

# Heterogeneous Synthesis of Chelating Resin Organophosphonic Acid-Functionalized Silica Gel and Its Adsorption Property of Heavy Metal Ions from Fuel Ethanol Solutions

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**ABSTRACT:** In this study, chelating resin silica gel chemically modified by poly(triethylenetetramine bis(methylenephosphonic acid)) (denoted as SG-Cl-T-P) was successfully developed by heterogeneous synthesis method and used for adsorptive removal of heavy metal ions from fuel ethanol solutions, and the relevant modified organic group was calculated by DFT method at the B3LYP/6-31 + G(d) level. SG-Cl-T-P was characterized by Fourier transform infrared spectrometer, scanning electron microscope, energy dispersive X-ray analysis system, porous

analysis, etc. SG-Cl-T-P has been used to investigate the adsorption of Hg(II), Cu(II), Mn(II), Co(II), Zn(II), Ni(II), Fe(III), and Cd(II) metal ions from ethanol solutions. The research results revealed that it has the better adsorption capacity for Hg(II) and Cd(II). © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** adsorption; composites; inorganic polymers; silica; heterogeneous synthesis; organophosphonic acid; fuel ethanol solutions

## INTRODUCTION

Porous materials have become more and more important both in science and technology, and they are gaining an increasing interest worldwide. Mesoporous silica gel (SG) was widely used as inorganic solid matrix or carrier in inorganic–organic composite materials due to the excellent mechanical and thermal stability, unique large surface area, a firm chemical union with the metals, and well-modified surface properties.<sup>1,2</sup> Such kinds of chelating resin SG materials have received a great deal of attention recently because of their superior properties and excellent performance in the field of chromatography, adsorption, and catalysis.<sup>3–6</sup> Generally, it is difficult for chelating ligands to bond to SG because of the relative inertness of the original surface of SG. However, bonding of chelating ligands to SG surface

can be achieved after surface activation. On the surface of active SG, there are a large number of silanol groups, which could react with silane coupling reagents that act as precursors for further immobilization of organic ligands. Then chemical modification of the skeleton of SG via the covalent coupling of an organic moiety is a promising approach to get such kind of modified SG materials.<sup>7</sup> The reaction of silane coupling reagents with surface silanol groups lead to the existence of desirable terminal functional groups on the surface of SG, where special chelating properties can be finally obtained, and this is mainly related to the structure of the organic ligands, the nature of the functional groups present and the incorporated donor atoms. Furthermore, it has been studied that the behavior of these synthesized chemically modified SG used as adsorbent are mainly dependent on the presence of active donor atoms such as O, S, and N of the incorporated organic moieties.<sup>8,9</sup> In a word, these inorganic–organic hybrid materials contain inorganic backbones, and organic ligands that could selectively bind target metal ions. They could be used as effective adsorption and separation materials for selective heavy metal ions removal.

Ethanol is one of the most important renewable biofuels contributing to the reduction of negative environmental impacts generated by the worldwide utilization of fossil fuels, and there has been a rapid growth in demand for fuel ethanol since 2000.

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However, the presence of some metal ions in ethanol fuel can introduce corrosion in the vehicle components in contact with the liquid.<sup>10</sup> Therefore, it is essential to develop cost-effective treatment methods to remove metals from fuel ethanol. Adsorption is highly effective and economical, and is a promising and widely applied method. Although it has been reported that modified mesoporous SGs have strong adsorption capabilities for heavy metal pollutants, the literature details the removal of heavy metal from ethanol solutions.<sup>11</sup> In this research, we explored chelating resin SG chemically modified by aminophosphonic acid SG-Cl-T-P by heterogeneous synthesis method, and found that it had excellent adsorption capability for heavy metal ions from fuel ethanol solutions, especially for Hg(II) and Cd(II).

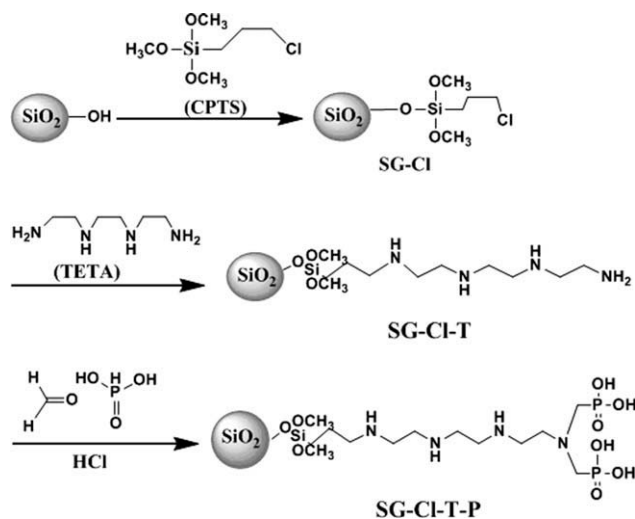
## EXPERIMENTAL

### Materials and methods

SG of chromatographic grade (80–100 mesh size) was obtained from Qingdao Silicon Create Fine Chemical, Shandong Province of China. Organic solvents toluene was redistilled just before use. 3-chloropropyltrimethoxysilane (CPTS) (Jiangnan Chemicals Factory, Jinzhou, China), triethylenetetramine (TETA) (Shanghai Chemical Factory of China), and the other reagents were used without further purification. Stock solutions of Hg(II) ( $0.1 \text{ mol L}^{-1}$ ) were prepared by dissolving  $\text{HgCl}_2$  in ethanol. Porous structure parameters were characterized using an automatic physisorption analyzer ASAP 2020 (Micromeritics Instruments, USA) by BET and BJH methods through  $\text{N}_2$  adsorption at 77 K. The morphology of the compounds was examined on JEOL JSM5600LV scanning electron microscope, JEOL, Japan. The energy dispersive X-ray analysis system (EDXAS) was performed on a NORAN LEVER-2 EDX analytical instrument. The concentration of metal ions was determined using a 932B-model atomic absorption spectrometer (GBC-932A, made in Australia), equipped with air-acetylene flame.

### Computational details

Theoretical calculations of the modified organic group have been performed with the Gaussian 03 program<sup>12</sup> using the B3LYP/6-31 + G(d) basis set to obtain the optimized molecular structure and vibrational wave numbers. The frequencies for the required structure were evaluated at the B3LYP/6-31 + G(d) level to ascertain the nature of stationary points, and harmonic vibrational wave numbers were calculated using the analytical second derivatives to confirm the convergence to a minimum of the potential surface. Moreover, Mulliken atomic



**Scheme 1** Synthetic routes of SG-Cl-T-P by heterogeneous method.

charges of the modified organic group were also obtained at the B3LYP/6-31 + G(d) level.

### Heterogeneous synthesis of SG-Cl-T-P

SGs were activated with nitric acid aqueous solution ( $\text{HNO}_3:\text{H}_2\text{O} = 1 : 1$ ) at refluxing temperature of  $112^\circ\text{C}$  for 3 h, then dipped in the hydrochloric acid aqueous solution ( $\text{HCl}:\text{H}_2\text{O} = 1 : 1$ ) at room temperature for 6 h, finally washed with distilled water, and dried in muffle at  $160^\circ\text{C}$  for 12 h. Under a nitrogen atmosphere, a mixture of 30.0 g of activated SG and 30.0 mL of CPTS were stirred at  $96^\circ\text{C}$  in the 120 mL of toluene solution for 12 h, and then the solid was filtered off and transferred to a Soxhlet extraction apparatus for reflux-extraction in ethanol for 24 h. The solid product was dried in vacuum at  $50^\circ\text{C}$  over 48 h, and it was referred to as SG-Cl.

Under a nitrogen atmosphere, a mixture of 20.0 g of activated SG and 46.7 mL of triethylenetetramine were stirred at  $90^\circ\text{C}$  in the 200 mL of ethanol solution for 12 h, and then the solid was filtered off and transferred to a Soxhlet extraction apparatus for reflux-extraction in ethanol for 24 h. The solid product was dried in vacuum at  $50^\circ\text{C}$  over 48 h, and it was referred to as SG-Cl-T. About 15.0 g of SG-Cl-T were added to 120 mL ethanol at room temperature for 12 h, then 3.0 g of paraformaldehyde (CAS number: 68476-52-8), 8.4 g of phosphorous acid, and 3.4 mL of hydrochloric acid were added. After being refluxed at  $90^\circ\text{C}$  for 12 h, the final product (SG-Cl-T-P) was filtered off, then washed thoroughly with distilled water and finally dried under vacuum over 48 h at  $50^\circ\text{C}$ . The whole synthetic route of SG-Cl-T-P was shown in Scheme 1.

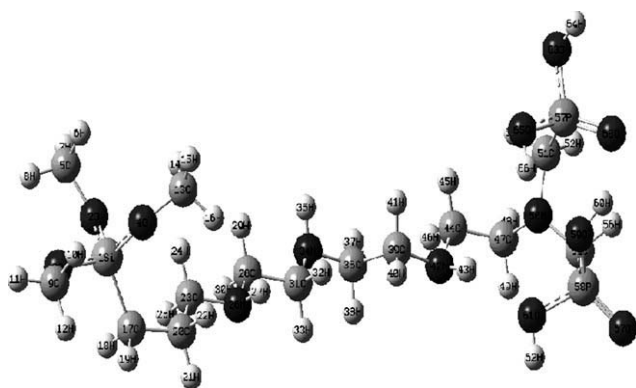


Figure 1 The optimized geometry of the modified organic group.

TABLE II  
Mulliken Atomic Charges of the Modified Organic Group at the B3LYP/6-31 + G(d) Level, and the Atom Labels are According to Figure 1

Atoms	Charges	Atoms	Charges
Si1	1.862	O59	-1.045
O2	-0.615	H60	0.586
O3	-0.659	O61	-0.950
O4	-0.646	H62	0.573
N26	-0.414	O63	-0.838
N34	-0.466	H64	0.521
N42	-0.368	O65	-0.825
N50	-0.160	H66	0.576
P57	1.761	O67	-0.688
P58	1.844	O68	-0.790

Adsorption experiments for transition metal ions

Static adsorption experiment was employed to determine the adsorption capacities of SG-Cl-T-P for different kinds of metal ions. The static adsorption

experiments were carried out with shaking. 0.02 g of resins with 20 mL of metal ion solution (0.5 mmol/L). The mixture was equilibrated for 24 h on a thermostat-cum-shaking assembly at 25°C. Then a certain volume of the solutions was separated from the

TABLE I  
The Optimized Geometrical Parameters Obtained at the B3LYP/6-31 + G(d) Level, and the Atom Labels are According to Figure 1

Bond length (Å)		Bond angle (°)		Dihedral angle (°)	
Si1—O2	1.6546	A(2, 1, 3)	107.5	D(3, 1, 2, 5)	45.6
Si1—C17	1.8769	A(2, 1, 4)	111.5	D(1, 2, 5, 6)	57.5
O2—C5	1.4261	A(2, 1, 17)	108.5	D(1, 3, 9, 10)	51.2
C17—C20	1.5439	A(3, 1, 4)	105.1	D(1, 4, 13, 14)	38.1
C20—C23	1.5312	A(3, 1, 17)	110.9	D(1, 17, 20, 21)	172.7
C23—N26	1.4641	A(4, 1, 17)	113.3	D(17, 20, 23, 24)	58.2
N26—C28	1.4611	A(1, 17, 20)	119.5	D(20, 23, 26, 27)	-57.4
C28—C31	1.5300	A(17, 20, 23)	114.3	D(23, 26, 28, 29)	57.5
C31—N34	1.4617	A(20, 23, 26)	110.9	D(26, 28, 31, 32)	-53.5
N34—C36	1.4627	A(23, 26, 28)	113.8	D(28, 31, 34, 35)	63.7
C36—C39	1.5420	A(26, 28, 31)	110.8	D(31, 34, 36, 37)	172.5
C39—N42	1.4617	A(28, 31, 34)	110.7	D(34, 36, 39, 40)	59.6
N42—C44	1.4583	A(31, 34, 36)	115.9	D(36, 39, 42, 43)	-149.6
C44—C47	1.5301	A(34, 36, 39)	115.9	D(39, 42, 44, 45)	41.6
C47—N50	1.4771	A(36, 39, 42)	112.3	D(42, 44, 47, 49)	45.4
N50—C51	1.4588	A(39, 42, 44)	115.4	D(44, 47, 50, 51)	-81.9
N50—C54	1.4656	A(42, 44, 47)	110.9	D(44, 47, 50, 54)	143.5
C51—P57	1.8321	A(44, 47, 50)	113.2	D(47, 50, 51, 57)	151.7
C54—P58	1.8481	A(47, 50, 51)	112.8	D(47, 50, 54, 58)	-109.6
P57—O63	1.6131	A(47, 50, 54)	115.3	D(50, 51, 57, 63)	-164.7
P57—O65	1.6151	A(50, 51, 57)	111.8	D(50, 51, 57, 65)	-57.0
P57—O68	1.5021	A(50, 54, 58)	113.7	D(50, 51, 57, 68)	69.8
P58—O59	1.6244	A(51, 57, 63)	111.8	D(50, 54, 58, 59)	-56.4
P58—O61	1.6307	A(51, 57, 65)	106.3	D(50, 54, 58, 61)	46.8
P58—O67	1.4862	A(51, 57, 68)	115.2	D(50, 54, 58, 67)	172.8
O59—H60	0.9915	A(54, 58, 59)	105.6	D(55, 54, 58, 61)	-76.7
O61—H62	0.9722	A(54, 58, 61)	104.9	D(56, 54, 58, 59)	67.0
O63—H64	0.9731	A(54, 58, 67)	113.7	D(51, 57, 63, 64)	-157.4
O65—H66	0.9808	A(58, 59, 60)	112.6	D(65, 57, 63, 64)	92.5
		A(58, 61, 62)	110.6	D(68, 57, 63, 64)	-32.0
		A(57, 63, 64)	112.8	D(51, 57, 65, 66)	84.3
		A(57, 65, 66)	110.0	D(63, 57, 65, 66)	-169.1
				D(54, 58, 59, 60)	-53.3
				D(67, 58, 59, 60)	75.1
				D(54, 58, 61, 62)	123.0
				D(67, 58, 61, 62)	-2.4
				D(59, 58, 61, 62)	-128.4

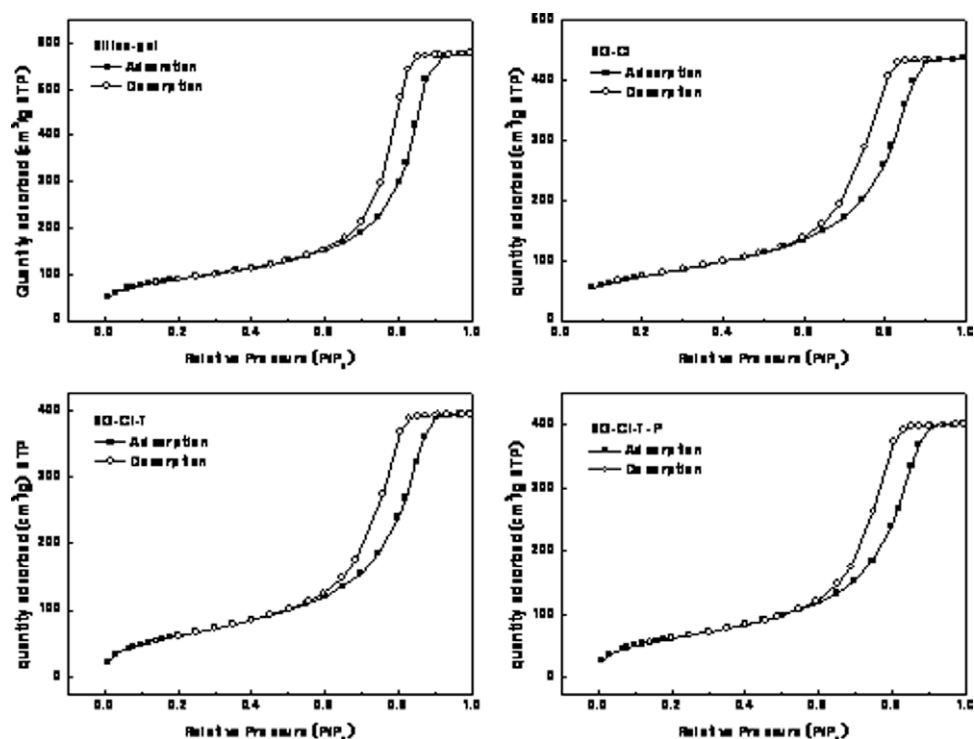


Figure 2 Nitrogen adsorption-desorption isotherms of SG, SG-Cl, SG-Cl-T, and SG-Cl-T-P.

adsorbents and the residual concentration of Hg(II) was detected by means of atomic absorption spectrometer. The adsorption amount was calculated according to the eq. (1):

$$q = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where  $q$  is the adsorption amount (mmol/g),  $C_0$  and  $C_e$  are the initial and equilibrium concentrations of metal ions (mmol/mL) in solution, respectively,  $V$  is the volume of the solution (mL), and  $W$  is the weight of SG-Cl-T-P (g).

## RESULTS AND DISCUSSION

### Theoretical calculation of the modified organic group

The introduction of the organic groups onto the activated SG can make this material form stable chelating compounds with many transition metal ions. The aim of chemical modification with aminophosphonic acid, which has both N donor atoms and O donor atoms, is to make the material have excellent coordination properties with metal ions and to obtain a novel adsorbent with a high loading capacity for metal ions. In order to design the title material, we theoretically calculated the modified organic group at the B3LYP/6-31 + G(d) level in advance. The optimized structure of the modified organic group was displayed in Figure 1, and the cor-

responding bond lengths and bond angles were presented in Table I. The P57-O68 and P58-O67 bond lengths were 1.5021 and 1.4862 Å, respectively, which agreed well with those values of phosphonic acid in Ref. <sup>13</sup> and was slightly longer than the experimental value (1.47 Å). Moreover, the P57-O63, P57-O65, P58-O59, and P58-O61 bond lengths were in the range (1.6131–1.6307 Å), comparable to those in phosphonic acid (1.59 to 1.63 Å).<sup>13</sup> Table II presented the Mulliken atomic charges of the modified organic phosphonic acid group, and showed that the oxygen atoms in phosphonic acid groups have more negative charges, and the Mulliken

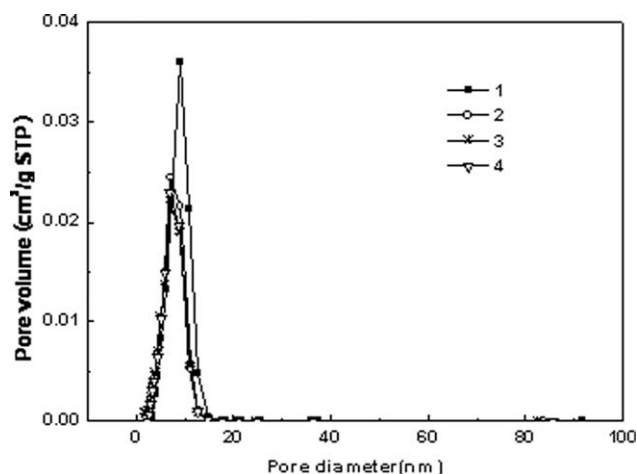


Figure 3 BJH desorption pore size distributions of SG (1), SG-Cl (2), SG-Cl-T (3), and SG-Cl-T-P (4).

**TABLE III**  
Parameters of Porous Structure of SG, SG-Cl, SG-Cl-T, and SG-Cl-T-P

Adsorbents	BET surface area (m <sup>2</sup> /g)	BJH desorption cumulative volume of pores (cm <sup>3</sup> /g) <sup>a</sup>	BJH desorption average pore diameter (nm)
SG	324.70	0.90	8.26
SG-Cl	279.35	0.68	7.21
SG-Cl-T	241.91	0.61	6.91
SG-Cl-T-P	238.11	0.62	7.18

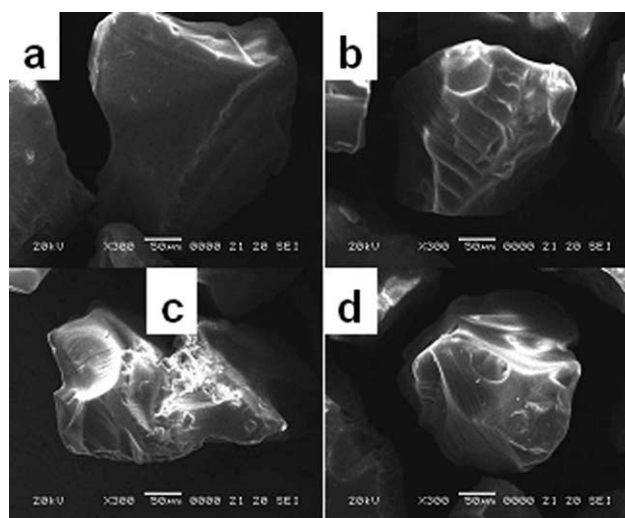
<sup>a</sup> The total volume of pores between 1.7 and 300 nm diameter.

electronic populations of O59, O61, O63, O65, O67, and O68 were -1.045, -0.950, -0.838, -0.825, -0.688, and -0.790, respectively, which made these oxygen atoms chelate with transition metal ions more easily. Therefore, the designed organic groups might provide a good adsorbent for use in adsorbing transition metal ions from aqueous solutions.

#### Characterizations of SG-Cl-T-P

The introduction of the organic groups onto the activated SG can make this material form stable chelating compounds with many transition metal ions. The aim of chemical modification with aminophosphonic acid, which has both N donor atoms and O donor atoms, is to make the material have excellent coordination properties with metal ions and to obtain a novel adsorbent with a high loading capacity for metal ions. In the heterogeneous route, the silane coupling reagent CPTS was first grafted onto SG and then reacted with TETA, subsequently paraformaldehyde and phosphorous acid to give a final product SG-Cl-T-P. For the reaction of TETA with chlorinated activated SG (SG-C), crosslinking reactions might carry out because the *N*-alkylation reaction could occur at primary amino and secondary amino groups in TETA. Figure 2 showed the nitrogen adsorption-desorption isotherms for SG and SG-Cl-T-P, and it could be seen that SG and the product SG-Cl-T-P were Type IV according to the IUPAC classification,<sup>14</sup> and each had a hysteresis loop that was representative of mesopores. The volume adsorbed steeply increases at a medium relative pressure ( $p/p^0$ ) indicating capillary condensation of nitrogen within the uniform mesoporous structure, and the two lines are approximately parallel representing that the pores of silica have uniform radius and are open. These open pores are very favorable for the bond reaction conducted on the surface of SG, and the inflection position shifted toward lower relative pressures and the volume of nitrogen adsorbed decreased with functionalization. Figure 3 displayed the BJH desorption pore size distributions of SG and SG-CL-T-P. As illustrated in Figure 3, the pores between 5 and 15 nm were dominant for all products. With the proceeding of the reaction, the

amount of the pores between 5 and 15 nm became smaller gradually and the pore size distribution moved to the smaller pore size. However, those relative values of SG-Cl-T-P became a little greater than those of SG-Cl-T. The porous structure parameters of the samples derived from the basis of the nitrogen adsorption data were summarized in Table III. As seen in Table III, the values of BET surface area, BJH desorption average pore radius and BJH desorption cumulative volume of pores for SG decreased with the functionalization reactions. The molecules of reagent first diffused into the interior of pores of SG, and then reacted with the active sites. With the formation of grafted pendant organic chains and cross-linking products, the pores size of SG became smaller and even some pores disappeared. In addition, the presence of pendant organic chains on the surface partially blocked the adsorption of nitrogen molecules. It should be noted that BET surface area, BJH desorption cumulative volume of pores and BJH desorption average pore radius of SG-Cl-T-P were 238.11 m<sup>2</sup>/g, 0.62 cm<sup>3</sup>/g, and 71.80 Å, respectively. The values of BJH desorption cumulative volume of pores and BJH desorption average pore radius were greater than those of SG-Cl-T, which could be interpreted by the formation of hydrogen bond between phosphonic acid group with



**Figure 4** The SEM images of SG (a), SG-Cl (b), SG-Cl-T (c), and SG-Cl-T-P(d).

TABLE IV  
Results of Energy Spectrum Analysis of SG-Cl, SG-Cl-T, and SG-Cl-T-P

W %	C	O	Si	Cl	N	P	F' (mmol/g)
SG-Cl	19.72	55.44	23.71	1.14	–	–	–
SG-Cl-T	20.27	50.22	21.86	0.54	7.12	–	–
SG-Cl-T-P	15.76	57.75	16.36	0.90	8.18	1.04	0.29

unreacted surface silanol as well as the partial hydrolysis of the sample with sodium hydroxide utilized to remove superfluous hydrochloric acid during the chemical modification process.

Morphologies of the SG and the product obtained from the relative synthesis process were characterized by scanning electron microscope (SEM) at 750 $\times$  and 5000 $\times$  magnification shown in Figure 4, and SEM was performed on the bare SG and chemically modified particles to detect differences in their surfaces. Apparently, the surface of bare SG was smooth and became rough after the modification reactions. Moreover, we observed that no clog between particles occurred during the preparation process, and the particles maintained regular lumpy shape. It could be seen that the particle appearance and size of these three samples were similar, demonstrating that the particles of SG had good mechanical stability and they had not been destroyed during the whole reaction process. Scanning electron micrographs of SG-Cl-T-P in Figure 4(2a) was displayed to clarify the unagglomeration of the SG particles after treatments to support the claiming of regular distribution of the functional group on the whole surface. Moreover, it was evident that the loaded functional groups were distributed on the whole surface that made the surface of the product SG-Cl-T-P become rough and may block part of the pore region, which would be verified by the following porous structure analysis. The EDXAS for SG-Cl, SG-Cl-T, and SG-Cl-T-P were summarized in Table IV. Generally, the degree of crosslinking of polyamine depends on the molar ratio of C/N, that is, the higher the molar ratio of C/N, the higher the degree of crosslinking. We could obtain the molar ratio value of SG-Cl-T from the calculation of EDXAS results, and it was 3.32, and its degree of crosslinking was a little higher. Moreover, the mass percentage of phosphor in SG-Cl-T-P was 1.04%, which confirmed the phosphonic acid groups were successfully introduced onto the amino-terminated chelating resin silica gel SG-Cl-T. Furthermore, it is possible to calculate the amount of attached functional groups onto the surface of SG ( $F'$ , mmol/g) from the percentage of phosphor in the functionalized SG, and the amounts of  $F'$  for SG-Cl-T-P was 0.29 mmol/g.

#### Static adsorption of SG-Cl-T-P for heavy metal ions from ethanol solutions

The aim of grafting functional aminophosphonic acid groups onto the surface of SG is to prepare the

modified SG with more excellent coordination properties. Saturated adsorption capacities for heavy metal ions were essential parameters for evaluating the ability of modified SG to bind and extract different transition metal ions from aqueous solutions. Figure 5 showed the static adsorption capacities of SG-Cl-T-P for Hg(II), Cu(II), Mn(II), Co(II), Zn(II), Ni(II), Fe(III), and Cd(II) metal ions. The saturated adsorption experiments for all these transition metal ions at pH 5.0 were studied at 25 $^{\circ}$ C, and 24 h of contact time was selected in this study to ensure the transition metal ions could be completely adsorbed. The research result displayed the static adsorption capacities for Hg(II), Cd(II), and Cu(II) were 0.3627, 0.3527, and 0.3019 mmol/g, respectively. However, those for Zn(II), Mn(II), Co(II), Ni(II), and Fe(III) metal ions were 0.2586, 0.1909, 0.2230, 0.1745, and 0.2347 mmol/g, respectively. Obviously, the as-synthesized adsorbent had good adsorption capability for Hg(II) and Cd(II) metal ions from aqueous solutions. Through the amino phosphonic acid groups, SG-Cl-T-P can form the stable chelating compounds with many transition metal ions, especially with Hg(II) and Cd(II). According to the theory of hard and soft acids and bases (HSAB) defined by Pearson, metal ions will have a preference for coordinating with ligands that have more or less same electronegative donor atoms. Chelating agents with N and O donor atoms are highly efficient for the selective sorption of Hg(II) and Cd(II) metal ions. There are

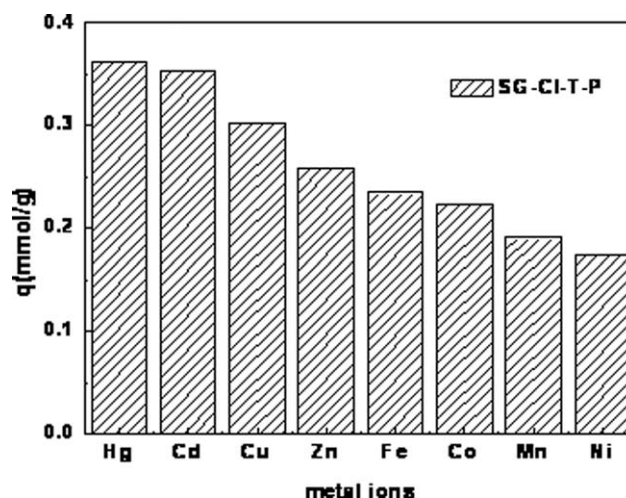


Figure 5 The saturated adsorption capacities of SG-Cl-T-P for heavy metal ions in ethanol solutions.

**TABLE V**  
**Adsorption Capacities of Different Adsorbents for Heavy Metal from Ethanol Solutions**

Adsorbents	References	Metal ions	Ethanol, $q_0$ (mmol g <sup>-1</sup> )
SG-Cl-T-P	Our work	Hg	0.36
		Cd	0.35
		Cu	0.30
		Zn	0.26
		Fe	0.23
		Co	0.22
		Mn	0.19
		Ni	0.17
SG chemically modified with benzimidazole	Ref. 17	Cu	0.26
		Cd	0.30
		Mn	0.14
ATZ-SSQ	Ref. 18	Co	0.09
		Zn	0.19
		Ni	0.09
		Fe	0.10
ATZ-SG	Ref. 18	Cu	0.21
		Co	0.04
		Zn	0.14
		Ni	0.05
		Fe	0.07
SG modified with 5-amino-1,3,4-thiadiazole-2-thiol (SiATT)	Ref. 19	Cu	0.20
		Co	0.10
		Ni	0.16
		Fe	0.20

many factors to affect the adsorption capacities of adsorbents for metal ions, including the class of chelating groups, species of metal ions, temperatures, contact time, solvent, etc. Some above-mentioned fact could be explained by the theory of hard and soft acids and bases (HSAB).<sup>15</sup> That is, soft ligand phosphorus tends to form stable complexes with soft acids such as Hg(II) and Cd(II), and transition base nitrogen and oxygen tends to form stable complexes with transition acids such as Cu(II), Zn(II), Fe(III), Co(II), Mn(II), and Ni(II). Thus, the introduction of phosphorus into SG-Cl-T-P resin was beneficial to the selective adsorption for Hg(II). Moreover, the Irving–Williams order is based on empirical observation and related to the increase in effective nuclear charge. Then, the results of this investigation are in agreement with the Irving–Williams order for Ni(II) < Cu(II) > Zn(II).<sup>16</sup>

As we compared the adsorption capacity of different types of adsorbents used for heavy metal adsorption (Table V), it was clear that the adsorption capacity of SG-Cl-T-P was relatively high when compared with several other adsorbents such as SG chemically modified with benzimidazole, ATZ-SSQ, ATZ-SG, and 5-amino-1,3,4-thiadiazole-2-thiol (SiATT).<sup>17–19</sup> The above-mentioned research results show that the novel inorganic-organic hybrid material SG chemically modified by poly(triethylenetetramine bis(methylenephosphonic acid)) SG-Cl-T-P is

favorable and useful for the removal of heavy metal from ethanol solutions, and the high adsorption capacity make it a good promising candidate material for heavy metal uptake.

## CONCLUSION

Metal ions in fuel ethanol can accelerate the corrosion of engines or promote the formation of gums and sediments, and the removal of heavy metal ions by modified mesoporous SG from ethanol solutions were studied. It was found that chelating resin SG supported via aminophosphonic acid SG-Cl-T-P had good adsorption capacity for Hg(II) and Cd(II). Therefore, it is concluded that modified mesoporous silica gel SG-Cl-T-P could be considered a potential and promising adsorbent for the removal of Hg(II) and Cd(II), typical heavy metal pollutants, from ethanol solutions.

## References

- Jin, Y.; Li, A.; Hazelton, S. G.; Liang, S.; John, C. L.; Selid, P. D.; Pierce, D. T.; Zhao, J. X. *Coord Chem Rev* 2009, 253, 2998.
- Liu, P.; Su, Z. *Mater Chem Phys* 2005, 94, 412.
- Wang, X.; Tseng, Y.; Chan, J.; Cheng, S. *Micropor Mesopor Mater* 2005, 85, 241.
- Ohta, K.; Morikawa, H.; Sando, M. *Anal Chim Acta* 2001, 439, 255.
- Im, H. J.; Barnes, C. E.; Dai, S.; Xue, Z. *Micropor Mesopor Mater* 2004, 70, 57.
- Zhang, Y.; Qu, R. J.; Sun, C. M.; Wang, C. H.; Ji, C. N.; Chen, H.; Yin, P. *Appl Surf Sci* 2009, 255, 5818.
- Lesaint, C.; Lebeau, B.; Marichal, C.; Patarin, J. *Micropor Mesopor Mater* 2005, 83, 76.
- Yokoi, T.; Tatsumi, T.; Yoshitake, H. *J Colloid Interface Sci* 2004, 274, 451.
- Walcarius, A.; Delacote, C. *Anal Chim Acta* 2005, 547, 3.
- Avelar, H. M.; Barbeira, P. S. *Fuel* 2007, 86, 299.
- Prado, A. G. S.; Pescara, I. C.; Evangelista, S. M.; Holanda, M. S.; Andrade, R. D.; Suarez, P. A. Z.; Zara, L. F. *Talanta* 2011, 84, 759.
- Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*; Gaussian: Pittsburgh, PA, 2003.

13. Joswig, J. O.; Hazebroucq, S.; Seifert, G. *J Mol Struct Theochem* 2007, 816, 119.
14. Sing, K. S. W.; Everett, D. H.; Haul, R. A. W.; Moscou, L.; Pierotti, R. A.; Rouquerol, J.; Siemieniewska, T. *Pure Appl Chem* 1985, 57, 603.
15. Pearson, R. G. *Science* 1966, 151, 172.
16. Irving, H.; Williams, R. J. P. *J Chem Soc* 1953, 637, 3192.
17. Filho, N. L. D.; Gushikem, Y.; Polito, W. L.; Moreira, J. C.; Ehirim, E. O. *Talanta* 1995, 42, 1625.
18. Filho, N. L. D.; Costa, R. M.; Marangoni, F. *Colloids Surf A Physicochem Eng Aspects* 2008, 317, 625.
19. Luis, A. M. G.; Pedro, M. P.; José, C. M.; Filho, N. L. D.; Yoshitaka, G. *J Brazil Chem Soc* 1998, 9, 494.