Formation of poly(acrylic acid)/alumina composite via in situ polymerization of acrylic acid adsorbed within oxide pores

Bin Wang^{1,*}, Ya-Ping Wang¹, Peng Zhou¹, Zhong-Qing Liu¹, Shi-Zhong Luo¹, Wei Chu¹,

Zhanhu Guo^{2,*}

¹College of Chemical Engineering, Sichuan University, Chengdu, Sichuan, 610065,

PR China

²Integrated Composites Laboratory (ICL), Chemical and Biomolecular Engineering

Department, University of Tennessee, Knoxville, Tennessee 37996, USA

Abstract

Poly(acrylic acid) (PAA) adsorption on alumina has been widely studied to provide composite materials. This work attempts to form PAA/alumina composites via in situ polymerization of acrylic acid pre-adsorbed on alumina. Effective acrylic acid adsorption in porous γ -alumina was realized with incipient wetness impregnation method. The adsorbed acrylic acid was then polymerized via reversible addition fragmentation transfer (RAFT) polymerization in aqueous medium. The solution properties of the as-prepared PAA/alumina composites were further investigated. Dissociation constant measurements illustrate that PAA molecules residing in alumina exhibited pK_a more basic than pure PAA. The composites showed higher lead adsorption capability than pristine alumina. However, there correlation of lead adsorption capability and the adsorbed PAA amount in PAA/alumina samples did not follow a straightforward pattern.

Ion adsorption difference among various PAA segments was proposed.

Keywords: lead ion sorption; poly(acrylic acid); polyelectrolyte dissociation constants; polymer/alumina composite; RAFT polymerization

*Corresponding author: Tel. (+86) 28-85464466; fax (+86) 28-85403422; E-mail
bin_wang@scu.edu.cn; zguo10@utk.edu

1. Introduction

Predetermined mechanical, chemical, or physical properties can be adjusted by combining inorganic and organic components at the molecular level to form composites [1]. In composite materials, the inorganic skeleton provides the mechanical stability to the hybrid, while the functional groups of the organic molecules can selectively perform various chemistries, such as absorbing heavy metal ions. Polymers are the most employed organic component in synthesizing composites. These composites can be synthesized via: polymer adsorption into the support pores or deposition inside layered silicates; polymerization of monomers inside the cavities of the support; covalently linking organic functionality to the support; or direct synthesis of the composites using the sol-gel process. Interactions between the inorganic and polymeric components of the composite can range from weak forces such as hydrogen bonding to strong covalent bonds.

Composites formed of infiltrated polymers inside inorganic support pores are of special interests. The polymeric network fully penetrating the inorganic skeleton presents entanglement properties not encountered in systems where polymers only adsorbed on the external surface [2]. The composites are expected to display high mechanical and chemical stability, as well as other unique properties. For example, the externally adsorbed polymers exhibit the glass transition similar to free polymers, the polymer chains embedded inside mesoporous silica channels do not display glass transition effect. Meanwhile, encapsulation of polymer chains within support pores provides protection against external environments such as aqueous solutions.

Start with pre-formed, industrially available inorganic support materials, composites with infiltrated polymers can be prepared either by polymer infiltration or in situ polymerization. The polymer infiltration process has been shown to take place in two stages, a rapid initial adsorption followed by a slow penetration into the pores. Pore size, polymer dimensions, ionic strength, and polymer concentration are the factors that affect the adsorption process. For example, Caruso et al. have studied the adsorption properties of polymer into metal oxide mesoporous pores [3,4]. Their studies conclude that polymer size and pore size are the most influential factors for the polymer infiltration in nano/mesoporous particles. Large pores are capable of adsorbing a broad range of molecular weight polymers.

Polymers have a certain degree of bulkiness that prevents them from infiltrating small openings/connections of the support pores. In order to fully fill the pore volume of the support materials, in situ polymerization of appropriate monomers offers a more promising means because monomer are much more feasible to penetrate narrow openings of the support. Atom transfer radical polymerization (ATRP) can be readily performed in aqueous or mixed aqueous media using monomers bearing various functional groups [5]. ATRP has been utilized to synthesize nanocomposite to provide a layer of well-defined polymer chains attached to inorganic particle surface [6,7].

Poly(acrylic acid) (PAA) is a well-known pH-responsive polymer that has been used as pharmaceutical carriers, anti-fouling agents, flocculants, and superabsorbers [8]. Acrylates with a wide range of side chains have been polymerized using the controlled free radical polymerization process [5]. When using ATRP to synthesize PAA, the

coordination between acrylic acid monomer and metal catalyst causes ill-controlled polymers [9]. Reversible addition fragmentation transfer (RAFT) polymerization of acrylic acid yields high molecular weight PAA with narrow polydispersity, as well as good miscibility with inorganic particles [10]. The RAFT polymerization of acrylic acid method can be readily employed in aqueous solution by using a trithiocarbonate chain transfer agent [11]. In the presence of inorganic support materials, acrylic acid has been incorporated into composite materials via in situ polymerization [5]. In the composites, the polymer layer demonstrates controlled thickness and functionality, affording the composite materials tailored physical properties such as wettability and etching resistance [5]. Exfoliation of layered double hydroxide [12] or montmorillonite [13–15] has been realized by intercalation of acrylic acid monomer followed by in situ living polymerization.

As for the inorganic support, we choose alumina that is one of the most studied metal oxides being widely utilized in water purification to remove dissolved inorganic and organic contaminants [16]. Among various forms, γ - Al_2O_3 is formed by heating boehmite $\text{AlO}(\text{OH})$ between 400 and 500 °C. It has a specific surface area of 100–300 m^2/g . Upon heating, adjacent $-\text{OH}$ groups can react to release water. The reported isoelectric point for alumina is pH 7.2–9 [17]. PAA/alumina interpenetrated composites have been synthesized via the in situ polymerization route in combination with sol-gel preparation of alumina [18,19]. Also, in situ radical polymerization of acrylic acid has been attempted in the presence of alumina powders dispersed in PAA aqueous solution [20]. Alumina particles are believed to be immobilized within the polymer matrix.

One application area of the PAA/alumina composites is for heavy metal ion removal. Alumina is a major component in soils, aquifer materials, and sediments that has active surface sites for sorption of metal ions [21]. Abundantly existing in natural environment, alumina particles adsorb organic matter, primarily humic substances, to form a hybrid complex. The properties of minerals can be significantly changed upon adsorption of humic substances [22]. Regarding metal ion sorption, humic substances can either increase metal ion sorption by offering complexation sites, or decrease sorption by blocking active sites on mineral surface. To better understand such processes, one commonly employed method is to use a binary system composed of a surrogate polymer that highly resembles humic substances, and alumina particles. Synthetic poly(acrylic acid) (PAA) has been widely used as such a surrogate [23]. Investigation of the binary PAA/alumina system becomes a valuable tool to illustrate the behavior of the humic substance and mineral hybrid that is extensively present in soil.

Interactions between PAA and alumina govern the properties of the PAA/alumina hybrid like adsorption and dispersion. Characteristics of the particles, polymer, and the mixing solution all contribute to the process [24]. The size, morphology, and charge of the inorganic material, the conformation, molecular weight, and concentration of the organic matter, and the ionic strength and pH of the reaction media have been studied to understand the interactions between PAA and alumina. We have previously investigated small molecular weight PAA adsorption into porous alumina channels [25]. We found the polymer conformation was critical for the chain adsorption inside the alumina pores. Per metal ion sorption of the composite materials, adsorption of Cd^{2+} onto the PAA/alumina

composite is influenced by the solution pH [21]. Below pH 6, the composite is advantageous for metal ion sorption. Above pH 6, a decreased metal ion sorption is discovered due to the enhanced Cd-PAA complex dissolution. The interpenetrated PAA/alumina composites synthesized by combined in situ polymerization of acrylic acid and sol-gel preparation of alumina have been shown to adsorb metal ions following Langmuir isotherms [19]. The sorption of different cations has been tested to demonstrate a sorption order: $\text{Ni}^{2+} < \text{Cu}^{2+} < \text{Cd}^{2+} < \text{Pb}^{2+}$.

In this study, we explore the preparation of PAA/alumina composites via the RAFT route starting from acrylic acid and alumina particles, with all manipulations performed in aqueous or mixed aqueous media. An in situ radical polymerization of monomer molecules pre-adsorbed on alumina was used to form poly(acrylic acid) inside alumina pores. Radical polymerization has been realized by chain growth inside the channels of micro- and mesoporous molecular sieves [26]. According to the article, pores of molecular sieves were filled with methacrylate molecules via gas phase infiltration to prepare the composite. In our experiment, we apply solution infiltration of monomer molecules for better industrial adaptability. Adsorption of acrylic acid on alumina is dominated by carboxylate group bridging two Al atoms [27]. The adsorption of mono- and dicarboxylic acids with 1–7 carbons on alumina surface is considered a self-assembled monolayer [28]. We expect it to be very viable to include acrylic acid inside γ -alumina pores in aqueous solution.

2. Experimental

2.1 Materials

Acrylic acid and carbon disulfide were acquired from Chengdu Kelong Chemical Co. (China). Ethanethiol, 2-bromobutyric acid, and 4,4'-azobis(4-cyanovaleric acid) (V501) were purchased from Chengdu Best Chemicals Co. Ltd. (China). γ -Alumina was obtained from Kemiou Chemical Co. (Tianjin, China), and its grinded powders in 40–60 mesh range were activated at 500 °C for 3 h prior to use. Other reagents were of analytical grade. Deionized water was used with a conductivity of $\leq 1.0 \mu\text{S cm}^{-1}$. All reagents were used as received without further purification unless stated otherwise.

2.2 Synthesis of RAFT chain transfer agent (CTA)

The RAFT chain transfer agent (CTA) was prepared following the literature route [11,29,30]. Briefly, a 50-mL three-neck flask charged with NaOH (1.2 g, in 50 wt.% solution), EtSH (2.25 mL, 30.0 mmol), CS₂ (1.68 mL, 28.0 mmol), acetone (1.5 mL), and water (5.0 mL) was reacted for 10 min and then placed in ice bath. 2-Bromobutyric acid (3.2 mL, 30.0 mmol) and 50% NaOH (2.4 mL) were added drop-wise in sequence. After addition, the ice bath was removed and water (5.0 mL) was added. The solution was stirred for 20 h, followed by quenching in ice water. The mixture was added with 50% HCl (10 mL), extracted with hexane (20 mL). The organic phase was further washed with water (20 mL) for five times until becoming colorless. The oil-like liquid was dried over MgSO₄, filtered, and then evaporated to remove hexane at 50 °C. The RAFT CTA was obtained as a dark-orange oil. Yield: 2.61 g (11.63 mmol), 41.5% based on CS₂.

¹H NMR (CDCl₃): 4.81 (1H, $-\text{CH}-\text{CH}_2-\text{CH}_3$), 3.37 (2H, $-\text{CH}_2-\text{CH}_3$), 2.00 (2H, $-\text{CH}-\text{CH}_2-\text{CH}_3$), 1.36 (3H, $-\text{CH}_2-\text{CH}_3$), 1.08 (3H, $-\text{CH}-\text{CH}_2-\text{CH}_3$) [11,29,30].

2.3 RAFT preparation of PAA/alumina composites

The preparation of PAA/alumina composites were conducted in two steps. The first step was the adsorption of acrylic acid (AA) in ethanol solution into alumina pores [10]. This was achieved in two fashions, wet impregnation and incipient wetness impregnation. During the RAFT process, acrylic acid monomers are usually distilled to remove added inhibitors. Our preliminary results demonstrated that in the presence of alumina particles, the impurities in monomers would not alter polymerization significantly so distillation operation was omitted. In the following operations, acrylic acid was used without prior distillation. AA was dissolved in ethanol to afford 10, 50, or 90 v.% solutions. In wet impregnation, 5.0 g of activated alumina was added to AA ethanol solution (50 mL), gently stirred for 12 h, filtered, and rinsed with water five times to removed externally adsorbed AA. In incipient wetness impregnation, alumina (5.0 g) was added with AA ethanol solution (2.0 mL) and standing for 1 h. The acrylic acid soaked alumina samples were labeled $M_{n,x}/Al$, where $n = 10, 50$, or 90% , and x stands for *wet* or *incipient wetness* impregnation.

After adsorption with acrylic acid, alumina (4.5 g) was added with CTA and V501 (both in 50% NaOH solution). The amounts of the two reagents were calculated according to adsorbed acrylic acid (determined via thermogravimetry): AA:CTA:V501 = 40:1:0.1 in molar ratios. The mixture was added with water (20 mL), stirred at 65 °C for 8 h, quenched with ice water. The mixture was then adjusted to pH 5.0–5.5 using NaOH, filtered and rinsed repeatedly, and dried at 60 °C for 10 h. The prepared samples were labeled $P_{n,x}/Al$, where n and x take the same meanings as in $M_{n,x}/Al$.

2.4 Solution properties of PAA/alumina composites

A batch equilibrium procedure was employed to analyze the solution properties of the formed composite materials. A certain amount of composite sample, based on measured PAA content, was dispersed with ~5 mL water. An aliquot of 0.20 mL of 0.025 M NaOH was titrated into the dispersion under swirling. After equilibration time, the pH value of the dispersion was taken.

A batch equilibrium procedure was employed to analyze the metal ion sorption properties of the composites while all results were reported as the average of a triplicate. Lead content of the supernatant was directly analyzed with atomic absorption spectrophotometry (AAS). When the lead content of a solid was to be determined, the solid was dissolved with 50% phosphoric acid, diluted with water, and analyzed with AAS. The lead sorption kinetics was analyzed by filtering the sorption solution at different time intervals and measuring the Pb content of the supernatant. The effect of Pb^{2+} concentration on sorption amount was tested in $\text{Pb}(\text{NO}_3)_2$ solutions. When preparing $\text{Pb}(\text{NO}_3)_2$ solution of high Pb^{2+} concentrations, the solution pH needed to be adjusted using NaOH. When the solution pH was above 5.5, the solution started to form precipitation. So $\text{Pb}(\text{NO}_3)_2$ solutions of pH 5.0–5.1 were used.

2.5 Characterization

Room temperature Fourier transform infrared (FT-IR) spectroscopy (Perkin Elmer Spectrum Two) was acquired from KBr pellets, of which ~1 wt.% was the sample, in the range of 4000–400 cm^{-1} . Proton nuclear magnetic resonance (^1H NMR) (Bruker Avance II-400MHz) was performed using CDCl_3 as the solvent. Mass spectrometry (Thermo

Finnigan TSA Quantum Ultra) was recorded in the range of $m/z = 100\text{--}300$. Thermogravimetry (TG) (HCT-2 Differential Thermal Balance, Beijing Hengjiu Scientific Instrument Co.) was operated in the range of $80\text{--}700\text{ }^{\circ}\text{C}$ in air. The sample was initially heated to $80\text{ }^{\circ}\text{C}$ for 20 min to remove atmospheric water. The process was monitored until the weight variation reached a level of $\leq 0.01\text{ mg}$. The sample was then heated to $130\text{ }^{\circ}\text{C}$ at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. After this point, the heating rate was changed to $2\text{ }^{\circ}\text{C min}^{-1}$ until $150\text{ }^{\circ}\text{C}$, and the sample was held for an additional 10 min at this temperature for the complete removal of AA (boiling point of $141\text{ }^{\circ}\text{C}$). Per experimental recording, decarboxylation occurred around $400\text{ }^{\circ}\text{C}$. From $150\text{ }^{\circ}\text{C}$, the heating rate was set to be $10\text{ }^{\circ}\text{C min}^{-1}$ until $350\text{ }^{\circ}\text{C}$. After this temperature, the heating rate was changed to $5\text{ }^{\circ}\text{C min}^{-1}$ until $500\text{ }^{\circ}\text{C}$ for the complete decomposition of organic matters. The specific surface areas, total pore volumes, and average pore diameters were determined from the nitrogen adsorption-desorption isotherms at $-196\text{ }^{\circ}\text{C}$, which were measured using an automated surface area and pore size analyzer (Quantachrome NOVA 1000e). Before each measurement, the samples were degassed in vacuum at $300\text{ }^{\circ}\text{C}$ for 3 h. Specific surface areas of samples were calculated by the Brunauer-Emmett-Teller (BET) method, and the pore size distribution and average pore diameter were determined according to the Barrett-Joyner-Halenda (BJH) method applied to desorption isotherms. Lead content was measured with atomic absorption spectrophotometry (AAS) (AA32DCRT, Shanghai Analytical Instrument Co., China). Aqueous lead standard solutions were prepared from $\text{Pb}(\text{NO}_3)_2$ to obtain standards for AAS.

2.6 Geometric parameters of infiltrated PAA

We combine the TG and BET/BJH results to estimate the geometric parameters of infiltrated PAA, and use values directly reported in Tables 1 and 2. The pristine alumina has an average surface area of $S_A \times 10^4 \text{ cm}^2$, pore diameter of $d_A = 2r_A \text{ nm}$ and pore volume of $V_A \text{ cm}^3 \text{ g}^{-1}$. Assume the predominant pore volume takes a tube form, then the total length of tubes in one gram of alumina is $l = \frac{V_A}{\pi r_A^2} \times 10^{14} \text{ cm}$. In one gram of composite sample, the mass of PAA measured with TG is $M \text{ mg}$. Take an approximate PAA density of 1.23 g cm^{-3} according to the supplier, this gives a volume of $0.813M \times 10^{-3} \text{ cm}^3$. Assume PAA covers alumina surface as a uniform, evenly distributed layer, the thickness of the layer becomes $h = \frac{0.813M}{\left(\frac{1000-M}{1000}\right)S_A} \text{ nm}$. Subtracting this value from the pristine alumina pore diameter, the composite sample should have a pore diameter of $2r_C = d_C = (d_A - 2h) \text{ nm}$. The corresponding volume is $V_C = \pi r_C^2 l \times 10^{-14} = \frac{r_C^2}{r_A^2} V_A \text{ cm}^3$, and surface area is $S_C = \pi d_C l \times 10^3 \text{ m}^2$ for the composite. The calculated such values of $P_{10,\text{in}}/\text{Al}$ and $P_{90,\text{in}}/\text{Al}$ are shown in Table 3, along with measured values.

3. Results and discussion

3.1 Synthesis of RAFT chain transfer agent (CTA)

The asymmetric trithiocarbonate RAFT chain transfer agent (CTA) was synthesized according to Scheme 1 following literature procedures. The FT-IR of the product shows S–H stretching at 2583 cm^{-1} [29,31], C=S stretching at 1265 and 1045 cm^{-1} [29,32–35], and C–S stretching at 653 cm^{-1} [35] (Figure 1). The ^1H NMR spectrum is shown in Figure 2. The peaks at 3.37 and 1.36 ppm are the combined contributions of the product CTA and the starting material EtSH [11,29,30]. To sufficiently remove the impurity EtSH, repeated purification

operations would be required that would have resulted in severely diminished product yield. Meanwhile, the presence of the impurity did not interfere with the RAFT reaction. Therefore, further purification of the product CTA was not performed. Mass spectrum of the product shows the molecular ion peak of $m/z = 224.66$ (Figure 3). The peak separated by 15 m/z is assigned to the loss of $-CH_3$, 27 m/z to $-CH_2CH_3$, and 54 m/z to two $-CH_2CH_3$.

3.2 Adsorption of acrylic acid (AA) in alumina

The adsorption of acrylic acid in alumina in aqueous solution was reported in the fashion of a monolayer acrylic acid coverage [36]. The FT-IR spectra of AA-adsorbed alumina samples are presented in Figure 4a. Compared to pristine alumina, acrylic acid adsorption was unveiled by the peak at 1722 cm^{-1} , assigned to the symmetric stretch of $-CO_2H$ [22]. The peaks at $1580\text{--}1550$ and $\sim 1460\text{ cm}^{-1}$ are assigned to the asymmetric and symmetric stretches of $-CO_2^-$, respectively, indicative of the dimeric binding mode [27]. Because of the strong $-OH$ bending vibration of alumina at 1640 cm^{-1} [25,37], the $C=C$ vibration of adsorbed acrylic acid at 1634 cm^{-1} was not observed in the spectra [12].

The TG traits of AA-adsorbed alumina samples are displayed in Figures 5a and 5c. Inflection points at 150 and 450 °C are due to heating program changes. We notice that there was minimal weight loss until 150 °C, arising from the loss of water and acrylic acid (boiling point 141 °C). The following degradation stages of the M/Al samples resemble that of P/Al samples, and will be discussed in the following section. Higher acrylic acid concentrations yielded more organic matter adsorbed in alumina for both wet and incipient wetness impregnation methods (Table 1). Adsorption efficiency indicates the ratio of organic matter measured via TG against the added acrylic acid amount in each

sample. For incipient wetness impregnation, the adsorbed acrylic acid was more efficiently retained at lower adsorbed amount after post-adsorption operations such as wash and drying. With 10% acrylic acid solution, wet impregnation afforded the least organic adsorption among all samples, 93 $\mu\text{g m}^{-2}$. Higher solution acrylic acid concentrations (50% and 90%) provided samples with $\sim 280 \mu\text{g m}^{-2}$ acrylic acid adsorption.

The oxide surface area occupied by adsorbed organic matter can be expressed in terms of monolayers. The occupied area of a molecule in the monolayer coverage pattern can be calculated according to the following equation [38]:

$$A = 6.354 \left(\frac{T_c}{p_c} \right)^{\frac{2}{3}} (\text{\AA}^2) \quad (1)$$

where T_c is the critical temperature, and p_c is the critical pressure. Using the values of T_c and p_c for acrylic acid [39], the calculated area for one acrylic acid molecule is $3.10 \times 10^{-19} \text{ m}^2$. Combine the area coverage and TG data, the values of acrylic acid monolayer coverage of alumina surface are listed in Table 1. The estimated acrylic acid coverage by using a single acrylic acid molecule area is close to that determined by TG discussed in the previous paragraph. The highest adsorbed acrylic acid from aqueous solution was determined to be $342 \mu\text{g m}^{-2}$ when the acrylic acid molecules were stacked in a monolayer fashion [36]. The adsorbed acrylic acid with the wet impregnation method in ethanol solution (50% and 90%) was close to the monolayer coverage. Using incipient wetness impregnation, higher acrylic acid adsorption than monolayer was achieved with solution concentrations of 50% and 90%. Incipient wetness impregnation appears a superior method for incorporating more acrylic acid in alumina. In the case of $\text{M}_{90,\text{in}}/\text{Al}$,

the adsorbed acrylic acid could occupy the alumina surface in a three-monolayer fashion.

3.3 RAFT preparation of PAA/alumina composites

In situ polymerization of acrylic acid in the presence of alumina particles was performed in aqueous solution. The FT-IR spectra of the composite samples are very similar to that of M/Al, showing peaks at 1580–1550 and $\sim 1460\text{ cm}^{-1}$ of CO_2^- (Figure 4b). Because the samples were neutralized after polymerization, the peak at 1722 cm^{-1} of CO_2H was absent.

The TG curves of the composite samples are displayed in Figures 5b, 5d. For pure PAA, a typical TG curve has three stages [15]. Below $150\text{ }^\circ\text{C}$, the release of water is accounted for the loss of mass. Between 150 to $350\text{ }^\circ\text{C}$, dehydration and decarboxylation of PAA contribute to the loss of mass. From 350 till $500\text{ }^\circ\text{C}$, the total chain breakdown and full combustion of the polymer occur. The P/Al samples demonstrate similar trends to that of pure PAA, especially those with relatively higher PAA contents ($\text{P}_{50,\text{in}}/\text{Al}$ and $\text{P}_{90,\text{in}}/\text{Al}$). An interesting point is that some acrylic acid monomer adsorbed samples (i.e., $\text{M}_{50,\text{in}}/\text{Al}$ and $\text{M}_{90,\text{in}}/\text{Al}$) present similar curves (Figure 5c). The phenomenon implies that polymerization of adsorbed acrylic acid monomers might have occurred during the heating process of TG measurement. There is loss of adsorbed acrylic acid during the polymerization process because all P/Al samples show retention efficiencies less than unity, some far from that (Table 2). Adsorbed acrylic acid molecules might be re-dissolved and re-distributed in the aqueous polymerization solution. During the RAFT polymerization, the acrylic acid molecules both inside and outside the alumina pores undergo polymerization to form PAA molecules, but those outside the pores will

be distributed on the outer walls of the oxide (Scheme 2). Retention efficiency is the ratio of the organic matter measured via TG against the adsorbed amount of acrylic acid monomer before polymerization. Again, incipient wetness impregnation affords higher PAA amounts in the composite than wet impregnation does. In a similar approach to that of monomer coverage, the alumina surface covered by PAA in terms of monolayer is given in Table 2.

The physical characterization in terms of specific surface area, pore diameter, and pore volume was performed on P_{10,in}/Al and P_{90,in}/Al (Table 3). The selection of these two composite samples was based on their adsorbed organic matter, i.e., the former having very small amount while the latter having the most among all composite samples. As expected, the pristine alumina presented the greatest BET specific surface area. After monomer adsorption and in situ polymerization, the composites samples experienced decreased specific surface areas because of polymer infiltration. If the adsorbed PAA would have taken a uniform coverage of the alumina surface, the theoretical specific surface area, pore volume, and pore diameter of samples P_{50,in}/Al and P_{90,in}/Al can be calculated based on the PAA content measured by TG (Table 3). Compare the calculated and measured values, the polymer distribution in these two samples seems contradictory. For P_{90,in}/Al with the highest adsorbed PAA amount, both calculated specific surface area and pore volume are smaller than the measured, and the pore diameter is greater. The explanation is that a significant portion of PAA existed on the outside surface of alumina particles and the pore infiltration by polymer chains was insufficient. On the other hand, for P_{10,in}/Al, the theoretical specific surface area and pore volume values are larger than

that of measured. The explanation of this discrepancy is that the pore channels of alumina were not uniform. Some narrower parts of the channels were clogged by the formed polymer, resulting some dead surface area and pore volume not accessible to N₂ molecules during the measurement.

3.4 Solution properties of PAA/alumina composites

Solution properties of composites P_{10,in}/Al and P_{90,in}/Al were analyzed by the pH titration method. The dissociation constant of PAA was determined by the pH titration method [40]:

$$K_a = [H^+] \left\{ \frac{[L^-]}{[HL]} \right\}^{\beta} \quad (2)$$

where β is a constant between 1 and 2. Rearrangement gives the relation between the pH and the degree of neutralization α in the modified Henderson–Hasselbach equation [40,41]:

$$pH = pK_a - \beta \log \left(\frac{1-\alpha}{\alpha} \right) \quad (3)$$

The equation states that for a given polymer type, the values of K_a and β are independent of polymerization degree. For a simple weak acid such as acetic acid, β is unity.

The pH value versus $\log[(1 - \alpha)/\alpha]$ is plotted in Figure 6. It is found that for P_{10,in}/Al, the plot is linear in the pH range of 4.95–7.38 while the pH range for P_{90,in}/Al is 4.90–6.74 with $R^2 \geq 0.999$ for both. Using the slope and intercept values, the pK_a and β values of the two composites were calculated (Table 4). The pK_a values of the two composites are higher than pristine PAA ($pK_a = 4.75$).⁴² Between the two composite samples, the more ratio of alumina (P_{10,in}/Al), the higher pK_a of the composite material. Sample P_{10,in}/Al has a higher β value than P_{90,in}/Al, indicating less carboxylic acid amount per material mass.

3.5 Lead sorption on PAA/alumina

Metal ion sorption on PAA/alumina composites depends on the solution pH range [21]. In the PAA/alumina composites, carboxylic acid groups are considered the predominant metal ion sorption sites. Metal ions on the composites may proceed through ion exchange with -COOH , or complexation with -COO^- [19]. On the other hand, the stability constant of Pb(II)-PAA (6.75–7.0) is higher than Pb(II)-alumina (6.0), but there exist enough strong-adsorbing sites on alumina for metal ion to bind [23].

Lead sorption on $\text{P}_{n,x}/\text{Al}$ samples were performed in a batch equilibrium procedure. In a typical experiment, an aliquot of Pb^{2+} solution (25 mL) was added with $\text{P}_{n,x}/\text{Al}$ (0.0100 ± 0.0002 g), standing for various time periods, and filtered. Examination of the adsorption curves of pristine alumina, $\text{P}_{10,\text{in}}/\text{Al}$, and $\text{P}_{90,\text{in}}/\text{Al}$ reveals that the three samples behaved highly similarly toward lead sorption (Figure 7a). After about 30 min, all samples had reached the adsorption plateau. The adsorption processes of the three samples with very different PAA amounts incorporated (0, 1/4-monolayer, 2-monolayer) highly resemble each other, suggesting that PAA directly attached to alumina surface contributed significantly to lead ion sorption (vide infra). The effect of metal ion concentration on lead sorption in pristine alumina, $\text{P}_{10,\text{in}}/\text{Al}$ and $\text{P}_{90,\text{in}}/\text{Al}$ was tested (Figure 7b). Adsorbed lead amount increased with higher Pb^{2+} solution concentration. Higher than 60 mg L^{-1} , the adsorbed lead amount increment became stagnated. The validity of lead sorption experiments was further tested by analyzing the combined lead amounts both in the supernatant and the solid after adsorption (Table 5). The data demonstrate that the lead amounts from the combined supernatant and solid matched the initial lead amounts very

well.

The adsorbed Pb(II) amount on each sample is shown in Figure 8 using a lead solution concentration of 60 mg L⁻¹. Pristine alumina had shown considerable Pb(II) sorption capacity, while composite samples with PAA incorporated showed higher Pb(II) sorption capacities. However, the Pb(II) sorption on the composite samples does not correlate with the adsorbed PAA amount on alumina. According to the previous analysis, P_{90,in}/Al would contain a significant amount of PAA on the outside surface of alumina particles. The carboxylic acid groups in the extra PAA chains did not show great contribution to Pb(II) sorption. Within experimental error, we find that all P_{n,x}/Al samples adsorbed similar amount of Pb(II). This implies that the PAA layer directly contacting alumina surface would be responsible for the metal ion sorption.

4. Conclusion

In situ polymerization of acrylic acid within γ -alumina pores was attempted to form PAA/alumina composites. The monomer molecules were adsorbed into the oxide pores via impregnation first, followed by RAFT polymerization in aqueous solution. The adsorbed monomer molecules might have re-dissolved in the solution during the polymerization process, leading to unevenly distributed polymer in the formed PAA/alumina composite samples. With high acrylic acid impregnation amount, a good portion of the formed PAA in the composite resided outside the alumina pores. With low acrylic acid impregnation amount, more of the formed PAA were located inside the oxide pores, but clogged some narrower channels. Thus there existed a discrepancy between

PAA amount measured via thermogravimetry and the physical data determined via gas absorption/desorption. The solution properties of the composites were further analyzed. The pK_a values of PAA in the composites became dependent on the alumina content. With higher alumina content in a composite sample, the pK_a value of PAA moved to the higher pH range. The metal ion sorption properties of the composites seemed to be independent of PAA content in each sample. It is suggested the PAA layer adjacent to alumina was responsible for metal ion sorption. Among the PAA/alumina composites prepared, the one with the highest acrylic acid loading via the incipient wetness impregnation contained the most PAA after in situ polymerization, and its lead sorption was the highest.

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Scheme 1. Schematic illustration of synthesis of asymmetric trithiocarbonate RAFT chain transfer agent (CTA) and in situ preparation of poly(acrylic acid) from acrylic acid in the presence of alumina.

Figure 1. FT-IR spectrum of trithiocarbonate RAFT chain transfer agent (CTA).

Figure 2. ¹H NMR spectrum of trithiocarbonate RAFT chain transfer agent (CTA).

Figure 3. Mass spectrum of trithiocarbonate RAFT chain transfer agent (CTA).

Figure 4. FT-IR spectra of alumina adsorbed with acrylic acid (a) and in situ polymerized PAA (b).

Figure 5. TG traits of alumina adsorbed with acrylic acid (a), (c) and in situ polymerized PAA (b) and (d).

Scheme 2. Schematic presentation of PAA distribution in the formed PAA/alumina composite after the RAFT polymerization of acrylic acid monomers adsorbed in alumina pores. Red dots represent acrylic acid molecules and red lines represent PAA chains.

Figure 6. Henderson–Hasselbach plot of PAA in composite samples titrated with NaOH.

Figure 7. Kinetics (a) and pH effects (b) of lead sorption on PAA/alumina composites.

Figure 8. Equilibrium lead sorption amounts and PAA adsorption amounts of wet impregnation (a) and incipient wetness impregnation (b) composite samples.

Table 1. Adsorption amount (μg m⁻²) and efficiency of acrylic acid in AA/γ-Al₂O₃ samples

Table 2. Adsorption amount ($\mu\text{g m}^{-2}$) and retention efficiency of PAA in PAA/ $\gamma\text{-Al}_2\text{O}_3$ samples

Table 3. Physicochemical characteristics of pristine alumina and select composites, and calculated values assumed uniform coverage of PAA on alumina surface in composites

Table 4. PAA solution dissociation constants of select composites

Table 5. Comparison of add-up Pb concentration (mg L^{-1}) by combined supernatant and digested measurements after composite adsorption versus initially concentration

T 1

	adsorption	adsorption	AA layers	
	amount	efficiency	<i>a</i>	<i>b</i>
M _{10,w} /Al	93.18	—	0.24	0.27
M _{50,w} /Al	272.55	—	0.71	0.80
M _{90,w} /Al	279.47	—	0.72	0.82
M _{10,in} /Al	173.58	79.89%	0.45	0.51
M _{50,in} /Al	631.09	58.09%	1.63	1.85
M _{90,in} /Al	1071.31	54.78%	2.78	3.13

a Calculated according to Eq. (1).

b Estimated using data from ref 36.

T 2

	adsorption	retention	PAA layers	
	amount	efficiency	<i>a</i>	<i>b</i>
P _{10,w} /Al	54.96	58.98%	0.14	0.16
P _{50,w} /Al	69.02	25.32%	0.18	0.20
P _{90,w} /Al	137.31	49.13%	0.36	0.40
P _{10,in} /Al	99.11	57.10%	0.26	0.29
P _{50,in} /Al	511.89	81.11%	1.33	1.50
P _{90,in} /Al	794.80	74.18%	2.06	2.32

a Calculated according to Eq. (1).

b Estimated using data from ref 36.

T 3

	BET area (m ² g ⁻¹)	pore volume (mLg ⁻¹)	pore diameter(nm)
γ -Al ₂ O ₃	174.5	0.3611	8.278
P _{10,in} /Al	155.4	0.3061	7.878
cal.	171.1	0.3471	8.117
P _{90,in} /Al	153.3	0.2496	6.513
cal.	147.2	0.2572	6.986

T 4

	β	K_a	pK _a	R^2
P _{10,in} /Al	1.697	6.42×10 ⁻⁷	6.192	0.999
P _{90,in} /Al	1.265	2.33×10 ⁻⁶	5.632	0.999

T 5

	initial	supernatant	digested	add-up	RSD
P _{10,in} /Al	60.000	26.477	35.374	61.851	3.09%
P _{90,in} /Al	60.000	23.754	36.936	60.690	1.15%

S1

F 1

F 2

F 3

F 4

F 5

S 2

F 6

F 7

(a)

(b)

F 8