Synthesis of polyaspartic acid–aminobenzenesulfonic acid grafted copolymer and its scale inhibition performance and dispersion capacity
Ying Xu, Lina Wang, Linlin Zhao and Yuanchen Cui

ABSTRACT
Polysuccinimide (abridged as PSI) was synthesized by urea and maleic anhydride. Aminobenzenesulfonic acid (ABSA) was introduced at different mole ratio to PSI to generate polyaspartic acid (abridged as PASP)/ABSA graft copolymer. The scale inhibition behavior of resultant PASP/ABSA copolymer was evaluated by using static scale inhibition method. The transmittance of the supernatant of the copolymer solution was measured to evaluate its dispersion ability for ferric oxide. The corrosion inhibition performance of the copolymer for iron plates immersed in the refined testing water (including 0.555 g of CaCl\(_2\cdot\)2H\(_2\)O, 0.493 g of MgSO\(_4\cdot\)7H\(_2\)O, 50 mg PASP/ABSA graft copolymer and 0.168 g of NaCl) was tested. It was found that PASP/ABSA copolymer was able to efficiently inhibit CaCO\(_3\) and Ca\(_3\)(PO\(_4\))\(_2\) scales and had good corrosion inhibition ability as well, and it also had good dispersion ability for Fe\(_2\)O\(_3\). Besides, the inhibition efficiency of PASP/ABSA against CaCO\(_3\) and Ca\(_3\)(PO\(_4\))\(_2\) scales and its dispersion capacity for Fe\(_2\)O\(_3\) was highly dependent on dosage. The reason may lie in that PASP/ABSA copolymer simultaneously possesses carboxylic ion and sulfonic group which can chelate Ca\(^{2+}\) to form stabilized and dissoluble chelates, resulting in increase of solubility of calcium salts in water. Also it may lie in that the introduction of acidic hydrophilic sulfonic group with a strong electrolytic capacity into PASP molecule simultaneously enhances the dispersion of the inhibitor molecules and hinders the formation of Ca\(_3\)(PO\(_4\))\(_2\) scale.

Key words | dispersion capacity, PASP graft copolymer, polysuccinimide, scale inhibition performance, sulfanilic acid

INTRODUCTION
The consumption of industrial water increases significantly with the rapid development of modern industry, which intensifies shortage of fresh water resource (Xiong et al. 2003). To alleviate the pressure on water resources, it is imperative to apply water-treatment agents to process industrial water for the purpose of retarding the formation of deposit and saving water. Early in 1950s, Kent M etc initially studied water-treatment agents. Since then, inorganic scale-corrosion inhibitor, polyphosphate salts scale-corrosion inhibitor, phosphate-based water-treatment agent and so on have been successfully developed (Ross et al. 1997). Particularly, the naissance of green chemistry concept in 1991 drew intensified attention among scientists all over the world, which has been promoting the development of low or non-phosphorus environmentally-friendly water-treatment agents. To date, four kinds of green water treatment agents, namely, polyaspartic acid, polyepoxysuccinic acid, alkyl epoxy carboxylic acid and natural polymers, are currently available. Most of natural polymer-based green water-treatment agents, however, have poor stability and low efficiency (Koskan & Low Kim 1992) and are inferior to corresponding synthetic ones in terms of scale inhibition ability and dispersion stability.

We are particularly interested in polyaspartic acid, because, thanks to a good reactivity, it allows ring-opening reaction under the catalysis by amine-group, and it is non-toxic, biodegradable and environmentally acceptable (Xiaojing et al. 2010), showing promising prospect as a green
water-treatment agent for circulated cooling water in industry. Nevertheless, polyaspartic acid has poor inhibition performance for Ca$_3$(PO$_4$)$_2$ scale and poor dispersion capacity for ferric oxide, which seriously limits its use (Nakato et al. 2000). To overcome those shortcomings and improve the service performance of polyaspartic acid, numerous efforts have been made to introduce hydrophobic group, carboxylic group, sulfonic group and phosphonyl to the side chain of PASP, which, based on the ring-opening reaction of polyaspartic acid by amine-group catalysis, is feasible (Tang & Davis 1998).

In the present research, by using aminobenzenesulfonic acid as the second ingredient, a sulfophenyl group was introduced into the side chain of PASP via amino-group ring opening in association with follow-up hydrolysis. Further, PASP/ABSA copolymer was fabricated, and its scale inhibition performance, dispersion performance, and corrosion inhibition performance were evaluated.

**EXPERIMENTAL SECTION**

**Instruments and agents**

Instruments used in the present research include DF-101S thermostatic magnetic stirrers, 722 grating spectrophotometer, FA1004A electronic balance, DHT thermostatic electric jacket equipped with a stirring, AUATAR-360 Fourier transform infrared spectrometer (FTIR) and JSM-7001F Field Emission Scanning Electron Microscope (SEM). Analytical grade maleic anhydride, urea, ethanol, acetone, sulfanilic acid, calcium chloride, and sodium tetraborate were used as the agent for synthesis.

**Preparation of poly(succinimide)**

9.8 g of maleic anhydride and a proper amount of water were added to a three-neck flask and heated at 60 °C, generating a colorless transparent liquid. Into the colorless transparent liquid was added 4.2 g of urea at an increased temperature of 80 °C, followed by 1 h reaction. At the end of the reaction, the mixed solution was concentrated and heated to 160 °C (Tang et al. 2000), followed by addition of 0.82 mL of mixed acids (H$_2$SO$_4$:H$_3$PO$_4$ = 1:1) and dehydration for 3 h. Resultant dehydrated solution was cooled to room temperature, washed with deionized water, filtered with an air pump, and dried, generating orange solid poly (succinimide) which was stored in a desiccator (ODA 2001). Relevant synthetic reaction is expressed as below:

![Synthesis of polyaspartic acid/aminobenzenesulfonic acid copolymer](image)

Inhibition performance of PASP/ABSA copolymer against CaCO$_3$ scale

Static scale inhibition tests were conducted according to China National Standard method (GB/T 16632-1996) to evaluate the scale inhibition efficiency of synthesized PASP/ABSA copolymer against CaCO$_3$ scale (Kasparova & Baldokhin 2007). Briefly, in a volumetric flask (capacity 1 L) was prepared an aqueous solution containing 250 mg/L Ca$^{2+}$ and 250 mg/L HCO$_3^-$\textsuperscript{-}. Resultant solution was uniformly mixed with a known amount of PASP/ABSA copolymer as the scale inhibitor and allowed to react in a water bath at 80 °C for 6 h. At the end of the reaction, resultant mixed solution was collected and cooled to room temperature. The concentration of Ca$^{2+}$ in the solution was measured using titration of ethylene diamine tetracetic acid (EDTA). The scale inhibition efficiency of the PASP/ABSA
A solution containing 150 mg/L Ca^{2+} and 5 mg/L PO_4^{3-} was prepared in a volumetric flask (capacity 1 L) in the same manner described in section 2.4. The pH value of resultant solution was adjusted to 9.0 with borax. Then the solution was evenly mixed with a known amount of scale inhibitor and allowed to react in a water bath at 80 °C for 10 h. At the end of the reaction, the mixed solution was cooled to room temperature and centrifugally separated. The content of PO_4^{3-} in the supernatant was measured with a 722-spectrophotometer (710 nm, 1 cm cuvette; in relation to distilled water) (Ochoa et al. 2003). The inhibition efficiency of the scale inhibitor against Ca_3(PO_4)_2 scale was calculated as below:

\[ \eta_{\text{Ca}_3(\text{PO}_4)_2} = \frac{\rho_1 - \rho_0}{\rho_2 - \rho_0} \times 100\% \]

Where \( \rho_0 \) is the mass concentration of PO_4^{3-} in the absence of scale inhibitor in to-be-tested solution; \( \rho_1 \) is the mass concentration of PO_4^{3-} in the presence of scale inhibitor in to-be-tested solution; and \( \rho_2 \) is the mass concentration of all PO_4^{3-} in to-be-tested solution.

Ability of PASP/ABSA copolymer to disperse ferric oxide

A solution containing 150 mg/L Ca^{2+} and 10 mg/L Fe^{3+} was prepared. The pH value of the solution was adjusted to 9.0 with borax. Then the solution was evenly mixed with a known amount of PASP/ABSA copolymer. Resultant mixed solution was stirred for 15 min and then heated at 50 °C for 5 h before being cooled to room temperature and centrifugally separated. The transmittance of the supernatant was measured with a 722-spectrophotometer (710 nm, 1 cm cuvette; in relation to distilled); and it was supposed that a smaller light transmittance referred to a better dispersion ability of the copolymer (Solmaz et al. 2007).

**Corrosion inhibition efficiency of PASP/ABSA copolymer**

Weight loss of rotating hung steel slices was measured to evaluate the corrosion inhibition efficiency of PASP/ABSA copolymer, which was conducted at a temperature of 45 °C, rotating speed of 80 rev/min, and a pre-coating time of 72 h (Touir et al. 2008). Briefly, the carbon steel with surface area of 28.00 cm^2 had the following composition of (wt%): C, 0.17–0.23% Si, 0.17–0.37% Mn, 0.35–0.65% Cr, ≤0.25% Ni, ≤0.3% Cu, ≤0.25% and Fe. The pre-coating solution consisting of 0.555 g of CaCl_2·2H_2O, 0.493 g of MgSO_4·7H_2O and 0.168 g of NaCl was mixed with a known amount of PASP/ABSA copolymer as the inhibitor. Into resultant mixture was added 0.168 g of NaCl, followed by being diluted to 1 L (Kobe et al. 2001). The corrosion rate and corrosion inhibition rate were determined according to China National Standard GB/T 18175-2000 ‘Performance measurement of corrosion inhibitor in water-treatment – with a rotating apparatus’. The corrosion efficiency was calculated as below:

\[ \eta = \frac{87,600 \times [(m_1 - m_0) - \Delta m]}{S \times T \times D} \]

Where \( m_1 \) is the mass of carbon steel hung slices before test; \( m_0 \) is the mass of carbon steel hung slices after test; \( \Delta m \) is the mass loss of carbon steel hung slices caused by washing in acid; \( S \) is the surface area carbon steel hung slice (28 cm^2); \( T \) is time test (72 h); \( D \) is density carbon steel hung slices (7.85 g/cm^3).

**RESULTS AND DISCUSSION**

**FTIR analysis of synthetic products**

Figure 1 shows the FTIR spectra of PASP and PASP/ABSA copolymer. It is seen that the characteristic absorption peaks of N–H bond stretching vibration appear within a wavenumber range of 3,000–3,400 cm\(^{-1}\) (Liu & He 1992). At the same time, the characteristic absorption peaks of carboxyl group appear at 1,200–875 cm\(^{-1}\) (Yanxing et al. 2010). The absorption peak at 1,599 cm\(^{-1}\) corresponds to
bending vibration of N–H bond; and those at 3,067 cm\(^{-1}\) and 1,040 cm\(^{-1}\) are attributed to bending vibration of C–H bond in benzene ring and –SO\(_3\)Na (Zhang et al. 2007), respectively. Thus it can be inferred that sulfophenyl group had been successfully introduced into the side chain of PASP molecules.

Scale inhibition performance of PASP/ABSA grafted copolymer

Different molar ratios of ABSA/PSI were obtained by different doses of ABSA and PSI. Table 1 shows different molar ratios of ABSA to PSI.

The inhibition efficiency of PASP/ABSA grafted copolymers (dosage 6 mg/L) obtained at different molar ratios of ABSA to PSI against Ca\(_3\)(PO\(_4\))\(_2\) scale is shown in Figure 2, where the scale inhibition rate is plotted vs. varying molar ratio of ABSA to PSI. It is seen that the PASP/ABSA grafted copolymer obtained at an ABSA to PSI molar ratio of 0.74:1 had the best inhibition efficiency against Ca\(_3\)(PO\(_4\))\(_2\) scale, and an inhibition rate of as high as 88.69% was reached.

### Table 1 | Different mole ratio of ABSA to PSI

<table>
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<tr>
<th>Product Code</th>
<th>The dosage of ABSA (g)</th>
<th>The dosage of PSI (g)</th>
<th>The mole ratio of ABSA/PSI</th>
</tr>
</thead>
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<tr>
<td>s-0</td>
<td>0</td>
<td>0.25</td>
<td>0</td>
</tr>
<tr>
<td>s-1</td>
<td>0.0799</td>
<td>0.2211</td>
<td>0.20:1</td>
</tr>
<tr>
<td>s-2</td>
<td>0.1982</td>
<td>0.2523</td>
<td>0.44:1</td>
</tr>
<tr>
<td>s-3</td>
<td>0.3340</td>
<td>0.2530</td>
<td>0.74:1</td>
</tr>
<tr>
<td>s-4</td>
<td>0.3745</td>
<td>0.2092</td>
<td>0.99:1</td>
</tr>
</tbody>
</table>

Figure 2 | Inhibition efficiency against Ca\(_3\)(PO\(_4\))\(_2\) scale in relation to varying molar ratio of ABSA to PSI.

**Figure 3** shows the variation of inhibition efficiency of PASP/ABSA copolymer against CaCO\(_3\) scale with concentration of the scale inhibitor. The inhibition efficiency against CaCO\(_3\) scale increased with increasing concentration of PASP/ABSA copolymer. The maximum inhibition efficiency, as high as 99.99%, was reached at an inhibitor concentration of 10 mg/L, beyond this concentration the inhibition efficiency remained nearly unchanged with further increase of concentration of the scale inhibitor. The excellent inhibition ability of PASP/ABSA copolymer against CaCO\(_3\) scale may be closely related to its simultaneous possession of carboxylic ion and sulfonic group. Both carboxylic ion and sulfonic
group can chelate $\text{Ca}^{2+}$ to form stabilized and dissoluble chelates (Robert et al. 1997). This results in increase of solubility of calcium salts and allows existence of more $\text{Ca}^{2+}$ in water, efficiently preventing $\text{CaCO}_3$ scale from deposition. Besides, it is likely that $\text{Ca}^{2+}$ ions were chelated with PASP/ABSA to the maximum extent when the dosage of the scale inhibitor was more than 12 mg/L. Therefore, the scale inhibition efficiency remained almost constant beyond 12 mg/L of scale inhibitor.

**SEM pictures of CaCO$_3$ crystals in the absence and presence of PASP/ABSA inhibitor**

The CaCO$_3$ scale deposits were observed by scanning electron microscope (SEM). As shown in Figure 4, without PASP/ABSA, CaCO$_3$ deposits show regular shape and glossy surface with a compact arrangement (Figure 4(a)). On the other hand, when PASP/ABSA was added to the solution, CaCO$_3$ deposits show flower and cascade patterns with floppy accumulation Figure 4(b), because CaCO$_3$ deposit fleetly, the crystal growth habits of CaCO$_3$ are blocked by the PASP/ABSA, and irregular shapes (flower and cascade) appeared. Consequently, the scale is floppy and can be removed easily.

**Influence of concentration of PASP/ABSA grafted copolymer on inhibition efficiency against Ca$_3$(PO$_4$)$_2$ scale**

This can be ascribed that with the increase of time, microcrystal particles move more quickly and the speed of particle colliding with each other is even faster, which accelerates the formation of scale easily. But, as well known, the adsorption of scale inhibitor polymer to the scale is exothermic, with the increase of the immersed time, the adsorption is weakened and adsorption quantity is reduced. Consequently, the efficiency inhibitor scale shows declining trend.

**Influence of time of PASP/ABSA grafted copolymer on inhibition efficiency against CaCO$_3$ scale**

As shown in Figure 5, scale inhibition efficiency is affected by immersed time. With time rising, the scale inhibition efficiency decline. Beyond 9 h, the efficiency decreases sharply.

**Figure 4** SEM picture for CaCO$_3$ deposits in the absence and presence of inhibitor. (a) CaCO$_3$ without PASP/ABSA. (b) CaCO$_3$ with PASP/ABSA.

**Figure 5** The influence of time on inhibition efficiency.

**Figure 6** shows the effect of PASP/ABSA concentration on inhibition efficiency against Ca$_3$(PO$_4$)$_2$ scale. PASP/ABSA
copolymer had excellent inhibition ability against \( \text{Ca}_3(\text{PO}_4)_2 \) scale. The inhibition rate was above 40\% even when the concentration of PASP/ABSA was as low as 2 mg/L. It drastically rose to over 85\% when the concentration of PASP/ABSA increased from 2 to 4 mg/L, and the maximum inhibition efficiency (98.96\%) was obtained at a scale inhibitor dosage of 24 mg/L. Beyond 24 mg/L, the inhibition rate against \( \text{Ca}_3(\text{PO}_4)_2 \) scale remained almost unchanged. The excellent inhibition ability of PASP/ABSA copolymer against \( \text{Ca}_3(\text{PO}_4)_2 \) scale could be well understood if one notices that introducing acidic hydrophilic sulfonic group with a strong electrolytic capacity (Koskan & Low Kim 1995) into PASP results in increased amount of negative charges in the copolymers and stronger ability for the copolymer to keep well stretched morphology in water (Koweton et al. 1997). In other words, sulfonic group simultaneously enhances the dispersion of the inhibitor molecules and hinders the formation of \( \text{Ca}_3(\text{PO}_4)_2 \) scale.

**Influence of concentration of PASP/ABSA on dispersion of ferric oxide**

Figure 7 shows the transmittance of the tested solutions vs. concentration of PASP/ABSA copolymer. The light transmittance of the tested solution decreased with increasing concentration of PASP/ABSA up to 15 mg/L, corresponding to improved dispersion efficiency for \( \text{Fe}_2\text{O}_3 \). The best dispersion efficiency for \( \text{Fe}_2\text{O}_3 \) was reached when 15 mg/L of PASP/ABSA was introduced into the tested solution, corresponding to 83.0\% of light transmittance of the solution. When the concentration of PASP/ABSA was within 15–30 mg/L, the dispersion efficiency for \( \text{Fe}_2\text{O}_3 \) varied slightly. Then it tended to decline to some extent with the increase of the inhibitor dosage from 30 to 40 mg/L and 50 mg/L. PASP/ABSA copolymer contains sulfonic group and can adsorb small crystal particles, resulting in change of charge state of particle surface via forming electric double layer (Amass et al. 1998). Such an electric double layer facilitated intramolecular repulsion owing to electrostatic interaction. As a result, particles were better dispersed in water. However, when the concentration of PASP/ABSA was over 30 mg/L, complex reaction might take place intra-molecularly, leading to decrease of dispersibility and dispersion efficiency for \( \text{Fe}_2\text{O}_3 \).

**Corrosion inhibition efficiency of PASP/ABSA copolymer**

Figure 8 shows the effect of PASP/ABSA concentration on corrosion inhibition efficiency. From Figure 8, we could...
conclude that the polymer had certain effect on corrosion inhibition. When the mole ratio of p-ABS and PSI is 0.74:1 and concentration of product was 50 mg/L, the inhibition efficiency could attain to 74.75%.

CONCLUSIONS

In the presence of poly(succinimide) as a corrosion and scale inhibitor, polyaspartic acid grafted copolymer containing benzenesulfonic acid group was synthesized using polyaspartate and sulphanilic acid as the starting materials. The inhibition performance of PASP/ABSA copolymer against CaCO₃ and Ca₃(PO₄)₂ scales was evaluated by using static scale inhibition method. Besides, surface topography of CaCO₃ deposit was studied by SEM. Furthermore, the influence of time on the inhibition efficiency was measured. At last, its dispersion ability for ferric oxide was examined, and its corrosion inhibition performance was also investigated. It has been found that PASP/ABSA copolymer is able to efficiently inhibit CaCO₃ and Ca₃(PO₄)₂ scales and possesses good dispersion capacity for Fe₂O₃ and good corrosion inhibition ability as well, while the scale inhibition performance of PASP/ABSA and its dispersion capacity for Fe₂O₃ was highly dependent on dosage. This is because both carboxylic ion and sulfonic group of PASP/ABSA copolymer can chelate Ca²⁺ to form stabilized and dissoluble chelates, increasing solubility of calcium salts in water. Also it may be because the acidic hydrophilic sulfonic group in the grafted copolymer can simultaneously enhance the dispersion of the inhibitor molecules and hinder the formation of Ca₃(PO₄)₂ scale.

REFERENCES


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