Thiolated Polyethyleneimine-Based Polymer Sponge for Selective Removal of Hg²⁺ from Aqueous Solution

Xiaoyi Gou, Yun Li,* Zia Ahmad, Xiuhua Zhu,* and Jiping Chen
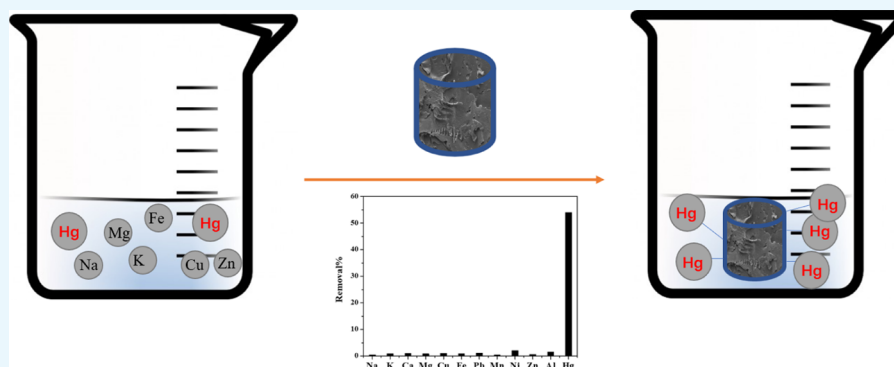
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ABSTRACT: Polymer sponges with molecular recognition provide a facile approach to water purification and industrial separation with easy operation. Herein, a thiolated polyethyleneimine (PEI)-based polymer sponge was prepared through cryo-polymerization of PEI, followed by grafting of PEI and then post-modification of the amine functionalities present within the hyperbranched structure with methyl mercaptoacetate, which afford high density of thiol functional groups on the surface of the sponge. The developed sponge was characterized by scanning electron microscopy and element analysis, and the adsorption kinetic and isotherm studies were conducted in detail. The sponge presents a remarkable maximum adsorption capacity of 2899.7 mg/g, which can be attributed to its high density of thiol functionalities. The sponge also shows excellent selectivity toward Hg²⁺ against other metal ions and natural organic matter, indicating its great potential in removing mercury from real water bodies. In addition, the sponge can be chemically regenerated and exhibits good reusability, which decreases the economic and environmental impacts. Hence, the high removal efficiency, high selectivity toward mercury, and good reusability of the sponge material highlight it as a promising sorbent for mercury removal in water pollution treatment.

1. INTRODUCTION

With the development of modern industry, water contamination by many pollutants especially heavy metals has gradually become a serious problem. Mercury has attracted special attention due to its high toxicity, long biological half-time, and bioaccumulation, which increase its potential for serious harm to the environment and human health.[1,2] Mercury can affect the human liver's function and cause a series of cardiovascular and cerebrovascular diseases. In addition, mercury in any form can become organomercury (such as methylmercury) under certain conditions that is extremely toxic to the nervous system and lethal at a dose of about 5 mg kg⁻¹ of body weight.[3] The culprit of Minamata disease, one of the world's eight major public hazards, in Kumamoto Prefecture, Japan, in 1956 was caused mainly by methylmercury in the industrial wastewater.[4] Due to the fact that trace amounts of mercury cannot be removed effectively in sewage treatment plants and its high mobility, mercury is accumulated in water bodies and becomes a global persistent pollutant in the aquatic environment.[5,6] In recent reports, mercury levels in groundwater have exceeded the maximum contaminant level of 2 μg L⁻¹ set by the US Environmental Protection Agency for drinking water.[7,8] Relatively high mercury levels (up to 5.4 μg L⁻¹) was reported for wastewater from hospitals. The discharge limit for mercury for industrial wastewater (50 μg L⁻¹), even the limit of 10 μg L⁻¹ is demanded by some local water authorities. The removal of mercury from the aquatic environment has so far been one of the greatest challenges and research hotspots.
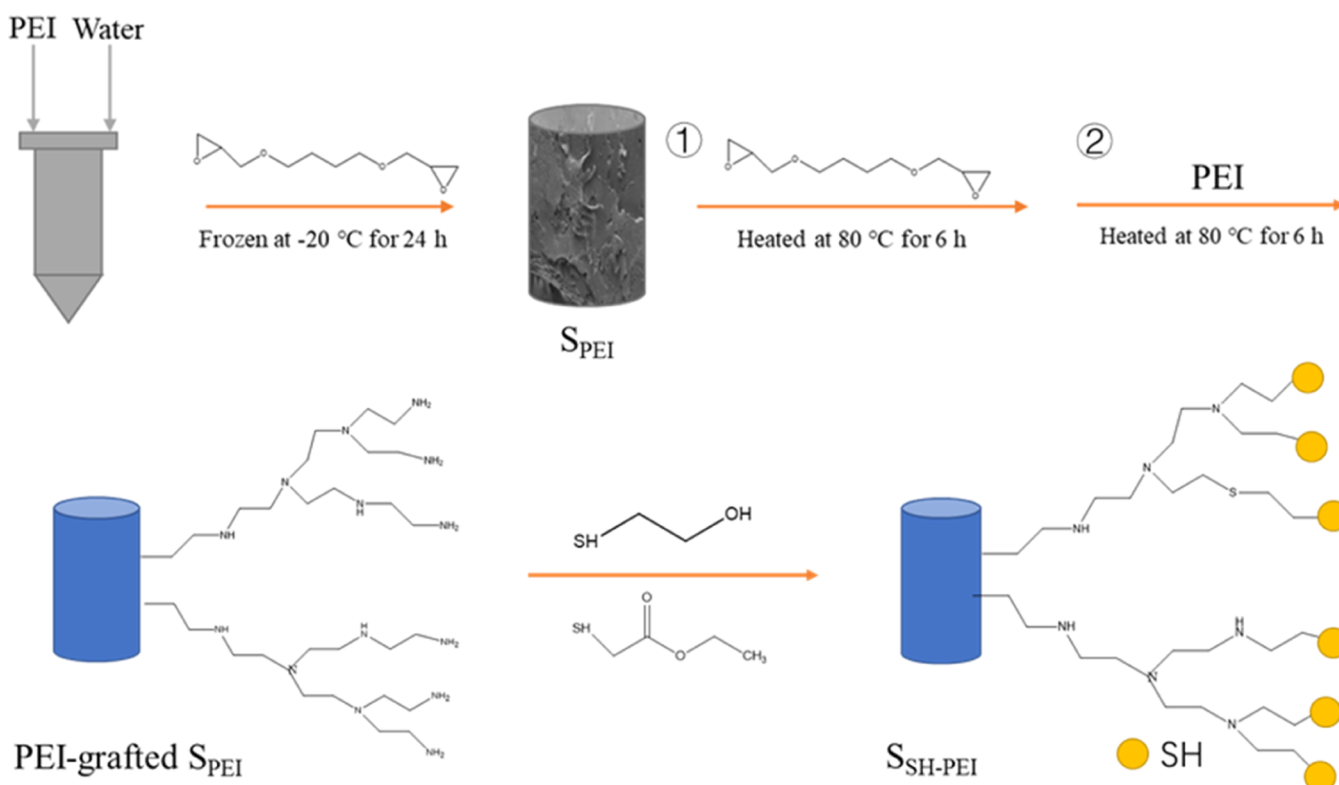
Figure 1. Schematic illustration of the fabrication.

Various processes and methods for removing mercury from wastewater have been developed including chemical precipitation,[9] electrochemical treatment,[10] ion exchange,[11] chemical oxidation or reduction, and chemical adsorption, and so forth.[12−14] However, most of these methods have some disadvantages or limitations such as causing secondary pollution, relatively high operating costs, and low removal efficiency. Among these different approaches, adsorption is an inexpensive and easily operated technique, with simple design in treatment facilities. Traditional adsorbents such as activated carbon, clay, chitosan, cellulose, silica gel, macroporous resin, and layered silicate have disadvantages of low selectivity, poor adsorption sites, and poor regeneration, which limit their practical applications in real mercury removal processes, especially for mercury at low levels.[15−18] Therefore, it is of great significance to explore and develop alternative adsorbent materials with high selectivity, high adsorption capacity, and the absence of secondary pollution. The creation or introduction of high density of chelating sites with high affinity on the surface of adsorbents would be a cost-effective method for mercury capture, especially for low concentration mercury.

Polyethyleneimine (PEI) as an outstanding adsorbent substrate has been widely used in the sewage treatment for heavy metals and organic pollutants. This typical hyperbranched polymer possesses numerous primary and secondary amine groups in its skeleton. It should be noted that the PEI-based monolithic adsorbents can take advantages of the combination of superior adsorption performance of PEI and facile separation from the solution. The sponge has unique properties such as high wettability, a large number of end groups, and internal molecular functional groups, which facilitate the penetration of waste water into the sponge and

full contact, and thus enables efficient and rapid adsorption of pollutants.[19] Liu et al. reported the preparation of macroporous polymeric sponges by ice templating of polyethylenimine aqueous solutions and their cross-linking in the frozen state. The large pore sizes of these sponges allow for rapid absorption of even high viscosity solvents such as pump oil.[20] Ahmad et al. presented the synthesis of bifunctionalized PEI-based sponges that simultaneously afforded a quaternary ammonium cation and phenyl functionalities via a bifunctional modification, for a highly selective removal anionic drug (diclofena), dye (methyl orange), and Cr (VI) species, respectively.[21] Privav et al. prepared PEI cryogels using three different cross-linking agents, which are applied in removal of heavy metals including Cu, Co, Ni, and Hg. However, PEI coordinates with most transition metals and cannot achieve highly selective and high-affinity recognition toward Hg, which greatly hinders its application in removing Hg at low concentration levels from complex water bodies.[22]

Herein, a hyperbranched thiol-functionalized spongy adsorbent for highly efficient removal of mercury in water was prepared via cross-linking, grafting, and thiolation, which exhibits remarkable properties including high selectivity, high adsorption capacity, good reusability, and low cost. Briefly, using hyperbranched PEI as the monomer and 1, 4-butanediol diglycidyl ether as the cross-linking agent, a polymeric sponge with a three-dimensional porous structure was first prepared by an ice templating method. An additional grafting of high molecular-weight PEI brought more plentiful amino functional groups on the surface of the spongy matrix, and the subsequent treatment with mercaptoacetic acid methyl ester yielded a large amount of thiol functionalities within the hyperbranched structure. According to the hard and soft acid−base theory, mercury has high affinity for sulfur. Therefore, thiol
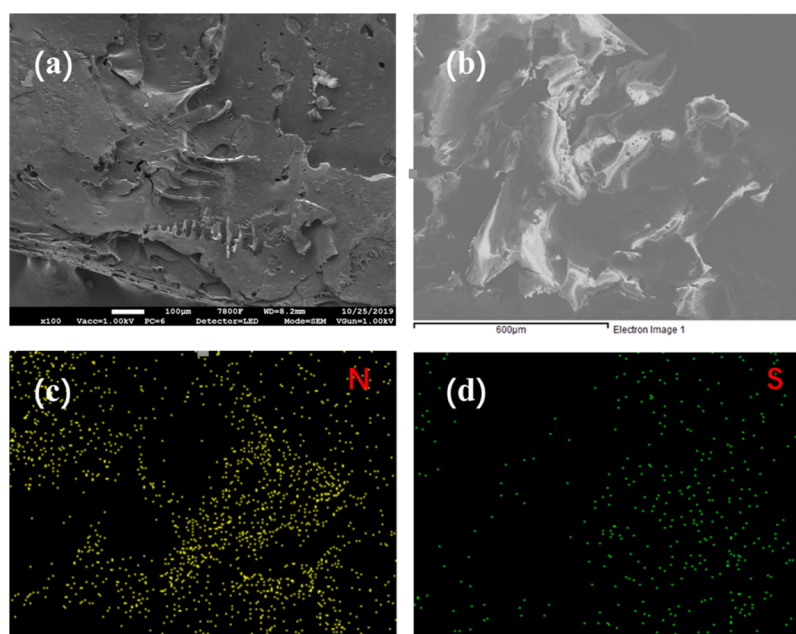
Figure 2. (a,b) SEM images of S_{SH-PEI} and (c,d) SEM/EDS mapping showing the distribution of nitrogen (N) and sulfur (S) in S_{SH-PEI}.

functionality prefers to coordinate with mercury ions in water to form extremely stable complexes. To evaluate the sponge's adsorption performance and understand the adsorption mechanism of mercury on it, the adsorption kinetic and isotherm, and the adsorption selectivity and reusability were investigated. As far as we know, at present, there is no report about the use of thiol-functionalized sponge for the removal of mercury in water.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterizations of S_{SH-PEI}. Figure 1 illustrates the preparation of a thiol-functionalized spongy material by transformation of reactive amine present at the surface of PEI-based sponge via grafting with hyperbranched polyethyleneimine (HPEI) and subsequent acrylation reaction. In detail, a spongy adsorption material with high content of amino groups was first prepared by cross-linking HPEI with 1,4-butanediol diglycidyl ether (BDDE) under cryogel conditions at −20 °C. In order to further increase the content of amino groups for subsequent thiolation, HPEI was grafted onto the surface of the obtained spongy material using diepoxide linkages, and the PEI grafted sponge was abbreviated as S_{PEI}. Subsequently, the S_{PEI} that contained plentiful amino groups on the surface was reacted with mercaptoacetic acid methyl ester to obtain thiolated S_{SH-PEI} via an amino intermediate.

For evaluation of the surface thiolation, both SEM/EDS and elemental analysis of the sulfur content were employed. As shown in Figure 2a, the S_{SH-PEI} presents a porous structure with pore sizes of 10−100 μm, which is conducive to the adsorption of Hg. The scanning electron microscopy (SEM) image (Figure 2a,b) of S_{SH-PEI} and the corresponding energy dispersive X-ray spectrometry (EDS) elemental mapping of N (Figure 2c) and S (Figure 2d) illustrate homogeneous distribution of N and S atoms in the skeleton of the dried S_{SH-PEI}. This result indicated that thiol groups have been successfully grafted on the S_{PEI} substrate. The elemental analysis results provided additional evidence for the successful

introduction of thiol groups. The sulfur contents before and after thiolation were 0% for S_{PEI} and 3% for S_{SH-PEI}, respectively. The decreased nitrogen content from 11.6% for S_{PEI} to 8.48% for S_{SH-PEI} also indirectly indicates the introduction of additional functionalities.

2.2. Adsorption Properties of SSH-PEI for Hg. *2.2.1. Effect of Solution pH.* Solution pH is a key factor that affects the accumulation and adsorption of heavy metal ions on the adsorbent because it influences both the chemical species of metal ions and the protonation and dissociation of the ligand. It is necessary to examine the influence of solution pH on removal efficiency of mercury in water using S_{SH-PEI}. The influence of pH on the removal of mercury was evaluated at various pH values (2, 3, 5, and 7) at a fixed metal ion concentration of 100 mg/L and an adsorbent dosage of 0.2 g/L at 25 °C. From Figure 3, it can be seen that the adsorption capacity of S_{SH-PEI} for mercury(II) ions increases with the
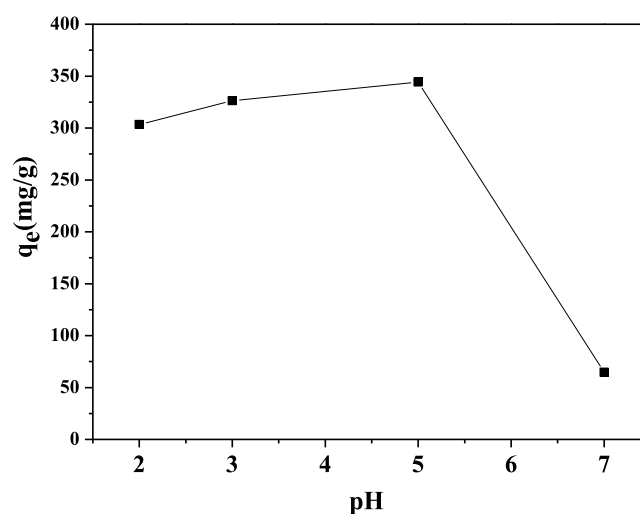

Figure 3. Effect of pH on the adsorption capacity of S_{SH-PEI} adsorbents. (conditions: C_0 = 100 mg/L, dosage = 0.2 g/L, t = 12 h).
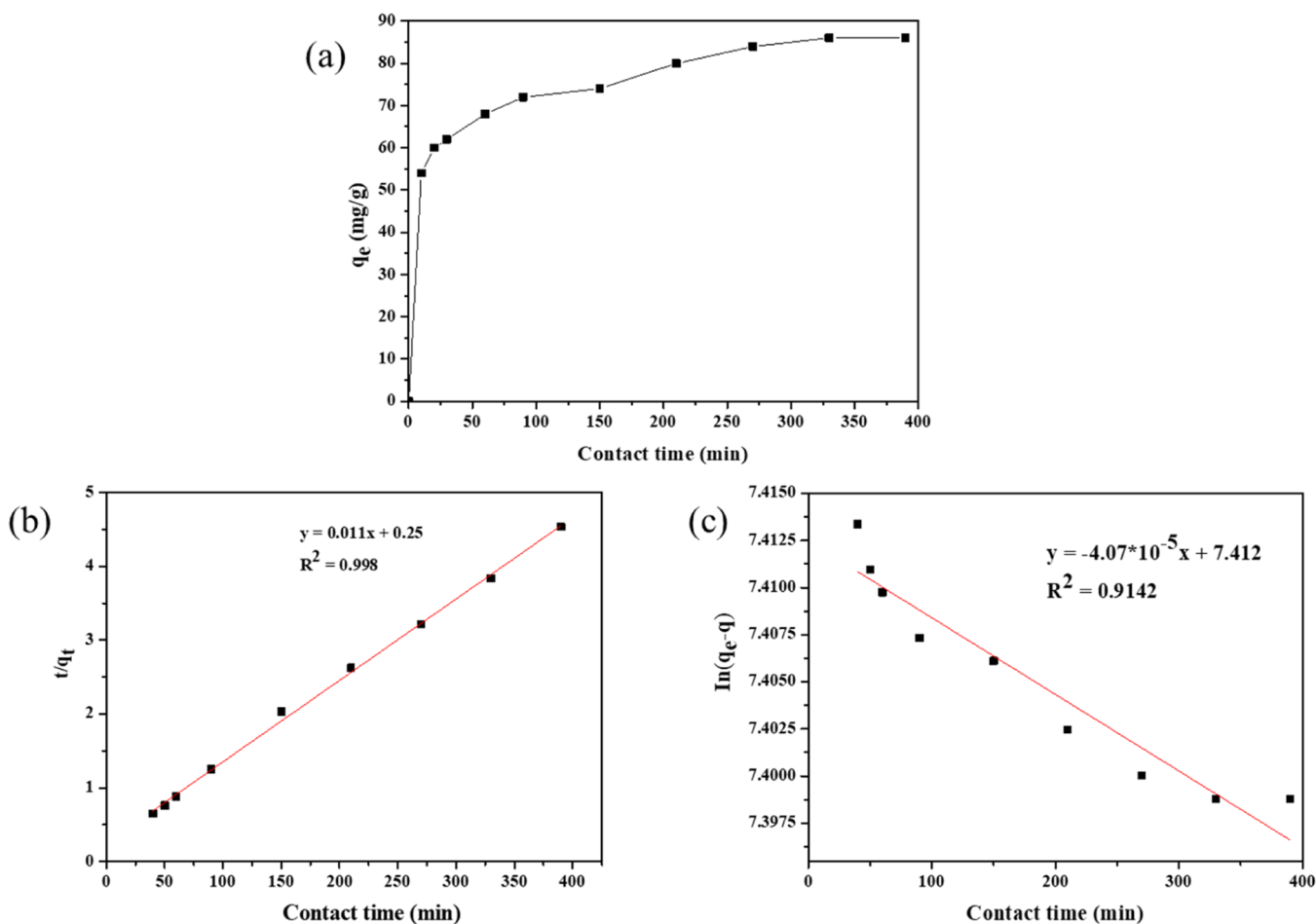
Figure 4. (a) Kinetic curves of adsorption process, (b) fitting for pseudo second-order equation, (c) fitting for pseudo first-order equation (conditions: C_0 = 100 mg/L, dosage = 0.2 g/L, pH = 5).

increase of pH at the ranges of 2−5. The adsorption capacity reaches a maximum of 344.3 mg/g at pH 5. The adsorption capacity of Hg^{2+} decreased from 344.3 to 64.8 mg/g when increasing the pH from 5 to 7. Hg(II) binding to the thiol-functionalized S_{SH-PEI} is strongly dependent on pH, especially in an acidic medium (pH < 5) where non-hydrolyzed Hg^{2+} species become dominant. In a more acidic medium, however, the sorption of the non-hydrolyzed Hg^{2+} species underwent dramatic loss of effectiveness, which resulted in lower capacities. They were interpreted on the basis of electrostatic considerations as the binding of Hg^{2+} to thiol groups leads to the generation of positively charged complexes in the host material. When the pH value was above 5, Hg(II) species were mainly in the form of $Hg(OH)_2$ and the obvious precipitation happened, which resulted in a sharp decrease in the adsorption capacity of S_{SH-PEI}.

It can also be seen from Table 2 that the adsorption capacity of S_{SH-PEI} for mercury(II) ions is higher than that of S_{PEI}, which indicates that the surface activity of the sponge obtains significant enhancement after grafting of thiol groups on the surface of the sponge. The result demonstrates that the introduction of −SH has a great promotion on the adsorption capacity of the PEI-based sponge, which is consistent with previous reports.[23−26]

2.2.2. Adsorption Kinetic Study. The Hg^{2+} adsorption levels at different time intervals are plotted against adsorption time and the results are shown in Figure 4. The results show that

68% of Hg^{2+} in the solution was adsorbed in the first 60 min, due to the presence of a large number of effective binding sites on the surface of the adsorbent. During the period from 60 min to 300 min, the adsorption tends to reach an equilibrium, which indicates that most of the adsorption sites on the adsorbent have been occupied, but there are still a small number of unoccupied binding sites that can absorb Hg. The adsorption of Hg reaches equilibrium after 330 min. These results suggest that a major limiting factor for Hg^{2+} adsorption by the sponge is likely molecular diffusion in the porous structure. Squeezing the sponge could reduce the equilibrium time to 30 min due to the faster diffusion and enhanced interaction between Hg^{2+} and S_{SH-PEI}. The affinity of S_{SH-PEI} for mercury can be evaluated by the distribution coefficient (K_d) defined as 0.61.

The kinetic models are used to fit and analyze the relevant data obtained in the adsorption kinetics experiment. The most widely used models for adsorption kinetics are the pseudo-first-order kinetic model (1) and the pseudo-second-order kinetic model (2).

$$\ln(q_e - q_t) = \ln q_e - k_1 \qquad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (2)$$

where q_e (mg/g) and q_t (mg/g) are the adsorption capacities at equilibrium time and time t (min), respectively. k_1 (1/min)

Table 1. Adsorption Kinetic Parameters of S_{PEI} and S_{SH-PEI} for Hg^{2+} Removal

materials	$q_{e,exp}$ (mg/g)	pseudo-first-order			pseudo-second-order		
		q_e (mg/g)	K_1 (min^{-1})	R^2	q_e (mg/g)	K_2 (g/mg·min)	R^2
S_{PEI}	480	310	0.008	0.933	445	0.00043	0.997
S_{SH-PEI}	1720	1590	0.06	0.948	1728	0.00012	0.998

Table 2. Characteristic Parameters of Langmuir and Freundlish Isotherms for the Adsorption of Hg^{2+} onto S_{PEI} and S_{SH-PEI}

materials	$q_{e,exp}$ (mg/g)	Langmuir isotherm				Freundlich isotherm		
		q_m (mg/g)	K_L (L mg^{-1})	R_L	R^2	K_f (L mg^{-1})	n	R^2
S_{PEI}	470.3	481.60	0.0055	0.045	0.833	57.82	3.86	0.800
S_{SH-PEI}	2899.7	3095.27	0.0008	0.078	0.861	22.96	1.74	0.994
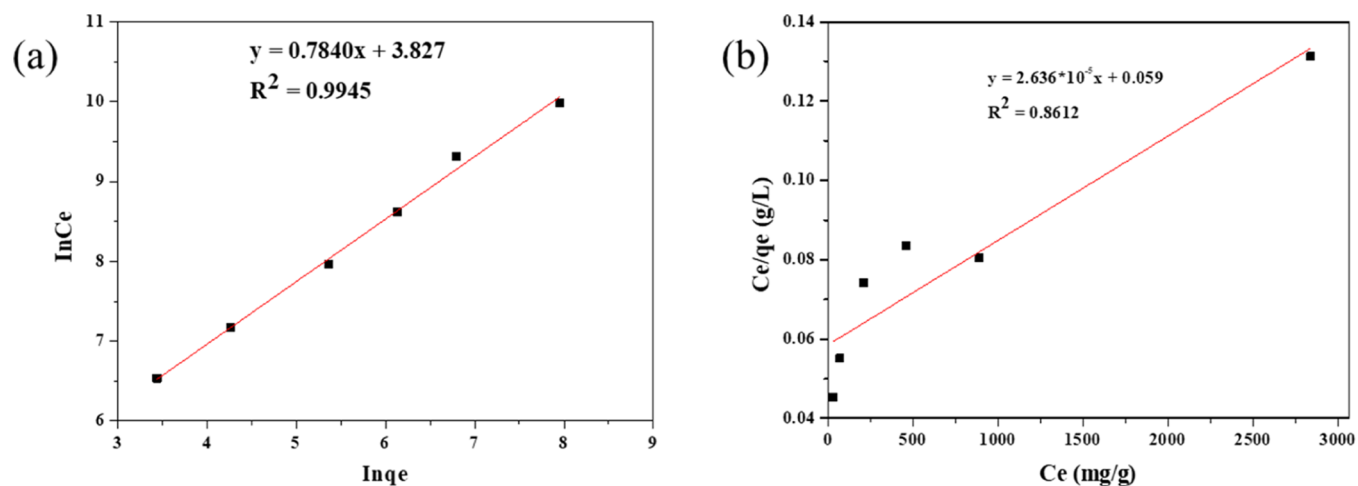
Figure 5. (a) Fitting for Freundlich equation, (b) fitting for Langmuir equation.

and k_2 [g/(mg·min)] are rate constants associated with pseudo-first-order and pseudo-second-order models, respectively. The slope and intercept values of linear plots of $\ln(q_e - q_t)$ vs (t) for pseudo-first-order and t/q_t vs (t) for pseudo-second-order are used to evaluate all corresponding parameters.

The results of Table 1 and Figure 4 show that the kinetic test data fit more with the pseudo-second-order kinetic model. The correlation coefficient (R^2) of the pseudo-second-order kinetic model (0.998) was higher than that of the pseudo-first-order kinetic model (0.948), and the equilibrium adsorption capacity calculated by which was closer to the experimental value. Therefore, the adsorption process of mercury onto S_{SH-PEI} can be better described by the pseudo-second-order kinetic model, which indicates that chemical bonding (interaction) between Hg^{2+} and functional groups on the surface of S_{SH-PEI} is responsible for the adsorption process.

2.2.3. Adsorption Isotherm Study. In order to further explore the thermodynamic behavior of S_{SH-PEI} adsorbing trace mercury in water, the thermodynamic parameters of the adsorption process were determined by performing a series of adsorption tests with initial concentrations ranging from 100 to 5000 mg L^{-1}. The experimental data of Hg^{2+} adsorption were analyzed using the Langmuir and Freundlish adsorption isotherm models as demonstrated by eqs 3 and 4.

$$q = q_m \frac{K_L C_e}{1 + K_L C_e} \tag{3}$$

$$q = K_f C_e^{1/n} \tag{4}$$

The analysis results in Table 2 and Figure 5 show that the thermodynamic experimental data are better described by the Langmuir model, with the corresponding correlation coefficient greater than 0.99 ($R^2 = 0.998$), in comparison to the Freundlich model ($R^2 = 0.914$). There is no difference between the maximum adsorption capacity value calculated according to the Langmuir model and the actual experimental value within the error range. Therefore, the adsorption process of Hg^{2+} onto S_{SH-PEI} is dominated by a continuous monolayer chemisorptions' process. This result is consistent with these obtained from the adsorption isotherms of sulfhydryl functionalized materials reported previously in the literature. Because the fitting has a high degree of consistency with the Freundlich model, but has no good correlation with the Langmuir model, the adsorption process occurs on a highly homogeneous surface.

2.2.4. Adsorption Selectivity. The adsorption selectivity is a key metric that quantifies the efficacy of any adsorbent in mixture separations. Real aquatic environment is very complicated and contains a lot of interfering ions and dissolved organics, which may occupy the adsorption sites of S_{SH-PEI} and thereby affect the adsorption efficiency toward mercury. The

most fundamental reason for using thiol-modified PEI-based sponge is that sulfur has a stronger affinity toward Hg than other metals. Na^+, K^+, Ca^{2+}, and Mg^{2+} are common metal ions in drinking or surface water, and some transition metal ionic pollutants such as Cu^{2+}, Pb^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, and Al^{3+} often occur in wastewater. The interference of K^+, Mg^{2+}, Na^+, Ca^{2+}, Cu^{2+}, Pb^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, and Al^{3+} metal cations for mercury adsorption in a mixed system were investigated. Figure 6 presents the removal efficiencies for 11 different metal
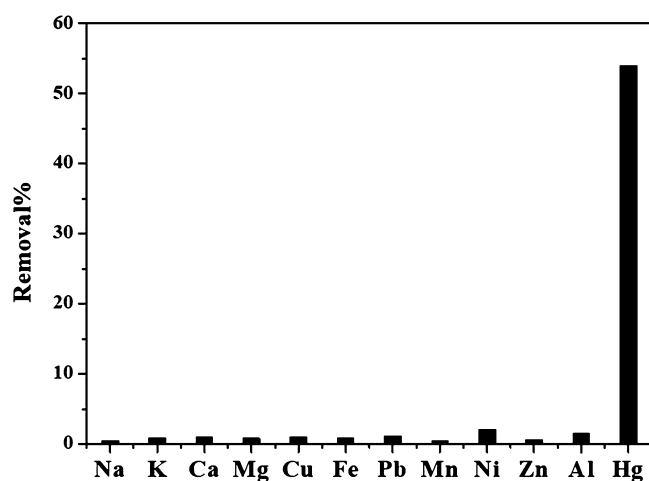

Figure 6. Selectivity for the detection of Hg^{2+} by SSH-PEI in the presence of other metal ions. (conditions: C_0 = 100 mg/L, dosage = 0.1 g/L, t = 12 h, pH = 5).

ions after exposure to S_{SH-PEI} for 6 h. The results showed that S_{SH-PEI} did not adsorb K^+, Mg^{2+}, Na^+, Ca^{2+}, and other transition metal ions presented a minor decrease of 0.4–2.1% in removal efficiency. Even with the presence of other interfering metal ions with equal mass concentrations, the mercury removal efficiency using S_{SH-PEI} was still the highest among the metal ions, showing an excellent selectivity toward mercury.

The effect of humic acid as a model for natural organic matter on mercury adsorption was investigated by treating ~5 mg of S_{SH-PEI} adsorbent in a 50 mL solution containing 100 mg/L of mercury with varying concentrations of HA from 0, 5, 10 to 20 mg/L. The results are listed in Figure 7. We can see that the presence of humic acid does not have a serious impact on mercury adsorption. As the concentration of humic acid increases up to 20 mg/L, the mercury removal efficiency decreases by only 5%. This is possibly due to the fact that higher concentration of humic acid occupies more adsorption sites.

The HPEI sponge has a three-dimensional network structure and a high adsorption rate, which facilitates the penetration of wastewater into the sponge and facilitates full contact, thereby enabling efficient and rapid adsorption of target pollutants. The sulfhydryl functionalized polymer material can remove mercury with high selectivity through coordination and chelation. These advantages make the material exhibit ultrahigh adsorption capacity. Compared with other adsorption materials, it also has great advantages. The data are listed in Table 3.

2.3. Regeneration and Reusability. In order to assess the recyclability/reusability of the sponge, sorbent regeneration and reuse experiments were performed. Figure 8 shows
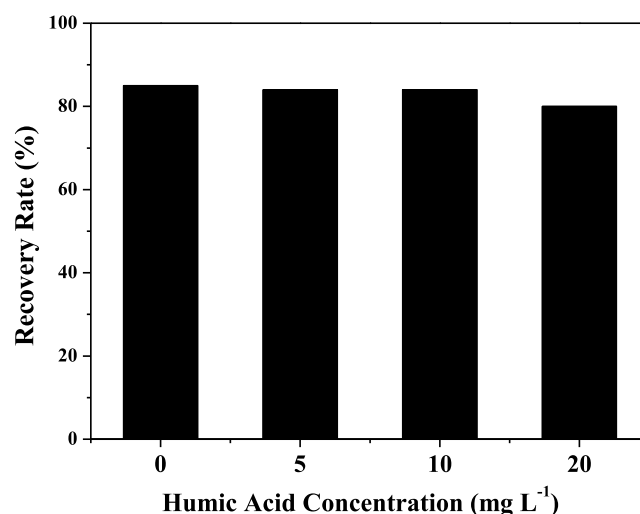

Figure 7. Selectivity for the detection of Hg^{2+} by S_{SH-PEI} in the presence of Humic acid. (conditions: dosage = 0.1 g/L, t = 12 h, pH = 5).

the removal efficiencies of mercury as a function of reuse cycles of regenerated S_{SH-PEI}. The adsorption performance of S_{SH-PEI} decreased only by 3% after four times of reuse. The main possible reason for the slight decrease in adsorption efficiency is that part of the adsorbed Hg firmly occupies the adsorption sites and cannot be eluted, and some inactive sites on the surface of the sponge are produced after multiple adsorptions and desorption processes. The good regeneration performance of S_{SH-PEI} for the removal of mercury further confirmed that the developed thiol-functionalized spongy material can be a promising adsorbent for removing mercury from water.

2.4. Removal of Hg^{2+} from Real Water. The S_{SH-PEI} was applied to real water samples for testing its performance, and bottled mineral water was used. Hg was not detected in the bottled mineral water using the current method, and 200 mL bottled mineral water samples that spiked at 10, 20, and 30 μg/L levels were adopted for adsorption experiments. The experiments show that at an adsorbent dosage of 0.025 g/L, the Hg^{2+} concentrations of 10, 20, and 30 μg/L spiked mineral water were reduced to 1.8, 3.3, and 5.3 μg/L, respectively.

3. CONCLUSIONS

In this study, a new type of sulfhydryl functionalized copolymer S_{SH-PEI} was developed and evaluated for removing mercury from water. The new sorbent technology is based on direct copolymerization, grafting, and thiolation of hyperbranched PEI. The effects of parameters such as pH, adsorption time, and initial concentration on the adsorption performance of this adsorbent were investigated. The results show that S_{SH-PEI} can be used to remove mercury in water in a wide acidic pH range, and can achieve high-efficiency removal of mercury in water in a short time (less than 2 h). The sponge presents a remarkable maximum adsorption capacity of 2899.7 mg/g, which can be attributed to its high density of thiol functionalities within the hyperbranched structure extended from PEI. The sponge also shows excellent selectivity toward Hg against other metal ions and natural organic matter, indicating its great potential in removing mercury from real water bodies. In addition, the sponge can be chemically regenerated and exhibits good reusability, which decreases the economic and environmental impacts. These findings

Table 3. Hg^{2+} Adsorption Performance of the Developed Sponge and other Reported Adsorbents

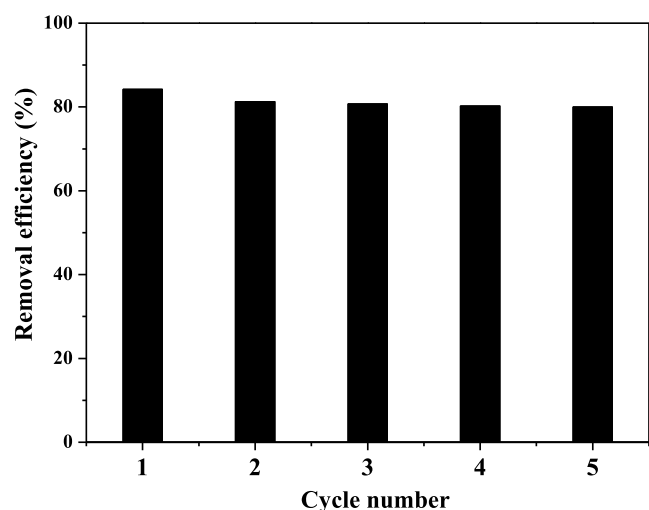|	adsorption conditions				
adsorbent	reuse times	equilibrium time for reaching drinking water level (min)	functionalized groups	q_{max} (mg/g)	refs
PAF-1-SH	3	7	thiol group	1000	27
M-MSPNPs	4	10	carboxy group	734	28
MFC-S	5	20	thiol group	282	29
TAPB-BMTTPA-COF	6	15	methyl sulfide units	734	30
SMP	4	3	sulfur atoms	595	31
S_{SH-PEI}	289	N/A	thiol group	2899	present work

Figure 8. Hg^{2+} removal efficiencies (%) by S_{SH-PEI} in 5 subsequent adsorption–desorption cycles. (conditions: C_0 = 100 mg/L, dosage = 0.2 g/L, t = 12 h, pH = 5).

suggested that the thiolated PEI-based sponge is a promising adsorbent for removing mercury from natural water bodies.

4. MATERIALS AND METHODS

4.1. Chemicals and Materials. Two HPEI (average Mw ∼ 1000 Da and ∼70 000 Da), methyl mercaptoacetate, and mercury standard solution (5000 μg/mL) were supplied by Sigma-Aldrich (Milwaukee, USA). BDDE (98%) was obtained from Alfa Aesar (Tianjin, China). Thioglycol was obtained from Acmec (Shanghai, China). Sodium hydroxide (NaOH), nitric acid (HNO_3), and methanol were supplied by Beijing Chemical Works (Beijing, China). The water used in all experiments was deionized water from a Milli-Q purification system (Billerica, MA, USA).

4.2. Preparation of Thiolated PEI-Based Sponge. A cryo-polymerization technique was used to prepare the PEI-based sponges via epoxy–amine reactions as described previously.[22] In a typical synthesis, 1.4 g of water and 1 g of 10% PEI solution (containing 2.38 mmol of CH_2CH_2N units) were vortex-mixed into an eppendorf tube, followed by the addition of 0.3 g of BDDE as a cross-linker to form a homogeneous solution. The precursor solution was immediately placed in a −20 °C freezer for 24 h for cryo-polymerization. The PEI cryogel was obtained by the procedure of thawing at room temperature, followed by washing with large amounts of water five times. In order to further improve the amount of amines for subsequent thiolation, a PEI functionalization step was performed by immersing the PEI-based sponge in 10% PEI aqueous solution at 80 °C for 4 h, followed by washing with large amounts of

water five times and drying in a vacuum oven at 50 °C for 12 h. The obtained sponge was abbreviated as S_{PEI}.

In order to get a thiol-functionalized sponge, the S_{PEI} obtained in the previous step was soaked in a solution of methyl mercaptoacetate and mercaptoethanol (v/v, 50/50), and then was heated at 80 °C for 24 h.[32] Finally, the mercaptoethylamide-modified sponge (abbreviated as S_{SH-PEI}) was washed repeatedly with ethanol and then water to remove unreacted reagents. Before adsorption, the adsorbent was dried overnight under vacuum at 50 °C and stored in a desiccator.

4.3. Characterizations and Instruments. The obtained materials were characterized by the following analytical techniques. A JSM-7800F scanning electron microscope (Peabody, MA, USA) with an SEM-EDS was used to observe the morphology of the sponge. Thermogravimetric analysis was carried out to test the thermal stability in the atmosphere of nitrogen at a heating rate of 10 °C/min over a temperature range of 40−780 °C, with an initial sample weight of approximately 10 mg, using a NETZSCH STA 449 F3 thermal analyzer. Inductively coupled plasma optical emission spectrometry (ICP-OES) measurements were performed with a PerkinElmer apparatus (NexION 300D). Determination of mercury content was performed on an AFS-230E double-channel atomic fluorescence spectrometer (AFS, Beijing Haiguang, China).

4.4. Batch Adsorption Experiments. The effect of initial solution pH, adsorption time, and initial concentrations on mercury adsorption onto S_{SH-PEI} were investigated using a batch adsorption study. Batch adsorption of mercury was conducted in 250 mL stoppered conical flasks containing 20 mg of S_{SH-PEI} in 100 mL of mercury solutions. The mixtures were shaken at 120 rpm for 2 h at 25 °C. After binding, the solutions were filtered through a 0.45 μm poly-(tetrafluoroethylene) membrane filter and determined using hydride generation AFS. Adsorption kinetics was obtained by taking the samples after different intervals (10, 20, 30, 60, 90, 150, 210, 270, 330, 390 min) with a fixed pharmaceutical starting concentration (50 mg L^{-1}). Adsorption isotherms were produced by varying the initial concentrations from 100 to 5000 mg L^{-1}, and the pH-dependent adsorption were generated with a fixed pharmaceuticals concentration (50 mg L^{-1}) and varying pH at 2, 3, 5, and 7. The solution pH was adjusted using 0.1 M NaOH or HCl to the desired value. In the adsorption test, the adsorbent dosage was fixed at 0.2 g L^{-1}. Except for the experiments for estimating the effect of pH, the solution pH was maintained at ∼5.

The effect of competitive metal ions on mercury adsorption was also evaluated by contacting 20 mg of S_{SH-PEI} with 200 mL of mixed solution containing an equal concentration of Cu, Fe, Pb, Mn, Ni, Zn, Al, and Hg ions (the concentration of each ion is 100 mg L^{-1}). The adsorption was carried out at optimized

pH for 12 h. The residual concentrations of different metal ions were analyzed by ICP-OES.

The removal efficiency (R_e %) and adsorption capacity at equilibrium (q_e) were calculated according to eqs 5 and 6, respectively.

$$R_e \% = (C_0 - C_e)\frac{100}{C_0} \tag{5}$$

$$q_e = (C_0 - C_e)\frac{V}{W} \tag{6}$$

where C_0 and C_e are the initial and equilibrium concentrations of metal ions in solution ($mg\ L^{-1}$), respectively; V is the volume of solution (L), and m (g) is the mass of adsorbent.

4.5. Regeneration and Recycling Studies. For the desorption experiments, the Hg-loaded sponge was collected from the solution and was slightly squeezed to force the solution out. Then, the Hg-loaded sponge was placed in a series of glass vials containing 10 mL of 6 M HCl, and the mixture was stirred at 25 °C for 2 h. The final concentration of Hg (II) ions in the eluent was determined by AFS. After desorption, the recovered adsorbent was treated with 0.005 M NaOH to restore the pH of the surface to pH 5 then washed with deionized water three times, and then subjected to the next four adsorption−desorption recycles with the same procedure described above.

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Notes
The authors declare no competing financial interest.

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