Novel Negatively Charged Hybrids. 2. Preparation of Silica-Based Hybrid Copolymers and Their Applications for Cu^{2+} Removal

Keyan Hu,[1] Junsheng Liu,[1] Hengzhou Wo,[2] Tao Li[1]

[1]Key Laboratory of Membrane Materials and Processes, Department of Chemical and Materials Engineering, Hefei University, Hefei 230022, China
[2]School of Machinery and Automobile Engineering, Institute of Tribology, Hefei University of Technology, Hefei 230009, China

ABSTRACT: A series of negatively charged silica-based hybrid copolymers were prepared via free radical polymerization of γ–methacryloxypropyl trimethoxy silane (MAPTMS), 4–vinylbenzylchloride (VBC), and styrene (St) monomers, and the sol–gel process. Their applications for Cu^{2+} removal from aqueous solution were investigated. TGA and DrTGA thermal analyses indicated that these hybrid copolymers can keep thermally stable up to 412°C. Their cation-exchange capacities (CIECs) are within the range of 0.49–1.25 mmol g^{-1}. Adsorption experiments indicated that the adsorption followed Langmuir isotherm model, suggesting that it is Langmuir monolayer adsorption. The electrostatic attraction between the ionic groups and Cu^{2+}, the content of ionic groups and the existence of reactive chloromethyl groups might be responsible for such trend. Based on these findings, it can be concluded that the incorporation of VBC in the hybrid copolymers conduces to the advance of Cu^{2+} adsorption capacity; however, the incorporation of St makes little contribution to the raise of Cu^{2+} adsorption capacity, suggesting that the adsorption performances of these silica-based hybrid copolymers can be artificially adjusted and have potentially application in the removal of Cu^{2+} from wastewater. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 42–51, 2010

Key words: negatively charged hybrid copolymer; silica-based hybrid copolymer; Cu^{2+} removal; adsorption; heavy metal ions

INTRODUCTION

With the wide application of copperplating technology and copperware, water pollution caused by Cu^{2+} ions has deserved escalating interest due to their negative effects on the environment and human health. To remove this toxic pollutant from waste water, a variety of methods have been developed in the past.[1–3] Among them, adsorption using hybrid materials with functional groups is considered as one of the most effective and versatile methods in that the metal ions can be bonded to the organic polymer/inorganic hybrids.[4–6] For examples, Chakraborty and coauthors[4] used aniline formaldehyde condensate (AFC) coated on silica gel as an adsorbent to remove Cu^{2+} from aqueous solution, they concluded that coordination bond formation between amine group and Cu^{2+} ion was the main mechanism of copper removal. Dey et al.[5] prepared one type of chelating material SiAPPMA using 1,4–bis(3–aminopropyl)piperazine and methylacrylate by a heterogeneous route, it showed higher adsorption ability towards Cu^{2+} than for Ni^{2+} and Co^{2+} in both competitive and noncompetitive conditions.

As one type of inorganic/organic hybrid polymeric material with positively or negatively charged groups, charged hybrid polymeric materials have caught numerous eyes in recent years.[7–15] This type of charged hybrid polymer not only combines the advantages of organic and inorganic materials, but also acquires some distinguished properties, such as structural flexibility, and thermal and mechanical stability. They have been successfully used to separate heavy metal ions from aqueous solution or wastewater,[11–15] indicating promising application in environmental protection fields.

Recently, the preparation and application of negatively charged hybrid polymers to remove heavy metal ions from aqueous solution were conducted in our laboratory.[11,12,15] In these earlier articles,[11,12] two novel approaches to the negatively charged hybrid materials were put forward and their applications to the removal of heavy metal ions from aqueous solution are investigated. One route to the negatively charged hybrid copolymers was initiated via free

TABLE I
Composition of the Prepared Negatively Charged
Silica-Based Hybrid Copolymers

Sample	MPTMS (mol)	VBC (mol)	St (mol)
(A)	0.1	0.1	0.1
(B)	0.1	0.1	0.2
(C)	0.1	0.2	0.1
(D)	0.1	0.2	0.2

radical polymerization of γ-methacryloxypropyl trimethoxy silane (MAPTMS) and acrylic acid (AA) monomers, and a subsequent sol–gel process of hybrid precursor. Their adsorption behaviors for heavy metal ions were carried out using the aqueous solution containing Cu^{2+} and Pb^{2+} ions as model heavy metal ions. Another approach to the negatively charged hybrid materials was initiated via sol–gel process and a subsequent epoxide ring-opening reaction, in which the $-SO_3H$ groups was created through the ring-opening reaction of epoxy groups in the 3–glycidoxypropyltrimethoxysilane (GPTMS) chains with sodium bisulfite ($NaSO_3H$). Their adsorption behaviors for heavy metal ions were evaluated for the removal of Pb^{2+} and Cu^{2+} ions from aqueous solution.

Our continuing interest in such charged hybrids stimulates us to make further effort. Herein, a series of negatively charged silica-based hybrid copolymers will be prepared via free radical polymerization of γ–methacryloxypropyl trimethoxy silane (MAPTMS), 4–vinylbenzylchloride (VBC), and styrene (St) monomers, and a subsequent sol–gel process. Compared with previous articles,[11,12] special attention will be paid to this new route: the inorganic ingredient is directly incorporated into the organic moiety via free radical polymerization of three different monomers, and the $-SO_3H$ groups are created by the sulfonation of phenyl groups. Furthermore, their adsorption properties for heavy metal ions removal will be evaluated using Cu^{2+} ions as model for the separation and recovery of heavy metal ions from aqueous medium.

EXPERIMENTAL

Materials

γ-Methacryloxypropyl trimethoxy silane (MPTMS), 4–vinylbenzylchloride (VBC), and styrene (St) monomers were purchased from Shanghai Chemical Reagent Co. (Shanghai, China); they were respectively purified by vacuum distillation (around 2–3 mmHg) over hydroquinone at 95 and 140°C before use. Initiator azobisisobutyronitrile (AIBN) was dissolved in warm methanol (35°C), recrystallized in an ice bath, and then dried in a vacuum oven at room temperature before use. Toluene was commercially obtained

Preparation of negatively charged hybrid copolymers

The negatively charged hybrid copolymers were prepared by reacting proper MPTMS, VBC, and St monomers in toluene solution (composition of these hybrid copolymers was shown in Table I), and a subsequent sulfonation of phenyl groups (as presented in Scheme 1). The preparation procedures can be described briefly as follows:

Firstly, into a three-necked round-bottom flask equipped with a stirrer, an N_2 inlet and a cooler/ heater, 0.05 mol of MPTMS solution dissolved in 150 mL of toluene solution was added, and then 0.03 g of AIBN was slowly added. Secondly, stoichiometric amount of VBC and St monomers was respectively added dropwise into the flask within 2 h (the molar ratios of MPTMS, VBC, and St monomers were listed in Table I). Thirdly, the mixed solution was heated at 70°C and stirred vigorously to undergo the free radical polymerization for additional 24 h, and then yellowed solution containing the hybrid precursor MPTMS-*co*-VBC-*co*-St could be observed.

After the completion of the above reaction, excessive fuming sulfuric acid (20% SO_3) (the molar ratio of sulfuric acid: MPTMS-*co*-VBC-*co*-St = 6 : 1) was
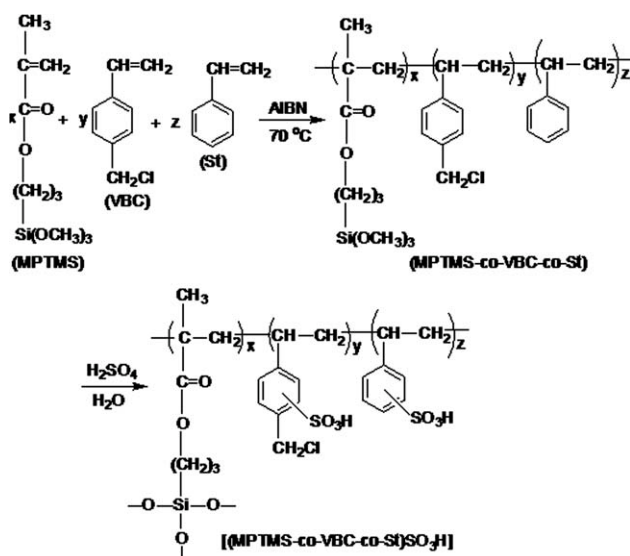
Scheme 1 Approach to the cation-exchange silica-based hybrid copolymers via free radical polymerization and sulfonation of phenyl groups, step1 is the free radical polymerization of MPTMS, VBC and St monomers to prepare the hybrid precursor, MPTMS-*co*-VBC-*co*-St, step 2 is the sulfonation of phenyl groups and sol-gel process to produce the cation-exchange hybrid copolymer (MPTMS-*co*-VBC-*co*-St)SO$_3$H.

added dropwise into the solution prepared earlier. The mixture was stirred vigorously for additional 12 h at the temperature, and then aqueous NaOH solution (0.01mol dm^{-3}) was added to neutralize the excessive sulfuric acid. Finally, the product was washed with deionized water and dried at 80°C to obtain the negatively charged hybrid copolymer, (MPTMS-co-VBC-co-St)SO$_3$H. Note that during the process of drying, the sol–gel reaction may simultaneously occur between Si and O to produce the Si—O—Si bonds in the copolymer backbone.

Sample characterizations

FTIR spectra of the step products were obtained using a Bruker Vector–22 Fourier transform infrared spectrometer in the region of 4000–400 cm^{-1}.

The degradation process and thermal stability were investigated via TGA and DTA analyses using a Shimadzu TGA-50H thermogravimetry analyzer, under a N$_2$ flow using a heating rate of 10°C/min from 30 to 700°C.

Ion-exchange capacity (IEC) was determined by titration.[8,9] The procedure was described briefly as follows. 1.0 g of the prepared copolymer was immersed in a large amount of deionized water for 24 h and washed several times to remove the impurity. Then, they were immersed in a Na$_2$SO$_4$ aqueous solution (0.1mol dm^{-3}) for 24 h to substitute H$^+$ with Na$^+$. The copolymer in the Na$^+$ form was titrated with a NaOH aqueous solution (0.01mol dm^{-3}), and the IEC could thus be determined based on the amount of H$^+$ ions exchanged by Na$^+$ ions. To decrease the test errors, the final results were the mean values of three independent measurements.

Adsorption experiments

The adsorption experiments were conducted in similar way as our previous studies.[11] The effects of pH (adjusted with NaAc–HAc buffer solution), the initial concentration of Cu^{2+} ions (in the range of 0.001–0.1 mol dm^{-3}) and solution temperature on the adsorption capacity were studied. Particularly, the procedure can be described as follows: about 0.5 g of particle sample was immersed in 0.01mol dm^{-3} Cu(NO$_3$)$_2$ for 24 h at pH 3 and 4, respectively, and then taken out and washed by deionized water. In the remaining solution, 10% KI solution was added; subsequently, a Na$_2$S$_2$O$_3$ aqueous solution (0.05 mol dm^{-3}) was used to titrate iodine so that the residual Cu^{2+} ions can be measured. The reactions can be expressed below:

$$2Cu^{2+} + 4I^- = 2CuI \downarrow + I_2 \qquad (1)$$

$$I_2 + 2S_2O_3^{2-} = 2I^- + S_4O_6^{2-} \qquad (2)$$
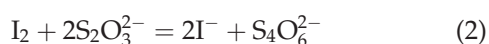
The adsorption capacity (q_{Cu2+}) of Cu^{2+} ion can be calculated as follows:

$$q_{Cu^{2+}} = \frac{(C_0 - C_R)V}{W} \qquad (3)$$

where C_0 and C_R are the concentrations of original and remaining Cu(NO$_3$)$_2$, respectively; V is the volume of Cu(NO$_3$)$_2$ solution; and W is the weight of copolymer.

RESULTS AND DISCUSSION

Preparation of negatively charged hybrid copolymers

As mentioned in the experimental section, the negatively charged silica-based hybrid copolymers were synthesized via the free radical polymerization among MAPTMS, VBC, and St monomers, and a subsequent sol–gel process, in which the —SO$_3$H groups was produced by the sulfonation of phenyl groups in the copolymer chains. As MAPTMS, VBC, and St three different monomers all have unsaturated double bonds, they can be polymerized in the presence of initiator AIBN and charged by sulfonating agent to create the —SO$_3$H groups in the molecular backbone. The possible reaction steps are shown in Scheme 1.

As presented in Scheme 1, Step 1 is the free radical polymerization reaction of MPTMS, VBC, and St monomers, and the product is hybrid copolymer precursor, MPTMS-co-VBC-co-St. To decrease the polymerization speed of these monomers, AIBN was first mixed with MPTMS and toluene solution. The main product of this step was determined by the molar ratio of MPTMS/VBC/St monomers (cf. Table I). Step 2 is the sulfonation of phenyl groups and sol–gel process to produce the negatively charged hybrid copolymer, (MPTMS-co-VBC-co-St)SO$_3$H. In this step, the alkoxysilane MPTMS conducted the hydrolysis and polycondensation to form the Si—O—Si bonds in the copolymer precursor prepared earlier. Meanwhile, the —SO$_3$H groups was produced by the sulfonation of phenyl groups in the copolymer chains. The negatively charged silica-based hybrid copolymer is thus prepared. This hybrid copolymer simultaneously contains both inorganic silica and —SO$_3$H groups, and can exchange H$^+$ ions with metal cations, it is therefore a negatively charged hybrid one.

Note that we made no effort to control the humidity. There exist some possibilities that the hydrolysis and polycondensation of alkoxysilane in step 2 is ahead of step 1 or both steps might occur simultaneously during the copolymer preparation. However, it does not affect any of the final product and its
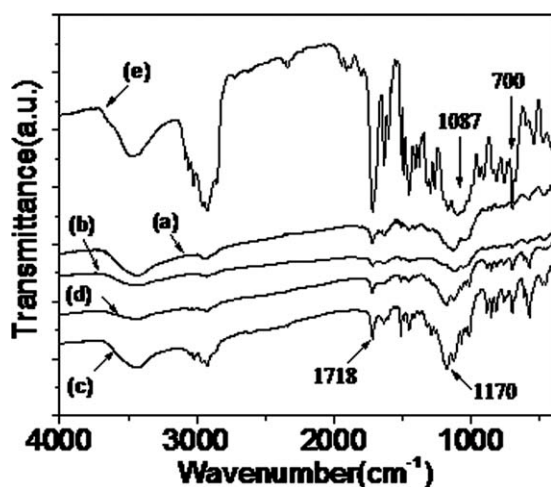
Figure 1 FTIR spectra of (a–d) were the samples (A), (B), (C), and (D), respectively. For comparison, the FTIR spectrum of the step product of sample (A) in step 1 was illustrated in the same plot as curve (e).

Figure 2 TGA curves of samples (A–D).

property because our only concern is the facilitation of the hydrolysis and polycondensation of alkoxysilane and the production of the Si-O-Si bond in hybrid matrix.

FTIR spectra

To confirm the reactions described in Scheme 1, FTIR spectra of samples (A-D) were examined and shown in Figure 1. For comparison, the FTIR spectrum of the step product of sample (A) in step 1 was illustrated in the same plot as curve (e).

As shown in curves (a–d), the large band at 3400 cm^{-1} was the stretching vibration of —OH groups. The adsorption peak near 3000 cm^{-1} can be ascribed to the stretching vibration of CH$_3$— and —CH$_2$— groups in the samples.[8,9] The peak at 1718 cm^{-1} was mainly from the stretching of —C=O in the polymer chains of MPTMS unit. The absorption peak at around 1087 cm^{-1} was the overlapping of asymmetric stretching vibration of Si—O—Si and Si—O—C bands from the trimethoxysilane groups of MPTMS unit.[10] The bands appeared at 2925 cm^{-1} and 1450–1600 cm^{-1} were the —C—H stretching vibration and C=C stretching vibration of aromatic absorption. The band at 700 cm^{-1} was the —C—Cl stretching vibration of chloromethyl group in VBC unit.[16]

Furthermore, from comparison of curve (a) with curve (e) in Figure 1, it is interesting to find that a new strong peak located at 1170 cm^{-1} appeared, which is in the range of 1100–1200 cm^{-1} corresponding to the asymmetric O=S=O stretching vibration of —SO$_3$H units,[17] suggesting the formation of —SO$_3$H groups in the polymer backbone. Based on these changes in adsorption peaks, it can be concluded that the sulfonation of phenyl groups had
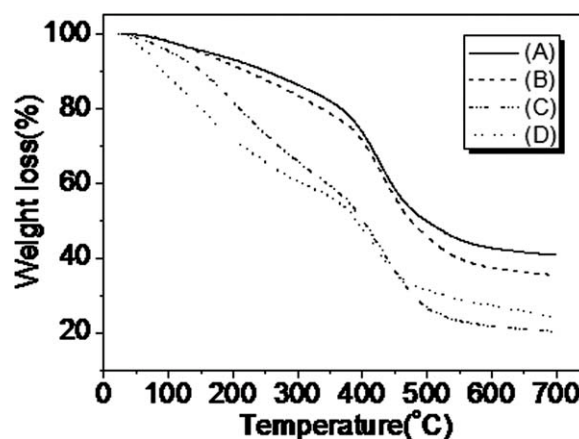
occurred during the copolymer preparation, further corroborating the reactions described in Scheme 1.

TGA and DTA analyses

Thermal stability is one primary property of a silica-based hybrid material. To have an insight into the thermal degradation behaviors of the synthesized hybrid copolymers (A-D), TGA, and DTA analyses were conducted and presented in Figures 2 and 3. Meanwhile, the thermal properties of these samples in TGA and DrTGA curves are summarized in Table II.

As shown in Figure 2, for samples (A) and (B), (C) and (D), their change trends in weight loss are similar, and two-step degradation can be clearly observed. Corresponding to these degradation processes, several markedly endothermic peaks in DrTGA curves can be discovered (cf. Fig. 3). Taking samples (A) and (B) into consideration, the endothermic peak temperature (T_{ep}) was 428.60 and 432.94°C, and the weight loss of them was near 35 and 38%, respectively, indicating the occurrence of
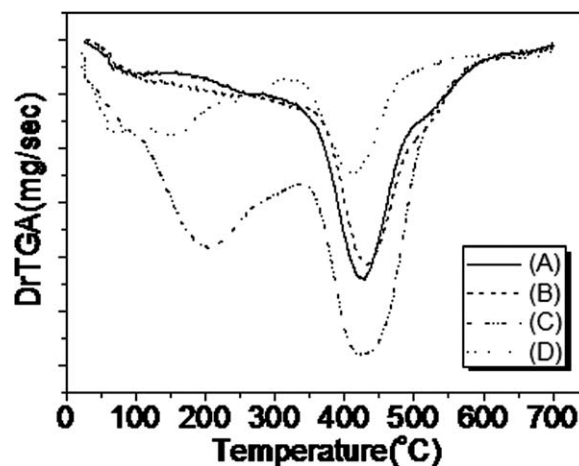

Figure 3 DrTGA curves of samples (A–D).

Sample	T_{d5} (°C)[a]	T_{d10} (°C)[a]	R_{700} (wt %)[b]	T_{ep} value (°C)		
				First	Second	Third
(A)	160.37	250.06	40.90	428.60		
(B)	150.44	220.27	35.47	432.94		
(C)	102.83	150.48	20.41	205.72	422.71	
(D)	66.51	91.76	24.15	66–78	150.41	412.29

[a] The thermal degradation temperature of 5 and 10% weight loss, respectively.
[b] The residual weight at 700°C.

decomposition. The thermal degradation temperature of 5 and 10% weight loss (labeled as T_{d5}, T_{d10}) of samples (A) and (B) respectively appeared at 160.37 and 250.06, 150.44 and 220.27 °C. By comparison these data of sample (A) with those of sample (B), it can be found that both T_{d5} and T_{d10} all decrease a little. However, the T_{ep} value increases slightly from 428.60 for sample (A) to 432.94°C for sample (B) (cf. Table II), indicating an upward trend when the St content in the hybrid copolymer chains increases. This result evidences that the incorporation of St in the hybrid copolymers can increase the thermal stability of the hybrid copolymers. As for sample (C), the T_{ep} values were 205.72 and 422.71°C, and the weight loss of these two endothermic peaks was near 19% and 55%, respectively. The T_{d5} and T_{d10} were 102.83 and 150.48°C, respectively, revealing a downward trend with the elevating VBC content in the hybrid copolymers when compared with that of sample (A). This finding suggests that the incorporation of VBC in the hybrid copolymers cannot increase the thermal stability of the prepared hybrid copolymers. Whereas considering sample (D), the T_{ep} values were 66–78, 150.41, and 412.29°C, and the weight loss of these three endothermic peaks was near within 5–8, 20, and 55, respectively. The T_{d5} and T_{d10} were 66.51 and 91.76°C, respectively, exhibiting a downward trend with the elevating St content in the hybrid copolymers when compared with that of sample (C). Moreover, the weight loss of these samples increases rapidly when the temperature exceed T_{d10}. These thermal decomposition behaviors can be explained as follows.

The weight loss below T_{d10} was the removal of the bonded water and solvent in these samples. Whereas the sharp weight loss beyond T_{d10} can be assigned to the decomposition of organic ingredients, mainly the elimination of the —SO$_3$H groups and methoxy groups, and the production of silica. As reported, when a polymer contains a pendant active methoxysilane group, the methoxy groups are eliminated to form crosslinked Si—O—Si bonds in the early stages of heating, resulting in the creation of silica.[18]

Table II lists the thermal analysis data of samples (A–D) in TGA and DrTGA curves. As shown in Table II, for samples (A), (B), (C), and (D), the T_{ep} value of first endothermic peak reveals the same downward changing trend as that of T_{d5} and T_{d10}, implying a decrease in the thermal stability of these samples. Meanwhile, the values of residual weight at 700°C (labeled as R_{700}) are 40.90, 35.47, 20.41, and 24.15%, respectively, which exhibit a similar changing trend with those of T_{d5} and T_{d10} except that of sample (C), demonstrating an increase of organic ingredients in the prepared hybrid copolymers.

Several dominating factors might be responsible for the above trends. One can be ascribed to an increase in the content of organic ingredients in the prepared hybrid copolymers. As shown in Table II, the residual SiO$_2$ in the samples decreases from sample (A) to (D) when both VBC and St contents increase, which is consistent with the theoretical one (i.e. the thermal degradation temperature decreases with an increase in the organic ingredient of a polymer); consequently, the R_{700} values indicate a decreasing trend. Another might be attributed to the fabrication of —SO$_3$H groups in the copolymer chains. From sample (A) to (D), the amount of —SO$_3$H groups increases, the hydrophilicity of these samples increases accordingly. As a result, their thermal degradation rate elevates and the thermal degradation temperature decreases as confirmed by T_{ep} values. In addition, the category of monomeric substance will be one of the chief factors. Compared sample (A) with (C), and (B) with (D), the higher amount of VBC was copolymerized in the hybrid copolymer (cf. Table I), and the main T_{ep} value respectively changes from 428.60 to 422.71, 432.94 to 412.29, which indicates a downward trend (cf. Table II), demonstrating that the incorporation of VBC in the hybrid copolymers cannot bring about any increase to the inherent thermal stability of the prepared hybrid copolymers. In contrast, polymerizing higher amount of St in the hybrid copolymers will increase the thermal stability of these hybrid copolymers as discussed above. If the structure stability of monomeric substance is considered, this is

TABLE III
Cation-Exchange Capacities (CIECs) of the Prepared Silica-Based Hybrid Copolymers

Sample	(A)	(B)	(C)	(D)
CIEC (mmol g^{-1})	0.56	0.49	1.25	1.12

reasonable and easily understood. As St has higher structure stability than that of VBC, thus its polymerization will block the inherent decomposition of the prepared hybrid copolymers, resulting in higher T_{ep} value as observed.

Note that, sample (C) has the minimal R_{700} value among the prepared samples (A–D), which polymerizes lower amount of St than sample (D). The reason can be assigned to the relatively lower thermal stability of poly(VBC) than that of polystyrene, leading to lower amount of residual organic ingredients in the final decomposition product.

Ion-exchange capacity (IEC)

Ion-exchange capacity (IEC) is an intrinsic property of a charged material or membrane, so IEC measurements of these samples were determined and shown in Table III.

It is interesting to find in Table III that the CIEC values don't exhibit a linear changing trend from sample (A) to (D). However, if the composition of hybrid copolymers was considered, it can be detected that the CIEC values change linearly. For example, from sample (A) to (B), and (C) to (D), in which the amount of St in them was elevated slowly (cf. Table I), their CIEC values indicate the same downward trend, suggesting that the incorporation of St in the hybrid copolymer make no contribution to an increase in CIECs of the prepared hybrid copolymers. However, from sample (A) to (C), and (B) to (D), in which the amount of VBC in the hybrid copolymers was also elevated slowly (cf. Table I), their CIECs exhibit the same upward trend, demonstrating that the incorporation of VBC in the hybrid copolymer conduces to an increase in their CIECs. Furthermore, by comparison the CIEC datum of sample (C) with that of sample (B), it can be noted that there is an obvious rise in the CIEC, indicating the positive influence of VBC on the CIECs. These findings demonstrate that monomer category incorporated into the hybrid copolymers plays an important role in the change of CIECs, and the incorporation of St and VBC in these hybrid copolymers has an opposite effect on the ion-exchange ability.

Several reasons might be responsible for such trends. One is related to the molecular structure stability of monomer unit and the reactivity of chloromethyl groups in the benzene ring. As we know St has relatively higher structure stability than that of VBC, meanwhile there is no reactive groups existed in benzene ring. Thus the sulfonation of phenyl groups in St unit is hard to be conducted. In contrast, the sulfonation of phenyl groups in VBC unit can be easily carried out due to the existence of reactive chloromethyl groups in the benzene ring, leading to an increase in the dissociation extent of —SO$_3$H groups and the boost of CIEC values. Another can be assigned to the steric hindrance of monomer unit, which will impact the ion exchange in the active sites, resulting in the difference of CIECs. Consequently, the CIECs of these negatively charged silica-based hybrid copolymers can be artificially adjusted by polymerizing different monomers onto the molecular backbone.

Adsorption of Cu^{2+} ions

Adsorption of divalent metal cations is regarded as cost-effective and environmental friendly method to remove environmental pollutants.[19,20] To have an insight into the adsorption behavior of the negatively charged silica-based hybrid copolymers, adsorption experiments were conducted using Cu^{2+} as model heavy metal ions. The factors examined include pH, the initial concentration of Cu^{2+} ions and solution temperature. The adsorption data were analyzed using Langmuir and Freundlich isotherm models.

Effect of pH on Cu^{2+} adsorption

pH is an important factor affecting the adsorption of heavy metal ions; however, considering the requirement on pH for determining Cu^{2+} content by titration, pH is chosen only within 3–4.[11] Figure 4 illustrates the relationship between the adsorption capacity (q_{Cu2+}) of Cu^{2+} vs. pH values. Obviously, pH = 3 is more suitable for Cu^{2+} adsorption.
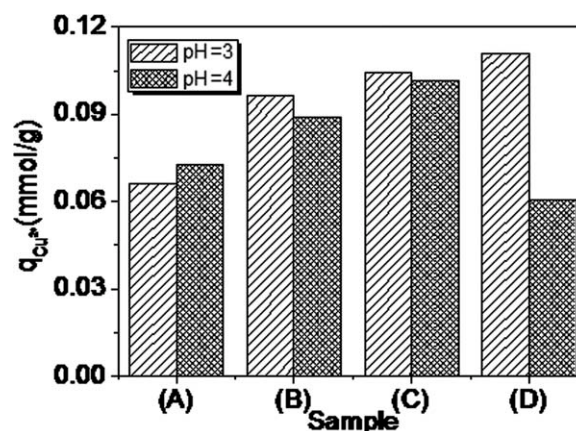

Figure 4 Plot of adsorption capacity of Cu^{2+} (q_{Cu2+}) vs. pH; the sample was immersed in 0.01 mol dm^{-3} Cu(NO$_3$)$_2$ solution for 24 h, respectively.
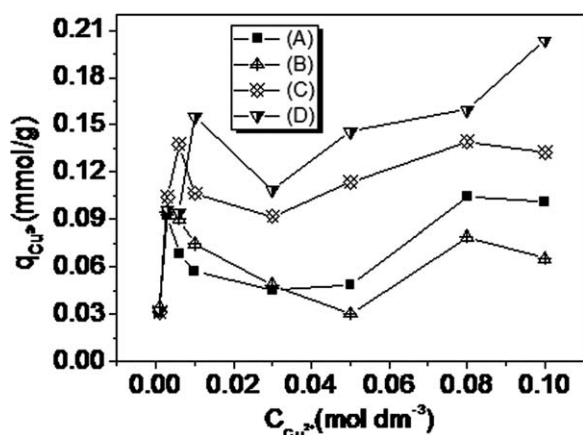
Figure 5 Effect of initial concentration of solution on Cu^{2+} adsorption at pH 3.

Accordingly, pH 3 was chosen to study the Cu^{2+} adsorption in this case, hereinafter.

Note that the adsorption capacity of Cu^{2+} on sample D decreases a little at pH 4 compared with that at pH 3. Such decrease may be related to the partial desorption of Cu^{2+} ions from sample D and the formation of metal hydrates in lower acidity of dilute solution. This is because sample D contains higher reactive chloromethyl groups and $-SO_3H$ groups in the copolymer chains, which possibly decrease the stability of adsorption product. This finding suggests that a decrease in the acidity of dilute solution doesn't favor the removal of metal ions by sample D.

Effect of initial concentration on Cu^{2+} adsorption

Figure 5 illustrates the effect of initial concentration of Cu^{2+} ions on the adsorption capacity at pH 3. It can be seen that for different samples, the adsorption amount of Cu^{2+} ions has different changing trends. When the initial concentration of Cu^{2+} is lowered to 0.03 mol dm^{-3}, the adsorption capacity of Cu^{2+} follows such order as: sample C > sample D > sample B > sample A. However, When the initial concentration of Cu^{2+} is higher than 0.03 mol dm^{-3}, the adsorption capacity of Cu^{2+} follows such order as: sample D > sample C > sample A > sample B.

By comparison the adsorption capacity of sample (A) to (C), and (B) to (D), in which the amount of VBC in the hybrid copolymers was elevated slowly (cf. Table I), it can be noted that their adsorption capacities reveal the same increasing changing trends as those of CIECs, suggesting that the incorporation of VBC in the hybrid copolymer can elevate Cu^{2+} adsorption capacity due to the existence of reactive chloromethyl groups in the benzene ring. In contrast, by comparison the adsorption capacity of sample (A) to (B), and (C) to (D), in which the amount of St in them was also elevated slowly

(cf. Table I), no clear changing trend can be found, implying that the incorporation of St in the hybrid copolymer doesn't significantly affect the adsorption capacity of Cu^{2+} ions due to the structural stability of benzene ring.

Taking individual sample into consideration, it can be noted that the adsorption capacity of Cu^{2+} ions on these samples increases with an increase in the initial concentration and approaches saturation at 0.08 mol dm^{-3} if the experimental error was ignored, which is consistent with the theoretical expectation.

The aforementioned findings suggest that the initial concentration of Cu^{2+} solution has different effects on Cu^{2+} adsorption due to the difference of incorporated monomer category.

It should be emphasized that although the CIEC value of sample B is lower than that of sample A (cf. Table III), the adsorption capacity of Cu^{2+} on sample B is higher than that on sample A when the initial concentration of Cu^{2+} solution was lowered to 0.03 mol dm^{-3}, which is inconsistent with the theoretical expectation, i.e. the uptake of metal ions on a charged polymer increases as the CIEC value elevates. It is difficult to exclusively explain such abnormal phenomenon within the authors' knowledge. The possible reason may be related to the impact of steric hindrance from chloromethyl groups on VBC unit, which may block the ion exchange of H from $-SO_3H$ groups in VBC unit with Cu^{2+} ions as the Cu^{2+} concentration decreases to dilute solution. In this case, water may firstly combine with Cu^{2+} ions to produce the metal hydroxide and thus further hinders the occurrence of Cu^{2+} adsorption. Comparing the molecular structure of sample A with sample B, it can be seen that sample A contains higher amount of chloromethyl groups in VBC unit and larger steric hindrance, consequently, the adsorption capacity of Cu^{2+} on sample A is lower than that on sample B. Moreover, the dissociation extent of $-SO_3H$ groups at dilute solution will also affect the adsorption of Cu^{2+}. Generally speaking, the dissociation extent of $-SO_3H$ groups increases with a decrease in solution concentration and the release of H^+ ions because of its strong dissociation property, such effect will favor ion exchange and the formation of metal complex. Accordingly, increase the adsorption capacity of metal ions. As listed in Table I, sample B comprises more amounts of St unit than those of sample A, the adsorption capacity of Cu^{2+} on sample B is therefore larger than that on sample A at dilute solution.

Adsorption isotherms

To explain the above phenomena, Langmuir and Freundlich isotherm models are used to analyze the
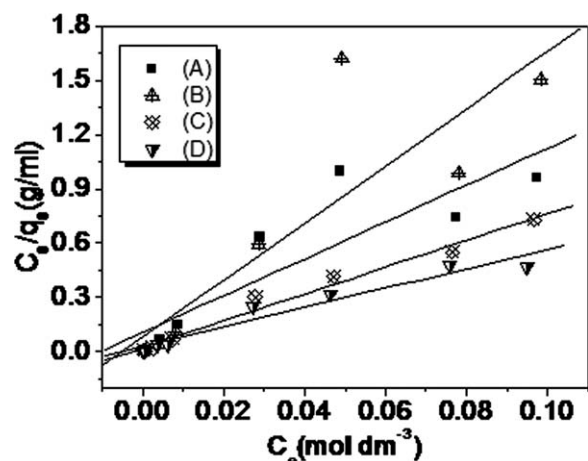
Figure 6 Langmuir adsorption isotherm of samples (A–D) for Cu^{2+} adsorption.

tested adsorption data. The Langmuir isotherm equation is based on monolayer adsorption on the active sites of the adsorbent; which can be expressed as eq. (4)[21,22]:

$$\frac{c_e}{q_e} = \frac{c_e}{Qm} + \frac{1}{Q_m b} \qquad (4)$$

where q_e and c_e are the equilibrium concentrations of metal ion in the adsorbed and liquid phases, respectively. Q_m and b are the Langmuir constants, which can be calculated from the intercept and slope of the linear plot based on c_e/q_e versus c_e.

Different from Langmuir isotherm model, Freundlich isotherm model is considered as the adsorption occurred on a heterogeneous surface with uniform energy; which can be expressed as eqs. (5a) and (5b)[4,21,22]:

$$q_e = k_F c_e^{\frac{1}{n}} \qquad (5a)$$

$$\text{or, } \log q_e = \log k_F + \frac{1}{n} \log c_e \qquad (5b)$$

where q_e and c_e are the equilibrium concentrations of metal ion in the adsorbed and liquid phases, respectively. k_F and n are the Freundlich constants, which can be calculated from the slope and intercept of the linear plot according to $\log q_e$ versus $\log c_e$.

Figure 6 illustrated the Langmuir adsorption isotherm of samples (A–D) for Cu^{2+} adsorption and the Langmuir isotherm parameters are listed in Table IV.

As shown in Figure 6, it can be seen that the experimental data fitted well with Langmuir isotherm model, especially for samples (C) and (D) [the regression coefficient (R^2) values are in the range of 0.77–0.98]. In contrast, these experimental data fitted worse with Freundlich isotherm model [due to the poor regression coefficient (R^2) values of Freundlich isotherm model, the plot of log (q_e) versus log (C_e) was not presented in the text]. Based on these results, it can be concluded that the adsorption process is monolayer adsorption rather than heterogeneous surface one and higher amount of CIECs will conduce to monolayer adsorption of Cu^{2+}. The reason might be related to such major factors: the electrostatic attraction between the ionic groups and Cu^{2+} ions, the content of ionic groups, etc,[21] and the influence of reactive chloromethyl groups.

For Langmuir isotherm model, separation factor or equilibrium parameter (R_L) can be used to predict the favourability of adsorption, which is defined by eq. (6)[21,22]:

$$R_L = \frac{1}{(1 + bC_0)} \qquad (6)$$

where C_0 is the initial Cu^{2+} concentration and b is the Langmuir adsorption equilibrium constant.

When the R_L value is within $0 < R_L < 1$, it is favorable adsorption. Otherwise, it is unfavorable adsorption. Table V lists the calculated R_L values based on the Langmuir isotherm parameters. Clearly, these R_L values are all in the range of $0 < R_L < 1$, suggesting that Cu^{2+} adsorption on the prepared hybrid copolymers is favorable. Consequently, the prepared negatively charged hybrid copolymers are promising adsorbents for Cu^{2+} removal from aqueous medium.

Furthermore, it can be seen that the adsorption of Cu^{2+} ions on these negatively charged hybrid

TABLE IV
Langmuir Isotherm Parameters for Cu^{2+} Adsorption

Sample	Q_m (mmol g^{-1})	b (dm^3/mol)	R^2
(A)	0.0981	95.873	0.784
(B)	0.0634	192.038	0.773
(C)	0.135	334.161	0.981
(D)	0.187	182.071	0.945

TABLE V
The Calculated R_L Values Based on the Langmuir Isotherm Parameter

C_0 (mol dm^{-3})	R_L Value			
	(A)	(B)	(C)	(D)
0.001	0.913	0.839	0.749	0.846
0.003	0.777	0.634	0.499	0.647
0.006	0.635	0.465	0.333	0.478
0.01	0.511	0.342	0.230	0.355
0.03	0.258	0.148	0.0907	0.155
0.05	0.173	0.0943	0.0565	0.0990
0.08	0.115	0.0611	0.0361	0.0642
0.1	0.0945	0.0495	0.0291	0.0521

copolymers was Langmuir monolayer adsorption, which is inconsistent with that reported in a previous article,[11] in which the adsorption of Cu^{2+} ions on negatively charged hybrid polymers followed Freundlich isotherm model, demonstrating that the adsorption of heavy metal ions on negatively charged hybrids doesn't follow the same type of theoretical model. This improvement in adsorption behaviors of a charged hybrid polymer would be very meaningful in the removal of heavy metal ions from aqueous solution, suggesting that the adsorption process of heavy metal ions can be artificially controlled by the design of hybrid polymer structure.

Effect of solution temperature on Cu^{2+} adsorption

To have an insight into the adsorption behaviors of Cu^{2+} ions on samples (A–D), the effect of solution temperature on Cu^{2+} adsorption was determined and presented in Figure 7.

As shown in Figure 7, it can be found that for different sample at the sample temperature, the adsorption capacity of Cu^{2+} ions increases from sample (B), (A), (C) to (D). Whereas, for the individual sample at different temperature, the adsorption capacity of Cu^{2+} ions increases with the elevated temperature [the linear regression coefficient (R^2) values are in the range of 0.85–0.95], suggesting that adsorption process of Cu^{2+} ions on these negatively charged hybrid copolymers is endothermic in nature. Two dominating factors might be responsible for such trend. One can be ascribed to an increase in the pore size and/or activation of the sample surface as the temperature increases.[21] Another can be assigned to the electrostatic attraction between Cu^{2+} ions and the negatively charged groups in the hybrid copolymers, which can be interpreted below.

Commonly, $-SO_3H$ groups are partially protonated and the partition degree increases with the elevated temperature in that the partition of $-SO_3H$ groups is an endothermic reaction, thus the amount of $-SO_3H$ groups transformed into $-SO_3^-$ groups will be promoted accordingly, resulting in an increase in the electrostatic attraction between metal ions such as Cu^{2+} ions and negatively charged groups in the copolymer chains. As a result, the adsorption capacity of Cu^{2+} ions increases slightly at high temperature. In this case, the partition or deprotonation-adsorption mechanism is the dominating control step and can be used to explain the adsorption behaviors [cf. eqs. (7a,b)]. Moreover, the Cu^{2+} ions may directly coordinate with $-SO_3H$ groups and conduct negatively charged reaction to produce the metal complexes, which will bring about an improvement of adsorption capacity when the temperature elevates. Thus they will follow the
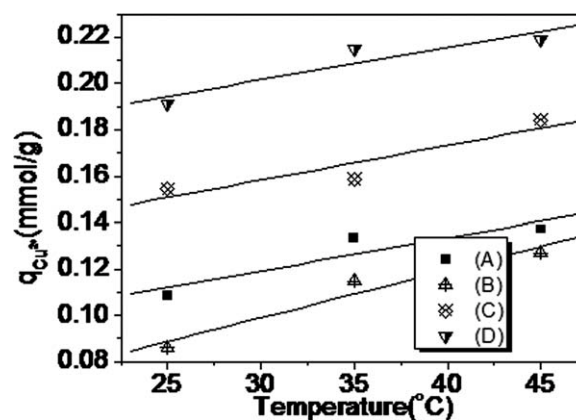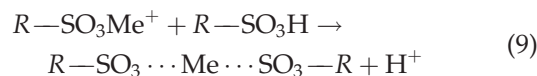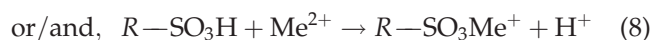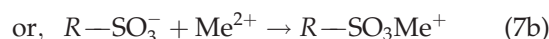

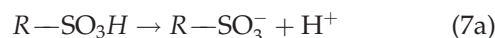**Figure 7** Effect of solution temperature on Cu^{2+} adsorption, the concentration of aqueous $Cu(NO_3)_2$ solution was 0. 1 mol dm^{-3}. at 25, 35, and 45°C for 24 h, respectively.

ion-exchange mechanism [cf. eq. (8)]. The proposed adsorption mechanism between divalent metal ions (Me^{2+}) and $-SO_3H$ groups can be briefly described as follows.

$$R-SO_3H \rightarrow R-SO_3^- + H^+ \tag{7a}$$

$$\text{or, } R-SO_3^- + Me^{2+} \rightarrow R-SO_3Me^+ \tag{7b}$$

$$\text{or/and, } R-SO_3H + Me^{2+} \rightarrow R-SO_3Me^+ + H^+ \tag{8}$$

$$\begin{aligned} R-SO_3Me^+ + R-SO_3H \rightarrow \\ R-SO_3 \cdots Me \cdots SO_3-R + H^+ \end{aligned} \tag{9}$$

Based on such suggested adsorption mechanism, it can be concluded that the combined effects of deprotonation and metal complex impact Cu^{2+} adsorption on the negatively charged hybrid copolymers, which would be very meaningful in the investigation of adsorption behaviors of charged hybrid polymer as discussed hereinbefore.

CONCLUSIONS

A novel approach to negatively charged hybrid copolymers was proposed and a series of silica-based hybrid copolymers were prepared from the free radical polymerization of MAPTMS, VBC, and St monomers, and a subsequent sol–gel process. These silica-based hybrid copolymers reveal higher thermal stabilities and their CIECs are within 0.49– 1.25 mmol g^{-1}. Adsorption experiments demonstrate that they can adsorb Cu^{2+} ions and such adsorption is an endothermic in nature. It is evidenced that the adsorption followed Langmuir isotherm model, suggesting that the adsorption process is Langmuir monolayer adsorption, which might be related to the electrostatic attraction between the ionic groups and Cu^{2+} ions, the content of ionic groups and the existence of reactive chloromethyl groups. In addition, by comparison the adsorption capacity, it is

confirmed that the incorporation of VBC in the hybrid copolymers have positive effects to the elevation of Cu^{2+} adsorption; in contrast, the incorporation of St in these copolymers makes no contributions to Cu^{2+} adsorption. These findings are very useful for the separation and recovery of heavy metal ions from wastewater or contaminated water.

References

1. Chen, A.-H.; Yang, C.-Y.; Chen, C.-Y.; Chen, C.-Y.; Chen, C.-W. J Hazard Mater 2009, 163, 1068.
2. Deveci, H.; Ahmetli, G.; Ersoz, M.; Kurbanli, R. J Appl Polym Sci 2009, 112, 1192.
3. Ğuzdoğan, E.; Denkbaş, E. B.; Öztürk, E.; Tuncel, S. A.; Kabasakal, O. S. J Hazard Mater 2009, 162, 1073.
4. Kumar, G. P.; Kumar, P. A.; Chakraborty, S.; Ray, M. Sep Purif Technol 2007, 57, 47.
5. Dey, R. K.; Airoldi, C. J Hazard Mater 2008, 156, 95.
6. Zhang, X. J.; Ma, T. Y.; Yuan, Z. Y. J Mater Chem 2008, 18, 2003.
7. Wu, C. M.; Xu, T. W.; Gong, M.; Yang, W. H. J Membr Sci 2004, 247, 111.
8. Wu, C. M.; Xu, T. W.; Yang, W. H. J Membr Sci 2003, 224, 117.
9. Luo, J. Y.; Wu, C. M.; Wu, Y. H.; Xu, T. W. J Membr Sci 2010, 347, 240.
10. Xu, T. W. J Membr Sci 2005, 263, 1.
11. Liu, J. S.; Wang, X. H.; Xu, T. W.; Shao, G. Q. Sep Purif Technol 2009, 66, 135.
12. Liu, J. S.; Li, T.; Hu, K. Y.; Shao, G. Q. J Appl Polym Sci 2009, 112, 2179.
13. Çavuş, S.; Gürdağ, G.; Sözgen, K.; Gürkaynak, M. A. Polym Adv Technol 2009, 20, 165.
14. Çavuş, S.; Gürdağ, G. Polym Adv Technol 2008, 19, 1209.
15. Liu, J. S.; Ma, Y.; Zhang, Y. P.; Shao, G. Q. J Hazard Mater 2010, 173, 438.
16. Shin, J.; Fei, G.; Kang, S.; Ko, B.; Kang, P.; Nho, Y. C. J Appl Polym Sci 2009, 113, 2858.
17. Göktepe, F.; Bozkurt, A.; Tgünday, S. Polym Int 2008, 57, 133.
18. Hou, S.-S.; Kuo, P.-L. Macromol Chem Phys 1999, 200, 2501.
19. Cao, Z. Y.; Ge, H. C.; Lai, S. L. Eur Polym J 2001, 37, 2141.
20. Maji, S. K.; Pal, A.; Pal, T.; Adak, A. Sep Purif Technol 2007, 56, 284.
21. Ramesh, A.; Hasegawa, H.; Maki, T.; Ueda, K. Sep Purif Technol 2007, 56, 90.
22. Wang, J.; Kuo, Y. J Appl Polym Sci 2007, 105, 1480.