Adsorption properties of hyperbranched aliphatic polyester grafted attapulgite towards heavy metal ions

Peng Liu [a,*], Tingmei Wang [b]

[a] State Key Laboratory of Applied Organic Chemistry, and Institute of Polymer Science and Engineering, College of Chemistry
and Chemical Engineering, Lanzhou University, Lanzhou, Gansu 730000, China
[b] State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics,
Chinese Academy of Sciences, Lanzhou 730000, China

Abstract

The AB_2 type monomer, 2,2-bis (hydroxymethyl) propionic acid (bis-MPA), was successfully grafted from the surfaces of the amino groups modified attapulgite nano-fibrillar clay (A-ATP) via a melt polycondensation method with *p*-toluenesulfonic acid (*p*-TSA) as catalyst. The competitive adsorption properties of the hyperbranched aliphatic polyester grafted attapulgite (HAPE-ATP) towards the heavy metal ions (Cu(II), Hg(II), Zn(II), and Cd(II)) were investigated preliminarily.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Hyperbranched aliphatic polyester; Attapulgite; Adsorption properties; Heavy metal ions

1. Introduction

In recent years, clay minerals are widely used for the removal of heavy metal ions [1], dyes [2], and other organics [3] from aqueous solutions because of their higher surface areas. Organo-modified clays are developed in order to enhance their selectivities [4].

The clay adsorbents are also applied in presence of water-soluble polymers, such as polyethylene oxide (PEO) [5], chitosan [6], and polyelectrolytes [7]. However, it is difficult to completely remove the free water-soluble polymers from the treated solutions. It is expected to overcome the disadvantage by bonding chemically the polymer chains onto the surfaces of the clay minerals. So the clays chemically modified with polymers might provide an optimal combination. In our previous work, polyacrylamide had been successfully grafted from the surfaces of the attapulgite nano-fibrillar clay (ATP) via the surface-initiated atom transfer radical polymerization technique. The adsorption experiments of the polyacrylamide grafted attapulgite towards the heavy metal ion and dyes showed the new adsorbent had not only the high adsorption capacities, but also the fast sedimentation rate [8].

Numbers of works reported the self-assembly of the hyperbranched polymers onto the flat surfaces or the surfaces of porous particles for many application, such as microcolumn packing for the on-line preconcentration and separation of the noble metal ions [9]; chiral stationary phase for use in HPLC [10]; effective catalysts for hydroformylation and Heck reaction by being complexed with Rh and Pd [11]; designable size exclusion chromatography columns [12]; corrosion-resistant coatings and chemical sensing [13]; photoacid-based lithography [14], and electrostatic immobilization of glucose oxidase [15], etc.

Nowadays, the preparation and application of the hyperbranched polymers grafted nano-surfaces has become an attractive research field [16,17]. For the preparation of the hyperbranched polymers grafted nano-surfaces, the one-pot method is simpler and more convenient [18,19]. They were all conducted by the solution method. In one of our previous work, the melt polycondensation had been used for the preparation of the hyperbranched polymers grafted nano-surfaces. It was found that the higher grafting efficiency could be achieved [20].

In the present work, the hyperbranched aliphatic polyester (HAPE) had been grafted from the surfaces of the ATP via the

---

* Corresponding author. Tel.: +86 931 8912516; fax: +86 931 8912582.
E-mail address: pliu@lzu.edu.cn (P. Liu).

melt polycondensation method and the product was investigated preliminarily as adsorbent for heavy metal ions.

2. Experimental

2.1. Materials and reagents

ATP with the average diameter of 325 meshes was provided by Gansu ATP Co. Ltd., Gansu, China. It was dried in vacuum at 110 °C for 48 h before use.

The γ-aminopropyltriethoxysilane (APTES) (Gaizhou Chemical Industrial Co. Ltd., Liaoning, China) was used as received. *p*-Toluenesulfonic acid (*p*-TSA) and 2,2-bis (hydroxymethyl) propionic acid (bis-MPA) were all analytical grade and used as received from Tianjin Chemical Co., Tianjin, China. Toluene, dimethyl formamide (DMF) and other solvents used were all analytical grade. The heavy metal ions aqueous solution was prepared with the acetates and acetic acid was used for the adjustment of pH of the solution.

2.2. Melt polycondensation

The γ-aminopropyltriethoxysilane was firstly self-assembled from the surfaces of the attapulgite according to the method reported previously [21].

Then the AB_2 monomer, bis-MPA, was melt polycondensated cored with the γ-aminopropyl attapulgite with surface active site, amino groups [20]: 2.0 g γ-aminopropyl attapulgite (A-ATP), 5.0 g bis-MPA and 0.50 g *p*-TSA were triturated in mortar to achieve a well-proportioned mixture. The polycondensation was performed at 200 °C (the melting point of the monomer: 189–191 °C) in nitrogen flow in a muffle for 30 min. The hyperbranched aliphatic polyester grafted attapulgite (HAPE-ATP) was separated from the non-grafted hyperbranched aliphatic polyester by several cycles of dispersion in DMF with ultrasonic vibrations for 30 min and precipitated by centrifugation at 10^4 rpm for 30 min. The ideal structure of HAPE-ATP is shown in Scheme 1.

2.3. Analysis and characterization

Elemental analysis (EA) of C, N, and H was performed on Elementar vario EL instrument. Bruker IFS 66 versus infrared spectrometer was used for the Fourier transform infrared (FT-IR) spectroscopy analysis. Thermogravimetric analysis (TGA) was performed with a Perkin-Elmer TGA-7 system (Perkin-Elmer Corporation, USA) at a scan rate of 10 °C min⁻¹ to 800 °C in N_2 atmosphere. X-ray diffraction (XRD) analysis was carried
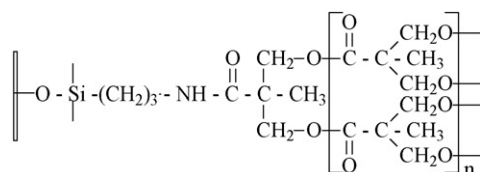
Scheme 1. The ideal structure of HAPE-ATP.

Table 1
Operation parameters of ICP-OES

RF power supply	Ar plasma gas flow	Ar auxiliary gas flow	Ar nebulizer gas flow	Viewing height
1100 W	14.0 L min⁻¹	0.5 L min⁻¹	1.0 L min⁻¹	11 mm
Detection lines	Cu	Zn	Cd	Hg
	327.3 nm	213.8 nm	226.5 nm	194.2 nm

out with a Shimadu XRD 6000 with Cu Kα radiation, operated at 50 kV and 80 mA over the range $10° < 2\theta < 100°$. X-ray photoelectron spectroscopy (XPS) was accomplished using a PHI-5702 multi-functional X-ray photoelectron spectrometer with pass energy of 29.35 eV and an Mg Kα line excitation source. The binding energy of C 1s (284.6 eV) was used as a reference. The morphologies of the bare ATP and HAPE-ATP were characterized with a JEM-1200 EX/S transmission electron microscope (TEM). The powders were dispersed in DMF in an ultrasonic bath for 5 min, and then deposited on a copper grid covered with a perforated carbon film.

2.4. Adsorption properties

The heavy metal ions uptake capacities of the adsorbents were determined preliminary as follows: 1.0 g adsorbent (bare ATP, A-ATP, or HAPE-ATP) was added into 100 mL heavy metal ions mixture solution (containing Cu(II), Zn(II), Cd(II), and Hg(II) with the same concentration of 0.36 mg/mL in pH 3.0) and then irradiated ultrasonically for 1 h at room temperature, respectively. Then the supernatant solutions were taken out for the ICP-OES (Perkin-Elmer ICP/6500 inductively coupled plasma spectrometer, operation parameters given in Table 1) determination.

3. Results and discussion

3.1. Melt polycondensation

After the assembly of γ-aminopropyltriethoxysilane onto the surfaces of attapulgite, the 2950 and 3295 cm⁻¹ band of methyl and methylene groups and the band at about 3400 cm⁻¹ of amino groups were found in the FT-IR spectrum of the product. The amino group content was found to be 0.6 mmol/g, calculated from the carbon and nitrogen elemental analyses.

After the "grafting from" polycondensation, the band at 1728 cm⁻¹ of ester groups was found in the FT-IR spectrum of the HAPE-ATP (Fig. 1). It showed the hyperbranched aliphatic polyester had been successfully grafted from the surfaces of the ATP nano-fibrillar clay by the proposed method. The presence of the characteristic band at about 1660 cm⁻¹ of amide groups also showed that the hyperbranched aliphatic polyester was grafted from the surfaces of the ATP nano-fibrillar clay via the amidation reaction between the carboxyl group of the monomer and the amino groups on the A-ATP, while the 1625 cm⁻¹ in the FT-IR spectrum of the bare attapulgite was assigned to the δH_2O absorbance [22]. It seemed that the absorbance at ~1600 cm⁻¹
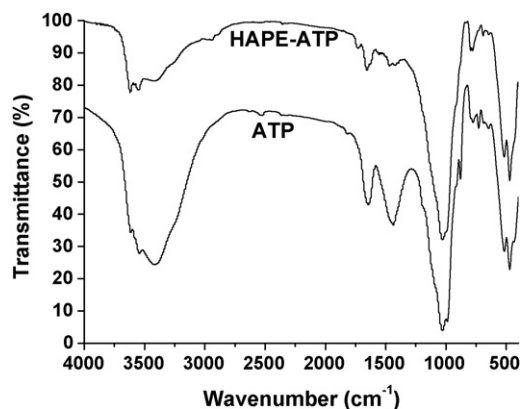
Fig. 1. FT-IR spectra of the bare ATP and HAPE-ATP.

Fig. 3. XPS survey spectra of: (a) bare ATP, (b) A-ATP, and (c) HAPE-ATP.

was weakened after the melt polycondensation. It was led from the breakout of the structure water (zeolitie water and crystal water) in ATP crystallines [23]. The presence of the band at about 3400 cm^{-1} of amino groups also showed that the amino groups of the A-ATP had not completely reacted with the carboxyl groups of the monomer or the nongrafted hyperbranched aliphatic polyester molecules with smaller molecular weights because of the space hindrance. The percentage of grafting (PG%, the weight ratio of the polymer grafted and attapulgite charged) was found to be 8.3% after only 30 min melt polycondensation, calculated from the carbon elemental analysis. The result was lower than that calculated from the weight loss in the thermogravimetric analysis (Fig. 2) of 9.4%. It was also caused by the breakout of the structure water in ATP crystallines [23].

3.2. Surface composition and crystal structure of the HAPE-ATP

The changes of the surface Si, Al, O, C, and N element content were demonstrated in the surface analyses of the bare ATP, A-ATP, and HAPE-ATP by X-ray photoelectron spectroscopy analysis (Fig. 3 and Table 2). It also validates that the surface grafting of the hyperbranched aliphatic polyester had been successfully grafted from the surfaces of the ATP nano-fibrillar clay with the mechanism shown in Scheme 1. The surface Al content decreased all through the two fabrication steps because both
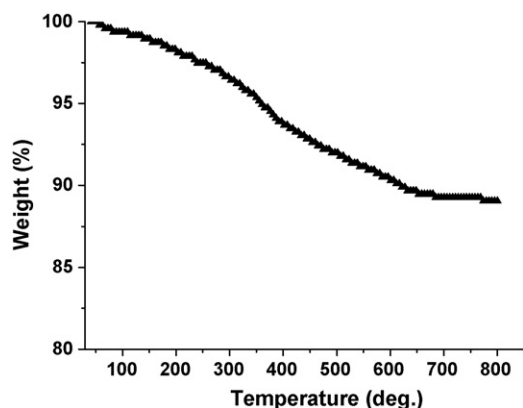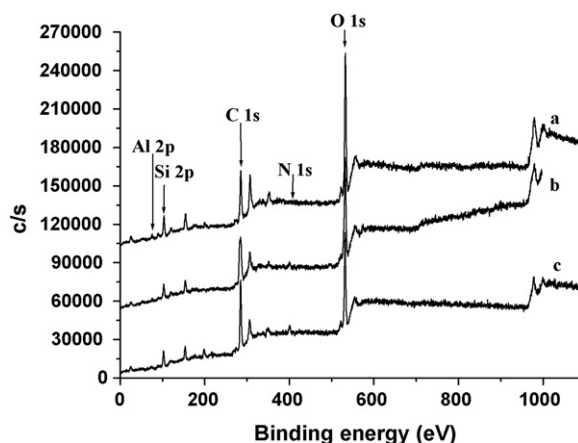
Table 2
The surface compositional data from XPS

Samples	XPS analysis (at.%)				
	Si	O	Al	C	N
ATP	8.25	45.67	7.28	38.17	0.63
A-ATP	8.40	32.85	2.95	51.39	4.41
HAPE-ATP	6.58	33.13	0.00	58.69	1.60

of the surface modified compounds do not contain Al element. However, the surface C content increased all through the two fabrication steps because both of the surface modified compounds contain C element. The surface Si and N element contents increased after the assembly of the functional silane and then decreased after the melt polycondensation because the silane contains the two elements and the monomer does not contain them. The surface O element content decreased after the assembly of the functional silane because the surface of the A-ATP had been covered with aminopropyl groups. Then it increased after the melt polycondensation because of the amount of O element present in the grafted hyperbranched aliphatic polyester.

The XRD patterns of the bare ATP, and the HAPE-ATP were given in Fig. 4. There was no change of the XRD patterns of the ATP after surface modifications with the hyperbranched aliphatic polyester. It could be concluded that the hyperbranched
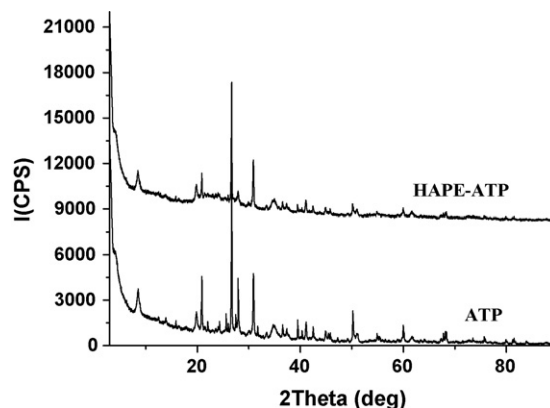

Fig. 2. TGA curves of the HAPE-ATP.

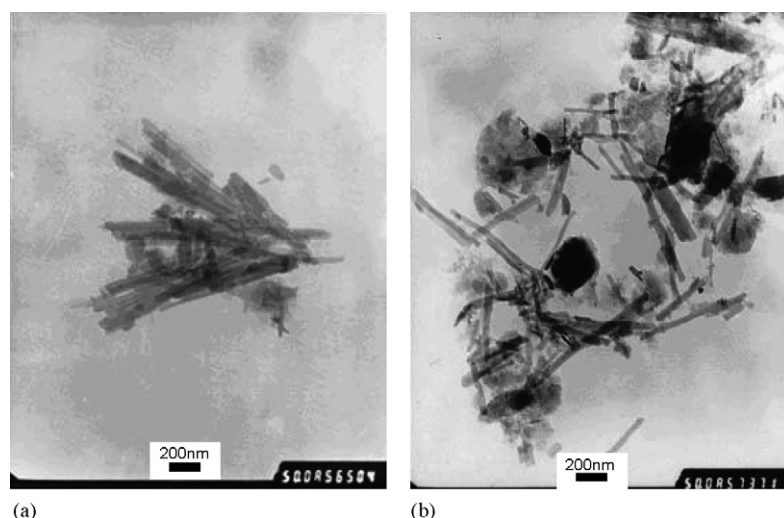Fig. 4. XRD patterns of the bare ATP and the HAPE-ATP.

Fig. 5. SEM images: (a) bare ATP and (b) HAPE-ATP.

Table 3
The competitive adsorption data of the ATP adsorbents

Samples	Conc. of the residual solution (mg/mL)					Adsorption capacities (mg/g)			
	Cu(II)	Hg(II)	Zn(II)	Cd(II)		Cu(II)	Hg(II)	Zn(II)	Cd(II)
Bare ATP	0.356	0.357	0.350	0.356		0.41	0.32	0.97	0.37
A-ATP	0.336	0.307	0.358	0.357		2.45	5.29	0.18	0.34
HAPE-ATP	0.342	0.325	0.355	0.357		1.76	3.52	0.45	0.29

aliphatic polyester was grafted from the surfaces of the nanofibril clay by the proposed method and it had no effect on the crystal structure of the nanofibril.

The transmission electron microscopy analyses (Fig. 5) showed that the dispersibility in DMF of HAPE-ATP was better than that of the bare ATP. It indicated that the suspension of the HAPE-ATP in DMF had much better stability than that of the bare ATP. The HAPE-ATP also has a big number of the surface hydroxyl groups after the proposed simple melt polycondensation of 2,2-bis propionic acid from the surfaces of the A-ATP.

3.3. Adsorption properties

The HAPE-ATP is expected to be used as adsorbent for the heavy metal ions because of the amounts of the ester groups in the polymer layer and the surface hydroxyl groups. The pH 3.0 was chosen because some components of the attapulgite could be dissolved in the strong acidic solutions [24].

After the ultrasonic irradiation, the mixture of heavy metal ion solutions with the three kinds of clay adsorbents for 1 h, the bare ATP and the HAPE-ATP adsorbents had deposited completely within 40 min. However, the suspension of the A-ATP adsorbent had the higher stability and hardly deposited because of the surface amino groups. So the suspension was centrifuged at 1.0×10^4 rpm for 1 h to separate the A-ATP adsorbent.

The competitive adsorption capacities of the three kinds of clay adsorbents towards the four heavy metal ions were summarized in Table 3. It was found that the bare ATP had the higher adsorption capacities for Zn(II) and Cd(II) ions. How-

ever, the A-ATP and the HAPE-ATP adsorbents had the higher adsorption capacities for Cu(II) and Hg(II) ions. Furthermore, the adsorption capacities for Cu(II) and Hg(II) ions of the HAPE-ATP clay adsorbent were lower slightly than those of the A-ATP clay adsorbent because the groups containing N element were enshrouded with the hyperbranched aliphatic polyester, which is not soluble in water. In addition, the ester and hydroxyl groups of the hyperbranched aliphatic polyester had the lower complexation abilities towards these heavy metal ions. However, the HAPE-ATP had faster sedimentating rate than the A-ATP. This is an advantage in the practical application.

4. Conclusion

The hyperbranched aliphatic polyester was successfully grafted from the surfaces of amino groups modified attapulgite nano-fibrillar clay prepared by the melt polycondensation of the AB₂ type monomer, 2-bis propionic acid, with *p*-TSA as catalyst. The competitive adsorption capacities of the three clay adsorbents, bare ATP, aminopropyl attapulgite (A-ATP), and HAPE-ATP, towards the four heavy metal ions (Cu(II), Hg(II), Zn(II), and Cd(II)), were also compared preliminarily.

References

[1] H.B. Bradl, Adsorption of heavy metal ions on soils and soils constituents, J. Colloid Interface Sci. 277 (2004) 1–18.
[2] F. Lopez Arbeloa, V. Martinez Martinez, J. Banuelos Prieto, I. Lopez Arbeloa, Adsorption of rhodamine 3B Dye on saponite colloidal particles in aqueous suspensions, Langmuir 18 (2002) 2658–2664.

[3] Y.Z. El-Nahhal, J.M. Safi, Adsorption of phenanthrene on organoclays from distilled and saline water, J. Colloid Interface Sci. 269 (2004) 265–273.

[4] N.L. Dias Filho, D.R. Do Carmo, Study of an organically modified clay: Selective adsorption of heavy metal ions and voltammetric determination of mercury(II), Talanta 68 (2006) 919–927.

[5] W.K. Mekhamer, F.F. Assaad, Flocculation and coagulation of Ca- and K-saturated montmorillonite in the presence of polyethylene oxide, J. Appl. Polym. Sci. 73 (1999) 659–662.

[6] M.Y. Chang, R.S. Juang, Adsorption of tannic acid, humic acid, and dyes from water using the composite of chitosan and activated clay, J. Colloid Interface Sci. 278 (2004) 18–25.

[7] G. Petzold, M. Mende, K. Lunkwitz, S. Schwarz, H.M. Buchhammer, Higher efficiency in the flocculation of clay suspensions by using combinations of oppositely charged polyelectrolytes, Colloids Surf. A Physicochem. Eng. Aspects 218 (2003) 47–57.

[8] P. Liu, J.S. Guo, Polyacrylamide grafted attapulgite (PAM-ATP) via surface-initiated atom transfer radical polymerization (SI-ATRP) for removal of Hg(II) ion and dyes, Colloids Surf. A Physicochem. Eng. Aspects 282–283 (2006) 498–503.

[9] X.Z. Wu, P. Liu, Q.S. Pu, Z.X. Su, Preparation of dendrimer-like polyamidoamine immobilized silica gel and its application to online pre-concentration and separation palladium prior to FAAS determination, Talanta 62 (2004) 918–923.

[10] B.T. Mathews, A.E. Beezer, M.J. Snowden, M.J. Hardy, J.C. Mitchell, The synthesis of immobilised chiral dendrimers, New J. Chem. 25 (2001) 807–818.

[11] K. Nozaki, Y. Itoi, F. Shibahara, E. Shirakawa, T. Ohta, H. Takaya, T. Hiyama, Asymmetric hydroformylation of olefins in a highly cross-linked polumer matrix, J. Am. Chem. Soc. 120 (1998) 4051–4502.

[12] K. Sakai, T.C. Teng, A. Katada, T. Harada, K. Yoshida, K. Yamanaka, Y. Asami, M. Sakata, C. Hirayama, M. Kunitake, Designable size exclusion chromatography colums based on dendritic polyner-modified porous silica particles, Chem. Mater. 15 (2003) 4091–4097.

[13] Y.F. Zhou, M.L. Bruening, D.E. Bergbreiter, R.M. Crooks, M. Wells, Preparation of hyperbranched polymer films grafted on self-assembled monolayers, J. Am. Chem. Soc. 118 (1996) 3773–3774.

[14] A. Aoki, P. Ghosh, R.M. Crooks, Micrometer-scale patterning of multiple dyes on hyperbranches ploymer thin films using photoacid-based lithography, Langmuir 15 (1999) 7418–7421.

[15] J.G. Franchina, W.M. Lackowski, D.L. Dermody, R.M. Crooks, D.E. Bergbreiter, K. Sirkar, R.J. Russell, M.V. Pishko, Electrostatic immobilization of glucose oxidase in a weak acid, polyelectrolyte hyperbranched ultrathin film on gold: fabrication, characterization, and enzymatic activity, Anal. Chem. 71 (1999) 3133–3139.

[16] P. Liu, Hyperbranched polymers grafted inorganic nanoparticles: A literature review, Mater. Res. Innov. 9 (2005) 103–105.

[17] P. Liu, J. Tian, W.M. Liu, Q.J. Xue, Fabrication dendrimer-like PAMAM based on silica nanoparticles, Chin. J. Chem. 21 (2003) 960–963.

[18] P. Liu, W.M. Liu, Q.J. Xue, Facile preparation and characterization of hyperbranched poly(amine ester) grafted silica nanoparticles, J. Mater. Sci. 39 (2004) 3825–3827.

[19] P. Liu, Hyperbranched aliphatic polyester grafted silica nanoparticles by a facile one-pot method, Surf. Rev. Lett. 12 (2005) 619–622.

[20] P. Liu, Q.J. Xue, J. Tian, W.M. Liu, Self-assembly of functional silanes onto nano-sized silica, Chin. J. Chem. Phys. 16 (2003) 481–486.

[21] P. Liu, Hyperbranched aliphatic polyester grafted attapulgite via a melt polycondensation process, Appl. Clay Sci. 35 (2007) 11–16.

[22] J. Herrero, J.A. Pajares, C. Blanco, Surface acidity of palygorskite-supported rhodium catalysts, Clays. Clay Miner. 39 (1991) 651–657.

[23] S. Lokanatha, B.K. Mathur, B.K. Samantaray, S. Bhattacherjee, Dehydration and phase transformation in attapulgite (palygorskite)—an R.D.F. study, J. Mater. Sci. Lett. 3 (1984) 1105–1108.

[24] M.S. Barrios, M.A.V. Rodriquez, Acid activation of palygorskite with HCl: development of physicochemical, textural and surface-properties, Appl. Clay Sci. 10 (1995) 247–258.