Gamma-irradiation synthesis of quaternary phosphonium cationic starch flocculants
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ABSTRACT
Quaternary phosphonium cationic starch (St-g-AM/ATPPB) flocculant was synthesized by using corn starch and acrylamide (AM), allyl triphenyl phosphonium bromide binary (ATPPB) through simultaneous gamma-irradiation. The chemical structure of the copolymer was characterized by FTIR (Fourier transform infrared spectroscopy) and $^1$H NMR (nuclear magnetic resonance) technologies. The effects of the absorbed dose in the range of 1 to 6 kGy, AM/ATPPB ratio and starch/(AM + ATPPB) ratio on grafting and flocculation were investigated. At a starch:AM:ATPPB wt ratio of 1:1.4:0.93, the graft ratio of AM/ATPPB reached maximum values at 3 and 6 kGy, and the cationic degree of St-g-AM/ATPPB increased with absorbed dose, while the turbidity reduction reached a maximum value at 5 kGy. At 3 kGy using a starch:(AM + ATPPB) wt. ratio of 1:2.33, the graft ratio of AM and ATPPB increased with AM/ATPPB ratio, while the cationic degree and turbidity reduction reached maximum values at AM:ATPPB wt. ratios of 1:0.67 and 1:0.5, respectively. At a constant AM:ATPPB wt. ratio of 1.067 and 3 kGy, the grafting ratio increased with starch/(AM + ATPPB), while the cationic degree and turbidity reduction simultaneously reached maximum values at a starch:(AM + ATPPB) wt. ratio of 1:2.67. Further study revealed that the higher the absorbed dose or the lower the starch/(AM + ATPPB) ratio, the lower the optimal flocculant concentration.

Key words | acrylamide, allyl triphenyl phosphonium bromide, cationic starch, flocculant, gamma-irradiation

INTRODUCTION
Water pollution due to toxic metals and organic compounds remains a serious environmental and public problem. Strict legislation on the discharge of these toxic products makes it necessary to develop efficient water treatment technologies for the removal of pollutants from wastewater (Crini 2005). The removal can be accomplished by gravitation (very slow), by coagulation (dependent on electric charge situation) and by flocculation (not dependent on electric charges and the fastest). Flocculation technology is widely used due to its high efficiency, economy and simplicity. Both inorganic and organic flocculants are in use. Inorganic flocculants (e.g., alum, ferrite flocculants and polyaluminum chloride) are used in very large quantities with large amounts of sludge left and are strongly affected by pH changes. Organic flocculants are typically polymeric in nature, and are used in ppm quantities. The organic flocculants can be classified into two groups, namely natural and synthetic (Brostow et al. 2009). Synthetic flocculants are further divided into anionic, cationic and non-ionic categories.

The majority of the cationic groups of organic flocculants are derived by introducing quaternary ammonium groups onto the polymer backbone, although polymers containing sulphonium and phosphonium groups are used to a limited extent. The most commonly used cationic polyelectrolytes are poly(dimethyldiallyl ammonium chloride) (polyDMDAAC), cationic polyacrylamide (CPAM), polymers from epichlorohydrin and dimethylamine (ECH/DMA). On the other hand, polyacrylamide as non-ionic flocculant is widely used due to its good water solubility, high molecular weight and the ability to create both anionic and cationic forms (Ziółkowski & Shyichuk 2011). Many types of cationic monomers can be homo- or copolymerized with acrylamide to yield water-soluble polymers with varying positive charge using peroxide catalyst as the initiator, which have found applications in paper making, water treatment and sludge conditioning (Wandrey & Jaeger 1984; Lin et al. 1988; Tripathy & De 2006). However, polyacrylamide is non-biodegradable and not shear resistant in flow. Natural
polymers – including starch – are fairly shear stable and biodegradable, but their flocculation efficiency is low, and their solutions and flocs lose stability and strength, respectively, due to biodegradability. In order to combine the best properties of both kinds of polymers, synthetic polymers are usually grafted onto backbones of natural polymers after purification (Shi et al. 2001; Brostaw et al. 2009; Banerjee et al. 2012; Cao et al. 2012; Gao & Xu 2012). Exemplifying this class of flocculants is cationic polyacrylamide-grafted starch (SPAM), which is an effective flocculant in suspensions of both low and high concentrations and has been widely used in many fields, such as paper making, spinning, petroleum well drilling, medicine, daily chemicals and flotation (Sableviciene et al. 2005; Pal et al. 2006; Guo et al. 2006; Ziółkowska & Słychuck 2011; Cao et al. 2012).

In fact, cationic SPAM can be synthesized by two grafting methods, i.e., the one-step method and the two-step method. The one-step method is simultaneously grafting AM and a cationic monomer (e.g., DMDAAC) to starch using chemical initiators. This method is simple and environmentally friendly, and the resulting cationic SPAM has strong flocculation capability. The so-called two-step method consists of first grafting acrylamide (AM) to starch, and then adding formaldehyde and dimethylamine through Mannich reaction (Guo et al. 2006; Cao et al. 2012).

Generally, starch-based flocculants containing cationic charge can be divided into three categories: ammonium (including amines), sulphonium and phosphonium quaternaries. However, reports regarding cationic starch-based flocculants containing phosphonium quaternaries have been rare in the literature during recent decades. Due to the polarizability difference between ammonium and phosphonium cationic centres, phosphonium-based cationic SPAM can be expected to have a different flocculating capability than their ammonium counterpart. In this paper, a series of phosphonium-based cationic SPAM (St-g-AM/ATPPB) are synthesized by grafting AM and allyl triphenyl phosphonium bromide (ATPPB) to corn starch, using the simultaneous gamma-irradiation technique. The graft ratio, cationic degree and flocculating activity of St-g-AM/ATPPB are investigated.

**METHODS**

**Materials**

Food grade corn starch powder was supplied by Henan Yongchang Starch Sugar Co., Ltd. Allyl triphenyl phosphonium bromide (ATPPB, analytical reagent) was purchased from Shandong Luyue Chemical Co., Ltd. AM analytical reagent was obtained from Tianjin No.3 Chemical Reagent Factory. Kaolin was purchased from Tianjin Kermel Chemical Reagent Co., Ltd. All other chemicals were analytical reagents. Double distilled water was used for preparation and measurements.

**Radiation process**

In order to study the effect of the absorbed dose on grafting and flocculation, a mixture of 6 g of corn starch powder and 60 mL of distilled water was continuously stirred using a mechanical stirrer under a nitrogen atmosphere in a water bath at 85 °C for 30 min. The gelatinized corn starch was mixed with 8.4 g of AM and 5.6 g of ATPPB, and continuously stirred to form a homogenous mixture under a nitrogen atmosphere. Thenceafter, the homogenous mixture was transferred into a bottle under nitrogen protection. The bottle was tightly closed with a cap. After the bottle was irradiated with cobalt 60 to a required absorbed dose at 40 Gy/min dose rate at 25 °C, a crude St-g-AM/ATPPB sample containing ungrafted poly (AM-co-ATPPB) and unreacted monomers was obtained.

In order to study the effect of AM/ATPPB ratio on grafting and flocculation, a gelatinized mixture of 6 g of corn starch powder and 60 mL of distilled water was mixed with 0.14 g to 11.2 g of AM and ATPPB, respectively. After a homogenous mixture was formed, the mixture was irradiated to 3 kGy by the same method mentioned in the previous paragraph, and then, a crude St-g-AM/ATPPB sample was obtained.

In order to study the effect of starch/(AM + ATPPB) ratio on grafting and flocculation, a gelatinized mixture of 6 g of corn starch powder and 60 mL of distilled water was mixed with AM and ATPPB using a fixed ratio of 8.4:5.6, whereas starch/(AM + ATPPB) ratio varied from 6:3 to 6:18, respectively. After a homogenous mixture was formed, the mixture was irradiated by the same method mentioned in the previous paragraph, and then, a crude St-g-AM/ATPPB sample was obtained.

**FTIR analysis**

The functional groups of St-g-AM/ATPPB were examined by Fourier transform infrared spectroscopy (FTIR), on a Bio-Rad FTS 135 spectrometer using a KBr pellet.

**NMR analysis**

Proton nuclear magnetic resonance (NMR) spectra were recorded in deuterium oxide (D₂O) on a Bruker Avance...
300 MHz, Germany. Chemical shifts were recorded as δ values in parts per million (ppm) and referenced to the solvent used (i.e., D₂O).

Determination of graft ratio

A crude sample was washed with ethanol and dried under vacuum at 60 °C for 24 hours. After the dried sample was ground into a powdered sample, the powder was extracted continuously for 18 hours in a Soxhlet extractor with a mixture of acetone and glacial acetic acid (1:1 v/v). After extraction, the sample was dried in a vacuum oven at 60 °C to a constant weight, and then a fine St-g-AM/ATPPB sample without ungrafted poly(AM-co-ATPPB) and unreacted monomers was obtained.

Graft performance in terms of percentage graft ratio was determined by weight measurement, and the percentage graft ratio was determined as:

\[
\text{Graft ratio} = \frac{\text{Weight of graft copolymer} - \text{Weight of starting starch}}{\text{Weight of starting starch}} \times 100\% 
\]

where weight of graft copolymer is the weight of the fine St-g-AM/ATPPB sample.

Determination of cationic degree

The cationic degree of St-g-AM/ATPPB was determined by titration (Mohr’s method) (Block & Waters 1967), which depended upon the content of ATPPB moiety in the copolymer. St-g-AM/ATPPB was weighed into a 250 ml Erlenmeyer flask and dissolved in 100 ml of distilled water. The pH value of the solution was adjusted to between 6.5 and 7.2. Potassium chromate served as the end point indicator in the titration of chloride ions with a silver nitrate standard solution. The colour change from yellow to brick-red signalled the end point of this titration. The cationic degree, which is defined as the mmol amount of ATPPB incorporated per gram of St-g-AM/ATPPB, used in mmol/g was determined as:

\[
\text{Cationic degree} = \frac{\text{Molarity of AgNO}_3 \times \left( V_{\text{AgNO}_3} - V_{\text{AgNO}_3}^0 \right)}{\text{Weight of starch grafted copolymer}} 
\]

where Molarity of AgNO₃ is used in mmol/mL, \( V_{\text{AgNO}_3} \) is the volume of the silver nitrate standard solution consumed during titration used in ml, \( V_{\text{AgNO}_3}^0 \) is the volume of the silver nitrate standard solution consumed during blank titration used in ml.

Floculation properties

The physical and chemical characteristics of kaolin are: specific surface area: 14.0 ± 0.1 m²/g (BET); cation exchange capacity: 9.1 cmol/kg; pH = 7.24; kaolinite: 89.0%; quartz: 5%; alunite: 6%.

Kaolin (0.6%) water solution was stirred using a mechanical stirrer at a speed of 500 r/min for 4 hours to form a suspension, and the pH of the colloidal suspension was adjusted to 7 using 0.1 N HCl solution, followed by 24 hours of settling time. A St-g-AM/ATPPB sample was put into 1,000 ml of the kaolin solution and mixed by stirring at a speed of 200 r/min for 0.5 hours, followed by 0.5 hours of settling time. The upper clear liquid was separated for further testing. The turbidity of the upper clear solution of kaolin was measured by a WZG-220 photoelectric turbidimeter (Shanghai Precision & Scientific Instrument). The turbidity reduction can be calculated by the following formula (Guo et al. 2006):

\[
\text{Turbidity reduction} = \frac{N_0 - N_i}{N_0} \times 100\% 
\]

where \( N_0 \) is the turbidity of the starting kaolin solution, \( N_i \) is the turbidity of the kaolin solution treated with flocculant. In this paper, the turbidity of the starting kaolin solution was 148 to 153 NTU.

RESULTS AND DISCUSSION

Characterization of St-g-AM/ATPPB by FTIR and NMR

The functional groups of St-g-AM/ATPPB were characterized by FTIR as shown in Figure 1. The IR spectrum of St-g-AM/ATPPB gives all the characteristic absorption peaks of corn starch (3,408 cm⁻¹ (s, broad); 2,928 cm⁻¹ (m); 1,153, 1,084 and 1,025 cm⁻¹ (s) for O-H, C-H and C-O stretching, respectively) and additional peaks at 3,202 cm⁻¹ (m), which are the characteristics of the –CONH₂ group contained in the acrylamide moiety. In addition, the peak at 1,413 cm⁻¹ (m) is for the weak band N-H out of plane bending. These were the typical absorption bands of the amide (Lanthong et al. 2006). Gamma-irradiation produced free radicals at active
sites of C-2 or C-3 hydroxyl of the starch backbones (Kiatkamjornwong et al. 2000). The grafting reaction emanated from those sites of the swollen starch to which AM and ATPPB molecules diffused from the aqueous phase to perform the grafting reaction.

To confirm that St-g-AM/ATPPB contained ATPPB, the proton (^1H) nuclear magnetic resonance spectra of the samples were recorded in deuterium (D2O). Although ^1H NMR of the graft polymer is complicated, the chemical shifts in 7.726, 7.637 and 7.574 ppm prove the presence of ATPPB moiety in St-g-AM/ATPPB (Figure 2).

Effect of the absorbed dose on grafting and flocculation

At a starch:AM:ATPPB wt. ratio of 1:1.4:0.93 (i.e., AM/ATPPB 1:0.124 mol), St-g-AM/ATPPB was synthesized in 60 mL water using gamma-irradiation at 40 Gy/min. The effects of the absorbed dose on the graft ratio and cationic degree of St-g-AM/ATPPB are given in Figure 3. The graft ratio increased initially with increasing absorbed dose up to 3 kGy and then decreased. However, the graft ratio increased once again as the absorbed dose further increased. As known, the irradiation of polymers generally produced simultaneous scission and cross-linking of polymeric chains (Clarlesby 1991). The initial increase in the graft ratio of AM/ATPPB was due to more active sites on the starch backbone in various initiation steps as the absorbed dose increased. The subsequent decline was caused by the intramolecular scission of starch backbones instead of AM/ATPPB graft chains at a higher dose, which can be proved by the continuous increase of cationic degree as the absorbed dose increased as shown in Figure 3. The high values of the graft ratio and cationic degree at 6 kGy were attributed to St-g-AM/ATPPB cross-linking predominating over its chain scission at this absorbed dose (Pande & Sharma 2002; El-Din et al. 2007; Mishra et al. 2007). The cationic degree of St-g-AM/ATPPB increased with the absorbed dose, which is different from that of
starch-graft-poly(acrylamide-co-dimethylallyl ammonium chloride) in previous work (Lv et al. 2013).

Kaolin (0.6%) water solution was stirred using a mechanical stirrer at a speed of 500 r/min for 4 hours to form a suspension, and the pH of the colloidal suspension was adjusted to 7 using 0.1 N HCl solution, followed by 24 hours of settling time. Two milligrams of St-g-AM/ATPPB were placed in 1,000 L of the kaolin solution and mixed by stirring at a speed of 200 r/min for 0.5 hour, followed by 0.5 hour of settling time. Then the turbidity was measured. The effect of the absorbed dose on the flocculating activity of St-g-AM/ATPPB is also given in Figure 3. The flocculating activity increased as the absorbed dose increased from 1 to 5 kGy. The cationic degree of St-g-AM/ATPPB increased with the absorbed dose increasing, which could enhance the bridging capability and, hence, improve the flocculating activity. However, when the absorbed dose was 6 kGy, St-g-AM/ATPPB cross-linking predominated over its chain scission, which made St-g-AM/ATPPB more difficult to dissolve in water, hence decreased movement of the molecular chains and functional groups, and, therefore, a slight decline in the flocculating activity.

**Effect of AM/ATPPB ratio on grafting and flocculation**

In order to investigate the effect of AM/ATPPB on grafting and flocculation, St-g-AM/ATPPB was synthesized at 3 kGy using a starch:AM:ATPPB wt. ratio of 1:1.4:0.93 in 60 mL water, whereas the AM:ATPPB wt. ratio varied from 0:14 to 1:0.5; the results are shown in Figure 4.

The graft ratio of St-g-AM/ATPPB increased with the increase of the AM/ATPPB ratio, which implied that ATPPB was less sensitive towards the graft copolymerization process compared with AM because of the steric hindrance effect; therefore, the higher the content of AM, the higher the graft ratio is. However, the cationic degree reached its highest value at an AM:ATPPB wt. ratio of 1:1 (i.e., AM/ATPPB 1:0.185 mol).

The flocculating activity of St-g-AM/ATPPB increased with the AM:ATPPB wt. ratio from 0:14 to 1:0.5; however, it showed a decreasing trend when the AM:ATPPB wt. ratio was more than 1:0.5 (i.e., AM/ATPPB 1:0.08 mol). As shown in Figure 4, the cationic degree, graft ratio and flocculating activity of St-g-AM/ATPPB increased to their highest values when AM:ATPPB wt. ratios were 1:1, 1:0.5 and 1:0.25, respectively. The reasonable explanation is due to a compromise between the cationic degree and the content of AM grafted onto starch backbones. The cationic groups were necessary for charge neutralization and attraction of the graft polymer to kaolin particle surface, and AM moieties (i.e., amide groups) were necessary for strong adsorption and bridging between two or more particles (Wandrey & Jaeger 1984; Bao et al. 2002; Bolto & Gregory 2007).

**Effect of starch/(AM + ATPPB) ratio on grafting and flocculation**

In order to investigate the effect of the starch/(AM + ATPPB) ratio on grafting and flocculation, St-g-AM/ATPPB was prepared using a constant AM:ATPPB wt. ratio of 1:0.67 (i.e., AM/ATPPB 1:0.124 mol) at 3 kGy in 60 ml water, whereas the starch:(AM + ATPPB) wt. ratio varied from 1:0.5 to 1:3. The results are shown in Figure 5.

As shown, the graft ratio increased almost linearly from 12% to 165% with the starch:(AM + ATPPB) wt. ratio. In comparison, by varying the starch:(AM + DMDAAC) wt.
ratio from 1.0:5 to 1.3, the graft ratio of the starch-graft-poly
(acrylamide-co-dimethyl diallyl ammonium chloride)
increased almost linearly from −10% to 267% (Lv et al.
2013). The cationic degree of St-g-AM/ATPPB increased
sharply from 0.137 to 0.564 mmol/g, and then increased
slightly to 0.566 mmol/g as the starch/(AM + ATPPB) ratio
increased. Moreover, in comparison, the cationic degree
increased from 0.74 to 1.17 mmol/g for starch-graft-poly
(acrylamide-co-dimethyl diallyl ammonium chloride) as the
starch:(AM + DMDAAC) wt. ratio increased from 1:0.5 to
1.5 (Lv et al. 2013). The flocculating activity of St-g-AM/
ATPPB increased sharply with the starch/(AM + ATPPB)
weight ratio initially, thereafter it tended to increase slightly. The
cationic degree and turbidity reduction showed the same
increasing trend, which implied that cationic degree was a pre-
dominant factor influencing turbidity reduction of St-g-AM/
ATPPB in the flocculating process.

Flocculation properties

As known, the dosage of flocculant affected the flocculating
effect. In order to estimate the flocculating effect of St-g-
AM/ATPPB as a flocculant, St-g-AM/ATPPB samples syn-
thetized at 2 and 5 kGy using starch:AM:ATPPB wt. ratios
of 1:1.4:0.93 and 1:0.6:0.4, were used. Aaolin (0.6%) water
solution was stirred using a mechanical stirrer at a speed
of 500 r/min for 4 hours to form a suspension, and the pH
of the colloidal suspension was adjusted to 7 using 0.1 N
HCl solution, followed by 24 hours of settling time. St-g-
AM/ATPPB samples were placed in 1,000 L of the kaolin
solution and mixed by stirring at a speed of 200 r/min for
0.5 hour, followed by 0.5 hour of settling time. Then the tur-
bidity was measured. Figure 6 shows the results.

As shown in Figure 6, the values of the turbidity
reduction increased with the dosage of flocculants. The opti-
mal flocculant concentration was 3 mg/L for the St-g-AM/
ATPPB sample synthesized using a starch:AM:ATPPB wt.
ratio of 1:1.4:0.93 at 5 kGy, and in comparison, 6 mg/L for
that at 2 kGy, which implied that the higher the absorbed
dose, the lower the optimal flocculant concentration. Moreover, the optimal flocculant concentration exceeded
10 ml/L for the St-g-AM/ATPPB samples synthesized using a
starch:AM:ATPPB wt. ratio of 1:0.6:0.4 at 5 and 2 kGy,
which implied that the higher the starch/(AM + ATPPB)
weight ratio, the higher the optimal flocculant concentration.

CONCLUSIONS

Quaternary ammonium-based flocculants have been known
about and produced for years, while quaternary phos-
phonium-based counterparts have been neglected in the
literature. Even so, it is meaningful to develop quaternary phosphonium-based flocculants, and these flocculants are
expected to have different characteristics to their quaternary
ammonium-based counterparts due to the higher electronic
polarizability of a phosphorus atom than that of a nitrogen
atom (Shabestary et al. 2007). In this paper, quaternary phosphonium-based starch (St-g-AM/ATPPB) flocculants were
synthesized by simultaneous gamma-irradiation. The
absorbed dose, the AM/ATPPB ratio and the starch/(AM +
ATPPB) ratio had an effect on the graft ratio, cationic
degree and flocculation properties of St-g-AM/ATPPB. An
increase in the absorbed dose in the range of 1 to 5 kGy,
was in favour of the flocculating activity of St-g-AM/ATPPB against the kaolin suspension. The flocculating activity of St-g-AM/ATPPB reached a maximum value at an AM:ATPPB wt. ratio of 1:0.5 using a constant starch/(AM + ATPPB) ratio, due to a compromise between the cationic degree and the content of AM grafted on starch backbones. At a constant AM:ATPPB wt. ratio of 1:0.5, the flocculating activity of St-g-AM/ATPPB increased sharply with the starch/(AM + ATPPB) ratio initially, thereafter it tended to increase slightly. Moreover, the higher the absorbed dose at the same value of the starch/AM/ATPPB ratio or the lower the optimal starch/(AM + ATPPB) ratio at a constant AM/ATPPB ratio, the lower the optimal flocculant concentration.

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