Poly-(acryl amine–co-dimethyl diallyl ammonium chloride) graft starch flocculant for cleaning-up of wastewater
Changhu Zhang, Juxiang Yang, Jiangtao Li, Zhenhua Fang and Yaping He

ABSTRACT
Graft starch flocculant (GSF) was synthesized by copolymerization of carboxymethylated soluble starch, acryl amine and dimethyl diallyl ammonium chloride using ceric ammonium nitrate \((\text{NH}_4)_2\text{Ce(NO}_3\text{)}_6\) as the polymerization initiator. The morphology was observed by scanning electron microscope, the structure was characterized by Fourier transform infrared spectroscopy and the surface area was measured by the Brunauer–Emmett–Teller method. The experimental results showed that the GSF had huge pore volume, high specific area and proper reaction groups, which could enhance its ability to adsorb heavy metal ions. The adsorption behavior was investigated through batch experiments in simulated \(\text{Cu}^{2+}\) and \(\text{Pb}^{2+}\) ions wastewater, and adsorption characteristics were affected by many factors, such as flocculant concentration, pH of the solution and adsorption time. Finally, the optimal adsorption parameters were gained, with GSF density of 0.024 mg·L\(^{-1}\)/\(C_0\), pH of 8 and a reaction time of 30 min. Application experiments adequately demonstrated that the removal ratio of \(\text{Cu}^{2+}\) and \(\text{Pb}^{2+}\) ions for the local wastewater reached about 50% based on the above optimized condition.

Key words | adsorption behavior, flocculant, starch copolymer

INTRODUCTION
With the rapid development of economy, the environmental problems caused by the chemicals are more and more prominent. In particular, poor quality of drinking water and sanitation were the major causes of preventable morbidity and mortality in the world due to water-borne and food-borne infections (Bodlund et al. 2014). Water pollution produced by humans is frequently laden with organic contaminants and toxic heavy metals such as mercury, chromium, cadmium, copper and lead. In particular, the issue of heavy metal pollution is very much of concern because of their toxicity for plant, animal and human beings and their lack of biodegradability (Singh & Prasad 2015). Various methods such as ion exchange, neutralization, reverse osmosis, precipitation, solvent extraction and adsorption have been developed to remove toxic metals from aqueous solution. Adsorption method provides a simple and universal approach for effective removal of various pollutants, particularly, the heavy metal ions. It is also an economical choice in that it is easy to handle, and has high efficiency in removing heavy metal ions with medium and low dosage in wastewater (Zhou et al. 2012).

Although the unmodified starch, such as rice starch, could be used as a coagulant/flocculant in treating real wastewater due to the characteristics of the starch (Teh et al. 2014a, 2014b), the modified starches, especially grafted ones, as a kind of cheaper and more effective absorbent, has widely been investigated because the raw starch was an inexpensive, biodegradable, and renewable resource. They have therefore been considered as a promising candidate for developing sustainable materials (Guo et al. 2015). Particularly, it has many primary active hydroxyls that are easy to trigger many reactions such as free radical reaction, esterification, halogenation, oxidation and etherification (Stenstad et al. 2008; Sun et al. 2014). Moreover, during modification, the physical and chemical properties of the grafted starches can be controlled and adjusted by regulation of the synthesis techniques or by modification of the surface of the groups (Yang et al. 2010). This will make the modified starch have suitable expansion, huge pore volume, high specific area and proper degree of substitution. Xiang et al. reported dithiocarbamate-modified starch derivatives with specific area up to 15–35 m\(^2\) g\(^{-1}\) (Xiang et al. 2016). Wierik et al.
prepared a new generation of potato starch products with surface area of 17–25 m² g⁻¹ (Wierik et al. 1996). Vatanasuchart et al. modified cassava starch with different UV irradiations to enhance baking expansion, with a specific volume of about 10–13 cm³ g⁻¹ (Vatanasuchart et al. 2005). These excellent performances greatly enhance the ability of the modified starch to adsorb dyes and heavy metal ions, exhibiting great application prospects in the water treatment field (Lin et al. 2015). Nikolic et al. (2014) reported that polystyrene-graft-starch copolymers obtained from freshly synthesized or waste polystyrene could be used as a water pollution alleviation technology for absorption of metal ions, or as biofiller for thermoplastics. Therefore, biodegradation of these copolymers was very important for environmental issues. Singh & Sharma (2007) prepared polystyrene-g-starch and polystyrene-g-poly (acrylic acid (AA))-co-starch films, and found that these polymeric networks developed from the waste polystyrene could be used for removal, separation and enrichment of hazardous metal ions in aqueous solutions, which was valuable for environmental remediation of municipal and industrial wastewaters. Kolya et al. (2014, 2015) synthesized a graft copolymer based on starch and a mixture of N-methyl acrylamide and AA, which was used as an efficient Hg(II) and Cr(VI) adsorbent. Yang et al. (2014) successfully synthesized a series of amphoteric starch-based grafting flocculants (3-chloro-2-hydroxypropyl trimethyl ammonium chloride modified starch-graft-poly-(acrylamide-co-acrylic acid)) denoted as SCPAMPAA with different grafting ratios that was used for the removal of different charged contaminants from water. Compared with pristine starch that has a sphere and smooth surface, the grafted starch microspheres were synthesized with several different types of thio- and/or amine-modified starch resin materials for adsorption of metal ions, because amide and -COOH functional groups are very effective for metal binding (Kolya et al. 2014).

Accordingly, the present study aims to synthesize a carboxymethylated soluble starch grafted with poly(dimethyl diallyl ammonium chloride-co-acrylamide) via a water-in-oil (W/O) emulsification cross-linking polymerization reaction, and thus to gain a grafted starch flocculant (GSF). The GSF contains some primary groups such as -COO⁻, -OH, -CONH₂, and -(CH₂CH₂)₂N⁺(CH₃)₂Cl⁻, and have high Brunauer-Emmett-Teller (BET) surface area of no less than 28.42 m² g⁻¹, far more than that of the original starch of 1.4436 m² g⁻¹ (Lin et al. 2015), and also higher than the data reported in the references (Wierik et al. 1996; Vatanasuchart et al. 2005; Xiang et al. 2016). This unique structure and its properties are expected to be beneficial for the removal of Pb²⁺ and Cu²⁺ ions coming from the effluent. The factors affecting the adsorption behavior including the pH effect, concentration factor and reaction time are investigated, and finally the desired absorption parameters are acquired. Based on the optimal parameters, experimental validations are carried out with the moat water and industrial wastewater from the western suburbs in Xi’an.

**EXPERIMENTAL**

**Materials**

Soluble starch, epoxy chloropropane (analytical grade or purity 99%), chloroacetic acid (analytical grade or purity 98%) and ethyl acetate (analytical grade or purity 99%) were purchased from Tianli Tech Co., Ltd (Tianjin, China), and used without further purification. Commercial soluble starch used in this study is produced by the partial acidolysis of potato starch. It is soluble in hot water, but insoluble in cold water. Ceric ammonium nitrate (NH₄)₂Ce(NO₃)₆, analytical grade or purity 99%) was obtained from Shangpu Chemical and Engineering Co., Ltd (Shanghai, China). Span 80, Tween 60 and acrylamide were purchased from Kemiu Chemical Reagent Co., Ltd (Tianjin, China). Methanol was obtained from Fuyu Chemical and Engineering Co., Ltd (Tianjin, China), and acetone was purchased from Ronlon Bohua (Tianjin) Pharmaceutical & Chemical Co., Ltd, China. Dimethylallyl ammonium chloride (DMDAC, purity 60%) was obtained from Aladdin Industrial Co., Ltd (Shanghai, China). Other reagents and solvents were of analytical grade and were used as received.

**Methods**

**Preparations of GSF**

The soluble starch (4.05 g), 130 mL ethanol aqueous solution, and 5 mL 10 mol·L⁻¹ NaOH solution were mixed in a three-neck flask, and 1.2 g chloroacetic acid was also added to gain a carboxymethylated soluble starch at 45 °C for 3 h. Alkali treatment at a high temperature was optimized to improve the hydrolysis of starch. Samples were filtered by suction filtration and washed with distilled water and ethanol to remove excess chloroacetic acid in sequence, and then dried and collected in glass bottles.
Then, 5 g carboxymethylated soluble starch was immersed in a 70 mL 2 mol·L\(^{-1}\) NaOH solution, and heated in a water bath at 80 °C for 40 min to destroy the hydrogen bonds of starch granule in cold water (Costa Garcia et al. 2016). The hot gelatinization solution was cooled to room temperature, and thus the water phase (W) was prepared. To obtain the oil phase (O), 2 g Span 80 and Tween 60 were dispersed in 80 mL cyclohexane and 20 mL chloroform, and then maintained at 60 °C until they were entirely dissolved. After 25 mL water phase was mixed with the above oil phase under mechanical agitation, the W/O emulsion was formed. Subsequently, 4.5 g acrylamide and 3 mL DMDAAC were added into the prepared emulsion to be emulsified in N\(_2\) for 30 min. Then, 0.3 g (NH\(_4\))\(_2\)Ce(NO\(_3\))\(_6\) was added into the prepared emulsion, and stirred with mechanical agitation of 250 rpm at 60 °C for 2 h. GSF samples were obtained after centrifuging and washing by ethyl acetate, acetone and absolute alcohol in sequence. Afterwards they were dried and collected in glass bottles. The dried GSF product was bundled with filter paper, washed and refluxed in acetone with a soxhlet extractor for 24 h, and dried in a vacuum oven at 105 °C until constant weight. The dry matter was used for further analysis and application. The synthetic scheme is shown in Figure 1.

Analysis

Fourier transform infrared (FT-IR) spectra of the samples were recorded in the range of 400–4,000 cm\(^{-1}\) using Nicolet-380 FT-IR spectroscopy. Those samples were prepared in pellet form with spectroscopic grade KBr. The morphologies of the samples were observed on an S-3400N-II scanning electron microscopy (SEM, Japan) operating with an accelerating voltage of 5 kV. The average diameter and number distribution of different size starch granules was conducted by laser-diffraction diameter tester (LS13320, Beckman Coulter Corporation). The specific surface area of the sample was determined by the BET method (ASAP 2020 M, Micromeritics Instrument Corporation).

Adsorption tests

A series of 50 mL turbid solutions were placed into several beakers separately, and then 1.0 g GSF was added into each beaker containing the solution. The beakers were placed in a constant temperature oscillator, and the solution was allowed to stand for 10, 20 and 30 min after agitation for 1 min. The photographs of flocculant at an equilibrium state were taken.

Cu\(^{2+}\) and Pb\(^{2+}\) standard concentration solutions were prepared in a range from 0 to 10 mg·L\(^{-1}\), the adsorption values of the two metal ions (Pb\(^{2+}\) and Cu\(^{2+}\) ions) were determined by an atomic adsorption spectroscopy (TAS-990A, China) with Pb and Cu element lamp, respectively. The determination conditions were as follows: for Pb\(^{2+}\), the determination was carried out at a wavenumber of 283.3 nm, an electrical current of 2 mA, a flow rate of C\(_2\)H\(_2\) 1,500 mL·min\(^{-1}\) and a height of 5 mm. For Cu\(^{2+}\), the wavenumber was 324.7 nm, the electrical current was 3 mA, the flow rate was C\(_2\)H\(_2\) 2,000 mL·min\(^{-1}\), and the height was 6 mm. Standard curve was attained according to an absorbance-concentration (A-C) in Figure 2. Three repetitions were performed for each assay, and the average values were presented in the ‘Results and discussion’ section.

The simulated wastewater solutions in the study were prepared by 8 mg·L\(^{-1}\) appropriate dilution solutions shaking (150 rpm) with an electronic thermostated shaker. To investigate the effect of flocculants dosage on adsorption performance, experiments were carried out with different dosages of the flocculants from 0.002 to 0.028 g·mL\(^{-1}\) for 24 hours adsorption in pH 7.0 at 25 °C. To study the effect

![Figure 1](https://iwaponline.com/wst/article-pdf/73/10/2394/461734/wst073102394.pdf)
of initial solution pH on adsorption performance, experiments were carried out at a flocculant concentration of 0.024 g·mL⁻¹ with different initial pH values from 2.0 to 9.0 at 25 °C. For reaction time studies, experiments were performed at a flocculant dosage of 0.024 g·mL⁻¹, pH 7.0, standing time for 20, 40, 60, 80, and 100 min after shaking at 25 °C. Experimental assays were carried out with moat water and industrial wastewater from the western suburbs in Xi’an. The concentrations of the metal ions were measured in the same way as described above. The removal ratio \( Q \) of metal ions by the flocculants was calculated by Equation (1).

\[
Q = \left( \frac{C_0 - C_1}{C_0} \right) \times 100\% \tag{1}
\]

where \( Q \) is the removal ratio of metal ions, and \( C_0 \) and \( C_1 \) are the initial and equilibrium concentration (mg·L⁻¹) of metal ions, respectively.

**Analysis by FT-IR spectroscopy**

In order to evaluate the structure of the as-prepared GSF materials, FT-IR analyses were used, as depicted in Figure 3. It was clear that the characteristic absorption peaks of the soluble starch generates were located at about 3,264–3,565 cm⁻¹, 2,890–2,930 cm⁻¹, 1,658 cm⁻¹ and 1,002–1,162 cm⁻¹, attributed to the stretching vibration modes of –OH, –C–H, –C=O and –C–O–, respectively (Xu et al. 2007; Shak & Wu 2014). In Figure 5(b), the GSF displays characteristic absorption peaks at 3,300–3,600 cm⁻¹ ascribed to –OH and amino groups, and the vibration peak at 2,930 cm⁻¹ assigned to the –C–H stretch, at 1,746–1,691 cm⁻¹ attributable to –C=O and at 1,642 cm⁻¹ ascribed to the amido-carbonyl stretch of the acrylamide samples. The peak at 2,946 cm⁻¹ was attributable to N⁺ related to –CH and –CH₃ originating from the DMDAAC (Da et al. 2011). The existence of characteristic peaks of the soluble starch and acrylamide confirmed the successful formation of the GSF.

**Microstructure and morphology of GSF**

Figure 4 shows the scanning electron micrographs of the native soluble starch and GSF, where obvious change was observed in the surface topologies and pore situation during modification. Compared with the raw starch (Figure 4(a)) that exhibits spheroidic or oval smooth surface, GSF showed irregular porous surface and a coarse structure. Average particle size of the GSF (Figure 4(b)) was also found to be significantly larger than starch granules. The morphology of the starch was destroyed when the original soluble starch solution was adequately heated (Patel & Seetharaman 2006). According to previous research, the continuous heating caused the granules to swell and crystallites to melt, leading to complete separation of amylose and amylopectin from the starch (Teh et al. 2014b). Meanwhile, the link force in the starch molecule chains was increased during cross-linking. Ultimately microspheres with spatial reticular structure were produced and precipitated from the water phase (Chern 2006; Chen et al. 2011). From the sample prepared by lyophilization in Figure 4(c), it can be noted that a large amount of pores may be observed. So it is not hard to understand that as the internal water molecules in the entirely-swollen GSF were extracted by freeze dryer, many microstructures were left. By contrast, the traditional flocculant, polyacrylamide, gave irregular and close-grained bulk morphology (Figure 4(d)). Furthermore, the granule size
distribution and BET surface area measurements in Table 1 reveal that the specific surface area of GSF was 18 times much more than the raw starch. The porosity structure devoting to the huge surface has great impact on adsorption behavior. In addition, it should be noted that the presence of the huge granules was superior to the small native starch in applications and recoverability.

Physical adsorption analysis

The photographs of the wastewater samples at different periods treated with GSF are vividly displayed in Figure 5. It was very clear that the original wastewater sample was brown, turbidity and opaque due to the existence of fine soil and sand, microorganism and soluble ions. With the increase of the treatment time, the transparency of turbid water was gradually increased. Particularly, the wastewater solution became significantly transparent after clean-up for 30 min. This was attributed to the porous structure and a big surface area of the GSF, which made the GSF exhibit strong adsorption ability. This GSF could even adsorb the suspending solid and microorganism during the treatment.

Effect of the GSF dosage on the removal of two metal ions

As shown in Figure 6(a), with increasing the flocculant dosage, the removal ratio of metal ions increased rapidly, which was in agreement with a previous reference (Zhang 2015). When the concentration of GSF was in a range from 0.008 to 0.020 g·mL⁻¹, the removal ratio of the GSF towards Cu²⁺ was less than that towards Pb²⁺, and from 0.020 to 0.024 g·mL⁻¹, the removal ratio towards Cu²⁺ was contrarily greater than that towards Pb²⁺. When the concentration of the flocculant was 0.024 g·mL⁻¹, the maximum removal ratio of Pb²⁺ was 37.2%, and the residual concentration of Pb²⁺ ions in the solution was 6.28 mg·L⁻¹. Meanwhile, the maximum removal ratio of Cu²⁺ was detected to be about 34.7%, and the residual concentration of Cu²⁺ was 6.53 mg·L⁻¹.

Table 1 | Size distribution and BET surface area of the different granules

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average diameter (μm)</th>
<th>Number distribution of different size granules (%)</th>
<th>BET surface area (m²·g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw starch</td>
<td>25.14 ± 0.56</td>
<td>43.03 ± 0.97</td>
<td>2.32</td>
</tr>
<tr>
<td></td>
<td>15.45 ± 0.19</td>
<td>48.53 ± 0.82</td>
<td>2.44</td>
</tr>
<tr>
<td></td>
<td>6.22 ± 0.04</td>
<td>10.45 ± 0.66</td>
<td>2.55</td>
</tr>
<tr>
<td>GSF</td>
<td>900.33 ± 2.34</td>
<td>70.45 ± 0.77</td>
<td>28.42</td>
</tr>
<tr>
<td></td>
<td>433.24 ± 1.98</td>
<td>19.32 ± 0.23</td>
<td>42.13</td>
</tr>
<tr>
<td></td>
<td>50.43 ± 1.23</td>
<td>10.42 ± 0.21</td>
<td>52.54</td>
</tr>
</tbody>
</table>
This trend that the high removal ratio of the metal ions with the increase of the flocculant dosage was consistent with the increased quantities of ionized carboxyl, amido and cationic groups coming from GSF, which led to the enhanced chelation of metal ions (Tan et al. 2015). On the other hand, the unique properties of heavy metal ions such as the polarization ability and atomic radius are also responsible for this high adsorption capacity. Although the Cu²⁺ and Pb²⁺ ions have different configurations, they have the same valence state. Their interaction force with the same anion (–COO⁻) changes in the light of the following order: the metal ions with the electron configuration 18 and 18 + 2 have larger force than those with the electronic configuration 8 (the outermost electron configuration of Cu²⁺ ions is 3s²3p⁶3d⁹, and for Pb²⁺ ions, it is 5s²5p⁶5d¹⁰6s²). Moreover, the radius of Pb²⁺ ions is larger than that of Cu²⁺ ions, which results in the formation of high coordination number (Morsali & Mahjoub 2004). As a result, the removal ratio towards Cu²⁺ was less than that towards Pb²⁺ at a low concentration of GSF from 0.008 to 0.020 g·mL⁻¹. With increasing the dosage of the GSF, the adsorption ability for the two ions was enhanced, but the extent of this enhancement was different from each other. According to the difference in the number of electronic shells for cations, the greater the number of electronic shells, the lower the coordination number resulting from a larger steric hindrance. Thus, the Cu²⁺ ions with small ionic radius were more readily entering into the flocculant particles than Pb²⁺ ions, and produced the complexation with internal active groups. Therefore, the adsorption capacity of the modified starch flocculant was Cu²⁺ > Pb²⁺ at a high concentration range of GSF from 0.020 to 0.028 g·mL⁻¹ (Rippey et al. 2008). As a result, the suitable dosage of GSF was 0.024 g·mL⁻¹.

**Effect of pH value on GSF adsorption performance**

From Figure 6(b), it is clearly noticed that the removal ratio greatly depended on the value of pH, and reached a maximum removal ratio at pH 8.0, because the H⁺ ions or pH had a great influence on both several ions in aqueous solution and the binding sites on the surface of the adsorbents (Zhu et al. 2007). At a low pH value, the H⁺ ions might contend with metal ions for the adsorption sites of the flocculants, and thereby prevented the adsorption of metal ions. Furthermore, the active groups of the GSF such as –NH₂, –OH and –COO⁻ were easily protonated at a low pH, thus leading to the reduction of the electrostatic attraction for the metal cations. But in a weak acidic or neutral condition, the removal ratio was sharply improved and even maintained an equilibrium value at pH = 8. The electrostatic attraction was mainly taking place between the metal ions and active groups of GSF. In a weak alkaline solution (pH = 7–9), Cu²⁺ and Pb²⁺ would be hydrolyzed into Cu(OH)⁺ and Pb(OH)⁺ ions so
that the removal ratio was slightly improved. In addition, at pH >9, there is a little Cu(OH)_2 and Pb(OH)_2 deposition.

In general, GSF could keep a well adsorption effect over a wide range of pH of 5.0–9.0. The pH variations significantly affect the adsorption of the metal ions onto the GSF. Therefore, the best pH value would be controlled at 8.0.

**Effect of adsorption time on GSF adsorption performance**

Figure 6(c) gives the adsorption curves of the GSF flocculant towards Pb^{2+} and Cu^{2+} ions at various cleaning-up times. It can be seen from Figure 6(c) that the removal ratio was sharply improved by increasing the clean-up time towards two metal ions. After 30 min, the removal ratio in the adsorption curve attained the equilibrium value. That was mainly considered as the fact that there were a large number of –COO⁻ groups and quaternary ammonium ions (–CH₂CH₂N⁺(CH₃)₂) and microporous structure on the GSF, which was devoted to excellent swelling properties during a short time, and an ample reaction space was left. Consequently, Pb^{2+} and Cu^{2+} ions were readily diffused within the GSF. Therefore, 30 min would be appropriate for two metal ions to react with GSF.

**Application of GSF for local wastewater**

Considering the influence of other metal ions or bad factors, wastewater coming from several different regions in Xi’an city containing various metal ions (Hg^{2+}, Cr^{3+}, Co^{3+}, Pb^{2+} and Cu^{2+}) was used to evaluate the removal capacity of GSF. The effect of the GSF dosage, pH of the solution and the reaction time on the absorption capacity are investigated in Figures 7(a)–7(c)). The lowest limit of the removal ratio was still reached up to 35% for the real and complex water. Finally, the desired cleaning-up conditions were gained, which included the dosage of GSF 0.024 g·mL⁻¹, pH of 8.0 and the absorption time of 30 min. Based on the above optimized conditions, the heartening results were obtained, and the removal ratio was 57.2% and 48.7% towards Pb^{2+} and Cu^{2+} coming from the moat water, respectively, and the removal ratio towards Pb^{2+} and Cu^{2+} were 52.2% and 46.2% coming from the industrial wastewater, respectively.

**CONCLUSIONS**

In conclusion, the GSF has been successfully prepared by inverse suspension polymerization method. The removal ratios of Pb^{2+} and Cu^{2+} ions from the simulated and real wastewater solutions was examined, and various factors affecting the removal ratios of the metal ions were investigated. These included the GSF dosage, the pH of the solution and the reaction time. Finally, the desired removal condition, such as the dosage of GSF 0.024 g·mL⁻¹, pH = 8.0 and the absorption time 30 min, were gained. Based on the ideal conditions, the adsorption behavior towards metal ions in wastewater from the moat and industrial zones were fully investigated, and the desired result close to 50% of the removal ratio was acquired. The improved surface adsorption originated from the two key factors, the hydrophilic groups such as –COO⁻, –OH, –CONH₂, –CH₂CH₂N⁺(CH₃)₂ and the intrinsic porosity, i.e. huge surface areas. The adsorption of the GSF for organic pollutants, microorganisms or liquid–solid separation should be thoroughly and deeply investigated in the future.

**ACKNOWLEDGEMENTS**

The authors express their sincere gratitude for the financial support for this work by the Science and Technology Project of Xi’an City (No. CXY1531WL32, No. CX12189WL30, and No. CXY1531WL26), the National Science Foundation of China (No. 21303135 and No. 21445004) and the Xi’an Science and Technology Project (No. CXY1531).
work was also supported by the Key Laboratory for Surface Engineering and Remanufacturing in Shaanxi Province, Xi’an University, China.

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