Environmental Science
Water Research & Technology

Flocculation of livestock wastewater using cationic starch prepared from potato peels

Journal:	*Environmental Science: Water Research & Technology*
Manuscript ID	EW-ART-10-2022-000794.R1
Article Type:	Paper

Water Impact Statement for:

Flocculation of livestock wastewater using cationic starch prepared from potato peels

Noor Haleem a,b, Augustina Osabutey a, Karlee Albert c, Cheng Zhang d, Kyungnan Min e,
Gary Anderson a, Xufei Yang a,*

a Department of Agricultural and Biosystems Engineering, South Dakota State University,
Brookings, SD 57007, USA

b Institute of Environmental Sciences and Engineering (IESE), National University of Sciences
and Technology (NUST), Islamabad 44000, Pakistan

c Department of Biology and Microbiology, South Dakota State University, Brookings, SD
57007, USA

d Department of Chemistry and Biochemistry, South Dakota State University, Brookings, SD
57007, USA

e Department of Civil and Environmental Engineering, South Dakota State University,
Brookings, SD 57007, USA

* Corresponding author; Tel: +1 605 688 5141; Email: xufei.yang@sdstate.edu

Solid separation is a key technology to mitigate odors and recover phosphorus from livestock wastewater. To enhance this, commercial coagulants, and flocculants such as alum, ferric sulfate, and polyacrylamide have been increasingly used. However, these agents are known to be toxic to ecosystems. This study represents the synthesis of a natural flocculant from locally available agricultural waste and recycle it for livestock wastewater treatment and facilitating the circular economy for livestock agriculture.

Flocculation of livestock wastewater using cationic starch prepared from potato peels

Noor Haleem,[ab] Augustina Osabutey,[a] Karlee Albert,[c] Cheng Zhang,[*d] Kyungnan Min,[e] Gary Anderson[a] and Xufei Yang[*a]

[a] Department of Agricultural and Biosystems Engineering, South Dakota State University, Brookings, SD 57007, USA

[b] Institute of Environmental Sciences and Engineering (IESE), National University of Sciences and Technology (NUST), Islamabad 44000, Pakistan

[c] Department of Biology and Microbiology, South Dakota State University, Brookings, SD 57007, USA

[d] Department of Chemistry and Biochemistry, South Dakota State University, Brookings, SD 57007, USA

[e] Department of Civil and Environmental Engineering, South Dakota State University, Brookings, SD 57007, USA

* Corresponding authors. Tel: +1 605 688 5141. E-mails: cheng.zhang@sdstate.edu; xufei.yang@sdstate.edu

Abstract

A cationic starch flocculant was prepared from potato peel waste (PPW) for enhanced solid-liquid separation of livestock wastewater, thereby promoting the agricultural circular economy. The starch extracted from PPW was cationized by incorporating a cationic moiety onto the backbone of starch via etherification with (3-chloro-2-hydroxypropyl)trimethylammonium chloride (CHPTAC). Using response surface methodology, a cationic starch sample with degree of substitution (DS)=0.86 was obtained from optimized reaction conditions: 1 wt% starch, 0.124 M CHPTAC, 2.0 M NaOH, isopropanol solvent, 60ºC and 5-h. ^{1}H NMR and FTIR confirmed the successful cationization of starch. A detailed analysis of the NMR spectra indicates that the substitution happened at all three OH groups of the anhydroglucose unit and some of the proton peak assignments in the literature are mistaken. The DS=0.86 sample was further studied for its flocculation performance. When used to treat undiluted swine and dairy wastewater (with high total suspended solid levels of 51.4 and 45.0 g/L), despite of a moderate suspended solid (SS) reduction (27.8 and 58.0%), the SS removal efficiency (72 and 162 suspended solid.9 mg TSS/mg flocculant achieved at the optimal dosages of 200 and 160 mg/L for swine and dairy wastewater, respectively) were greater than commercial flocculant PAM and some other flocculants in the literature that were used to treat highly diluted livestock wastewater.

Keywords

Flocculation, livestock wastewater, solid separation, cationic starch, waste valorization

1. Introduction

Potato (*Solanum Tuberosum*) is the fourth most consumed crop worldwide, with the annual production of ~370.43 million metric tons in 2019.[1, 2] A massive amount (70-140×10^3 tons) of potato peel waste (PPW) is produced per year, accounting for 15-40 % of the mass of primary potato products.[3] Most of the produced PPW is disposed of in landfill as a solid waste. Starch is the single most abundant component, accounting for up to 52% of dry potato peel mass.[4] Other abundant components include non-starch polysaccharides, lignin,, protein,[5] and low-molecular-weight phenolic compounds such as garlic acids and flavonoids.[6] Assuming the same composition as potato starch, PPW would contain 73-79 % amylopectin and 12-27 % amylose.[7] The starch can be utilized for various purposes such as ethanol fermentation,[8] novel material synthesis,[9] and enzyme production,[10] despite of the starch's poor water solubility, easy retrogradation after gelatinization, and high gelatinization temperature.[11]

Another potential application of PPW is production of cationic starch flocculants for wastewater treatment. This involves the chemical modification of starch granules extracted from PPW. Various chemical methods (e.g., esterification, etherification, oxidation, carbonization, and crosslinking with other polymers) are available for starch modification with desired functional groups at C2, C3 and C6 in starch backbones.[12] Etherification reactions have been employed to introduce quaternary ammonium groups onto starch[13, 14] using common reagents like glycidyltrimethyl ammonium chloride (GTAC) and 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC).[13] Alkaline bases such as NaOH, $NH_4(OH)$, and $Ca(OH)_2$ were required for reaction with these two reagents. When the reaction is carried out in alkaline water, the solution's viscosity rises, leading to gelatinization which hinders the reaction. It was found that gelatinization could be prevented by adding a nonsolvent or reagent to reduce swelling of starch.[15, 16]

The organic particles in manure are often negatively charged and are therefore suited for flocculation using cationic flocculants.[17] Livestock farming along with poultry farming generate the third largest source of water pollution (after industrial and domestic sources).[18] Solid separation is considered a key technology to mitigate odors and recover phosphorus from livestock wastewater[19-22] because most of the phosphorus occurs as solid particles rather than in dissolved forms. The suspended solids can be removed with gravitational settling, mechanical, and chemical methods. An example of the chemical methods is using flocculants/coagulants to enlarge the particle size, thereby facilitating solid separation.[23, 24] Beside phosphorus recovery, other benefits of solid separation include reduced odor nuisance[25] and improved suitability of livestock wastewater for irrigation and anaerobic digestion.[19]

Metal salts such as polyaluminium chloride and synthetic polymers such as polyacrylamide (PAM) are often used as coagulants and flocculants. However, these agents can introduce hazardous metal ions and acrylamide monomers into water.[26,27] Biopolymer-based flocculants have been intensively studied as potential substitutes for inorganic coagulants and synthetic polymer flocculants for their wide availability, environmental friendliness, and biodegradability.[28] Many biopolymers, such as chitosan,[29] starch,[30] cellulose,[31] lignin,[32] etc. can be chemically modified to function as flocculants. These biopolymers are modified with different functionalities using various reactions such as graft copolymerization, etherification, amination, esterification, acylation, oxidation, cross-linking, and Mannich reaction.[28] Biopolymer-based flocculants perform flocculation with by different mechanisms such as adsorption, bridging, charge neutralization, net trapping, and sweeping.[28]

Cationic starch has been explored as a natural flocculant for years. Unlike organic polymer flocculants, it is non-toxic and causes no secondary pollution.[33] However, only a few studies reported its preparation from potato peels[13, 14] and no application of cationic potato peel starch for livestock wastewater treatment was reported. To address growing livestock wastewater management challenges, we wish to present our synthesis of cationic starch from PPW via etherification with CHPTAC and the testing results of solid removal from livestock and dairy wastewater samples. In this work, we optimized cationic starch (CS) synthesis parameters via response surface methodology (RSM),[34] characterized the prepared CS flocculants and examined the effectiveness of the CS' in solid removal from swine and livestock wastewater. In ^{1}H NMR analysis, we paid special attention to the assignment of the key signals of CS and found some of the assignments in the literature are mistaken.

2. Methods and Materials

2.1. Materials

Materials for extraction of starch were generated in the lab (Sec. (2.1.1)). The cationization agent, 3-chloro-2-hydroxypropyl) trimethyl ammonium chloride (CHPTAC) with 60 wt% in water, d = 1.154 g/mL, MW = 188.1g/mol), isopropanol (91%) and ethanol (99.5%) were supplied by Sigma-Aldrich. Hydrochloric acid (HCl), and sodium hydroxide (NaOH) was obtained from Fisher Scientific. All the reagents used in this work were of analytical grade and were used as received without any further purification.

2.2. *Flocculant Preparation*

2.2.1. Starch extraction from potato peels

Around 1.8 kg of brown skin potatoes acquired from a local supermarket were manually peeled after rigorous washing with hot water. The peels (~176 g) were chopped into small pieces and further ground to fine granules using a coffee grinder. Deionized water was then added to the granules to create a slurry. After being homogenized for 30 min, the slurry was sieved using a 135-mesh polyester screen and the obtained filtrate was centrifuged at 3000 rpm for 12 min. The solid was air dried at room temperature and then ground into fine powders.

2.2.2. Preparation of cationic starch (CS)

The preparation adopted a protocol revised from reference.[35] It involved two steps: alkalization and etherification (Fig. 1). For alkalization, a mixture of 2.00 g (12.3 mmol of AGU) of the starch and 200 mL of isopropanol was stirred at 300 rpm for 15 min. Ten mL of a NaOH solution (0.500, 1.00, 1.50, 2.00, or 2.50 M) was then added dropwise, and the stirring was continued for another 60 min. During etherification, 3-7 mL (i.e., 0.053-0.124M or 10.6-24.8 mmol) of 60% 3-chloro-2-hydroxypropyltrimethyl ammonium chloride (CHPTAC) was added subsequently to the alkalized starch at ~60ºC and stirring was continued at the temperature for 2-5 hrs. After being cooled down to room temperature, the reaction was quenched with 0.1 M HCl to pH ~6.2. The product was further precipitated by adding 100 mL of ethanol (99%), collected by vacuum filtration, washed 3-5 times with 99% ethanol to remove unreacted reagents and byproducts and air-dried overnight in an oven at 40 ºC. The details of the reaction parameters, including the mole ratio of the reactants and reaction time are shown in Table 1.

<Fig. 1>

2.2.3. Determination of degree of substitution (DS) and reaction efficiency

For CS, DS is defined as the average number of hydroxyl groups in each anhydroglucoside unit (AGU) substituted by quaternary ammonium groups.[36] DS was calculated as [37]:

$$DS = \frac{162.15 \times N}{14.01 \times 100 - 151.5 \times N} \tag{1}$$

Where 162.15 is the molecular weight of AGU, 151.5 is the MW of cationic substituent, N% refers to the content of total nitrogen in a CS sample and it was determined in five replicates per sample using a TNT plus 826 test kit (Hach Method 10208) [38] with a standard deviation < 0.5%.

The efficiency of the cationization reaction is defined as

$$RE = \frac{DS}{n} \times 100\%, \tag{2}$$

Where n is the molar ratio of CHPTAC and AGU in the reaction.

2.2.4. Optimization of preparation conditions

Design Expert 11.0 (Stat-Ease Inc., Minneapolis, MN, USA) was used for experimental design and associated statistical analysis. Three independent variables (reaction parameters) were examined: reaction time, volume of 60% CHPTAC used, and NaOH concentration, with DS as the response. Following the central composite design (CCD), a prevalent response surface methodology (RSM) method, twenty sets of reaction conditions were investigated (Table 1). For each set of conditions, the reaction was run in triplicate in order to obtain an average DS value. The acquired data were analyzed with ANOVA and further fitted with a polynomial regression equation (Eq. 3 in Section 3.1), following a procedure described by Boulifi et al.[39]

<Table 1>

2.3. Flocculation Experiments

Raw swine wastewater samples were acquired from a wean-to-finish barn managed through the Swine Education & Research Facility of South Dakota State University (Flandreau, SD, USA). The barn housed ~1200 head of hogs and used a 2.4-m deep pit under slatted concrete floors for waste collection and storage. Raw dairy wastewater samples were acquired from a 2000-head dairy farm near Lake Benton, MN, USA. The farm used a sand-bedded free-stall system and sand lanes to separate sands from wastewater before feeding it to an anaerobic digester. The wastewater was collected after sand separation. All the acquired wastewater samples were prescreened with a 35-mesh sieve to remove large solid particles and then kept in a refrigerator at 4 ºC before flocculation experiments. The wastewater samples remained vertically homogeneous after one-month's storage.

The flocculation experiments (i.e., jar testing) were performed on a six-paddle jar tester (Phipps & Bird Model 7790-901B; Fisher Scientific Inc., Richmond, VA, USA). A standard protocol[40] was followed during the experiments. First, 1.00 g of CS was stir-mixed with 100.0 mL deionized water for 30-40 min to create a colloidal solution. Then, the prepared flocculant solution was added into 0.5-L swine and dairy wastewater at a target dosage (80, 125, 150, 200 and 250 mg/L). Three jar test replicates were carried out at each dosage. Before adding flocculants, the pH of swine wastewater in each jar was adjusted to 8.0 using a diluted HCl solution, while no pH adjustment of dairy wastewater was conducted because its pH value was 6.5, already very close to neutral. The flocculant solution was added in all six beakers simultaneously. To stimulate coagulation, the wastewater samples were stirred intensively at 300 rpm for 1.0 min, then gently at 20 rpm for 20 min to promote flock formation. The mixtures were allowed to sit for 24 h for the flocks to settle down. In beakers with CS added, stratification of swine and dairy wastewater was observed, with some solids settling on the bottom of each beaker. In beakers with no CS added (controlled samples), no stratification was seen. Liquid samples (5 mL) were taken from each beaker at ~2 cm depth from the top. The total suspended solids (TSS) of the liquid samples and control samples (i.e., wastewater with no CS added) were measured using glass fiber filters (Whatman GF/A, with 1.6-µm pore size) based on the classic gravimetric method.[41]

2.4. Characterization of Cationic Starch (CS)

Morphological analysis was done with a Hitachi S-3400N scanning electron microscope (SEM) (Hitachi Ltd., Tokyo, Japan) at an accelerating voltage of 10.0 kV. A ~1.0-mg starch or CS was loaded onto a two-sided adhesive carbon tape and coated with a thin gold layer. Images were taken at multiple magnifications to examine the size and shape of starch granules.

IR spectra were measured with a Perkin-Elmer Spectrum 100 FT-IR spectrometer (PerkinElmer Inc., Waltham, MA, USA). A powdered sample was mixed with KBr (2:98 w/w) and pressed into a transparent disk. A transmittance spectrum was derived from 28 scans of the sample at a resolution of 4 cm^{-1}. The purpose of FT-IR analysis was to identify functional groups indicative of successful starch modification.

DSC analysis was conducted on a Perkin-Elmer DSC 6000 analyzer (PerkinElmer Inc., Waltham, MA). A ~10-mg sample was loaded in an aluminum sample pan and purged with N_2 at a flow rate of 20 mL/min. The sample was heated from 20 ºC to 450 ºC at a ramp rate of 10 ºC/min. The purpose of the analysis was to compare glass transition (T_g) and decomposition temperatures of original starch and CS samples. A down shift in the temperatures is usually taken as an indicator of a successful modification.[42]

Similar to FT-IR, NMR was used to determine the functional groups indicative of the presence of the ammonium group in the CS samples. The analysis (^1H NMR) was conducted on a Bruker Avance 600 MHz NMR spectrometer (Bruker Corp., Billerica, MA). Tetramethyl silane was used as an internal reference. Samples were dissolved in dimethyl sulfoxide-d6 (DMSO-d6).

3. Results and Discussion

3.1. Optimization of Preparation Conditions

Three experimental parameters were examined: NaOH concentrations, volume of 60% CHPTAC and reaction time. DS characterizes the average number of substituted ammonium groups per AGU. Thus, it was selected as the benchmark measure of the quality of prepared CS. As aforementioned, 20 preparation conditions following the CCD design (Table 1) were applied to determine the optimal preparation condition (Fig. 2), as reported by Hivechi et al.,[43] for optimizing DS. Through the experiments, a second-order polynomial equation was obtained (Eq. 3).

$$DS = 0.670914 + 0.883388A - 0.138120B - 0.357549C + 0.000892AB - 0.000661A + 0.031826BC - 0.218739A^2 + 0.003564B^2 + 0.029004C^2 \quad (3)$$

where, A, B, and C correspond to NaOH concentrations, the volume of CHPTAC added, and the reaction time, respectively.

<Fig. 2>

The analysis of variance (ANOVA) test was conducted to further investigate the effect of each item (e.g., A and AB) in Eq. 3 (Table S1). Four significant influential items were identified: A ($p<0.0001$), BC ($p<0.0001$), A^2 ($p<0.0001$), and C^2 ($p=0.0017$), since their p values were below 0.05. The same threshold ($p<0.05$) was commonly used in RSM-CCD analysis to determine the significance of correlation.[44] The most significant factor was found to be NaOH concentration. As a measure of the goodness-of-fit, the adjusted determination of coefficient was calculated (Adj $R^2 = 0.9827$), along with the predicted determination of coefficient (Pred $R^2 = 0.8349$). The high R^2 values and a low coefficient of variation (CV = 5.92%) indicate that the experiments were precise and reliable.[45] A comparison of the model-predicted versus actual DS was shown in Fig. S1, which again affirms the good fitting performance of Eq. 3.

The effect of NaOH concentrations was further examined since it was identified as a top influential factor. As shown in Fig. S2 (Note: a graph created by the Design Expert software), DS increased with the molar concentration of NaOH until it reached DS=0.86 at 2.0 M NaOH. This DS value is even slightly higher than the DS value (0.84) reported in a recent methodology paper on starch cationization using the same reagent (CHPTAC). A further increase in NaOH concentrations led to a decrease in DS. The existence of an optimum NaOH concentration is the result of the balance between the need for NaOH to deprotonate starch OH groups for etherification and the side reaction that involves CHPTAC and sodium hydroxide.[46] At the optimum NaOH concentration, the reaction efficiency (the % of CHPTAC that ended up in the product) is calculated to be 24.6% using Eq. 2. The reaction efficiency is limited by the conditions used in the synthesis method (use of a lot of solvent – isopropanol) since alcohol can also react with CHPTAC despite the low reactivity of isopropanol due to its greater steric hindrance for the substitution reaction as compared to the primary alcohol at the C6 of AGU and its lower chance to be deprotonated as compared to the C2-OH and C3-OH in AGUs. The AGU OH groups are considered slightly more acidic than isopropanol because the carbon atoms in an AGU are more electron-deficient due to oxygenation of every carbon atom. The semidry method with addition of CaO described in a recent paper[15] permits a higher reaction efficiency (84%) for preparation of a CS with a similar DS (0.84).

3.2. Characterization of Cationic Starch (CS)

3.2.1. Morphology

Fig 3 shows the SEM images of potato peel starch (DS=0) and CS samples (DS=0.12 & DS=0.86). The unmodified starch (DS=0) largely consisted of oval granules with smooth surface and some curtailed sides. No obvious defect or impurity particles were observed (Fig. 3a). The same morphology was reported by Nasir and his coworkers.[38] For CS samples, unreacted cationic reagent and by-products were removed during the purification step. However, the removal can be incomplete, as indicated by NaCl crystals trapped on the surface of some CS granules (Fig. 3c). A similar observation was made by Almonaityte et al.[15] The cationization reaction was considered to disrupt the structure of starch, reduce the hydrogen bonding, and facilitate water uptake, thereby increasing the water solubility/dispersibility of cationic starch.[47]

<Fig. 3>

3.2.2. FTIR spectra

FTIR analysis also confirms the successful cationization of potato peel starch (Fig. 4). At the first glance, the spectra of the modified starch samples look similar to that of unmodified. This is because only $\leq$0.86/3 of hydroxyl groups on the starch backbone are substituted. Compared with the unmodified starch sample, new peaks at 959 cm^{-1} and 1480 cm^{-1} are observed for the modified samples (DS=0.12 and DS=0.86). This peak can be assigned to the stretching vibration of the C–N bond of quaternary ammonium groups and, thus, is an indication of the successful incorporation of trimethyl ammonium groups.[47] All the spectra are dominated by the broad bands at 3399 and 2937 cm^{-1}, which are attributed to the O-H and C-H bond stretching vibrations, respectively;[48] and the peaks at 990, 1086, and 1157 cm^{-1} are the characteristic absorption bands of AGU.[49]

<Fig. 4>

3.2.3. NMR spectra

Another evidence of successful cationization is provided by NMR analysis. The NMR spectra of raw starch extracted from potato peels (DS=0) and CS with DS=0.12, 0.86 are shown in Fig. 5. Due to the low solubilities of all samples, the spectra are dominated by the signals of trace water at 3.35 ppm and trace DMSO-d_5 at 2.50 ppm even though the anhydrous DMSO-d_6 was used and NMR sample preparation was done in a N_2 glovebox. Spectra in Fig. 5b-d are blown-up and truncated, and the C1 proton peaks at 5.773 ppm are normalized to better compare the intensities of other peaks visually. Beside DMSO and moisture, common organic solvents present in the glovebox such as THF and, to a less extent, EtOAc (with peaks at 4.106, 2.07 and 1.05 ppm), are also found in the spectra. Nevertheless, NMR analysis provides strong evidence of successful cationization. According to the literature,[50] ^{1}H NMR signal at ~3.1 ppm was ascribed to $CH_3–N^+$. This spectral region is shown in Fig. 5e-g for DS=0, 0.12 and 0.86 samples. Three new singlets at 3.125, 3.142 and 3.160 ppm are seen in Fig. 5f and 5g and can be assigned to the methyl groups in the ammonium groups that are attached to the starch at different sites (C2, C3 and C6). An apparent doublet is found in the same spectral region of the raw starch, which is likely from an impurity in the starch and is also present in the spectra of the two CS samples and partially overlaps with the 3.160 ppm peak of the ammonium. The peaks of the raw starch between 4.5 and 5.6 ppm were from OH groups on the glucose unit and impurities such as lignin. Upon modification with CHPTAC, the intensities of OH peaks all decreased, indicating that all OH groups on C2, C3 and C6 could be etherified. The region of 3.50-3.80 ppm, which is dominated by the trace THF, is where the peaks of the hydrogens on the glucose carbons (except C-1) are located. In the literature, the peaks between 4.5 and 5.6 ppm were mistakenly ascribed to the hydrogen atoms in the starch backbone (meaning the Hs on backbone carbon),[50] and the peak at 3.6 ppm was mistakenly ascribed to O-H groups.[51] A small amount of lignin is present in the starch as indicated by the peaks in the aromatic region of 7.0-7.6 ppm. No effort was made to remove it since it also contains OH groups and can be cationized as the starch.[50]

<Fig. 5>

3.3.4. DSC thermograms

DSC analysis results also supported the successful cationization of potato peel starch (Fig. S3). The glass transition temperature (T_g) of the DS=0.86 sample (87.3ºC) was lower than that of the unmodified starch sample (96ºC). The decrease in T_g may be attributed to the introduction of quaternary ammonium groups into the starch polymer. The incorporation of the ammonium groups increases the mobility of polymers due to the associated reduction in structure regularity. The thermal degradation of the DS=0.86 sample started at 231˚C, substantially lower than that of unmodified starch (281˚C). A similar finding was reported in the literature.[50, 52]

3.3. Flocculation Performance

In this study, the suspended solid (SS) contents of original swine and dairy wastewater samples were as high as 73,950 and 79,070 mg/L, respectively. After screening with a 35-mesh sieve, the SS concentration was reduced by 30.4% for the swine wastewater and 43.1% for the dairy wastewater. Flocculation experiments were conducted with the prescreened wastewater. Only the results of the experiments using the DS=0.86 flocculant were presented here. CS samples with lower DS values were found to deliver lower flocculation performances.

The experimental results are presented in Table 2. The suspended solid reduction was generally greater for dairy (36-58%) than swine wastewater (22-28%). This is likely related to a difference in their solid compositions. The swine wastewater in this study had a higher pH value (pH=8.6) and total nitrogen content (TN=6172 mg/L) than the dairy wastewater (pH = 6.5 and

TN= 1631 mg/L). Such a difference may be caused by differences in feed diet, animals' digestive systems, and waste management systems. For example, due to the use of sand beddings, the wastewater from sand-bedded free-stall dairies contained more minerals (e.g., silicon and carbonates) than swine wastewater.[53, 54] The adjustment of the pH value of swine wastewater from 8.6 to 8.0 is believed to have negatively affected SS reduction because some surface amino groups are certainly protonated, thus reducing the negative charge density of the surface of suspended particles. The effect of pH of swine wastewater on flocculation has been reported: a pH value of 11 or more was best for PAM to flocculate and precipitate the suspended solid.[55]

<Table 2>

CS dosage had a significant impact on SS reduction. For both swine and dairy wastewater, an optimal dosage existed within the studied concentration range (60-250 mg/L); and it was 200 mg/L for swine and 160 mg/L for dairy wastewater. Both under- and over-dosing could result in poor solid-liquid separation.[56] Flocculation/coagulation is a complex process and it involves multiple mechanisms such as charge neutralization, sweep coagulation, bridging, and patch flocculation.[57] Excessive CS could lead to covering of suspended particles with the flocculant, resulting re-stabilization the suspended solids.[58] In addition to SS reduction, SS removal efficiency, which is defined as the SS removal (mg) per mg of flocculant added, is also calculated. It decreases with the dosage for both swine and dairy wastewater. This makes sense since large suspended particles, with less curved surfaces and thus larger contact area, have greater interaction with CS granules and thus coagulated preferentially as compared to smaller particles.

A comparison of SS reduction and SS removal efficiency of the CS with reported flocculants for livestock wastewater treatment is given in Table 3. The CS did not outperform other flocculants in terms of SS reduction. Commercial flocculants, such as polyacrylamide (PAM) and chitosan, can remove >95% of SS in livestock wastewater upon optimization. The low SS reduction (27.9%) for CS is possibly limited by the percentage content of negatively charged particles among the TSS. A low SS reduction (41%) was also reported by Rolf et al.[59] The near quantitative SS reduction by PAM can be attributed to its high charge density (59%)[60]. It is noteworthy that most of the previous studies listed in Table 3 used diluted or pretreated livestock wastewater with substantially lower initial total suspended solid (TSS) levels than in this study. In terms of SS removal efficiency (72 and 162.9 mg TSS/mg flocculant for swine and dairy wastewater, respectively, at the optimal dosages), the prepared CS outperformed most of the listed flocculants. This is encouraging from a management standpoint because most livestock wastewater contains exceptionally high TSS levels and high flocculant dosages are undesired due to cost and water quality considerations.

The only other flocculant that outperformed our flocculant in terms of SS removal efficiency is a commercial cationic potato starch with a SS removal efficiency of 187 mg TSS/mg flocculant for swine wastewater.[59] However, the performances of these two flocculants may not be directly comparable because our tests were conducted using the whole CS, while it is not clear whether the commercial cationic potato starch[59] is consisted of the whole cationic starch or just the water soluble/dispersible fraction. Also, the pH value of the raw swine manure slurry used in this literature was 8.05, while our raw swine manure slurry had a pH of 8.6, indicating a higher content of basic species (such as amine) in our sample. As stated earlier, adjustment of the pH from 8.6 to 8.0 by addition of dilute HCl is expected to reduce SS removal efficiency. Nevertheless, the results demonstrate the potential of cationic starch for livestock wastewater solid and nutrient removal.

<Table 3>

4. Conclusion

Converting agricultural byproducts into value-added products is beneficial for agricultural sustainability and contributes to the establishment of a circular economy. In this study, we extracted starch from PPW, an abundant agricultural byproduct, and convert it to cationic starch through a simple wet chemistry process. The preparation cationic starch samples showed good performance in flocculation removal of SS from swine and dairy wastewater with SS removal efficiencies of 72 and 162.9 mg TSS/mg flocculant for swine and dairy wastewater respectively. The SS reduction are 27.9% and 58% for swine and dairy wastewater respectively. It could be improved by further increasing the DS of cationic starch via the use of different catalysts or solvents. Since microbes in livestock wastewater are generally negatively charged, efforts will be made to further study the flocculation removal of waterborne Coliforms and antibiotic resistant bacteria.

CRediT authorship contribution statement

Noor Haleem: conceptualization, methodology, experiment, formal analysis, investigation & draft manuscript preparatin. Augustina Osabutey: experiment. Karlee Albert: experiment. Cheng Zhang: formal analysis, investigation, research mentoring, manuscript revision, response to reviewers. Kyungnan Min: experiment. Gary Anderson: formal analysis. Xufei Yang: conceptualization, investigations, review & editing, project administration, supervision.

Declaration of Conflict of 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.

Acknowledgements

The study was sponsored by a USDA NIFA Multistate Hatch Project (SD00R690-20) through the South Dakota Agricultural Experimental Station. We wish to thank Dr. Ryan Samuel and his students for helping us acquire swine wastewater samples for this research.

References

1. Djaman, K.; Irmak, S.; Koudahe, K.; Allen, S., Irrigation Management in Potato (Solanum tuberosum L.) Production: A Review. *Sustainability* **2021,** *13*, (3).
2. Waste ManagementStat, F., Statistical Database. Food and Agriculture Organization(FAO). In 2012.
3. Sepelev, I.; Galoburda, R., Industrial potato peel waste application in food production: a review. *Res Rural Dev* **2015,** *1*, 130-136.
4. Arapoglou, D.; Varzakas, T.; Vlyssides, A.; Israilides, C., Ethanol production from potato peel waste (PPW). *Waste Management* **2010,** *30*, (10), 1898-1902.
5. Camire, M. E.; Violette, D.; Dougherty, M. P.; McLaughlin, M. A., Potato peel dietary fiber composition: effects of peeling and extrusion cooking processes. *Journal of Agricultural and Food Chemistry* **1997,** *45*, (4), 1404-1408.
6. Sampaio, S. L.; Petropoulos, S. A.; Alexopoulos, A.; Heleno, S. A.; Santos-Buelga, C.; Barros, L.; Ferreira, I. C. F. R., Potato peels as sources of functional compounds for the food industry: A review. *Trends in Food Science & Technology* **2020,** *103*, 118-129.
7. Zhang, H.; He, F.; Wang, T.; Chen, G., Thermal, pasting, and rheological properties of potato starch dual-treated with CaCl2 and dry heat. *LWT* **2021,** *146*, 111467.
8. Lin, C.-W.; Tran, D.-T.; Lai, C.-Y.; I, Y.-P.; Wu, C.-H., Response surface optimization for ethanol production from Pennisetum Alopecoider by Klebsiella oxytoca THLC0409. *Biomass and Bioenergy* **2010,** *34*, (12), 1922-1929.
9. Hussein, M. F.; Abo El Naga, A. O.; El Saied, M.; AbuBaker, M. M.; Shaban, S. A.; El Kady, F. Y., Potato peel waste-derived carbon-based solid acid for the esterification of oleic acid to biodiesel. *Environmental Technology & Innovation* **2021,** *21*, 101355.
10. dos Santos, T. C.; Gomes, D. P. P.; Bonomo, R. C. F.; Franco, M., Optimisation of solid state fermentation of potato peel for the production of cellulolytic enzymes. *Food Chemistry* **2012,** *133*, (4), 1299-1304.
11. Ge, X.; Shen, H.; Su, C.; Zhang, B.; Zhang, Q.; Jiang, H.; Yuan, L.; Yu, X.; Li, W., Pullulanase modification of granular sweet potato starch: Assistant effect of dielectric barrier discharge plasma on multi-scale structure, physicochemical properties. *Carbohydrate Polymers* **2021,** *272*, 118481.
12. Fan, Y.; Picchioni, F., Modification of starch: A review on the application of “green” solvents and controlled functionalization. *Carbohydrate Polymers* **2020,** *241*, 116350.
13. Liu, Y.; Liu, M.; Zhang, L.; Cao, W.; Wang, H.; Chen, G.; Wang, S., Preparation and properties of biodegradable films made of cationic potato-peel starch and loaded with curcumin. *Food Hydrocolloids* **2022**, 107690.
14. Lappalainen, K.; Kärkkäinen, J.; Niemelä, M.; Vartiainen, H.; Rissanen, O.; Korva, H., Preparation of cationized starch from food industry waste biomass and its utilization in sulfate removal from aqueous solution. *Carbohydrate Polymers* **2017,** *178*, 331-337.

15. Almonaityte, K.; Bendoraitiene, J.; Babelyte, M.; Rosliuk, D.; Rutkaite, R., Structure and properties of cationic starches synthesized by using 3-chloro-2-hydroxypropyltrimethylammonium chloride. *International Journal of Biological Macromolecules* **2020,** *164*, 2010-2017.

16. Li, W.; Yu, Y.; Peng, J.; Dai, Z.; Wu, J.; Wang, Z., Effects of the degree of substitution of OSA on the properties of starch microparticle-stabilized emulsions. *Carbohydrate Polymers* **2021,** *255*, 117546.

17. Garcia, M. C., Vanotti, M. B., Szogi, A. A., Simultaneous separation of phosphorus sludge and manure solids with polymers. *Transactions of the ASABE* **2007,** *50*, (6), 2205–2215.

18. Zhang, T.; Gao, N.; Wang, T. F.; Liu, H. X.; Jiang, Z. C., Global dynamics of a model for treating microorganisms in sewage by periodically adding microbial flocculants. *Math Biosci Eng* **2019,** *17*, (1), 179-201.

19. Burton, C., The potential contribution of separation technologies to the management of livestock manure. *Livestock Science* **2007,** *112*, (3), 208-216.

20. Hjorth, M.; Christensen, K. V.; Christensen, M. L.; Sommer, S. G., Solid–liquid separation of animal slurry in theory and practice. In *Sustainable Agriculture Volume 2*, Springer: 2011; pp 953-986.

21. Umar, A.; Khan, M. S.; Alam, S.; Zekker, I.; Burlakovs, J.; dC Rubin, S. S.; Bhowmick, G. D.; Kallistova, A.; Pimenov, N.; Zahoor, M., Synthesis and Characterization of Pd-Ni Bimetallic Nanoparticles as Efficient Adsorbent for the Removal of Acid Orange 8 Present in Wastewater. In *Water*, 2021; Vol. 13.

22. Jabeen, S.; Sufaid Khan, M.; Khattak, R.; Zekker, I.; Burlakovs, J.; Rubin, S. S. d.; Ghangrekar, M. M.; Kallistova, A.; Pimenov, N.; Zahoor, M.; Khan, G. S., Palladium-Supported Zirconia-Based Catalytic Degradation of Rhodamine-B Dye from Wastewater. In *Water*, 2021; Vol. 13.

23. Garcia, M. C.; Szogi, A. A.; Vanotti, M. B.; Chastain, J. P.; Millner, P. D., Enhanced solid–liquid separation of dairy manure with natural flocculants. *Bioresource Technology* **2009,** *100*, (22), 5417-5423.

24. Osabutey, A.; Haleem, N.; Uguz, S.; Min, K.; Samuel, R.; Albert, K.; Anderson, G.; Yang, X., Growth of Scenedesmus dimorphus in swine wastewater with versus without solid–liquid separation pretreatment. *Bioresource Technology* **2023,** *369*, 128434.

25. H. Zhang, R.; W. Westerman, P., SOLID-LIQUID SEPARATION OF ANNUAL MANURE FOR ODOR CONTROL AND NUTRIENT MANAGEMENT. *Applied Engineering in Agriculture* **1997,** *13*, (3), 385-393.

26. Renault, F.; Sancey, B.; Badot, P. M.; Crini, G., Chitosan for coagulation/flocculation processes – An eco-friendly approach. *European Polymer Journal* **2009,** *45*, (5), 1337-1348.

27. Lapointe, M.; Barbeau, B., Dual starch–polyacrylamide polymer system for improved flocculation. *Water Research* **2017,** *124*, 202-209.

28. Jiang, X.; Li, Y.; Tang, X.; Jiang, J.; He, Q.; Xiong, Z.; Zheng, H. J. E. S.; Research, P., Biopolymer-based flocculants: A review of recent technologies. **2021,** *28*, 46934-46963.

29. Rebello, S.; Sali, S.; Jisha, M.; Reshmy, R.; Pugazhendhi, A.; Madhavan, A.; Binod, P.; Awasthi, M. K.; Pandey, A.; Sindhu, R. J. S. C.; Pharmacy, Chitosan a versatile adsorbent in environmental remediation in the era of circular economy-a mini review. **2023,** *32*, 101004.

30. Asharuddin, S. M.; Othman, N.; Altowayti, W. A. H.; Bakar, N. A.; Hassan, A. J. E. T.; Innovation, Recent advancement in starch modification and its application as water treatment agent. **2021,** *23*, 101637.

31. Zhang, Y.; Zhang, Y.; Xu, W.; Wu, H.; Shao, Y.; Han, X.; Zhou, M.; Gu, P.; Li, Z. J. C.; Communications, I. S., Preparation methods of cellulose nanocrystal and its application in treatment of environmental pollution: A mini-review. **2023,** *53*, 100707.

32. Wang, B.; Wang, S.-F.; Lam, S. S.; Sonne, C.; Yuan, T.-Q.; Song, G.-Y.; Sun, R.-C. J. R.; Reviews, S. E., A review on production of lignin-based flocculants: Sustainable feedstock and low carbon footprint applications. **2020,** *134*, 110384.

33. Chang, Y.; Hu, Z.; Wang, P.; Zhou, J., Synthesis, characterization, and flocculation performance of cationic starch nanoparticles. *Carbohydrate Polymers* **2021,** *269*, 118337.

34. Haleem, N.; Jamal, Y.; Khan, S. N.; Baig, M. A.; Wahab, M.; Yang, X., Synthesis of Carbon Nanotubes (CNTs) from Poultry Litter for Removal of Chromium (Cr (VI)) from Wastewater. *Materials (Basel)* **2021,** *14*, (18).

35. Chittapun, S.; Jangyubol, K.; Charoenrat, T.; Piyapittayanun, C.; Kasemwong, K., Cationic cassava starch and its composite as flocculants for microalgal biomass separation. *International Journal of Biological Macromolecules* **2020,** *161*, 917-926.

36. Abdul Hadi, N.; Wiege, B.; Stabenau, S.; Marefati, A.; Rayner, M., Comparison of Three Methods to Determine the Degree of Substitution of Quinoa and Rice Starch Acetates, Propionates, and Butyrates: Direct Stoichiometry, FTIR, and (1)H-NMR. *Foods* **2020,** *9*, (1).

37. You, Y.; Yang, L.; Sun, X.; Chen, H.; Wang, H.; Wang, N.; Li, S., Synthesized cationic starch grafted tannin as a novel flocculant for efficient microalgae harvesting. *Journal of Cleaner Production* **2022,** *344*, 131042.

38. Md Nasir, N.; Abdulmalek, E.; Zainuddin, N., Preparation and Optimization of Water-Soluble Cationic Sago Starch with a High Degree of Substitution Using Response Surface Methodology. *Polymers (Basel)* **2020,** *12*, (11).

39. Boulifi, N. E.; Aracil, J.; Martínez, M., Lipase-catalyzed synthesis of isosorbide monoricinoleate: Process optimization by response surface methodology. *Bioresource Technology* **2010,** *101*, (22), 8520-8525.

40. Yamamura, H.; Putri, E. U.; Kawakami, T.; Suzuki, A.; Ariesyady, H. D.; Ishii, T., Dosage optimization of polyaluminum chloride by the application of convolutional neural network to the floc images captured in jar tests. *Separation and Purification Technology* **2020,** *237*, 116467.

41. Hansel, P. A.; Guy Riefler, R.; Stuart, B. J., Efficient flocculation of microalgae for biomass production using cationic starch. *Algal Research* **2014,** *5*, 133-139.

42. El-Naggar, M. E.; Abdel-Aty, A. M.; Wassel, A. R.; Elaraby, N. M.; Mohamed, S. A., Immobilization of horseradish peroxidase on cationic microporous starch: Physico-bio-chemical characterization and removal of phenolic compounds. *International Journal of Biological Macromolecules* **2021,** *181*, 734-742.

43. Hivechi, A.; Bahrami, S. H.; Arami, M.; Karimi, A., Ultrasonic mediated production of carboxymethyl cellulose: Optimization of conditions using response surface methodology. *Carbohydrate Polymers* **2015,** *134*, 278-284.

44. Lin, R.; Li, H.; Long, H.; Su, J.; Huang, W.; Wang, S., Optimization of lipase-catalyzed rosin acid starch synthesis by response surface methodology. *Journal of Molecular Catalysis B: Enzymatic* **2014,** *105*, 104-110.

45. Yetilmezsoy, K.; Demirel, S.; Vanderbei, R. J., Response surface modeling of Pb(II) removal from aqueous solution by Pistacia vera L.: Box–Behnken experimental design. *Journal of Hazardous Materials* **2009,** *171*, (1), 551-562.

46. Sableviciene, D.; Klimaviciute, R.; Bendoraitiene, J.; Zemaitaitis, A., Flocculation properties of high-substituted cationic starches. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2005,** *259*, (1), 23-30.

47. Pi-xin, W.; Xiu-li, W.; Xue, D.-h.; Xu, K.; Tan, Y.; Du, X.-b.; Li, W.-b., Preparation and characterization of cationic corn starch with a high degree of substitution in dioxane–THF–water media. *Carbohydrate Research* **2009,** *344*, (7), 851-855.

48. Pal, S.; Mal, D.; Singh, R., Cationic Starch: An effective flocculating agent. *Carbohydrate Polymers* **2005,** *59*, 417-423.

49. Wei, Y.; Cheng, F.; Zheng, H., Synthesis and flocculating properties of cationic starch derivatives. *Carbohydrate Polymers* **2008,** *74*, (3), 673-679.

50. Wang, Y.; Xie, W., Synthesis of cationic starch with a high degree of substitution in an ionic liquid. *Carbohydrate Polymers* **2010,** *80*, (4), 1172-1177.

51. Heinze, T.; Haack, V.; Rensing, S. J. S. S., Starch derivatives of high degree of functionalization. 7. Preparation of cationic 2-hydroxypropyltrimethylammonium chloride starches. **2004,** *56*, (7), 288-296.

52. Aggarwal, P.; Dollimore, D., The effect of chemical modification on starch studied using thermal analysis. *Thermochimica Acta* **1998,** *324*, (1), 1-8.

53. Rabinovich, A.; Rouff, A. A.; Lew, B.; Ramlogan, M. V., Aerated fluidized bed treatment for phosphate recovery from dairy and swine wastewater. *ACS Sustainable Chemistry & Engineering* **2018,** *6*, (1), 652-659.

54. Khan, I.; Saeed, K.; Zekker, I.; Zhang, B.; Hendi, A. H.; Ahmad, A.; Ahmad, S.; Zada, N.; Ahmad, H.; Shah, L. A.; Shah, T.; Khan, I., Review on Methylene Blue: Its Properties, Uses, Toxicity and Photodegradation. In *Water*, 2022; Vol. 14.

55. Lee, W.-C.; Chang, C.-C. J. S., Effectively Recycling Swine Wastewater by Coagulation–Flocculation of Nonionic Polyacrylamide. **2022,** *14*, (3), 1742.

56. Mohseni, A.; Fan, L.; Roddick, F.; Li, H.; Gao, Y.; Liu, Z., Cationic starch: an effective flocculant for separating algal biomass from wastewater RO concentrate treated by microalgae. *Journal of Applied Phycology* **2021,** *33*, (2), 917-928.

57. Suopajärvi, T., Functionalized nanocelluloses in wastewater treatment applications. *Acta Universitatis Ouluensis C* **2015,** *526*.

58. Maraschin, M.; Ferrari, K. F. S. H.; da Silva, A. P. H.; Carissimi, E., Aluminum sludge thickening: Novel helical pipes for aggregation by dual flocculation and thickening by filtration applied to water treatment plants. *Separation and Purification Technology* **2020,** *241*, 116560.

59. Rolf, J.; Weide, T.; Brügging, E.; Wetter, C., The Application of Biodegradable Flocculants Derived From Potato Starch for Nutrient Recovery in Pig Manure. *Global Journal of Agricultural Research* **2021,** *9*, 1-15.

60. Walker, P.; Kelley, T., Solids, organic load and nutrient concentration reductions in swine waste slurry using a polyacrylamide (PAM)-aided solids flocculation treatment. *Bioresource Technology* **2003,** *90*, (2), 151-158.

61. González-Fernández, C.; Nieto-Diez, P. P.; León-Cofreces, C.; García-Encina, P. A., Solids and nutrients removals from the liquid fraction of swine slurry through screening and flocculation treatment and influence of these processes on anaerobic biodegradability. *Bioresource Technology* **2008,** *99*, (14), 6233-6239.

62. Chelme-Ayala, P.; El-Din, M. G.; Smith, R.; Code, K. R.; Leonard, J., Advanced treatment of liquid swine manure using physico-chemical treatment. *Journal of Hazardous Materials* **2011,** *186*, (2), 1632-1638.

63. Pacheco, I. d. S.; Alves, A. G. T.; Santana, L. C.; Ribeiro, E. A. M.; Canobre, S. C.; Amaral, F. A., Performance of cationic hemicelluloses arising from peanut shell residue from agroindustry in application as primary coagulant in physical-chemical treatment of dairy wastewater. *Journal of Water Process Engineering* **2022,** *47*, 102661.

Figure Captions

Fig. 1. Conversion of potato peel starch to CS through etherification reactions with 3- chloro-2-hydroxypropyl trimethylammonium chloride (CHPTAC).

Fig. 2. Response surface plots showing the co-effects of NaOH concentration, the volume of cationic reagent, and reaction time on the DS of CS.

Fig. 3. Scanning electron microscope (SEM) images of (a) raw starch extracted from potato peels (DS=0), (b) CS with DS=0.12, and (c) CS with DS=0.86. All the images were taken at ×300 magnification.

Fig. 4. FTIR spectra (wave number: 700-4000 cm^{-1}) for raw starch extracted from potato peels (DS=0), CS with DS=0.12, and CS with DS=0.86. Shown in the insert is the FTIR spectra of the three samples between 1460 and 1500 cm^{-1}. A peak at 1480 cm^{-1} indicates the occurrence of $C\text{-}N^+$ groups.

Fig. 5. ^1H NMR spectra of (a) CS with DS=0.86, (b) raw starch extracted from potato peels (DS=0), (c) spectrum b with no truncation to the highest peaks, and (d) & (e) spectral region of 3.2-3.1 ppm of DS=0.86 and DS=0 samples, respectively.

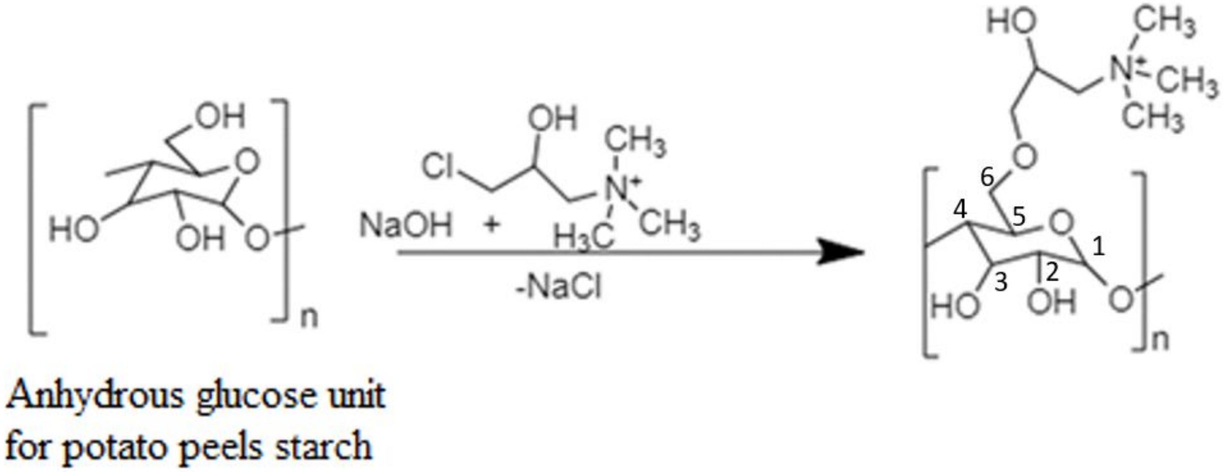

Fig. 1. Conversion of potato peel starch to CS through etherification reactions with 3-chloro-2-hydroxypropyl trimethylammonium chloride (CHPTAC). The carbon atoms in the AGU are labeled.

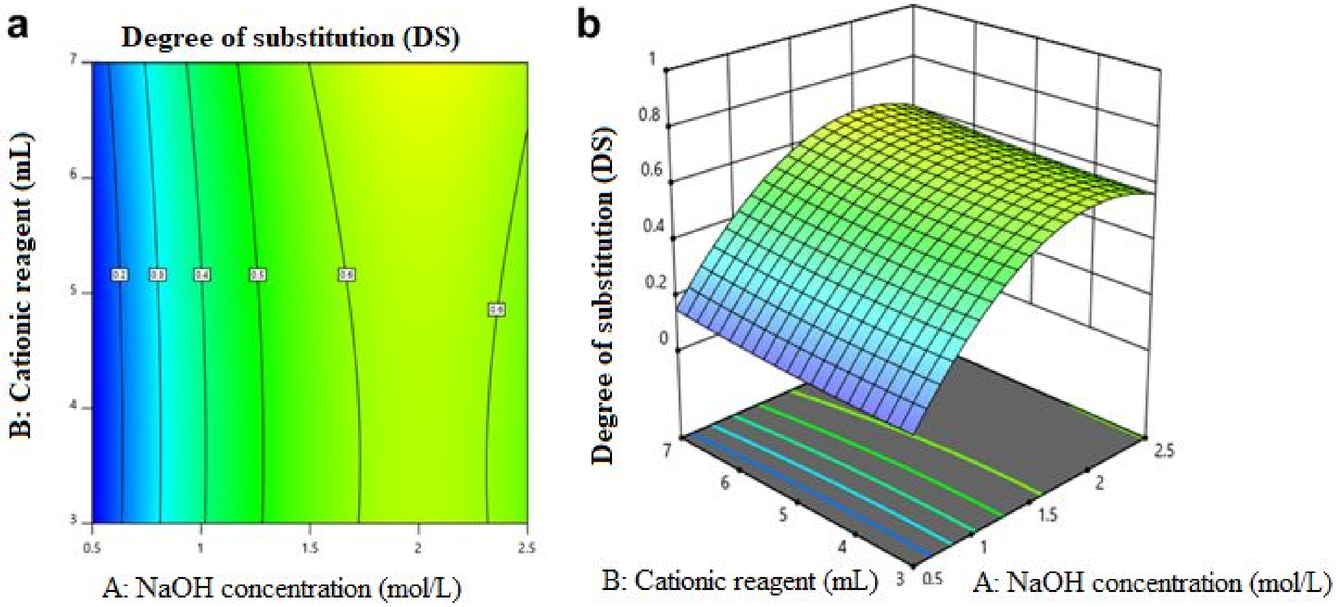

Fig. 2. Response surface plots showing the co-effects of NaOH concentration, volume of cationic reagent, and reaction time on the DS of CS.

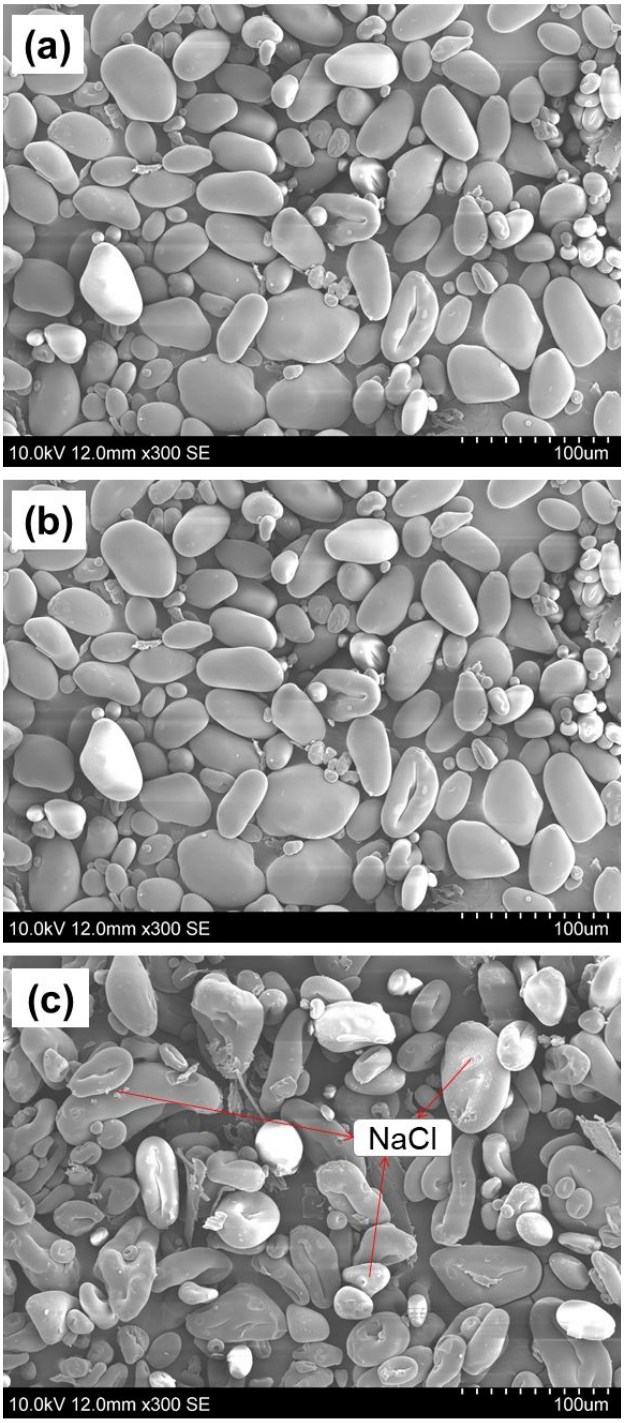

Fig. 3. Scanning electron microscope (SEM) images of (a) raw starch extracted from potato peels (DS=0), (b) CS with DS=0.12, and (c) CS with DS=0.86. All the images were taken at ×300 magnification.

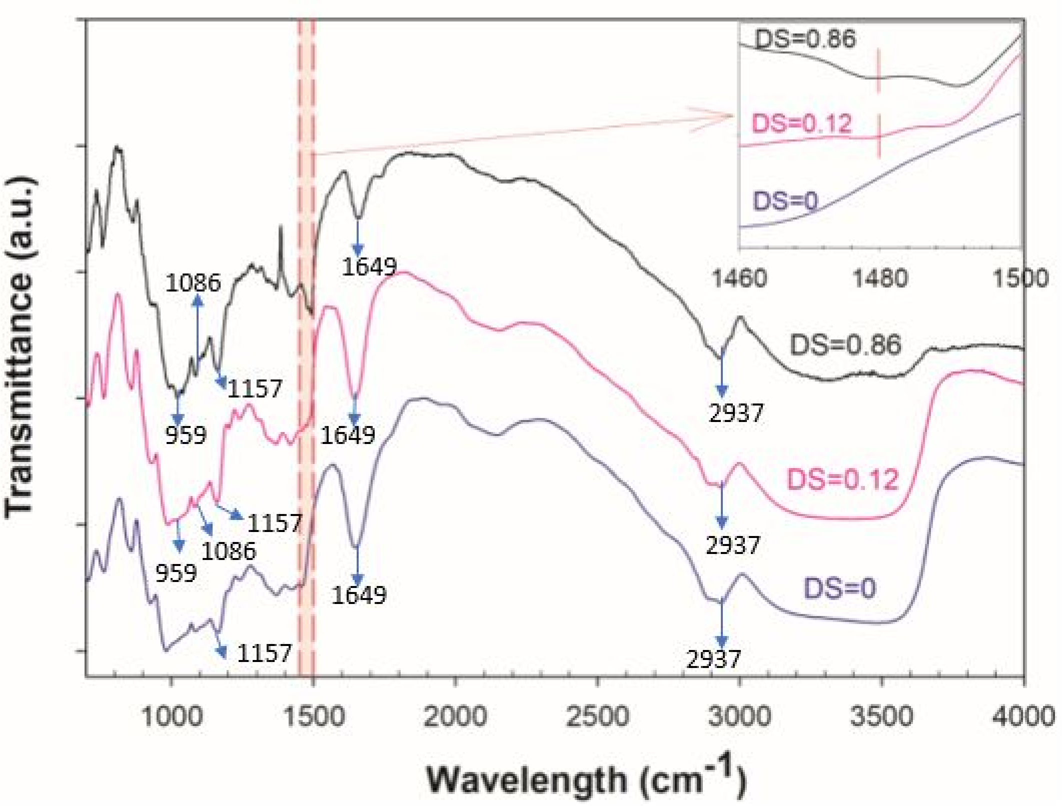

Fig. 4. FTIR spectra (wave number 0-4000 cm^{-1}) for (a) raw starch extracted from potato peels (DS=0), (b) CS with DS=0.12, and (c) CS with DS=0.86.

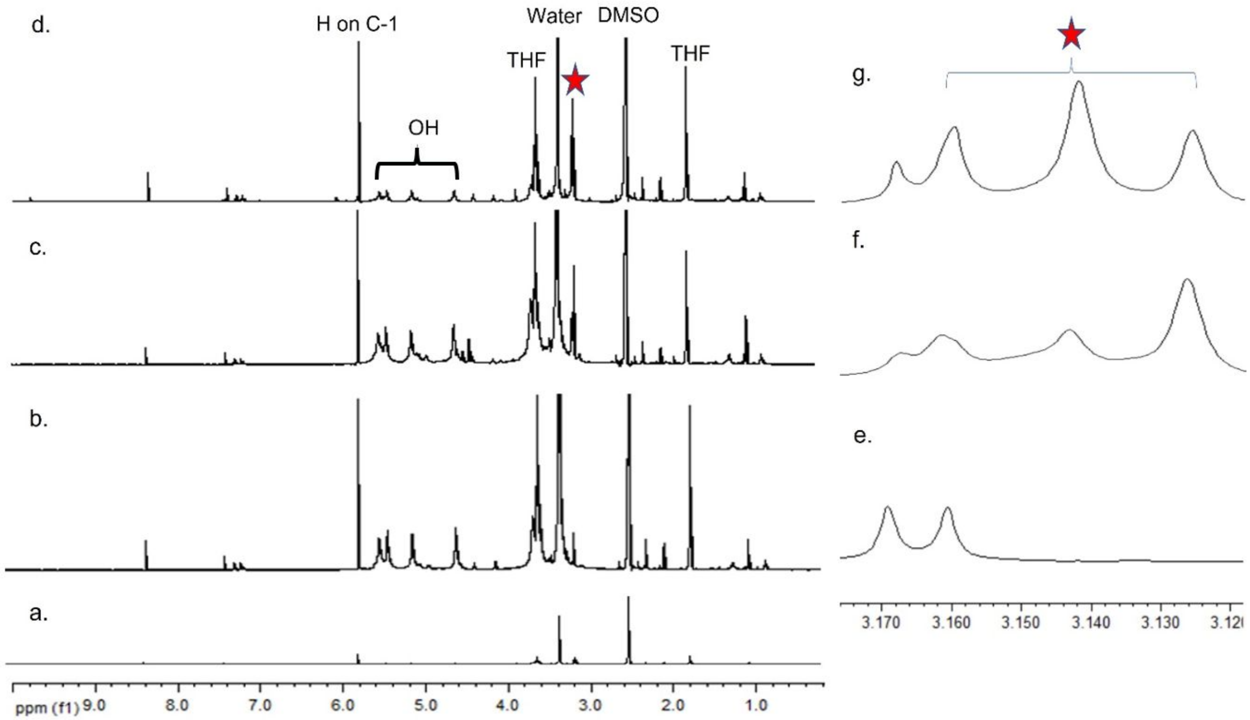

Fig. 5. ^{1}H NMR spectra of raw starch (a,b) extracted from potato peels (DS=0), CS with DS=0.12 (c), and CS with DS=0.86 (d). The spectral region of 3.176-3.120ppm of DS=0, 0.12 and 0.86 are shown in e, f, and g, respectively.

3.125, 3.142 and 3.160 ppm

Table 1. Experimental design for optimizing cation starch preparation conditions.

Experiment No.	**Factor 1** **A: NaOH concentration (mol/L)**	**Factor 2** **B: Cationic reagent (mL)**	**Factor 3** **C: Reaction time (min)**	**Response 1** **Degree of substitution (DS)**
1	1.5	5	4	0.57
2	2.5	7	2	0.55
3	0.5	5	2	0.17
4	2	4	2	0.74
5	2.5	3	5	0.54
6	1	6	5	0.49
7	1.5	5	4	0.57
8	0.5	5	2	0.17
9	1	6	3	0.43
10	0.5	3	4	0.12
11	1.5	5	4	0.57
12	0.5	7	4	0.19
13	1	3	3	0.39
14	1.5	7	2	0.58
15	2.5	7	4	0.64
16	1.5	5	4	0.57
17	2	4	2	0.74
18	0.5	4	5	0.15
19	2	7	5	0.86
20	2.5	6	3	0.60

Table 2. SS removal from dairy and swine wastewater using the prepared CS.

Dosage (/)	**Average TSS (mg/L)**	**SS reduction (%)**	**SS removal efficiency** [a]
Swine wastewater, with initial [TSS] = 51,433 ± 1607 (mg/L)			
80	40,210 ± 1392	21.8	140.3
125	39,617 ± 1077	23.0	94.5
160	37,517 ± 993	27.1	87.0
200	36,950 ± 1905	27.9	72.0
250	38,417 ± 1487	25.3	52.1
Dairy wastewater, with initial [TSS] = 44,968 ± 104 (mg/L)			
80	28,750 ± 132	36.1	202.7
125	25,400 ± 379	43.5	156.5
160	18,900 ± 275	58.0	162.9
200	25,850 ± 180	42.2	95.6
250	27,500 ± 29	38.8	69.9

[a] SS removal efficiency is defined as the SS removal (mg SS/mg of flocculant used).

Table 3. SS reduction and SS removal efficiency: A comparison with the literature results on SS flocculation for swine and dairy wastewater.

Wastewater	**Flocculant** [a]	**Initial TSS (mg/L)**	**Dosage (mg/L)**	**SS reduction (%)**	**SS removal efficiency (mg SS/mg flocculant)**	**References**
Swine	PAM	177.3	375	99.6 [b]	0.452	[60]
	PAM	2900	80-200	37-64 [c]	13.44-5.37	[61]
	SAP	4375	1250	33	1.16	[62]
	Cationic starch	51,433	167	27.9	187	[59]
	CS	76,000	200	41	72.0	This study
Dairy	Chitosan	11540	540	98.7 [d]	21.1	[23]
	Cationic hemicelluloses	336	400	80 [e]	0.67	[63]
	CS	44,968	160	58.0	162.9	This study

[a] PAM – polyacrylamide; SAP – superabsorbent polymer. [b] The study tested multiple different swine wastewater. To be relevant, only the results from grower-finisher swine wastewater was included. The SS concentration of raw wastewater was low (177.3 mg/L). [c] The study tested multiple different swine wastewater. To be relevant, only the results from pre-sieved feeder-to-finish swine wastewater was included. [d] The reduction efficiency was achieved through flocculant addition followed by sieving (with 1-mm screens). [e] The reduction efficiency was achieved at pH = 9.0. The raw wastewater was diluted with a SS concentration of 336 mg/L.