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Enhancing extraction of alginate like extracellular polymers (ALE) from flocculent sludge by surfactants

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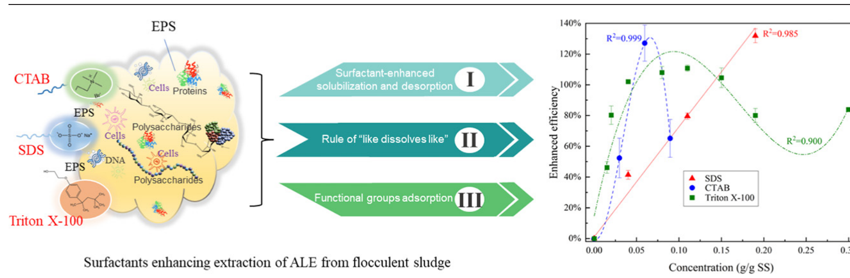
HIGHLIGHTS

- Three surfactants could enhance the ALE extraction from 12.4% to 22.3–28.2% VSS.
- The surfactants could improve the alginate purity from 50% to 54%–70%.
- Triton X-100 had the best performance on ALE extraction, followed by CTAB and SDS.
- Micelles of the surfactants could solubilize flocs and extracellular biopolymers.
- Functional groups adsorption could facilitate the ALE release from matrixes.

GRAPHICAL ABSTRACT



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ABSTRACT

Alginate like extracellular polymers (ALE) recovered from flocculent sludge has been identified as a kind of highly valuable biomaterials. However, the extraction protocols limit the production of biopolymers as ALE extracted from flocculent sludge is at a lower level, around 90–190 mg/g VSS. Under this circumstance, the eco-friendly and effective optimizations for the ALE extraction protocols are expected, and thus surfactants have gained an attention to enhancing the ALE extraction. With this study, different surfactants with different structures and chemical characteristics, such as sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB) and octyl phenyl polyoxyethylene ether (Triton X-100), were experimented to improve the ALE extraction, and in turn the optimal conditions and the associated mechanisms were evaluated and figured out. The experimental results indicated that surfactants could enhance the ALE extraction but also improve the alginate purification of ALE. With the optimal dosage of surfactants, the ALE extraction increased from 124.1 mg/g VSS to about 222.8–281.9 mg/g VSS, and the alginate purify was at around 54%–70%, in which the efficiency of the ALE extraction was improved by 79.5%–127.2%. Among others, Triton X-100 had the best performance on improving the ALE extraction, followed by CTAB and SDS. The mechanisms of surfactants on enhancing the ALE extraction and improving the alginate purify can be attributed to: i) surfactants micelles, which can solubilize flocs and extracellular biopolymers; ii) similar structures of surfactants and ALE, which follows the rule of "like dissolves like"; iii) functional groups adsorption, which facilitates the ALE release from matrixes. In a word, the optimized extraction protocol by using surfactants can be effectively applied to extract ALE from flocculent sludge.

1. Introduction

Recovering biopolymers from excess sludge produced in wastewater treatment has become intensive for research and attractive for applications (Kim et al., 2020; Li et al., 2021; Lin et al., 2015; Loosdrecht and Brdjanovic, 2014). Nowadays, the applications of biopolymers in some areas have become economically viable. Among them, alginate like extracellular polymers (ALE) extracted from microbial aggregates of aerobic granular sludge (AGS) and/or flocculent sludge have been identified as the highly valuable biomaterials with widely promising applications (Kim et al., 2020; Li et al., 2021; Lin et al., 2015). For example, ALE was evaluated to be of a

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good performance as non-flammable surface coating (Lin et al., 2015), which complies with the aviation requirements for aircraft interiors by the Federal Aviation Regulations (FAR) (Kim et al., 2020). However, the ALE production extracted from flocculent sludge is at the lower level, around 90–190 mg/g VSS (Li et al., 2021; Lin et al., 2013; Schambeck et al., 2020; Zhang et al., 2021), compared to AGS with the ALE extraction of 200–350 mg/g VSS (Adav and Lee, 2008; Boleij et al., 2019; Felz et al., 2016; Kim et al., 2020; Lin et al., 2010; Zhu et al., 2015). On the other hands, conventional activated sludge processes are still the main trend for biological wastewater treatment now, and thus extracting/recovering ALE from flocculent sludge becomes more interesting and promising.

ALE extraction from flocculent sludge is mainly limited by the less ALE formation in flocs matrixes and also the lower efficiency with existing extracted protocols. Among them, different medium compositions and operational conditions including influent substrate, temperature, solid retention times (SRT), etc. have some significant effects on ALE formation (Li et al., 2022; Liu et al., 2010; More et al., 2014; Ye et al., 2011a; Ye et al., 2011b). Although the ALE formation could be improved by adjusting some parameters mentioned above, the associated strategies are often not cost-effective and unrealistic in practice. For example, the previous study have concluded that starch-rich influent and low temperature are favorable to enrich ALE formation in flocculent sludge (Li et al., 2022). However, these conditions only occur in the special scenarios and are also not supportive of high biological nutrient removal performance.

On the other hand, conventional protocols of extracting biopolymers have either a lower efficiency or a less economic value of extraction for practical applications (Sheng et al., 2010; Felz et al., 2016). For this reason, optimizing the existing protocols become necessary and urgent for the ALE recovered from flocculent sludge. There have been some studies on investigating the modifications on the existing protocols, such as using different chemicals, adjusting working conditions (ultrasonic power and pulse time, centrifugal speed and time, etc.) and/or environmental parameters (pH, temperature, etc.) (Cao et al., 2021; Feng et al., 2019; Lin et al., 2015; Meng et al., 2019; Sheng et al., 2010). However, these optimized approaches are energy- and/or time-consuming and have some negative effects on total environment due to their possible pollutions. Although Lin et al. (2010) optimized the existing extraction protocol of alginate extraction from the seaweed by heating-Na_2CO_3 and successfully recovered ALE from AGS with a higher production, this approach was not effective for the ALE extraction from flocculent sludge as the efficiency was so low as 72 ± 6 mg/g VSS (Lin et al., 2013), 187 ± 94 mg/g VSS (Schambeck et al., 2020) and 65 ± 22 mg/g VSS (Zhang et al., 2021), due to the different structures of flocs aggregates and EPS matrixes from AGS.

Under this circumstance, effective and sustainable approaches have to be developed and evaluated to recover highly valuable biopolymers from flocculent sludge (Ras et al., 2011; Sheng et al., 2010). Such surfactants as sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) are one of the most versatile chemical products. Previous studies revealed that the presence of surfactants in pre-treatment of excess sludge has obviously some positive effects on extracting biopolymers, due to lowering the surface tension and/or altering cell structures (Cao et al., 2021; Kavitha et al., 2014; Taghavijeloudar et al., 2021). Kavitha et al. (2014 and 2016) reported that SDS could dissolve suspended solids and thus increase the soluble organics content in anaerobic digestion, which could ultimately improve the energy conversion efficiency. Lai et al. (2016 and 2018) also implied that surfactants destabilized sludge flocs and released extracellular biopolymers (such as protein and polysaccharides) into the liquid phase due to its solubilization capacities. Lin et al. (2018) figured out that the heat-Na_2CO_3 method with only 0.1% SDS added could dissolve and separate extracellular biopolymers in AGS and achieved the higher production of glycosylated amyloid-like proteins, up to 480 ± 90 mg/g VSS. Moreover, Taghavijeloudar et al. (2021) found that four different surfactants could improve the EPS extracted efficiency from the microalgae. Cao et al. (2021) also concluded that the ultrasonic method plus CTAB and SDS could enhance the EPS extraction from flocculent sludge by 76.5% and 53.1%, respectively. However, the effects and the associated mechanisms of different surfactants on improving the ALE extraction from flocculent sludge have not been well analyzed and documented.

With this study, the method of heating-Na_2CO_3 for the ALE extraction was optimized by adding designed dosages of surfactants. Three different types of surfactants were applied for experiments, including anionic surfactant SDS, cationic surfactant CTAB and nonionic surfactant Triton X-100. The enhanced efficiency of surfactants on the ALE extraction were also evaluated to figure out the optimal strategies for the effective ALE recovery. At the same time, the compositions and structures of the extracted ALE were characterized and analyzed to ascertain the involved mechanisms of surfactants enhancing ALE extraction.

2. Materials and methods

2.1. Optimization of extraction protocols

Flocculent sludge used in this study was collected from a typical municipal wastewater treatment plant (WWTP) with the AAO process in Beijing, China. The collected flocculent sludge was concentrated by a 0.15-mm filter, sieved, and then stored in a refrigerator (4 °C) for use. The characteristics of concentrated flocculent sludge are listed in Table 1.

Three types of surfactants, anionic SDS, cationic CTAB and nonionic Triton X-100, were chosen for experiments. Prior to extraction, flocculent sludge was centrifuged at 4000 ×g and 4 °C for 20 min; after the supernatant was decanted, the equal volume (to the supernatant) of deionized water was supplemented into the centrifuge tube to wash residual solids. Then, the washed flocculent sludge was added with the designed dosages of different surfactants as listed in Table 2. These mixtures were stirred at 500 rpm/min for 5 min, then at 150 rpm/min for 20 min and finally settled for 3 h. Finally, all the samples were heated at 80 °C for 35 min with Na_2CO_3 (0.5%, w/v, analytical reagent) in a water bath and then centrifuged at 4000 ×g and 4 °C for 20 min. Supernatants were collected and pellets (for baffling) were removed respectively. pH of the supernatants was adjusted to 2.2 with 1 M HCl for alginate purification and also for separating the residual surfactants. Then, the acidified supernatants were again centrifuged at 4000 ×g and 4 °C for 20 min. The pellets containing ALE was collected and re-dissolved with 1 M NaOH at pH 8.5. The dissolved biopolymers were dialyzed for 24 h in a dialysis bag with a molecular weight cut-off of 3.5 kDa to remove the solubilized ions. Finally, the ALE samples were frozen at −50 °C and then freeze-dried in freeze drier (Felz et al., 2016, 2019; Lin et al., 2010). Extraction of ALE from flocculent sludge with different types and/or dosages of surfactants were conducted in duplicate.

Importantly, surfactants in the mixtures were be separated and discarded at the stage of adjusting the supernatants to 2.2 with 1 M HCl for alginate purification. Moreover, in the final dialysis process with a molecular weight cut-off of 3.5 kDa, all solubilized ions including surfactants could be removed. Therefore, the residual surfactants in the extracted ALE were negligible in this study.

Table 1
Properties of the concentrated flocculent sludge.

Parameters	Value	Parameters	Value
MLSS (g/L)	28.1 ± 0.8	CST (s)	43.8 ± 1.1
MLVSS (g/L)	15.1 ± 0.9	MV (μm)[a]	16.36 ± 0.2
MLVSS/MLSS	53.7%	CS (m^2/cm^3)[b]	0.182 ± 0.05
Water content (%)	97.1 ± 0.3	D[50] (μm)[c]	200.2 ± 4.2
pH	7.23 ± 0.2	D[95] (μm)[d]	891.1 ± 7.6

[a] MV: mean diameter of the volume distribution, μm;
[b] CS, calculated specific surface area, m^2/cm^3;
[c] D[50], median diameter, particle parameter representing cumulative 50% distribution of a cumulative curve, μm;
[d] D[90]: Particle parameter representing cumulative 90% distribution of a cumulative curve, μm.

Table 2
Designed dosages of surfactants for optimizing alginate like extracellular polymers (ALE) extraction.

Surfactants[a]	Abbreviates	Types	Dosage							
Sodium dodecyl sulfate (g/L)	SDS	Anionic	0		1.0		3.0		5.0	
Cetyltrimethylammonium bromide (g/L)	CTAB	Cationic	0		0.4		0.8		1.2	
Triton X-100 (mL/L)	Triton X-100	Nonionic	0	0.5	0.75	1.25	2.5	3.75	5.0	10

[a] Mixed liquor suspended solids (MLSS) of the mixture after pre-treatment was at 26.3 g/L. Corresponded mass ratio of surfactants to MLSS of flocculent sludge were as follows: SDS = 0, 0.04, 0.11, 0.19 g/g SS; CTAB = 0, 0.03, 0.06, 0.09 g/g SS; Triton X-100 = 0, 0.015, 0.02 0.04, 0.08, 0.11, 0.15, 0.30 g/g SS.

2.2. Analytical methods

Polysaccharide (PS) and protein (PN) analyses were detected by a phenol-sulfuric acid assay with D-glucose as the standard and the Lorry assay with bovine serum albumin respectively, based on the conceptual framework proposed by Dubois et al. (1951) and Lowry et al. (1951). Alginate is the main structural component in extracellular biopolymers and thus could be used to determines the functionalities of the recovered biomaterials. Therefore, the commercial alginate (extracted from brown-algae, viscosity 4–12 cP, 1% in H_2O, analytical reagent) was chosen as the standard with the phenol-sulfuric acid assay to evaluate the amount of alginate equivalents, which represented the alginate purity of the extracted ALE (Felz et al., 2019; Li et al., 2021; Lin et al., 2010). Total organic carbon (TOC) was determined with a TOC analyzer (vario total organic carbon analyzer, DKSH company/Swiss) to analyze the organic proportions in the ALE extraction. The ALE solution prior to the final freeze-drying step was used to measure the particle size distributions and specific surface area using a laser particle size analyzer (Microtrac S3500, American Mickey Co., Ltd./USA).

The fractionations of the isolated biopolymers, including a family of copolymers comprising of mannuronic acid (M) and guluronic acid (G) units arranged in an irregular block pattern of varying proportions of GG, MG and MM blocks, were detected by the methods of partial acid hydrolysis as described in supplementary materials Text S1 (Lin et al., 2013). Detailed information about these different kinds of blocks in alginate was also shown in supplementary materials Text S2. Ionic hydrogel formation was tested with 2.5% (w/v) $CaCl_2$ solution according to the procedures described by Lin et al. (2013) and Felz et al. (2016). The ALE was cross-linked in the $CaCl_2$ solution at room temperature for about 16–18 h.

The chemical functional groups were analyzed and evaluated by a Thermo Fisher Fourier transform infrared spectrometer (FT-IR). Spectra of biopolymers were measured at the wavenumber of 4000–400 cm^{-1} with KBr pellets (98 mg KBr + 2 mg sample, spectrum pure). The spectra of commercial sodium alginate were also recorded as the standard to estimate of the quantitative similarity of chemical functional groups between different biopolymers and commercial alginate by the FT-IR software (Li et al., 2019).

Capillary suction time (CST) of the concentrated sludge samples was determined with a CST instrument. Moreover, water content, mixed liquor suspended solids (MLSS), mixed liquor volatile suspended solids (MLVSS) and pH were detected according to the standard methods (Isolation, 1999).

2.3. Statistical analysis

Enhanced efficiency was estimated to quantitatively analyze and evaluate the effects of surfactants on ALE production comparing to the blank tests (no surfactants), according to the following equation:

$$Enhanced\ efficiency = \frac{ALE_{Surfactants} - ALE_{Blank}}{ALE_{Blank}} \quad (1)$$

where, $ALE_{Surfactants}$ and ALE_{Blank} is the ALE extraction with and without surfactants, respectively.

Moreover, a one-way ANOVA was used to compare the difference of the ALE extraction from flocculent sludge with different surfactants addition. The significance level at 95% were based on the data obtained from the duplicated experiments. Values of different parameters were expressed as the mean ± standard deviation.

3. Results and discussion

3.1. Anionic surfactant, SDS

The ALE extraction enhanced by adding anionic surfactant, SDS, are shown in Fig. 1. As depicted in Fig. 1a, the ALE extraction increased sharply from 124.1 ± 12.3 mg/g VSS to 287.7 ± 5.6 mg/g VSS along with the increased dosage of SDS from 0 to 5.0 g/L. The corresponding enhanced efficiency was so high as 132%, which demonstrates that SDS had a very positive effect on the ALE extraction from flocculent sludge.

The alginate equivalent of the extracted ALE was evaluated and the results are shown in Fig. 1b. The content of alginate in the extracted ALE was at 697.5 ± 31.5 mg/g ALE with SDS = 3.0 g/L, which was much higher than that of the extracted ALE without SDS added (525.4 ± 14.7 mg/g ALE). Moreover, the fraction of GG, MG and MM blocks are also depicted in Fig. 1b. The recovery yield of all blocks from flocculent sludge was at 45%–65%, with about 20%–33% GG blocks and 17%–28% MG blocks in the chemical structures of extracted ALE. The GG block in the extracted ALE with SDS = 3.0 g/L had the highest composition, up to 33.3% ± 2.3%, which benefited more compactly gelling capacities of the ALE extraction (Felz et al., 2016; Lin et al., 2013). The monomer ratios of G:M of the extracted ALE with different dosage of SDS was at the range of 2.0–3.0. Moreover, the ionic hydrogel formation tests revealed that Ca^{2+}-ALE beads displayed the good stabilities among the different ALE extraction. These results indicate that SDS could not only promote the extracted efficiency of ALE from flocculent sludge but also improve the alginate purity of the biopolymers, which could make the great gel formation capacities for wide applications.

With SDS = 5.0 g/L, however, the alginate equivalent of the extracted ALE sharply declined to about 348.2 ± 2.6 mg/g ALE. The results of TOC (Fig. 1c) also indicated that the over-dosing SDS (≥5.0 g/L) resulted in more inorganic components contained in the extracted ALE. The quantitative similarity of chemical functional groups between the extracted ALE and the commercial alginate were evaluated by FT-IR spectra and the results are listed in Table 3. As shown in Table 3, the similarity of chemical functional groups was at the range of 67%–75% with SDS ≤ 3.0 g/L, while no obvious similarity was detected with SDS = 5.0 g/L, which indicates that the appropriate concentration of SDS would enhance the ALE extraction and over-dosing SDS would destroy the properties and structures of the extracted ALE. These results were consistent with the above analysis of GG, MG and MM blocks in the ALE extraction.

Fig. 1d shows the contents of PS and PN contained in the extracted ALE. The PS content slightly decreased from 82.3 ± 9.7 mg/g ALE to 33.5 ± 9.3 mg/g ALE along with the increased dosage of SDS = 0 to 5.0 g/L, while the PN content increased from 337.8 ± 26.6 mg/g ALE (SDS = 0) to 367.52 ± 3.03 mg/g ALE (SDS = 1.0 g/L) and then declined back to around 323.6 ± 5.9 mg/g ALE (SDS = 5.0 g/L). The ratio of PN/PS gradually increased from about 4.1 to 5.5 but sharply reached to 10.0 with SDS = 5.0 g/L, which is obviously beyond the normal range of ALE at 3.0–6.0 (Mahendran et al., 2012; Zhu et al., 2012). These results demonstrated that different dosage of SDS might have effects on the composition of the extracted ALE. The detailed explanation is described in the following parts.

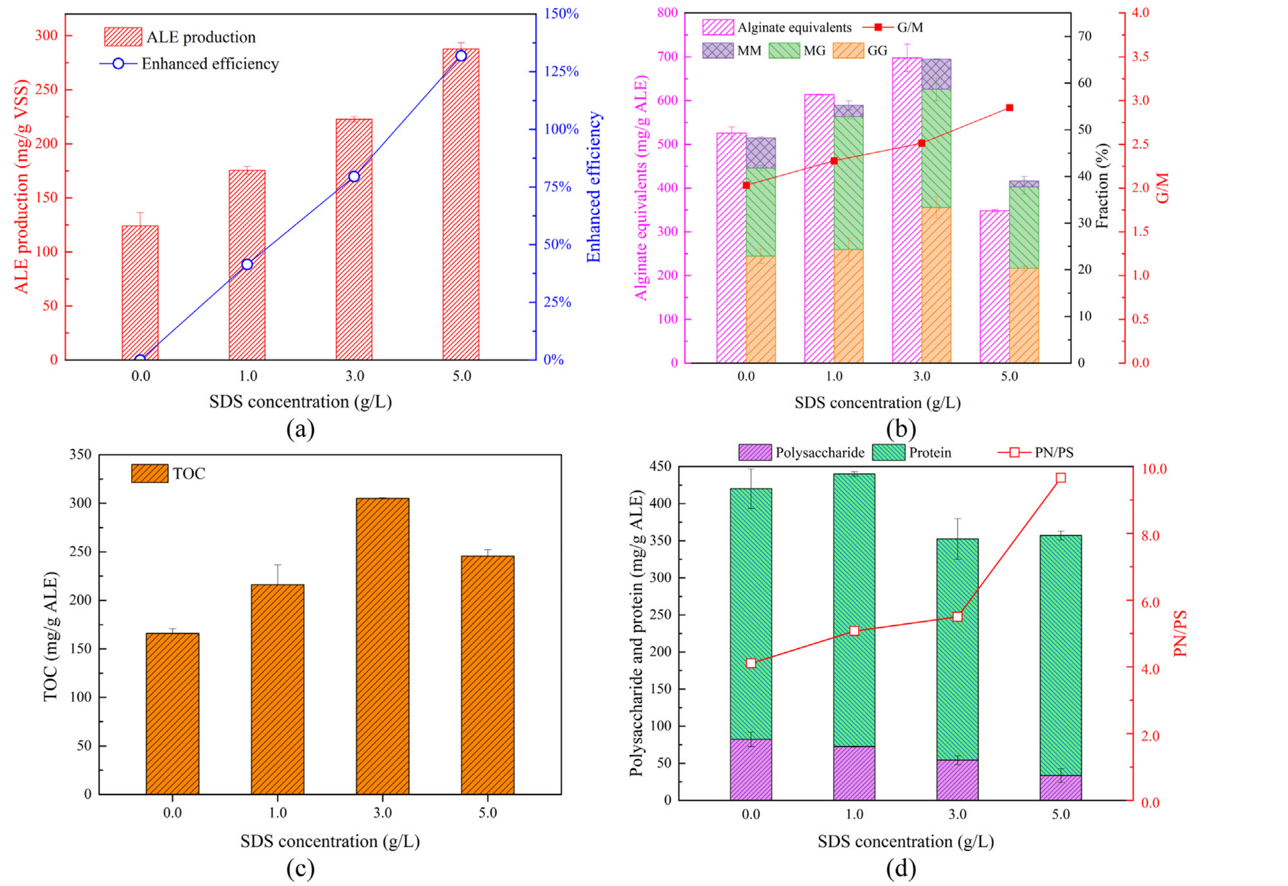


Fig. 1. Alginate like extracellular polymers (ALE) extraction from flocculent sludge with different dosages of anionic surfactant, SDS: a) ALE extraction; b) alginate equivalents of ALE; c) total organic carbon (TOC); d) polysaccharide (PS) and protein (PN) content.

With the dosage of SDS = 3.0 g/L, anyway, the ALE extraction was at 222.8 mg/g VSS and the enhanced efficiency reached to 79.5%, corresponding to the purity of 70%. Although over-dosing SDS could increase the ALE production, but the alginate purity would decrease.

3.2. Cationic surfactant, CTAB

The ALE extraction by cationic surfactant, CTAB, are shown in Fig. 2. As shown in Fig. 2a, CTAB at 0.4 g/L could improve the ALE extraction, from 121.1 ± 8.9 mg/g VSS to 189.2 ± 16.0 mg/g VSS and CTAB at 0.8 g/L made the ALE extraction reach to the maximum level, 281.9 ± 14.6 mg/g VSS. However, the ALE extraction dropped to about 205.0 ± 15.2 mg/g VSS with CTAB at 1.2 g/L. Clearly, CTAB could also enhance the ALE extraction and the optimum dosage of CTAB was at 0.8 g/L, with the enhanced efficiency of 127.2%.

As shown in Fig. 2b, however, there were a minor difference ($p > 0.05$) on both the alginate equivalent and the recovery yield of blocks (G and M) of the extracted ALE with the different dosages of CTAB. The alginate equivalent was at the range of 535–630 mg/g ALE and the fraction of MG and GG were stably at 20%–22%, respectively. The similar trend also occurred for TOC (Fig. 2c), keeping at around 275 mg/g ALE. The similarity of chemical functional groups was at around 58%–67% as shown in Table 3. The PS and PN content (Fig. 2d) also kept constantly at 150–170 mg/g ALE and 360–370 mg/g ALE, respectively.

These results indicate that CTAB seemed to have a positive effect on the ALE extraction and to have a minor effect on the associated compositions and chemical characteristics. The dosage of CTAB at 0.8 g/L achieved the highest extraction of 281.9 mg/g VSS and the enhanced efficiency was at 127.2%.

Table 3
Similarity between the extracted ALE and the commercial alginate.

SDS (g/L)	0		1.0		3.0		5.0	
Similarity	67.4 ± 2.3%		75.7 ± 0.6%		73.9 ± 1.4%		/	
CTAB (g/L)	0		0.4		0.8		1.2	
Similarity	67.4 ± 0.4%		65.4 ± 1.4%		61.1 ± 0.3%		58.5 ± 0.6%	
Triton X-100 (mL/L)	0	0.5	0.75	1.25	2.5	3.75	5.0	10
Similarity	67.4 ± 0.5%	70.3 ± 1.0%	76.9 ± 0.5%	55.7 ± 0.4%	76.2 ± 1.5%	74.2 ± 0.3%	74.2 ± 0.7%	75.7 ± 0.6%

3.3. Nonionic surfactant, Triton X-100

Nonionic surfactant, Triton X-100, was also selected to improve the ALE extraction and the results are shown in Fig. 3. Fig. 3a indicated that Triton X-100 significantly enhanced the ALE extraction from flocculent sludge. With Triton X-100 increased from 0 mL/L to 3.75 mL/L, the ALE extraction increased from 120.1 ± 2.3 mg/g VSS to 260.0 ± 2.5 mg/g VSS, and the enhanced efficiency was about 110%. However, the ALE extraction was only at about 230.0 mg/g VSS with Triton X-100 = 10.0 mL/L, which indicate the over dosage of Triton X-100 slightly declined the ALE extraction.

Fig. 3b showed that the alginate equivalent of the extracted ALE rapidly increased from 584.4 ± 11.6 mg/g ALE (Triton X-100 = 0 mL/L) to 676.9 ± 40.3 mg/g ALE (Triton X-100 = 0.5 mL/L). However, it declined to the lowest level of about 518.3 ± 14.4 mg/g ALE with Triton X-100 = 10.0 mL/L. This implied that the small amount of Triton X-100 could promote the ALE extraction and also have an obvious positive effect on the alginate purity, but over dosage would reduce the alginate purify in the ALE

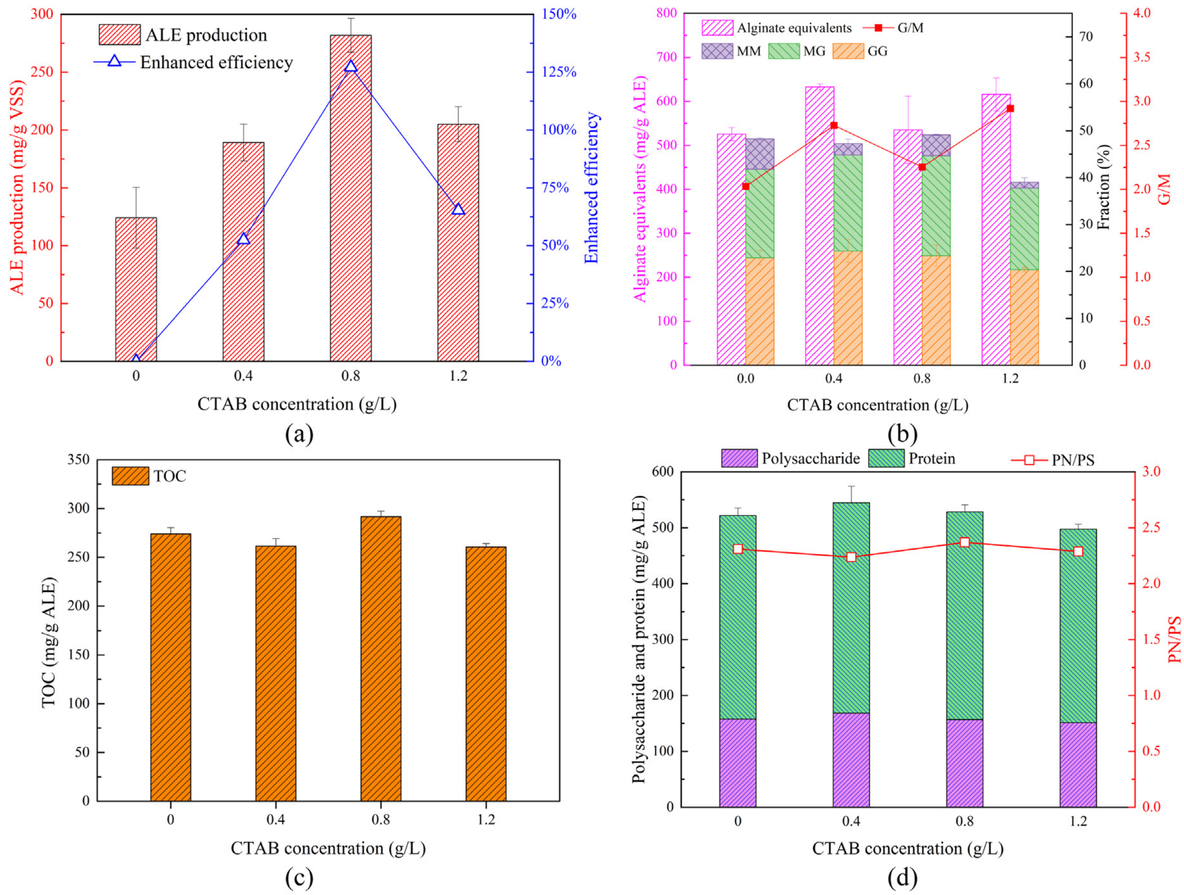


Fig. 2. Alginate like extracellular polymers (ALE) extraction from flocculent sludge with cationic surfactant, CTAB: a) ALE extraction; b) alginate equivalent of ALE; c) total organic carbon (TOC); d) polysaccharide (PS) and protein (PN) content.

extraction. The fraction of MG and GG also sharply increased and then sightly declined along with continuously adding Triton X-100.

TOC (Fig. 3c) gradually increased with Triton X-100 < 2.5 mL/L, and then decreased to a lower level. Moreover, Fig. 3d showed a decreasing trend of PS, from 157.7 ± 2.5 mg/g ALE (Triton X-100 = 0 mL/L) to 109.00 ± 5.4 mg/g ALE (Triton X-100 = 10.0 mL/L). However, the PN content did not change significantly and was at the range of 320–360 mg/g ALE. These results demonstrate that the increased TOC content was not from the compositions of PS or PN. Based on the analysis of FT-IR results, it could be speculated that it came from the aromatic and humic substances in the extracted ALE.

In the end, Triton X-100 = 1.25 mL/L could enhance the ALE extraction and obtain the highest extracted level of 250.6 mg/g VSS and the enhanced efficiency reached to 102%, corresponding to the alginate purity of 63%.

3.4. Summary

The modified extraction protocols by using different surfactants had the positive effects on enhancing the ALE extraction from flocculent sludge. The ALE extraction could increase from the initial 12% VSS to around 25%–28% VSS with the different dosages of surfactants. These results implies that the maximum ALE content in flocculent sludge was not so high, only around 280 mg/g VSS, which is indeed different from that from AGS (normally >300 mg/g VSS). As a result, the ALE extraction from flocculent sludge is mainly limited by the lower ALE formation in its flocs matrixes. Therefore, the higher ALE extraction from flocculent sludge has to be further enhanced by adjusting influent characteristics and operational parameters (Li et al., 2021, 2022). Moreover, the analysis of the alginate equivalent and different fractionations in the extracted ALE also indicate that surfactants improve the purity of ALE, which benefit the gelling capacities and feasibility of substitute as commercial alginates. Anyway, surfactants could help to achieve wider applications of ALE extracted from flocculent sludge as the highly valuable raw biomaterials.

Surfactants improved the ALE extraction mainly by destroying the microbial aggregates and releasing the extracellular polymers from the matrixes. Thus, the function of surfactants should be also evaluated by the mass ratio of dosed surfactants to mixed suspended solids of flocculent sludge, as shown in Fig. 4. Fig. 4 illustrates that the ALE extraction tended to linearly increase below 0.075 g surfactant per gram of SS; the same ALE extraction up to 28% VSS was respectively achieved by Triton X-100 = 0.04 g/g SS, CTAB = 0.06 g/g SS and SDS = 0.15 g/g SS, which means that Triton X-100 had the best performance on enhancing the ALE extraction, followed by CTAB and SDS. Clearly, over-dosage of both Triton X-100 and CTAB had the negative effect on the ALE extraction. Anyway, the enhancement of the ALE extraction was depended not only on the type of surfactants but also on the added concentration. For this reason, it is necessary to further analyze the associated mechanisms of surfactants on enhancing the ALE extraction.

4. Mechanisms of enhancement by surfactants

4.1. Surfactant-enhanced solubilization and desorption

Surfactant molecules could aggregate into micelles with hydrophobic groups bound at the core of clusters. The concentration relating to the formation of surfactant micelle is defined as a critical micelle concentration (CMC). Some previous studies revealed that the concentration of surfactants approaching to CMC could improve the solubility of hydrophobic substances (Lai et al., 2016, 2018; Zhou et al., 2018). On the surface of micelles, hydrophilic groups would reduce the Gibbs free energy of the

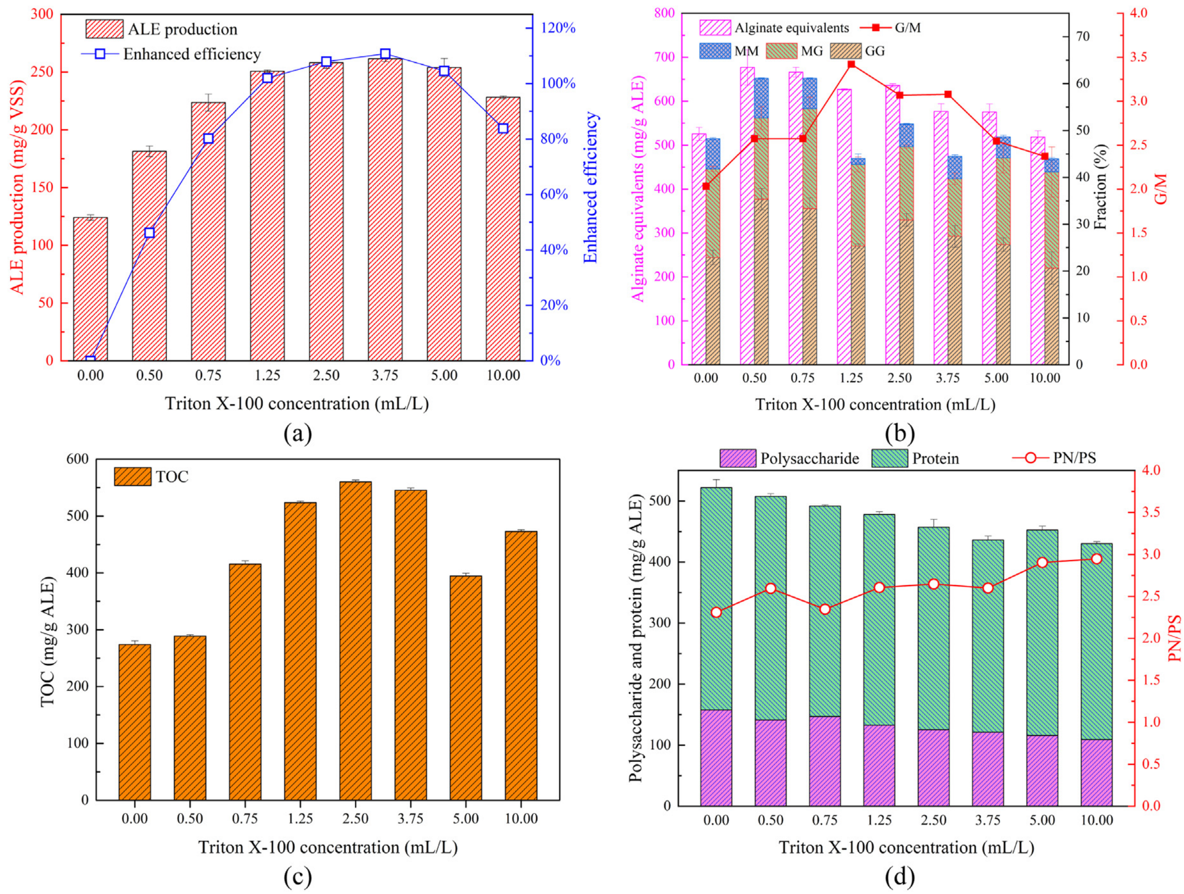


Fig. 3. Alginate like extracellular polymers (ALE) extraction from flocculent sludge with nonionic surfactant, Triton X-100: a) ALE extraction; b) alginate equivalent of ALE; c) total organic carbon (TOC); d) polysaccharide (PS) and protein (PN) content.

system, which resulted in dissolving more hydrophobic organic compounds or other insoluble and/or slightly soluble substances (Macakova, 2007; Ying, 2006).

ALE exists as insoluble calcium alginate (Ca^{2+}-Alg) in the EPS matrixes. Surfactants could disrupt the structures of Ca^{2+}-Alg in sludge flocs and thus dissolve them into the aqueous phase. The phenomena of ion exchange interaction between Na^{+} (originating from Na_2CO_3) and Ca^{2+} could be enhanced, which resulted in more ALE separation and extraction from the

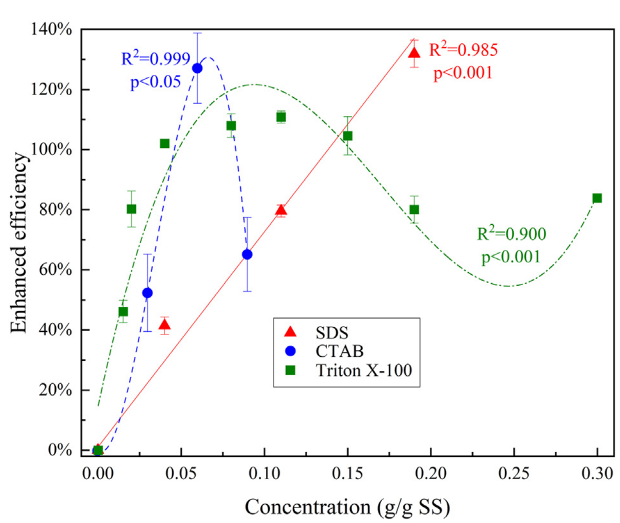
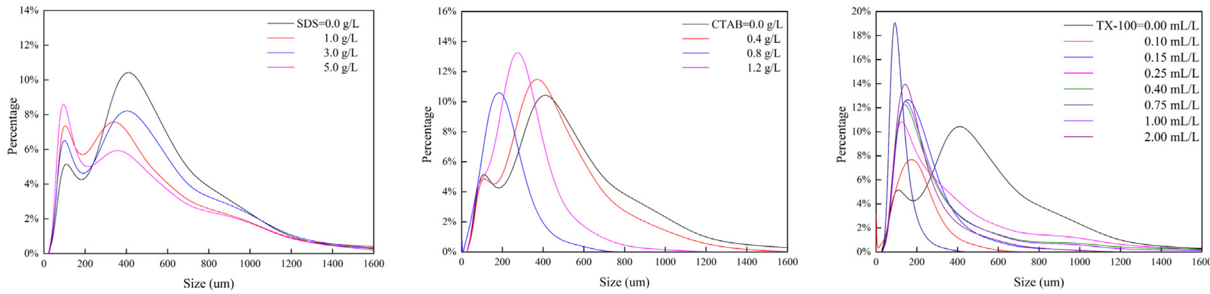


Fig. 4. Relation between added surfactant concentration and the enhanced efficiency of the alginate like extracellular polymers (ALE) extraction.

sludge flocs. On the other hand, surfactants could also destroy cell flocs and release extracellular substances from the EPS matrixes, resulting in the higher ALE extraction (Taghavijeloudar et al., 2021).

Surfactant-enhanced solubilization and desorption can be confirmed by the results of particle size distribution of the extracted ALE, as depicted in Fig. 5. The detailed information about particle size distribution is also listed in Tables S3–5. The particle size of ALE without surfactants added was mostly at the range of 400–600 μm, but reduced to about 200 μm or even lower than 100 μm with surfactants added, which indicates that the solubility of sludge flocs or the EPS matrixes should be improved by surfactants and thus the network of ALE structures was dispersed in the aqueous phase. Moreover, the results also reveal that the improved solubility depended heavily on the high dosage of surfactants and that higher dosage of surfactants resulted in smaller particles sizes. These findings are also consistent with Taghavijeloudar et al. (2021) who concluded that surfactants could enhance the solubilization and desorption of the microalgae and thus improve the soluble biopolymers in the aqueous phase.

CMC and other properties of the three surfactants used in this study are listed in Table 4 (Taghavijeloudar et al., 2021; Yu et al., 2007). Previous study already described that the solubilization capacity of different surfactants with the same hydrophobic groups was based on CMC and that a lower CMC value had the stronger performance (Rajesh Banu et al., 2020; Wang et al., 2018). The CMC value of Triton X-100 is 0.2 mmol/L (= 129.4 mg/L), which is much lower than CTAB = 0.89 mmol/L (= 324.4 mg/L) and SDS = 8.2 mmol/L (= 2364.6 mg/L) in Table 4. For the extracted ALE with Triton X-100 addition (Tables S3–5), the particle size distribution parameter of D [90] was 142 μm, which was also lower than D90 = 569 μm of SDS and D90 = 256 μm of CTAB. Thus, Triton X-100 achieved the highest solubilization and desorption of organic substances at a relatively lower concentration and had the best performance of



(a) SDS (b) CTAB (c) Triton X-100

Fig. 5. Particle size distribution of alginate like extracellular polymers (ALE) with different surfactants: (a) SDS, D [50] (median diameter) decreased from 291.0 μm to 145.2–228.5 μm; (b) CTAB, D [50] decreased from 291.0 μm to 127.0–276.1 μm; (c) Triton X-100, D [50] decreased from 291.0 μm to 80.3–146.0 μm.

enhancing the ALE extraction from flocculent sludge. The similar phenomena were also identified by Taghavijeloudar et al. (2021) and Yu et al. (2007) and they found such an order: nonionic surfactants > cationic surfactants > anionic surfactants. Moreover, as listed in Table 4, cationic surfactants (CTAB) with positive charges (+61.5 mV) on the outside was unfavorable for disrupting the structures of Ca^{2+}-Alg in sludge flocs, which resulted in less alginates dissolving into the aqueous phase. Therefore, as shown in Fig. 2, with the addition of over-dosing CTAB (1.2 g/L), the ALE extraction dropped to about 205.0 ± 15.2 mg/g VSS.

4.2. Rule of "Like dissolves like"

Surfactants could also follow the rule of "like dissolves like" in enhancing the ALE extraction. The chemical structures of alginate and three surfactants are shown in Fig. 6 (Hay et al., 2013). The main structure of alginate is linear long-chains which are similar to the structures of SDS and CTAB. As a result, "like dissolves like" should work here and thus promote the synergistic dissolution for each other. More linear long-chains polysaccharide including the ALE biopolymers could deport from flocs and dissolve into the aqueous phase, resulting in the higher ALE extraction (Lai et al., 2018; Zhou et al., 2018). The higher enhanced efficiency of CTAB could be attributed to the longer alkyl chain structure of CTAB (16 C atoms) than SDS (14 C atoms).

As shown in Fig. 6, moreover, the main structure of Triton X-100 with benzene rings are also very similar to the monomers of alginate polymers with the ring structure (Hay et al., 2013). These similar blocks could benefit more alginate structures to be dissolved and thus extracted from sludge flocs, while other impurities, such as proteins or humic substances were remained in the EPS matrixes. Thus, Triton X-100 addition could increase the alginate purity of ALE.

4.3. Functional groups adsorption

Different surfactants contain many different functional sites including hydrophobic and hydrophilic groups, which would be bound to functional groups of biopolymer structures in sludge flocs by the interactions of electrostatic force, hydrogen bonding or hydrophobic interaction (Zhong et al., 2018). Thus, the adsorption sites of flocs are occupied and could

Table 4
Properties of different surfactants used in this study (Taghavijeloudar et al., 2021; Yu et al., 2007).

Surfactants	Types	Surface charge (mV)	Molecular weight (g/mol)	Critical micelle concentration (CMC, 25 °C)	
				mmol/L	mg/L
SDS	Anionic	−49.9	288.37	8.2	2364.6
CTAB	Cationic	+61.5	364.45	0.89	324.4
Triton X-100	Nonionic	NA	647.00	0.2	129.4

facilitate the release of calcium alginate biopolymers from sludge matrixes. The opportunities of Ca^{2+}-Alg replace by Na^{+} would be increased and the conversion efficiency of insoluble Ca^{2+}-Alg to dissolved Na^{+}-Alg would be also improved.

The functional groups were detected and analyzed by FT-IR spectra to figure out the associated mechanisms, and the results are shown in Fig. 7. The more detailed information of different band assignments for the FT-IR spectral features are listed in Table S6 (Jia et al., 2017; Niu et al., 2016; Yin et al., 2015; Zhang et al., 2019). The vibration of main functional groups, including polysaccharide-related functional groups (CH stretching groups at 2930 cm^{-1} in CH_2 structure, CH plane bending vibration group at 1072 cm^{-1}) and protein-related functional groups (amide CO at 1655 cm^{-1}, amide NH bending vibration at 1530 cm^{-1}) in ALE with surfactants added, were weakened or strengthened to an extent. It was speculated that the sites of ALE functional groups were adsorbed and occupied by surfactants. The adsorption would enrich more ALE biopolymers with special functional groups into the aqueous phase. This might be the reason why surfactants could achieve the enhancement of the ALE extraction and also the alginate purity.

Fig. 7 also reveals that over-dosing surfactants resulted in apparent changes in the peak vibration for some functional groups, such as amide CN stretching vibration at 1233 cm^{-1} and CH stretching groups at 2960 cm^{-1} in CH_3 structure, which indicates that the excessive amphoteric functional groups of surfactants might also combined and adsorbed with other complex substances such as humic substances, soluble tyrosine aromatic protein, soluble microbial metabolites (protein-like compounds), etc. and thus destroy chemical properties and/or decrease the alginate purity of the ALE extraction (Kavitha et al., 2016; LaSarre and Federle, 2013; Macakova, 2007; Nikpay et al., 2017). Anyway, the improvement of the ALE extraction enhanced by over-dosing surfactants could reduce the economic value of biopolymers for future applications. Different surfactants would have variable interactions with sludge flocs and thus cause different effects on the ALE extraction. Like the structures of three surfactants shown in Fig. 6, the most obvious differences among them are the type of tail-tied ligands. Due to the end of SDS tied with the sulfate group, the higher dosage of SDS with the sulfate groups would destroy the non-covalent bonds in the EPS matrixes such as ionic bonds and hydrogen bonds and thus could completely destroy the sludge flocs.

CTAB is linked to the quaternary ammonium salt group, which could adsorb the functional groups of protein and polysaccharides and improve the ALE extraction (Gonze et al., 2003; Vallom and McLoughlin, 1984). Moreover, the positive charges of CTAB could neutralize the negative charge groups in sludge flocs and thus destroy the stability of aggregates. These synergic effects resulted in the better performance of CTAB than SDS on enhancing the ALE extraction.

Even though the nonionic surfactant Triton X-100 was weak on adsorption and binding, it could also destroy lipid bilayer structures and most of protein molecules in flocs. Thus, sludge flocs would be disintegrated, which benefited to extracting ALE. With Triton X-100 added, the supernatant after the gels participation step (pH adjusted to 2.2) became browner than the other two surfactants, and the color gradually was deepened

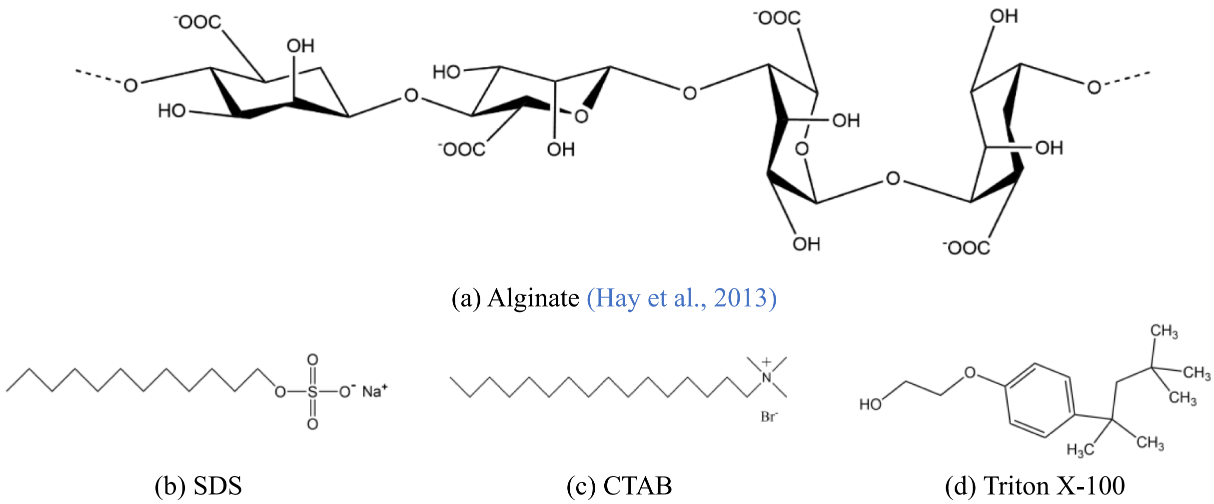


Fig. 6. Chemical structures of alginate and three different surfactants: (a) alginate; (b) SDS; (c) CTAB; (d) Triton X-100.

with Triton X-100 concentration increased, which indicates that Triton X-100 could help discard other impurities (such as humic substances, Li et al. (2019)) and improve the alginate purity of ALE.

5. Conclusions

The ALE extraction from flocculent sludge could be enhanced by surfactants, and also the alginate purity of the ALE extraction could be improved. With three different surfactants (cationic-SDS, anionic-CTAB and nonionic-Triton X-100), the experiments were initiated and main conclusions can be made as follows:

i. SDS (3.0 g/L), CTAB (0.8 g/L) and Triton X-100 (1.25 mL/L) were their optimal dosages on enhancing the ALE extraction, which resulted in the ALE extraction increasing from 124.1 mg/g VSS to 222.8, 281.9 and 250.6 mg/g VSS respectively, with the enhanced efficiency by 79.5%, 127.2% and 102.0%, corresponding to the alginate purity increasing from 50% to 70%, 54% and 63%.
ii. Based on the mass ratio, the optimal dosages of three surfactants achieving the similar ALE extraction ratio (25%–28% VSS) were found to be at 0.04 g/g SS (Triton X-100) < 0.06 g/g SS (CTAB) < 0.19 g/g SS (SDS).
iii. Surfactants enhanced the ALE extraction by surfactant-enhanced solubilization and desorption when micelles were formed at the critical micelle concentration (CMC). Among the three surfactants, Triton X-100 had the lowest CMC value and thus the best performance on enhancing the ALE extraction.
iv. Surfactants enhancing the ALE extraction could also follow the rule of "like dissolves like". Moreover, Triton X-100 could improve the alginate purify of the extracted ALE by this rule.
v. Absorption from functional groups could also be attributed to enhancing the ALE extraction and improving the alginate purify, which depended heavily on the different functional groups of different surfactants.

CRediT authorship contribution statement

Ji Li: Conceptualization, Methodology, Investigation, Writing - Original draft preparation. **Xiaodi Hao**: Supervision, Writing - Reviewing and Editing, Project administration. **Wei Gan**: Investigation, Formal analysis, Writing - Original draft preparation. **Mark C. M. van Loosdrecht**: Supervision**. Yuanyuan Wu**: Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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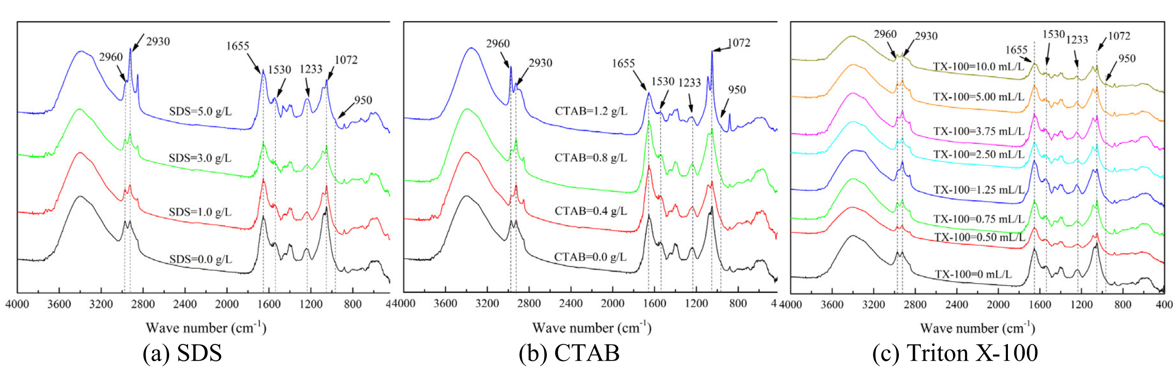

Fig. 7. FT-IR spectra of alginate like extracellular polymers (ALE) with different surfactants added: a) SDS; (b) CTAB; (c) Triton X-100.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2022.155673.

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