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Adsorption and photosensitized oxidation of sulfide ions on aluminum tetrasulfophthalocyanine-loaded anionic resin

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Abstract

Oxidation of inorganic sulfide in water by molecular oxygen was studied under visible light ($\lambda \geq 450$ nm) irradiation in the presence of immobilized aluminum tetrasulfophthalocyanine (AlPcTS) on a commercial anionic resin Amberlite IRA 400. The composite catalyst exhibited not only a good capacity for uptake of sulfide ions from water, but also a higher photoactivity for the sensitized oxidation of sulfide, as compared to the unbound AlPcTS. Ionic chromatography analysis showed that sulfite and thiosulfate were the reaction intermediates, which were finally oxidized into sulfate. Although the intermediates competed with sulfide for the adsorption sites and active oxygen, the final product of sulfate did not show significant effect both on the adsorption and photosensitized oxidation of sulfide. Five repeated experiments showed that the immobilized sensitizer was reasonably stable and could be repeatedly used for the sulfide oxidation by molecular oxygen under visible light irradiation. The effects of experimental parameters such as AlPcTS loading and sulfide concentration were also examined and discussed in the text.
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1. Introduction

Sulfide and hydrogen sulfide are well known pollutants in industrial wastewater and communal wastewater. The presence of sulfide ions in water has a mortal effect on the bacterial strains used for biological purification and reduces the dissolved oxygen amount as well. Thus, proper conversion of sulfide into less dangerous substance before discharge into waterways is required. There have been several reports on the sulfide oxidation by molecular oxygen, catalyzed by water soluble complexes of metal phthalocyanine such as CoPcTS and CuPcTS [1,2]. The catalyzed oxidation is proposed to proceed via the formation of a tertiary-activated complex in which HS$^-$ and O$_2$ reversibly bind with MPcTS. However, the catalyzed oxidation of sulfide is incomplete, often giving colloidal sulfur as the product with concomitant formation of polysulfides, polythiosulfates and sulfate [1,2]. Interestingly, the deep oxidation of sulfide, sulfite and thiosulfate into sulfate could be achieved under visible light irradiation in an aerated aqueous solution of ZnPcTS or zinc

phthalocyaninecarboxylate (ZnPcTC) [3]. In this process, singlet oxygen is proposed as the main reactive species, which is generated via energy transfer from the electronically excited complex to triplet dioxygen. Immobilization of the metal complex onto different supports of Al$_2$O$_3$, SiO$_2$, TiO$_2$, WO$_3$, zeolite, clay and metal chalcogenides has been successfully made for sulfide oxidation and catalyst separation [4–9]. However, the immobilized ZnPcTS and ZnPcTC are not stable against visible light irradiation, which gradually decompose into small fragment during the photosensitized oxidation of sulfide [4,6]. The analogical complexes of Co and Cu are very stable against the photobleaching, but their activities in the photosensitized generation of singlet oxygen are very low, as compared to the zinc complexes.

As an environmental photosensitizer, phthalocyanine complexes are worthy of further development for sulfide oxidation. They are easily synthesized at a low cost, and can collect about 50% of the energy available in the solar spectrum. Thus, it would make it possible to utilize solar light and molecular oxygen for waste treatment. For a practical application, the sensitizer should possess not only a high quantum yield of singlet oxygen, but also a high stability against photobleaching. This could be easily achieved, since both the photophysical and redox properties

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of metal complex are greatly influenced by the central metal and substitute groups on the Pc ring [10–12]. In general, the complexes containing a metal ion with filled electron shells or d-orbitals such as Al(III) and Zn(II) have high triplet lifetimes and thus high quantum yield of singlet oxygen formation, whereas the complexes that contain paramagnetic transitional metal ions such as Co(II) have much lower quantum yield. Attachment of electron-attracting groups such as $-SO_3^-$ and $-NO_2$ to the Pc ring may result to reduction in the electron density and thus improvement in the complex (photo)stability. On the other hand, an ideal support used for the complex immobilization should possess several functions. First of all, it is only a simple support of the catalyst for facile separation. Secondly, it should be able to make the photosensitizer dispersed in a monomeric form, since the aggregated complex is much less photoactive than the corresponding monomer. Thirdly, the support is also a good sorbent for uptake of sulfide ions from water, which may result into enhancement in the photosensitized oxidation of sulfide at the catalyst.

With this in mind, the present work has examined an anionic resin as the support of aluminum(III) tetrasulfophthalocyanine (AlPcTS), for the photosensitized oxidation of sulfide in water under visible light ($\lambda \geq 450$ nm) irradiation. It is known that the anionic resin has strong affinity toward anionic ions from water via ionic exchange. Comparatively, AlPcTS is much stable than ZnPcTS against the photobleaching. The result showed that the immobilized AlPcTS was not only a good sorbent for uptake of sulfide from water, but also exhibited notably enhanced activity for the photosensitized oxidation of sulfide, as compared to the unbound AlPcTS in a homogenous solution. With the aid of ionic chromatography, sulfite and thiosulfate were detected as the reaction intermediates, but they could be ultimately oxidized into sulfate in situ. Five consecutive experiments demonstrated that the immobilized catalyst could be repeatedly used, without significant loss both in adsorption capacity and photosensitization activity. The optimal loading of AlPcTS was only about 1.5 wt.%.

2. Experimental

The sodium salt of aluminum(III) tetrasulfophthalocyanine (AlPcTS) was prepared as described [13]. The anionic complex was then immobilized into anionic resin, Amberlite IRA 400, via an ionic exchange [14]. Briefly, 2 g of resin was dispersed into an aqueous solution of AlPcTS (100 mL) at a certain concentration. After the suspension was stirred in the dark overnight, followed by filtration, the resulting blue solid was washed with water, and dried at room temperature for several days. Since no AlPcTS in the filtrate was detectable by a spectrophotometer, all the used AlPcTs for the synthesis was considered to be completely immobilized onto the resin. Based on that, the loading of AlPcTS into the resin was calculated at 0–2.5% by weight. Note that after the solid was re-immersed in water overnight, no AlPcS was found in the filtrate, further confirming that AlPcTS was firmly bound into the resin. The solid spectrum was recorded on an Agilent 8453 UV–vis spectrometer with an attachment of Labsphere RSA-HP-53.

The adsorption isotherm of sulfide on the catalyst from water was measured in the dark at pH 9.3 in the presence of air (note that although sulfide could be oxidized by molecular oxygen, such oxidation was extremely slow, as will be shown in Fig. 3b). The aqueous suspension containing 0.025 g of catalyst and 50 mL of Na_2S solution (0.15–2.5 mM) was shaken in the dark overnight. The sulfide concentration was determined by using a sulfide-selective electrode on a pHS-3C meter (Shanghai Kangning), following the procedure as described [15]. The concentration of sulfide before and after the adsorption was presented in the text by C_0 and C_e, respectively, whereas the amount of sulfide adsorption, Q_e, expressed as mole of the adsorbed sulfide per gram of catalyst.

The photochemical reaction was carried out in a Pyrex glass-made reactor thermostated at 20 °C. The irradiation source was a Halogen lamp (500 W, Shanghai Yamin) filtered by a solution of dichromate ($\lambda \geq 450$ nm). Before light irradiation, the suspension containing necessary components was sufficiently equilibrated overnight (note that the equilibrium was actually reached at less than 1 h). At certain intervals of irradiation, small aliquots of the suspension were withdrawn, filtered and analyzed on a sulfide-selective electrode. The reaction intermediates and products were analyzed on a Dionex ICS-2000 Ionic Chromatography instrument, equipped with a GP50 gradient pump and an AS18 column (2 mm × 250 mm). The eluent was an aqueous solution of KOH (33%) at a flow rate of 0.25 mL/min.

Repeated experiments for evaluation of the catalyst stability were performed as follows. The suspension containing 1% AlPcS-loaded resin (50 mg) and sulfide solution (50 mL, 2 mM) at pH 9.3 was equilibrated first in the dark overnight. At a given time interval of irradiation, 1.0 mL of the suspension was withdrawn, and analyzed as described above. After each run was completed, 5.0 mL of stock sulfide solution (20 mM, pH 9.3) was supplied to restore the initial concentration of sulfide at ca. 2 mM. After stirring in the dark for 1 h, the suspension was irradiated again, and analyzed as described above.

3. Results and discussion

Fig. 1 shows the adsorption isotherm of sulfide on 1.0 wt.% AlPcTS-loaded resin from aqueous solution at pH 9.3. The amount of sulfide adsorption, Q_e, increased with the equilibrium concentration of sulfide, C_e, in the bulk solution. Since the isotherm was not the Langmuir-type, as clarified by the plot of C_e/Q_e versus C_e, it suggested that the sulfide adsorption proceeded predominantly via an ionic exchange. After the adsorbed sample was re-dispersed in water, only about 1% of the adsorbed sulfide was desorbed from the solid. When AlPcTS loading in the resin increased from 0.5 to 2.5 wt.%, the amount of sulfide adsorption was almost unchanged (Fig. 1b). No free AlPcS species was detected in the filtrate solution after the sulfide adsorption completed. It indicated that the sulfide ion exchanged with the Cl^- sites of resin, other than the immobilized AlPcTS anions. This could be understood by the fact that $AlPcTS^{4-}$ has a higher negative charge than S^{2-}, and thus a stronger interaction with the framework of the anionic resin.
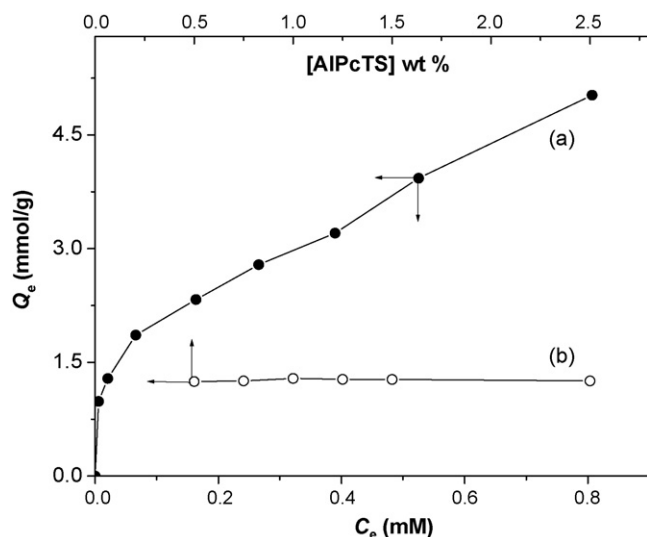
Fig. 1. (a) Adsorption isotherms of sulfide on the immobilized catalyst at 1 wt.% AlPcTS. (b) Effect of AlPcTS loading in the catalyst on the sulfide adsorption (initial sulfide concentration was 0.66 mM). The experiment was determined in water at pH 9.3 over a catalyst at 0.50 g/L.

Fig. 3. Oxidation of sulfide in water at pH 9.3 under different conditions: (a) in the presence of blank resin under visible light irradiation; (b) in the presence of 1.0 wt.% AlPcTS resin in the dark; (c) in the presence of 1.0 wt.% AlPcTS resin under visible light irradiation; (d) in the homogenous solution of AlPcTS (6 μM, right *y*-axis). The initial concentration of sulfide was 4.13 mM, and the catalyst was 0.50 g/L.

The immobilized AlPcTS existed mainly in a monomeric form, as revealed by diffuse reflectance spectral analysis (Fig. 2). The unbound AlPcTS, like other metal phthalocyaninesulfonates, was highly aggregated in water. The absorption band at 618 nm was assigned to the aggregates, which was much higher than that of the corresponding monomer at 673 nm (Fig. 2, the dotted line). After AlPcTS was immobilized into the resin, however, the composite catalyst displayed a spectrum mostly contributed by the monomeric species. The monomer band at 673 nm was higher than that of aggregates at 618 nm, different
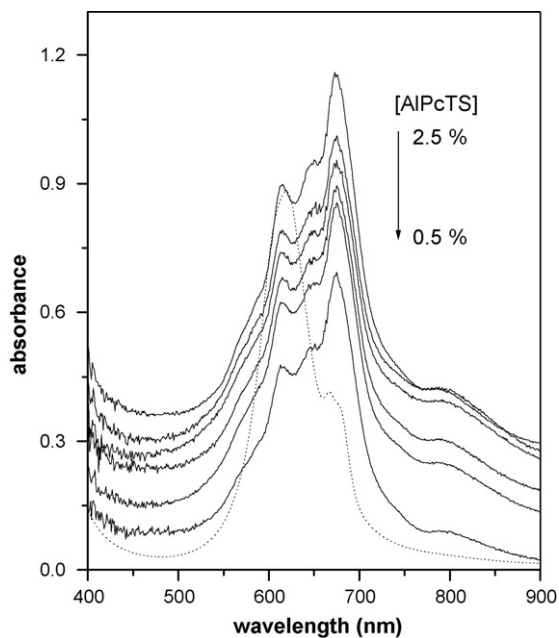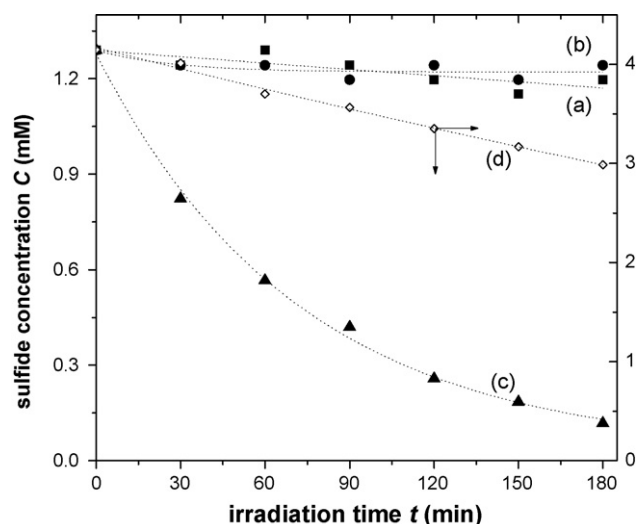

Fig. 2. Diffuse reflectance spectra of the immobilized AlPcTS samples containing different amount of AlPcTS at 0.5, 0.75, 1.0, 0.75, 1.5 and 2.5 wt.%. The dotted line was the spectrum of AlPcTS in an aqueous solution at pH 7.

greatly from the spectrum recorded for AlPcTS alone in an aqueous solution. It suggests that during the ionic exchange process, the monomer of AlPcTS enters easily into the porous resin as compared to the aggregates, probably due to steric factor. This spectral property of the immobilized AlPcTS would facilitate generation of singlet oxygen upon visible light irradiation and subsequently the sulfide oxidation. Several previous studies have demonstrated that the dye aggregation decreases the photosensitization activity for sulfide oxidation in a homogeneous solution, due to enhanced self-quenching of the excited dye [3–5,10–12].

The photosensitized oxidation of sulfide ion occurred efficiently in water at pH 9.3 on the resin-supported AlPcTS under visible light ($\lambda \geq 450$ nm) irradiation (Fig. 3c). The sulfide concentration measured in the bulk solution continuously decreased with irradiation time. After 3 h of irradiation, about 90% of sulfide ions disappeared. The time profile was well fitted into the first-order equation, giving the apparent rate constant $k_{app} = 0.013$ min^{-1}. The control experiments in the dark (Fig. 3b) or under irradiation in the presence of blank resin (Fig. 3a) showed that the sulfide ion was scarcely oxidized in such aerated aqueous medium. The catalyst contained AlPcTS at about 10.6 μmol/g, equivalent to 6 μM AlPcTS in solution. A parallel photoreaction in a homogeneous solution under similar conditions (Fig. 3d) gave $k_{app} = 0.0019$ min^{-1}, much smaller than that obtained in a heterogeneous medium (Fig. 3c). A reasonable explanation for such enhanced sulfide oxidation over the immobilized catalyst is that the immobilized AlPcTS exists mainly in a monomeric form, whereas the free AlPcTS in water is highly aggregated (Fig. 2). During the photosensitized oxidation of thiosulfate and 2-mercaptoethanol over ZnPcTS or ZnPcTC in a homogeneous aqueous solution, Iliev and co-workers have demonstrated that the rate of substrate oxidation increases with the concentration of monomeric dye, attributed to enhanced gen-
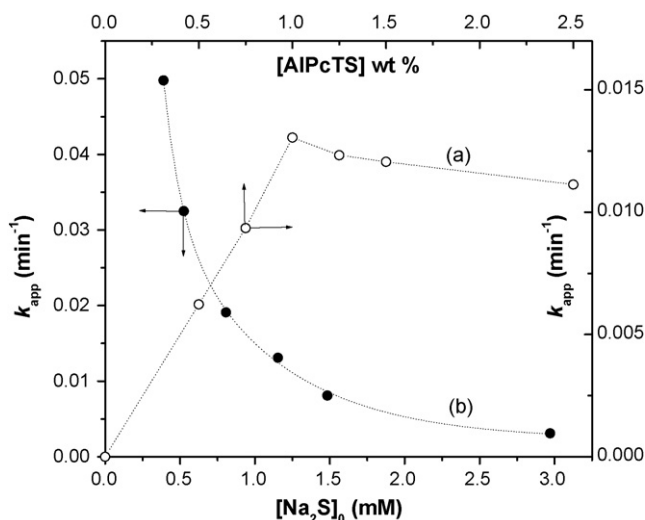
Fig. 4. Effects of (a) AlPcTS loading and (b) initial sulfide concentration on the photooxidation of sulfide at pH 9.3 in water. For (a), the initial concentration of sulfide was 4.15 mM, and for (b) the catalyst was 1.0 wt.% AlPcTS-loaded resin. The catalyst concentration was 0.50 g/L.
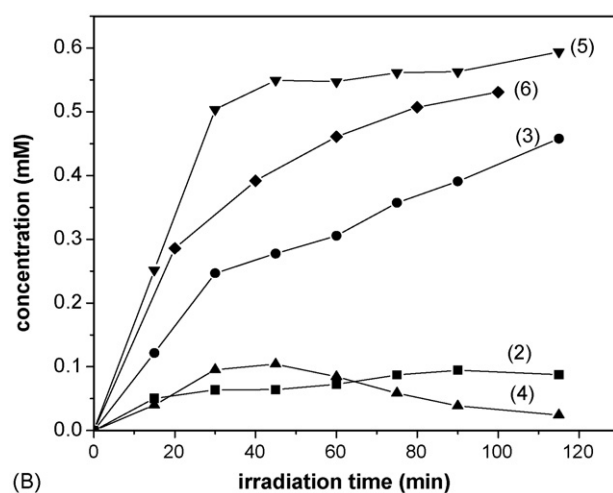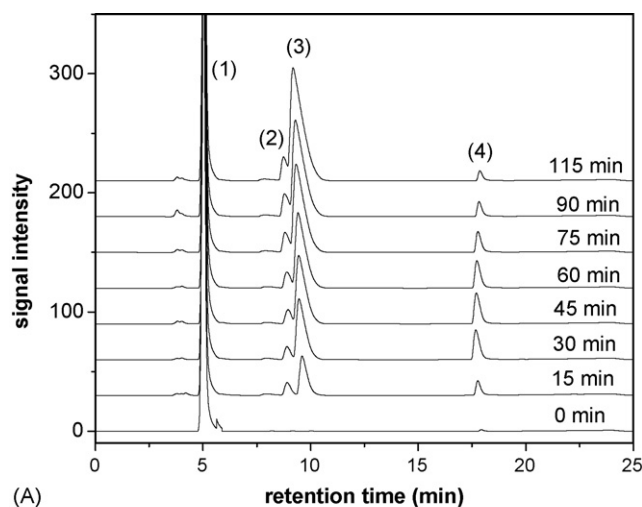

Fig. 5. Formation of the intermediates detected in the filtrate of sulfide oxidation. (A) The profiles recorded by ionic chromatography at different irradiation time. (B) The profiles of substrate concentrations as a function of irradiation time. The legends represent: (1) chloride ions released from the resin; (2) sulfite; (3) sulfate; (4) thiosulfate; (5) total concentration of all the detected ions (sulfite, sulfate and thiosulfate); (6) total loss of sulfide in the solution detected by sulfide-selective electrode. Conditions: initial sulfide concentration was 2.0 mM, and the catalyst of 1.0 wt.% AlPcTS resin at 0.50 g/L.

eration of singlet oxygen ($^1O_2$) [3–5]. The present result suggests that the resin is not only a good support for AlPcTS fixation, but also an excellent reagent for dispersing the immobilized photosensitizer in a monomeric form. This would lead to great enhancement in the rate of $^1O_2$ production and thus in the rate of sulfide oxidation.

The heterogeneous photosensitization reaction was influenced by AlPcTS loading in the catalyst (Fig. 4a) and by the initial concentration of sulfide as well (Fig. 4b). As the loading of AlPcTS increased, the rate of sulfide oxidation increased almost linearly at low loading (up to 1.5 wt.%), and then decreased slightly at high loading. Since the sulfide oxidation is initiated by $^1O_2$, the increase in total concentration of monomeric AlPcTS with AlPcTS loading (Fig. 2) would increase the rate of $^1O_2$ generation and thus the rate of sulfide oxidation. As the loading of AlPcTS further increased, the dye aggregation becomes slightly increased (Fig. 2), which would slow down the generation of $^1O_2$ and thus the sulfide oxidation (Fig. 4a). In this regard, the optimal loading of AlPcTS is about 1.5 wt.%. It means that all the light is harvested at 1.5 wt.% AlPcTS in the catalyst or 5.3 μM of net AlPcTS in solution.

However, the rate of sulfide oxidation was observed to decrease with the initial concentration of sulfide used (Fig. 4b). This was not the result we previously expected. The singlet oxygen once formed from the immobilized AlPcTS would not diffuse far way from the solid, and it would prefer to react with the adsorbed sulfide nearby on the catalyst. In this regard, the rate of sulfide oxidation is expected to increase with the initial amount of sulfide adsorbed. Such positive effect of substrate adsorption has been observed for the photosensitized oxidation of chlorophenol over organoclay-supported AlPc, where both photosensitizer (AlPc) and target substrate (chlorophenol) are located in the hydrophobic interlayers of composite clay [16]. The negative effect of sulfide adsorption observed here for sulfide oxidation might suggest that in the positively charged

network of resin, the adsorbed sulfide and/or singlet oxygen could not migrate at rates competitive with $^1O_2$ deactivation. Alternatively, the excited AlPcTS may be physically quenched by the adsorbed sulfide and/or the reaction intermediates nearby, lowering the efficiency of $^1O_2$ formation.

The reaction intermediates and products of sulfide photooxidation over the immobilized AlPcTS were monitored by ionic chromatography (IC) (Fig. 5A). The species 1 was assigned to be chloride ions released from parent resin as a result of sulfide exchange, whereas the species 2, 3 and 4 were identified as sulfite, sulfate and thiosulfate, respectively. The time profile of concentration change (Fig. 5B) showed that sulfite and thiosulfate were the reaction intermediates formed from sulfide oxidation. These intermediates could be further oxidized in situ, forming sulfate as the final product. In thermal catalysis, it is relatively difficult to oxidize thiosulfate by ground dioxygen, as

compared to sulfide and sulfite [2,3]. However, this is not the case in the present system. The thiosulfate intermediate could be efficiently converted to sulfate. After 2 h of irradiation, a mixture of 80% sulfate, 15% sulfite and 4% thiosulfate were detected in the filtrate by IC. However, the total concentration of the detected ions (Fig. 5B, curve 5) was higher than the sulfide concentration decreased in the bulk solution (Fig. 5B, curve 6), and much lower than the total sulfide added (2.0 mM). It indicated that either 3 h of irradiation was not enough, or the reaction intermediates/products, once formed from sulfide oxidation on the catalyst, were not completely desorbed into the solution, limiting the sulfide adsorption during the reaction process. A separate experiment showed that the sulfide adsorption was notably decreased in the presence of thiosulfate or sulfite or sulfate. But the magnitude of such negative effect was different from one anion to another, following the order of sulfate < thiosulfate < sulfite. It implies that among these anions, sulfate is easily released from the resin in the presence of sulfide, whereas sulfite is hardly released into the solution. However, strong adsorption of sulfite would benefit its oxidation by $^1O_2$ into sulfate. Another experiment in a homogeneous solution confirmed that both sulfite and thiosulfate competed with sulfide for $^1O_2$, but sulfate showed no effect on the sulfide oxidation. The experiment also showed that thiosulfate was more difficultly oxidized by $^1O_2$ than sulfite. Because of that, a maximal concentration of thiosulfate in bulk was reached at 50 min, whereas the concentration of sulfite was always kept at a low level. Due to faster oxidation of the adsorbed sulfite and faster desorption of the adsorbed sulfate, the sulfate concentration in bulk solution was high, increasing continuously with the reaction time. Since the sulfide adsorption on the catalyst was stronger than any of another three anions (sulfate, thiosulfate and sulfite), due to smaller ionic size, the total loss of sulfide in solution (Fig. 5B, curve 6), monitored by a sulfide-selective electrode, was lower than the sum of three anions detected by IC in solution (Fig. 5B, curve 5).

Although the reaction intermediates (sulfite and thiosulfate) adsorbed highly on the catalyst, they could be finally oxidized into sulfate over the immobilized catalyst in situ under visible light irradiation. This was verified by a repeated experiment, together with an aim to testify the catalyst stability (Fig. 6). During five consecutive runs, the rate of sulfide oxidation decreased gradually from one run to another, with k_{app} equal to 0.0481, 0.0469, 0.0423, 0.0302, and 0.0256 min^{-1}, respectively. This decrease in the rate constant was in agreement with the catalyst capacity toward sulfide adsorption, which also decreased from one run to another. Both the decreases in the sulfide adsorption and in the sulfide oxidation were mainly attributed to the intermediate competition with sulfide for the adsorptive sites and for $^1O_2$. It was also partially due to the catalyst concentration that was slightly decreased from one run to another, since for each data analysis 1.00 mL of the suspension was taken out from the system. After the forth run, however, the sulfide adsorption was still relatively large, and the photoreaction was still efficient. This indicates that the adsorbed intermediates could be replaced by sulfide. This is probably the mostly understanding advantage of the anionic resin used in the present system for sulfide oxidation. The result demonstrates that the resin-supported AlPcTS is
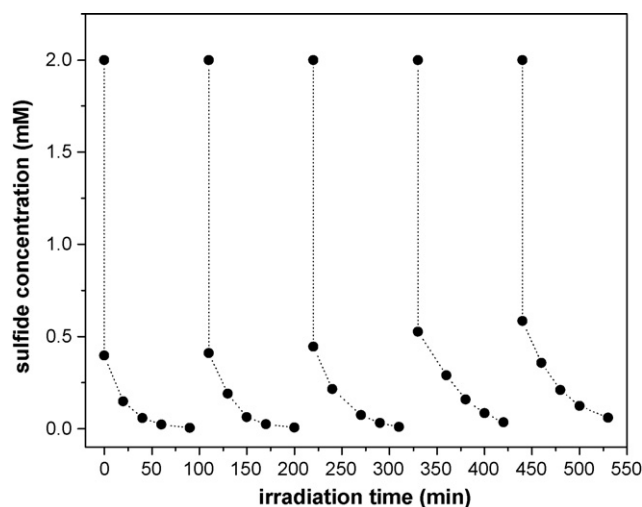

Fig. 6. Repeated experiments for the sulfide oxidation over 1.0 wt.% AlPcTS-loaded resin in water at pH 9.3 under visible light irradiation. Conditions were as described in Section 2.

efficient and relatively stable for adsorption and photosensitized oxidation of sulfide in the aerated aqueous medium.

4. Conclusions

An efficient strategy to photooxidize sulfide ion by visible light irradiation in an aerated aqueous medium has been developed. The resin-supported AlPcTS exhibits not only a high capacity for uptake of sulfide ion from water, but also a higher photosensitization activity for sulfide oxidation, as compared to the unbound AlPcTS. Although the intermediates (sulfite and thiosulfate) once formed adsorb and compete for the sorptive sites and $^1O_2$, they could be finally oxidized into sulfate in situ. Among all the anions, the final product of sulfate is easily desorbed from the solid into solution, especially in the presence of sulfide. This is the mostly understanding advantage of the anionic resin found in this work, although the support is also an excellent dispersing reagent for immobilization of the photosensitizer in a form of more photoactive monomer. The composite catalyst was relatively stable and could be used repeatedly. This system was also efficient for the photosensitized oxidation of sulfur-containing organic compounds such as vinyl ethyl thioether and thiophenol. Further improvement of the catalyst activity is highly possible for practical treatment of sulfide-containing wastewater by solar light and molecular oxygen.

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