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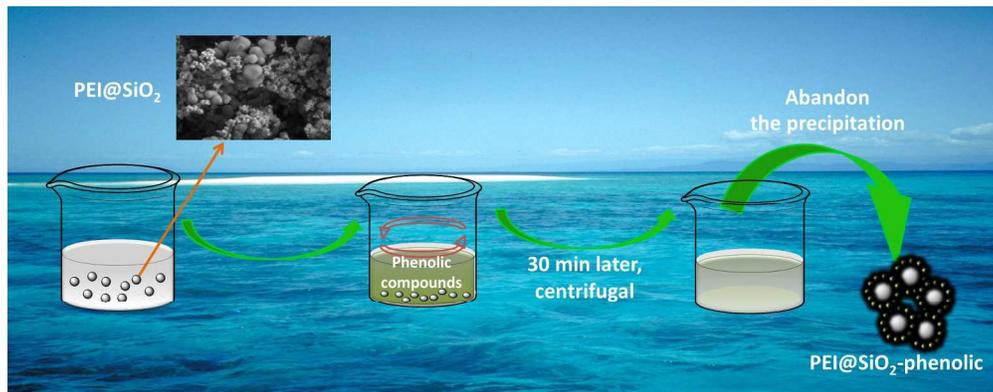


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PAPER

PEI@SiO₂: synthesis from diatomite and application for capturing phenolic compounds from aqueous solution

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The "dissolving and rebuilding" way was applied to prepare the diatomite - ethyleneimine polymer (PEI) hybrid composite and its structure and topography were characterized by XRD, SEM, TEM, FTIR, DTG, elemental analysis and ζ-potential. The result indicated that the PEI was efficiently assembled into the SiO₂ framework formed from diatomite. The composite was tried to remove phenolic pollutants e.g. phenol, *o*-chlorophenol and bisphenol A (BPA) from aqueous solution. These adsorptions were to match lipid-water partition law and their *K_{ow}* values were calculated to be 79.1 L/kg for phenol, 37.3 L/kg for *o*-chlorophenol and 24.2 L/kg for BPA.

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1. Introduction

Phenolic compounds are nearly ubiquitous contaminants because of their widespread appearance in wastewater of discharged oil refineries, paint, drug and pesticide industries, as the intermediates of processes¹. The potential toxicity of phenol derivatives has received increasing attention, and some of them have been proven²⁻⁵. For example, bisphenol A (BPA) can cause damage to reproductive system and affect cellular development⁵⁻⁷. Chlorophenol may cause inflammation in the digestive system and increase blood pressure⁸. Due to their toxicity, phenolic compounds are the two classes of compounds widely prevalent and classified by the US Environmental Protection Agency as priority pollutants⁹. Per the recommendation of the World Health Organization, the threshold concentration of phenol in drinking water should fall below 1.0 μg/L¹⁰.

During the past decades, the development of efficient techniques for removal of highly toxic organic compounds such as pesticides, fertilizers, hydrocarbons, phenols and plasticizers from wastewater, has drawn significant interests¹¹⁻¹⁴. Adsorption technique was quite popular due to its simplicity, as well as the availability of a wide range of adsorbents¹⁵⁻¹⁶. For the adsorption of phenolic compounds from aqueous solution, various adsorbents such as granular activated carbon and fibrous activated carbon¹⁷, mesoporous alumina-aluminium phosphates¹⁸, synthetic polymers¹⁹ and ion exchange resins²⁰ have been used. In recent years, a strategy to remove organic pollutants by using natural mineral was well developed owing to the flexibility, general applicability and low cost²¹⁻²³. However, the low adsorption capacity and poor selectivity restrict their application of original natural mineral²⁴. Recently, further efforts in the chemical modification of the pristine minerals have offered new possibilities to prepare new materials with superior performances for a variety of applications. For instance, Bhardwaj *et al*

modified clinoptilolite and zeolite Y for adsorbing 2,4-dichlorophenoxyacetic acid²⁵; Xie *et al* demonstrated a versatile chitosan modified zeolite for the removal of different pollutants from water²⁶. So far, impregnating, acid pickling, calcining and ionic-exchanging have been often employed to modify the natural pristine mineral. However, the conventional surface modification usually brings out some serious defects, for example unapparent improvement on the adsorption capacity and easy separation of active group^{10, 27-28}.

PEI, which is composed of a large number of primary and secondary amine groups²⁹, exhibits an outstanding adsorption ability to various pollutants³⁰⁻³¹ e.g. carbon dioxide³², heavy metals^{29, 33} and phenols³⁴. Diatomite is known as an adsorbent for pollution control³⁵⁻³⁷. It can be dissolved easily to form abundant amorphous silica (SiO₂·nH₂O) under hydrothermal conditions. In previous papers, mesoporous materials, such as MCM-41³⁸⁻⁴¹, mordenite⁴² and ZSM-5 zeolites⁴³⁻⁴⁴, have been obtained from natural diatomite under hydrothermal conditions. Thus it is possible to turn diatomite and PEI into a multifunctional hybrid adsorbent for phenols by a "dissolving and rebuilding" way.

In the present work, an innovative approach i.e. dissolving and rebuilding was utilized to prepare a hybrid composite PEI@SiO₂ by dissolving PEI in the diatomite alkaline solution. As an excellent sorbent, it was used to adsorb the phenolic compounds with a high adsorption capacity. The simple synthesis overcomes the above disadvantages of the traditional surface modification.

2. Experimental

2.1 Apparatus and materials

A photodiode array spectrometer (Model S4100, Scinco, Korea) was used to determine phenolic compounds in aqueous solutions. The concentrations of mixed phenolic compounds in

the supernatants were measured by high-performance liquid chromatography (HPLC) with a DAD detector (Model LC 2000, Hitachi, Japan). The elemental analysis device (Model Vario EL III, Germany) was used to determine C, N and H content of the hybrid composite. The microstructure and morphology of the material was measured by scanning electronic microscopy (SEM) (Model Quanta 200 FEG, FEI Co., USA) was used to measure and transmission electron microscopy (TEM) with energy dispersive X-ray detector (Model TECNAI G2 S-TWIN, FEI Co., USA). The FT-IR spectra of the hybrid composite were obtained, using an infrared spectrometer system (Model Equinox/hyperion 2000, BRUKER Co., Germany). The X-ray diffraction (XRD) (Model Bruker D8 Advance, Germany) was recorded using CuK radiation in range of $10 - 90^\circ 2\theta$ at 40 kV and 40 mA. A thermal analysis system (Model Q600 SDT Simultaneous DSC/TGA, TA instruments, USA) was used for thermogravimetry analysis (TGA) of the materials. A ζ -potential instrument (Zetasizer Nano Z, Malvern, United Kingdom) was used to determine the surface potential of the PEI@SiO₂ composite. An inductively coupled plasma optical emission spectrometer (ICP-OES) (Model Optima 2100 DV, PerkinElmer, USA) was used to determine metal contents in materials.

Diatomite (Aladdin Agents, China), sodium hydroxide (Aladdin Agents, China), PEI (M.W. 600, Aladdin Agents, China), sodium chloride (Aladdin Agents, China), hydrochloric acid (Sinopharm Chemical Reagent Co., Ltd, China) were used. Three phenolic compounds i.e. phenol, *o*-chlorophenol and BPA (Aladdin Agents, China) adsorbing on the PEI@SiO₂ were investigated. (As, Bi, Cd, Cu, Cr, Fe, Hg, Mn, Ni, Se, Pb, Zn) multi-element mixed standard solution (100ppm, Aladdin Agents, China) were used.

2.2 Synthesis and characterization of the PEI@SiO₂

20 g of diatomite was added into 1000 mL of 2 mol/L sodium hydroxide, stirred at 500 rpm for 24 h at 363 K. The mixture was centrifuged to remove insoluble residue into the supernatant containing 17.66 g/L diatomite, 0.21 M PEI was added and the solution was adjusted to pH 10 with 1 M HCl under stirring. After 24 h, the PEI@SiO₂ suspension was centrifuged and washed for several times with deionized water. The PEI@SiO₂ product was dried and ground into powder for characterization of the structure, composition and morphology. The PEI content was calculated by determining C content with an elemental analysis device. The PEI@SiO₂ powder was digested with 2.0 M sodium hydroxide and the Al, Fe and Si content in the supernatant were determined by ICP-OES. With the same method, the SiO₂ - only product formed from diatomite was prepared where PEI was not added.

2.3 Adsorption of phenolic compounds

The adsorption capacity of the PEI@SiO₂ composite to three phenolic compounds was determined. The phenol solutions from 6 to 500 mg/L were treated with 0.3% of the PEI@SiO₂ composite. All of the liquids were mixed for 30 min at 500 rpm by magnetic stirrer and then centrifuged to separate adsorbent residue. The phenol concentration remained in the supernatants

were determined by UV spectrophotometry. With the same method, the *o*-chlorophenol solutions from 6 to 650 mg/L and the BPA solutions from 3 to 400 mg/L were treated.

The influences of pH from 3 to 11, ionic strength from 0 to 0.25 M, temperature from 298 to 328 K and the mixing time from 0 to 30 min were investigated for three phenolic compounds adsorbing in the PEI@SiO₂ composite.

2.4 Treatment of phenolic wastewater and disposal of the waste

The three phenolic wastewaters respectively containing 20 mg/L phenol, 42 mg/L *o*-chlorophenol and 38 mg/L BPA were treated with the PEI@SiO₂ from 0.1 to 1.8%. The phenolic compound remained in each supernatant was determined by UV spectrophotometry. In addition, their mixed solution was treated with the PEI@SiO₂ from 0.1 to 1.8%, too. The phenolic compounds in the supernatants were determined by the high-performance liquid chromatography (HPLC) with a DAD detector (Model LC 2000, Hitachi, Japan), where phenol was detected at 270 nm at 5.64 min, *o*-chlorophenol at 275 nm at 6.56 min and BPA at 286 nm at 8.36 min. The flow phase consisted of CH₃OH and H₂O according to 50:50 (V:V) at 0.5 mL/min of the flow speed through a chromatographic column (Model Allsphere ODS-25 μ m, Length 250 mm). The injection volume was 20 μ L.

20 g of the phenol-PEI@SiO₂ waste produced above was calcined for 6 h at 550 °C with a Muffle furnace (Model SXL-1008, Shanghai Jinghong Lab Equipments Co., China). The residue was ground into powder approximately being 200 mesh. The 0.5 % (w/v) of the phenol-PEI@SiO₂ waste calcined respectively was added into the (As, Bi, Cd, Cu, Cr, Fe, Mn, Ni, Se, Pb) multi-element mixed standard solution (1 mg/L) at pH 5 under stirring for 2 h. After the mixtures were centrifuged, the removal rates of pollutants in the supernatants were determined by ICP.

3. Results and discussion

3.1 Interaction of PEI with diatomite

By hybridizing PEI with diatomite to prepare the PEI@SiO₂ composite, the hybridization amount of PEI increases with increase of the PEI dosage and then approaches equilibrium (Fig. 1A). The hybridization of PEI obeys the Langmuir isotherm model (Fig. 1B), i.e. $c_e/q_e = 1/K_f q_\infty + c_e/q_\infty$, where c_e is the equilibrium molarity of PEI in mol/L, q_e is the amount of PEI embedding in diatomite in mg/g, q_∞ is the saturation hybridization amount of PEI in mg/g and K_f is the binding constant of PEI. The maximum of PEI embedding in the PEI@SiO₂ composite approaches 258 mg/g and the K_f is calculated to be 25.4 M⁻¹. A strong interaction, i.e. high affinity occurs³⁴ between PEI and diatomite. The Gibbs free energy (ΔG) is less than zero, indicative of the spontaneous interaction of the PEI@SiO₂. From the effect of pH on the hybridization of PEI (Fig. 1C), the hybridization amount of PEI increases with increase of pH from 7 to 10 and then declines very slightly. Thus, the preparation of the hybrid material is carried out at pH 10. Diatomite is hydrolyzed to form the dissolved diatomite. The dissolved diatomite and PEI

with the initial weight ratio 1: 7 are applied to prepare the PEI@SiO₂ at pH 10 (see the experiment section).

The basic chain structure of PEI is the alkyl chain (-[CH₂-CH₂-NH]_n), so there are a large number of nitrogen atoms of amino groups on the macromolecular chains of PEI. In aqueous solution, they may combine easily with H⁺ to form -[CH₂-CH₂-NH₂⁺]_n^{11, 46-47}, that means that majority of amino groups on PEI chains are protonated. The chain of PEI may be positively charged, i.e. forming cationic polyelectrolyte³⁴. Whereas diatomite particles are negatively charged, so both attract each other and PEI is adsorbed compactly to the surface of diatomite particles. The ζ-potential of diatomite-only is determined to be -34.0 mV in aqueous media while that of the PEI@SiO₂ composite changes to +12.9 mV. After hybridizing, the electric property of the surface of diatomite changes substantially, it depends on the character of macromolecule PEI, so the surface of modified diatomite has positive charge because of the strong acceptability of N atoms of PEI chains for protons. Thus, the electrostatic interaction occurs between PEI⁺ and diatomite.

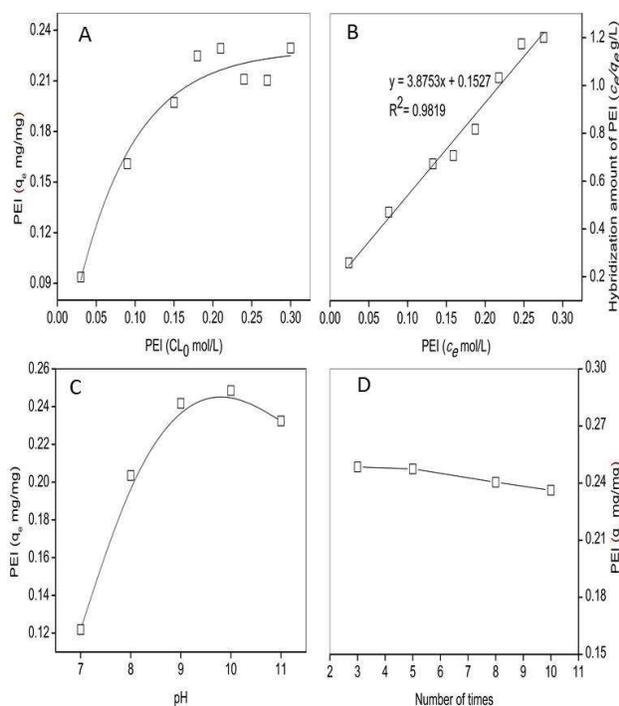


Fig. 1 Effect of PEI on the hybridization. A: plots q_e vs c_0 , B: Plots c_e/q_e vs c_e . C: Effect of pH on the hybridization of PEI. D: Effect of water washing on the hybridization of PEI.

It is well known that the main composition of diatomite is SiO₂ (88%), Al₂O₃ and Fe₂O₃⁴⁸. The molar ratio of PEI to Si, Al and Fe is calculated 1 : 248.5 : 61.8 : 2.6 in the PEI@SiO₂, which is determined by element analysis and ICP. It provides an evidence for the formation of the PEI@SiO₂ composite. Approximately 248.5 mg/g PEI is embedded in the composite, which is much more than one of the others reported. In previous papers, Gao introduced an interesting study for modifying diatomite by PEI impregnating and the maximum of PEI embedding in the diatomite approached 128 mg/g³⁴, Öztekin employed bentonite clay particles to adsorb PEI the maximum of PEI embedding approached 145 mg/g⁴⁹. Then the “dissolving and rebuilding” approach increases more hybridization capacity of PEI than the

conventional surface modification approach. In addition, easy migration of active groups and causing secondary pollution are some serious defects of the conventional surface modification⁵⁰⁻⁵¹. They limit the applications of the conventional surface modification. From the effect of water washing on the hybridization of PEI (Fig. 1D), PEI cannot be separated from the PEI@SiO₂ composite by washing with water, which shows that the “dissolving and rebuilding” approached exhibits a better resistant to migration of active groups than the conventional surface modification. Therefore, the composite is suitable for treatment of wastewater.

3.2 Structure and morphology of the PEI@SiO₂

As shown in Fig. 2A, the absorption peaks at 2935 (C-H stretching), 2819 (C-H stretching), 1756 (-NH₂ and -NH-deformation) and 1471 (-NH₂ and -NH- deformation) cm⁻¹ indicate PEI embedding in the PEI@SiO₂ composite is confirmed from its infrared spectra (IR). The Si-O absorption peak is at 1059 cm⁻¹. The XRD patterns for only-SiO₂ and the PEI@SiO₂ are shown in Fig. 2B. XRD patterns of only-SiO₂ and the PEI@SiO₂ all show a broad diffraction peak from 2θ = 15-30°, which indicates that SiO₂ holds mainly amorphous silica structure and there is no prominent difference that occurred due to PEI in the PEI@SiO₂ composite⁵²⁻⁵⁴, which shows that the main structure of the hybrid composite remains unchanged. If there is a nanocrystalline silica material, corresponding peaks should be observed at a definite diffraction angle⁵⁵. Similar work based on the addition of Ionic liquid coated sulfonic acid⁵⁴, β-cyclodextrin⁵⁶ and nanosized NiO particles⁵⁷ with functionalized amorphous silica composites have been reported with the prominent XRD peaks. As seen in the thermal gravimetric analysis (TGA) differential thermal gravity of the PEI@SiO₂ (Fig. 2C), the first step in the range of 40 to 200 °C is attributed to the removal of the physisorbed water and interlayer water⁵⁸. Additional observed weight loss steps indicated the behavioral complexity of decomposition of the various covalently attached organic phases⁵⁹. The second step in the range of 200 to 400 °C is due to the removal of branched chain group of PEI and the third step in the range of 400 to 500 °C due to the removal of straight chain of PEI. Similar TGA weight losses profiling also arose from previous reports⁵⁹⁻⁶¹. The loss of weight between 200 and 500 °C indicates approximately 25.3% PEI is embedded into the PEI@SiO₂ composite, which accords with the above reaction rate of PEI. From the differential thermogravimetry analysis (DTG) curves (Fig. 2C and Fig. S1, Supporting Information†), a new peak appears around 272 °C for the PEI@SiO₂ composite. It indicates the intermolecular interaction of PEI with SiO₂. Fig. 2D illustrates the N₂ sorption isotherm and the pore-size distribution with Barrett-Joyner-Halenda method of PEI@SiO₂. The isotherm is classical type IV, which refers to the mesoporous materials. Furthermore, the isotherms have two hysteresis loops, indicating a bimodal pore size distribution in the mesoporous regions. At the high relative pressure between 0.8 and 0.9, the hysteresis loops are type H1, suggesting the presence of cylindrical mesopores⁶². The bimodal pore-size distribution is confirmed by the pore-size distribution in Fig. 4d. From the pore plots, no peak appeared in the pore, indicating the presence of

irregular mesopores. The mesopores may be formed by the SiO₂. The BET analysis of the material indicates that the specific

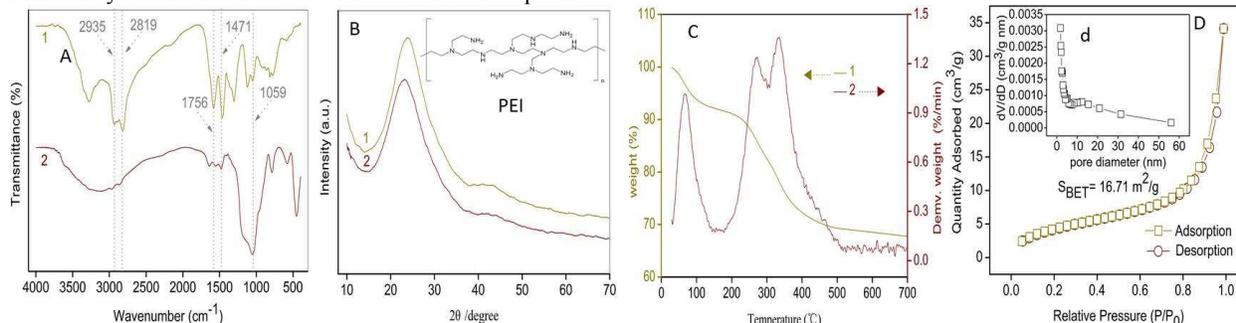


Fig. 2 IR spectra (A) of PEI (A1), the PEI@SiO₂ (A2) and XRD (B) of only-SiO₂ (B1), the PEI@SiO₂ (B2), DTA of the PEI@SiO₂ (C1), TGA of the PEI@SiO₂ (C2) and N₂ absorption-desorption isotherm and pore-size distribution (inset) for PEI@SiO₂ (D, d).

From the SEM images, diatomite is consisted of the tiny aquatic organism remain fossilized (Fig. 3C). The PEI@SiO₂ particles are irregular in the size of 100 to 500 nm and stack up of the reticular structure (Fig. 3 A and B), where all the macropores (>50 nm) disappear (Fig. 3B). The pore size distribution (see Fig. S2, Supporting Information†) is also similar for many amorphous silica studied⁶³. The C, N, O, Al and Si are observed in interior of the PEI@SiO₂ composite from the EDX (Fig. 3Aa). Just as one kind of adhesive, PEI is bridging among SiO₂ particles so as to change the morphology of the PEI@SiO₂ composite (Fig. 3D). The stripes (red) of the SiO₂ particles and the irregular block (blue) of PEI are found (Fig. 3E). The lattice spacing of the crystal grain is 0.20 nm (Fig. 3F). It indicates the Al₂O₃ crystal grains (yellow) formed (Fig. 3E).

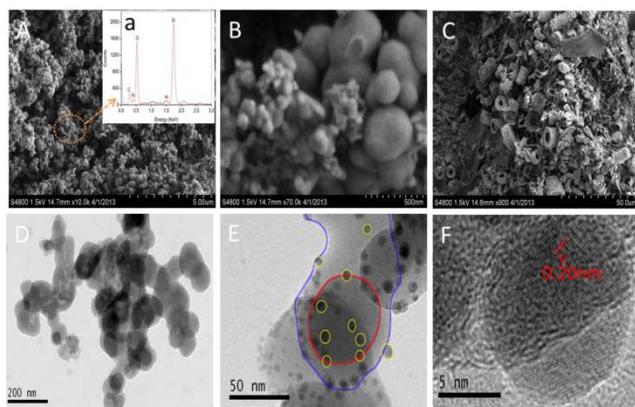


Fig. 3 SEM images of the PEI@SiO₂ (A, B), diatomite (C), EDX of the PEI@SiO₂ (Aa) and TEM of the PEI@SiO₂ (D, E, F).

3.3 Adsorption of solo phenolic compounds on the PEI@SiO₂

PEI contains lots of long hydrophobic chains so that the PEI@SiO₂ composite carries a large amount of hydrophobicity. $\lg K_{ow}$ is the logarithm of the *n*-octanol – water partition coefficient, which underestimates the partition of organic compounds between *n*-octanol and water phases. It is well known that *o*-chlorophenol ($\lg K_{ow} = 3.06$) and BPA ($\lg K_{ow} = 3.32$) are difficult to be remove from water-drinking body by the conventional methods, e.g. flocculation and disinfection⁶⁴. A few studies have suggested that phenolic compounds can be adsorbed by sorbent through intermolecular acting force (mainly

surface area of PEI@SiO₂ is determined to be 16.71 m²/g.

hydrophobic interaction)³⁴. The adsorption of phenol, *o*-chlorophenol and BPA in the PEI@SiO₂ composite is to accord with the lipid-water partition law (Fig. 4A). The partition coefficient (K_{aw}) of phenol is calculated to be 79.1 L/kg, i.e. $\lg K_{aw} = 3.90$, which is more than $\lg K_{ow}$. In addition, $\lg K_{aw} = 1.38$ for *o*-chlorophenol and 1.35 for BPA. The adsorption constant of phenol is 10^{-9.98}. The benzene ring of the phenolic compounds may interact with the hydrophobic vinyl of PEI *via* the hydrophobic interaction. In addition, hydrogen bond may form between PEI of the PEI@SiO₂ composite and phenol.

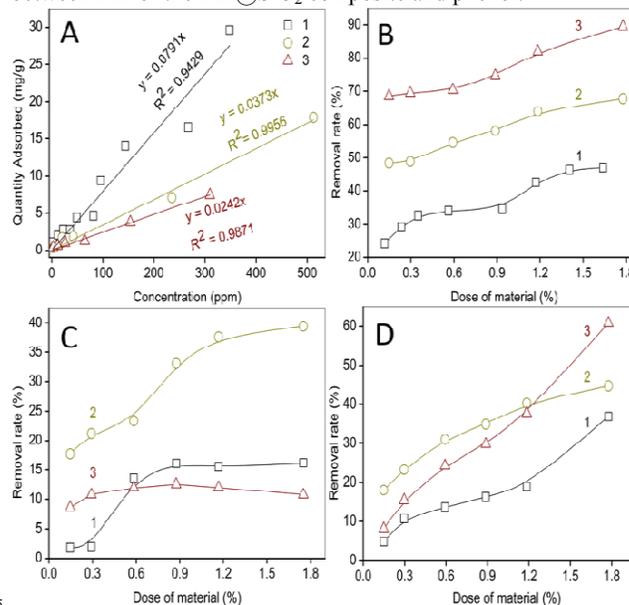


Fig. 4 A: adsorption of phenol (1), *o*-chlorophenol (2) and BPA (3) with the PEI@SiO₂. B: The removal rate of phenol (1), *o*-chlorophenol (2) and BPA (3) with the PEI@SiO₂. Conditions-material dosage, 1.7–18 mg/mL. C: The removal rate of phenol (1), *o*-chlorophenol (2) and BPA (3) with the diatomite. Conditions-material dosage, 1.7–18 mg/mL. D: the removal rate of phenol (1), *o*-chlorophenol (2) and BPA (3) from their mixed solution with the PEI@SiO₂. Conditions-material dosage, 1.5–18 mg/mL.

The adsorption equilibrium is completed in 10 min (Fig. S3A, Supporting Information†), which is much faster than that of activated carbon and the other polymer sorbents⁶⁵⁻⁶⁸. It is considered that a hydrophobic interaction between adsorbent and organic compounds might be attributed to the rapid adsorption rate⁶⁹. The rapid adsorption of phenolic compounds on the PEI@SiO₂ ensures that sufficient time is available for adsorption

equilibration to get at the usual operator condition of the adsorption. The pH of solution hasn't seriously affected the adsorption of those phenolic compounds (Fig. S3B, Supporting Information†). However, in previous paper, the adsorption capacities of diatomite with the conventional surface modification are very different under different conditions of pH values³⁴. The sorption of phenolic compounds on diatomite modified by the conventional surface is the mode of monomolecular layer adsorption^{49, 70-71}, while the adsorption of phenolic compounds in the PEI@SiO₂ composite is to accord with the lipid-water partition law. Diatomite modified by the conventional surface interacts with phenolic compounds *via* hydrogen bond interaction and the hydrogen bond interaction between PEI on diatomite surface and phenolic compounds are affected by the change of pH values³⁴. However, the PEI@SiO₂ interacts with phenolic compounds *via* the hydrophobic interaction and the hydrophobic interaction keep steady at different pH values. With ionic strength increasing from 0.05 to 0.2 mol/L, q_e of phenol, *o*-chlorophenol and BPA increase by 31.5%, 15.1% and 6.4% respectively (Fig. S3C, Supporting Information†). It is considered that the hydrogen bonding between phenolic compounds and H₂O becomes weak at higher ionic strength, which makes phenolic compound molecules freely available⁷²⁻⁷⁴. Hence, it is attributed to the fact that ionic strength can strengthen the hydrophobic interaction between phenolic compounds and the PEI@SiO₂. Temperature is an important parameter for any separation process⁷⁵. With the temperature increasing from 297 to 315 K, q_e of phenol decreases by 17.8%, while that of *o*-chlorophenol and BPA remains almost constant (Fig. S3D, Supporting Information†). It is obvious the equilibrium adsorption capacity increases with increment of the equilibrium concentration whilst decreases with increasing of the temperature, suggesting that the adsorption is a favorable while an exothermic process⁷⁶. A change in the adsorption capacity with temperature is possibly due to that the adsorbate has a tendency to escape from the solid phase to the solution when the interaction is exothermic⁷².

3.4 Effect of adsorbent dosage

Effects of the PEI@SiO₂ composite's dosage are determined on adsorption of three phenolic compounds mixture (20 mg/L phenol, 42 mg/L *o*-chlorophenol and 38 mg/L BPA) and the results are shown in Fig. 4 B and C. The removal rates of three phenolic compounds increase with increase of the dosage. The PEI@SiO₂ composite removed 47% phenol, 68% *o*-chlorophenol and 89% BPA. However, diatomite removed only 16% phenol, 39% *o*-chlorophenol and 11% BPA (Fig. 4B). Also, being different from the PEI@SiO₂ composite, diatomite adsorbing phenolic compounds obeys the Freundlich model (Fig. 4C)^{36, 45}. Therefore, diatomite interacting with phenolic compounds is different with the PEI@SiO₂ composite. The most possible reason is that the active group -O of diatomite interacted with phenolic compounds *via* hydrogen bond. The PEI chain embedding into the PEI@SiO₂ composite bound to phenolic compounds *via* hydrophobic interaction.

The mixture solution of 20 mg/l phenol, 42 mg/l *o*-chlorophenol and 38 mg/l BPA is treated with the PEI@SiO₂

composite. From the results showing in Fig. 4D, 0.18% of the PEI@SiO₂ composite removed 37% phenol, 45% *o*-chlorophenol and 60% BPA. Comparing with those in Fig. 4 B, the adsorption of phenol, *o*-chloropheno and BPA decreased by 21%, 34% and 33% respectively. When three solutes compete for sorption in the trisolute system, the sorption amount of each solute is less than that in a single-solute system. It indicated that the competitive adsorption occurred among three phenolic compounds. Due to limited active sites of the PEI@SiO₂, the competitive hydrophobic interactions of three phenolic compounds are expected to be the mechanism for the inhibited desorption^{17, 77}.

3.5 Treatment of heavy metals with the phenol-PEI@SiO₂ waste calcined

In order to avoid the secondary pollution and increase the comprehensive use of resource, recycling of the spent materials is often necessary⁷⁸. After the PEI@SiO₂ sludge with phenol is calcined at 550 °C, all organic compounds (phenol and PEI) are decomposed. The material calcined is consisted of SiO₂ and Al₂O₃, which is capable of adsorbing metals⁷⁹. The removal rates of Bi³⁺, Fe³⁺ and Cu²⁺ are more than 75% (Fig. 5).

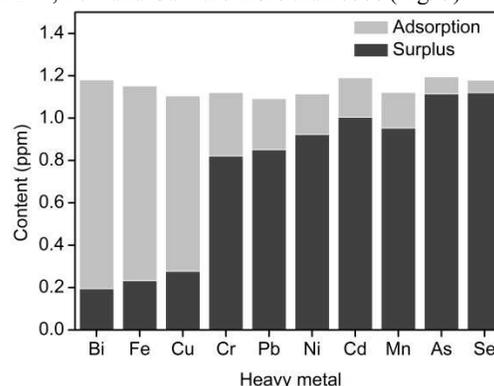


Fig. 5 the adsorption of multi-metals mixed with the phenol-PEI@SiO₂ waste calcined

4. Conclusions

We demonstrated an innovative method (dissolving and rebuilding) to produce hybrid adsorbent for by using the natural mineral and organic polymer. Such a material has more hybrid amount of PEI, compared with reported materials³⁴. More than 22.9% PEI is embedded so that the sorbent contains a large numbers of active sites, which results in an exceptional adsorption capacity towards phenolic compounds. It conforms to the lipid-water partition law and the K_{aw} of phenol, *o*-chlorophenol and BPA is 79.1 L/kg, 37.3 L/kg and 24.2 L/kg. After calcinations of the used PEI@SiO₂, the formed the phenol-PEI@SiO₂ waste calcined exhibits a good sorption capacity to heavy metals and also can be used to eliminate heavy metal pollutant. This work has provided a novel approach for the preparation of environment-friendly inorganic-organic hybrids.

Notes and references

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- † Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/
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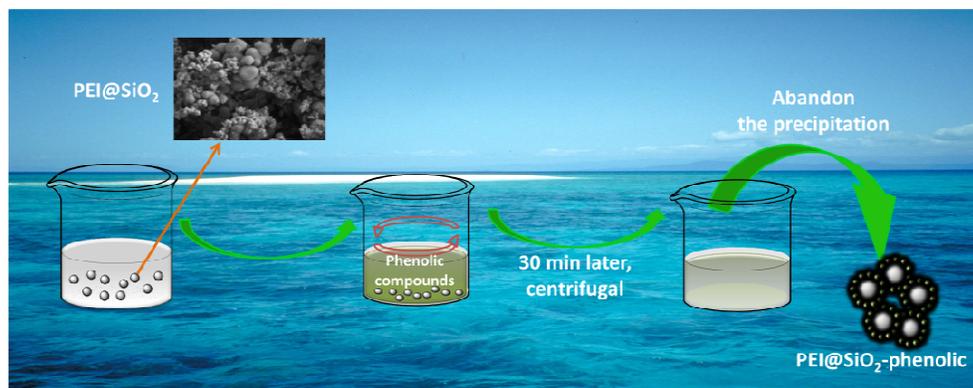
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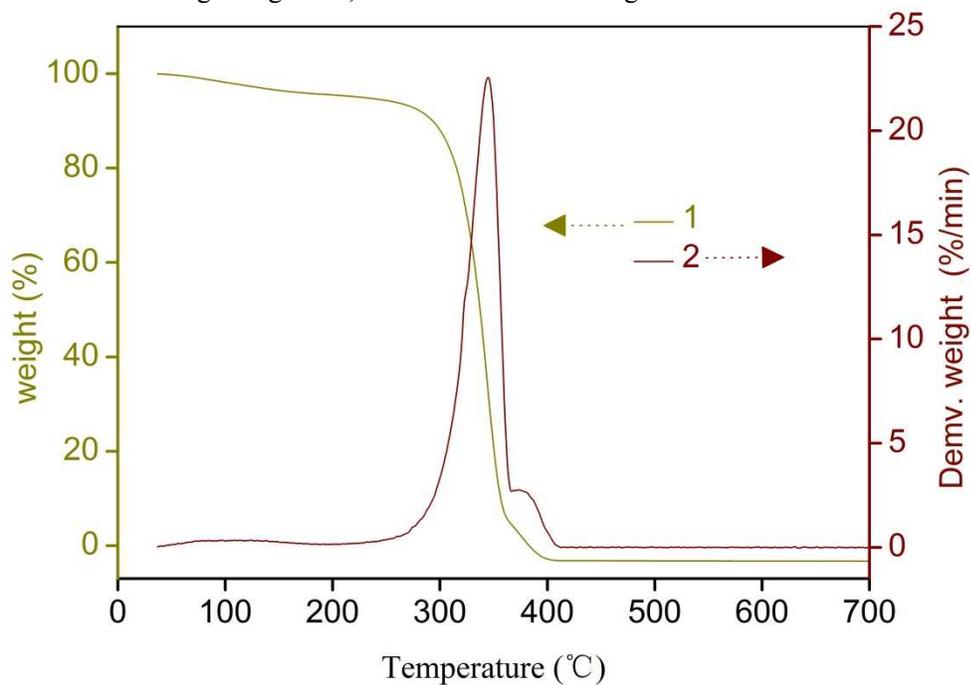
PEI@SiO₂: synthesis from diatomite and application for capturing phenolic compounds from aqueous solution

Zheng-Yong Chen,^a Ya-Yuan He^a and Hong-Wen Gao^{*a}

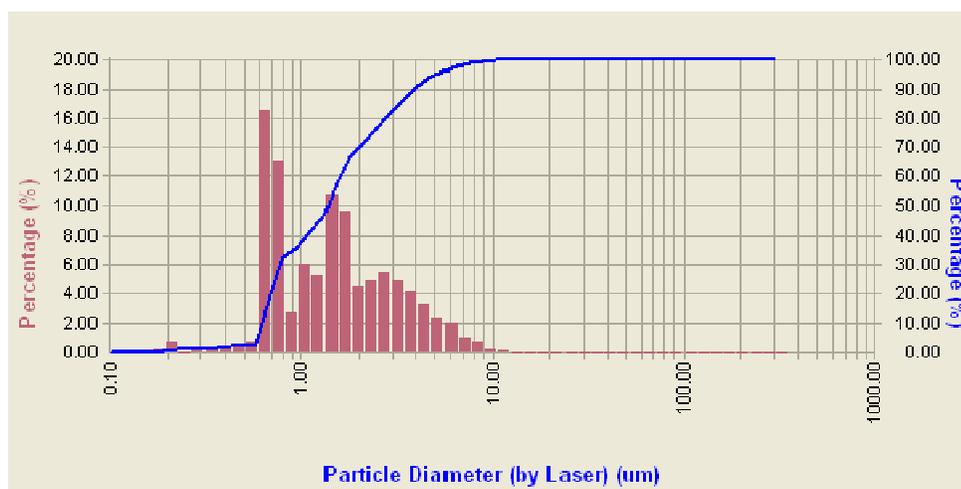
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The PEI@SiO₂ hybrid composite was synthesized for sorption of phenolic compounds.



Electronic Supplementary Information**PEI@SiO₂: synthesis from diatomite and application for capturing phenolic compounds from aqueous solution**Zheng-Yong Chen,^a Ya-Yuan He^a and Hong-Wen Gao^{*a}

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Fig. S1 DTA (1) and TGA of PEI (2)**Fig. S2** Particle size distribution of the PEI@SiO₂

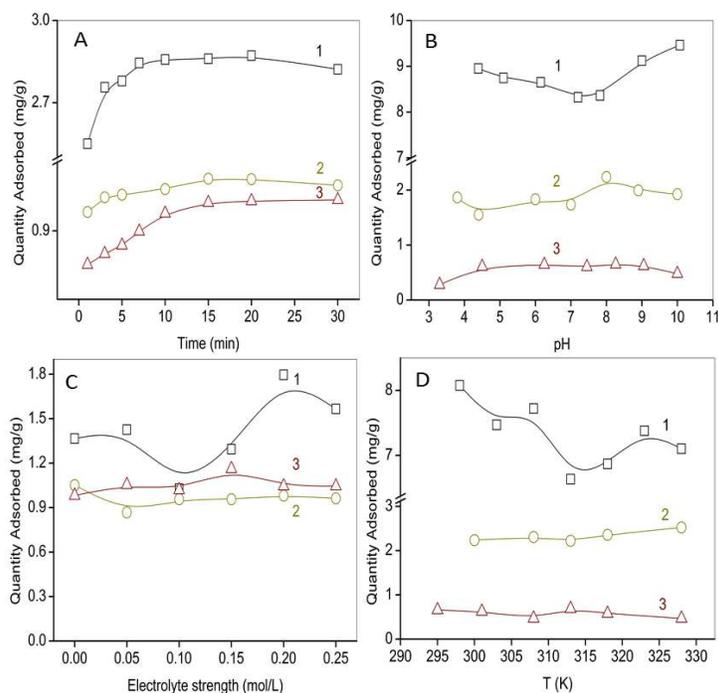


Fig. S3 **A:** the sorption curve of phenolic compounds (1- phenol, *o*-chlorophenol and 3- BPA) to the the PEI@SiO₂ at different times. **B:** the sorption curve of phenolic compounds (1- phenol, 2- *o*-chlorophenol and 3- BPA) to the the PEI@SiO₂ at different pH. **C:** the sorption curve of phenolic compounds (1- phenol, 2- *o*-chlorophenol and 3- BPA) to the the PEI@SiO₂ at different ionic strength. **D:** the sorption curve of phenolic compounds (1- phenol, 2- *o*-chlorophenol and 3- BPA) to the the PEI@SiO₂ at different temperature.

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