution was determined by LASER diffraction using a Malvern Mastersizer (Master-sizer 3000, Malvern Instruments Limited, UK); this particle size analyzer provided particle size distributions from 0.01 μm to 3500 μm . The values 1.73 and 1.33 were used for the refractive indexes of cloud particles and dispersion phase, respectively, and 0.1 was used for the absorption index of cloud particles. Samples were introduced into the volume presentation unit, which already contained deionized water (obscuration of 42 %). In this unit, the diluted sample was stirred at 1500 rpm and pumped through the optical cell; in these experimental conditions, particle size distribution was verified to be not affected by stirring and pumping. Due to the polydispersity of the liquor particles and to the importance of the specific surface in flocculation mechanism, the Sauter mean diameter, expressed as SMD, was calculated. The surface area mean diameter is commonly defined as the diameter of a sphere that has the same volume/surface area ratio as the set of particles; it is widely used in the characterization of dispersions because it links the area of the dispersed phase to its volume and hence to mass transfers and chemical interactions with the surrounding environment.

Total solids (TS) content

A well-mixed sample is evaporated in a weighed dish and dried to constant weight in an oven at 103–105 °C. The increase in weight over that of the empty dish represents the total solids. Total solids include total suspended solids and total dissolved solids (Method 2540 B [21]).

Total suspended solids (TSS) content

A well-mixed sample is filtered through a weighed standard glass-fiber filter (1.2 μm) and the residue retained on the filter is dried to a constant weight at 103–105 °C. The increase in weight of the filter represents the total suspended solids (Method 2540 D [21]).

Experimental procedure for the treatment of liquor

The (P) emulsion polymers should be pre-diluted in tap water before use. The functionalized chitosan was in the dry form; solutions were prepared in tap water of the dry product to obtain the applied concentration.

The test working conditions were given in Table 2; the choice of the concentration range (expressed in mg per g of liquor total solids) was assessed by the supplier for the P agent and by preliminary flocculation tests for the functionalized chitosan.

Table 2: Test working conditions.

Tests	Temperature	PH	Flocculating agent	Concentration mg/gTS
T1	23 ± 2	7.9 ± 0.3	(CHF)	25
T2				50
T3				100
T4	23 ± 2	7.9 ± 0.3	(P)	5
T5				10
T6				20

The prepared P and CHF solutions were respectively mixed with 300 mL of liquor using the methodology of Rico et al. [22]. This method (pouring method) was used, preferentially to the jar test method, due to the high solids concentration and the viscosity of the liquor. The mixture, composed of the flocculating solution and the liquor sample, was passed successively from one beaker to the other. After 10 transfers, optimal and achieved flocculation was verified and the mixture particle size distribution was measured.

Then liquid and solid fractions were pre-separated using a 125 μm screen, collecting the large flocculated solid fraction and the liquid fraction separately; this liquid fraction was then allowed to settle for 2 h (Fig. 1). The volume of the supernatant, as well as its total solids content, was measured.

The mixing and solid separation strategies are presented in Fig. 1.

Results and discussion

Synthesis of chitosan carrying quaternary ammonium salt

The commercial chitosan was analyzed by GPC in aqueous media to determine its average molar mass, and a value of 135 000 g/mol as M_w with pullulan standards (Fig. 2).

Reaction of chitosan with epoxy functions results in nucleophilic substitution and opening of epoxy ring. Illy et al. [15] have characterized the better reactivity of amine with epoxy groups compared to others nucleophilic centers as hydroxyl group. The chitosan with quaternary ammonium salt was prepared by reacting chitosan with GTMAC in neutral conditions according to Loubaki et al. [23] (Scheme 1). After 24 h and a three-fold excess of GTMAC, the reaction was quantitative at 85 °C. The structure of modified chitosan was confirmed using ^1H NMR recorded in deuterium oxide (Fig. 3). The most important signal at 3.1 ppm was attributed to methyl ammonium. The integrations of H8, H2-9 and H7 signals, 0.96, 2.94 and 2.0, respectively, allowed confirming a complete conversion. Lastly, the integration of acetyl proton (H11) gave the acetylation ratio of modified chitosan around 7–8 %. In conclusion the amount of quaternary ammonium on chitosan was 92 %.

Fig. 1: Mixing and solid separation strategies.

Fig. 2: GPC chromatogram of chitosan before chemical modification.

Scheme 1: Synthesis of chitosan with quaternary ammonium salt.

Fig. 3: ^1H NMR spectrum of chitosan with quaternary ammonium salt in D_2O solvent.

Liquor characterization

Solids content

Table 1 presents, for each tested liquor, TS and TSS contents, as well as the ratio TSS/TS. Liquors 1, 4, 7 and 8 were considered as high TS content-liquors; the liquor 8 presented the specificity to show low TSS, while a

great majority of TS of the liquor 7 was constituted of suspended solids. The liquor 3 and 5 were considered as low-TS content liquors with a relatively low part of TSS (around 20 % of the TS).

The solids present in the liquor are composed of suspended particles ($> 1.2 \mu\text{m}$) but also of coarse colloids (from $1.2 \mu\text{m}$ to $0.45 \mu\text{m}$), of fine colloids (from $0.45 \mu\text{m}$ to 1 kDa) and of dissolved matter ($< 1 \text{ kDa}$) [24]. The estimation of the TSS made it possible to quantify the solid particles with size higher than $1.2 \mu\text{m}$; the ratio between TSS and TS contents allowed identifying the share of the suspended solids to the total solids in the liquor samples. In our study, this identification revealed that the liquors tested differed not only in the solids content but also in the size of these solids. This solids diversity in the liquor samples, certainly related to the different nature of the feedstocks [25], was interesting for estimating the CHF ability to flocculate a large variety of solids from the liquors.

Impact of functionalized chitosan (CHF) and polyelectrolyte (P) addition on granulometric distribution and Sauter diameter of digestate liquors

Figure 4 presents the size distribution of the liquor particles; according to the particle size analyzer ability, only suspended particles and some colloids (with size higher to $0.01 \mu\text{m}$) could be significantly observed.

The particle size distributions of the liquors 1, 4, 6 and 8 were relatively close to each other; the large spread distributions revealed a polydispersity in size of these liquors. If the polydispersity of the liquors 2, 3, 5 and 7 was also observed, bimodal distributions were obtained, demonstrating the presence of two significant fractions of particles in these liquors.

The influence of functionalized chitosan and polyelectrolyte addition on liquor particle size distribution is presented in Figs. 5 and 6.

The results demonstrated that the addition of P could be totally inefficient in terms of particle aggregation with some of the liquors (liquors 4 and 8). The addition of P, however, tended to modify the size

Fig. 4: Granulometric distribution of liquors 1–8.

Fig. 5: Granulometric distribution of liquors 1, 4, 6 and 8, in Test 1–6.

distribution of the other liquors, promoting aggregation; nonetheless a relative polydispersity was generally maintained despite this aggregation.

The addition of CHF was globally more efficient in terms of size distribution modification. Indeed, whatever the type of liquor, the distribution was modified by an increased presence of high-size particles. Moreover, CHF addition tended to homogenize the size of the particles, which could facilitate the choice of the liquid-solid separation process. This homogenization was particularly observed for the liquor initially highly dispersed in size, i.e. liquors 1, 4, 6 and 8.

Fig. 6: Granulometric distribution of liquors 2, 3, 5 and 7, in Test 1–6.

It should be mentioned that the concentration of polyelectrolyte or functionalized chitosan added to the liquor, in the tested range, had no significant influence on the obtained results. Thus, in the following discussions about the effect of flocculating agent addition, an average of the data obtained in different concentration conditions was considered.

Figure 7 presents the SMD before and after addition of the flocculating agents. Except for liquor 7, functionalized chitosan addition resulted in larger SMD than polyelectrolyte (P) addition.

Fig. 7: SMD before and after addition of the flocculating agents.

This overall size measurement confirmed that CHF addition could promote bonds with liquor macroscopic and colloidal particles, which could result in an efficient flocculation and thus in an optimal liquid-solid separation.

Impact of functionalized chitosan (CHF) and polyelectrolyte (P) addition on liquid-solid separation of digestate liquors

The performance of the liquid-solid separation was estimated through the determination of two parameters measured after the screening- settling of the mixture liquor/flocculating agent:

- (i) the separation efficiency (EV), corresponding to the ratio of the supernatant volume obtained after the mixture screening-settling on the initial mixture volume,
- (ii) the TS removal efficiency (ETS), corresponding to the ratio of the removed TS (i.e. TS of the mixture minus TS of the supernatant) on the TS of the mixture.

An optimal liquid-solid separation is characterized by a large volume of supernatant, containing low solids content, i.e. when both parameters EV and ETS are high. Figure 8 presents EV and ETS for each mixture.

The addition of CHF or P had different impact on the separation efficiency, as well as on the removal of the TS content of the liquid phase.

For the liquors 7 and 8, the liquid-solid separation appeared to be very difficult in our operating conditions with a few disposal of a liquid fraction, whatever the flocculent agent was. However, it appeared that addition of CHF increased the TS removal, particularly for the sludge 8, certainly in relation with the important modification of the particle size distribution comparing with the one observed after P addition.

As regards the liquors 3 and 5, a large amount of liquid fraction was obtained, certainly due to relatively low initial TS content that could facilitate the settle ability of the liquor. For these two liquors, CHF addition led to better TS removal.

For the liquors 1, 2 and 4, if P addition led to a better phase separation than the one obtained after CHF addition, TS removal was better after an addition of CHF.

For liquor 6, it appeared clearly that an addition of P is preferable to an addition of CHF in terms of both separation efficiency and removal of the TS content.

In conclusion, the results demonstrated that CHF could present some advantages in comparison with a usual flocculating agent; this advantage lied essentially in a better solids capture during the liquid-solid separation due certainly to an increase in size of the liquor particles accompanied by a size homogenization.

Fig. 8: EV and ETS for liquors after addition of functionalized chitosan (CHF) or polyelectrolyte (P).

Conclusion

These results provide an overview of the performance of the liquid-solid separation after an addition of functionalized chitosan in various liquors, in comparison with the one of a polyelectrolyte usually used for this utilization. These preliminary tests demonstrated the potentiality to the functionalized chitosan to obtain a great modification of the granulometry of the liquor, with a homogenization in size of the suspended particles and coarse colloids; this homogenization could facilitate the choice of the separation technology and of the related working conditions, and could allow better liquid-solid separation performances. This separation enhancement is very important because liquid-solid separation is an essential first step in valorization or further treatment of anaerobic liquors. Nowadays, there are emerging valorization routes for the utilization of AD liquor apart from the classical farmland application as fertilizer [26]. Thus, the liquor, exempt of suspended solids, could be used as a substrate for algae production, could be subjected to ammonia stripping and recovery as ammonium-sulfate, to struvite crystallization for nitrogen and phosphorous recovery... The success of these different valorization strategies and others hinges on the solid-liquid separation step. While efficient phase separation has proven possible through the use of functionalized chitosan, bearing quaternary ammonium salt, further complementary research aiming at identifying the flocculation mechanisms are required with the objective to adopt a functionalization specifically adapted to one or several liquors. The economics remain challenging; to assess the real economic and environmental benefits, this complementary approach is necessary.

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