Synthesize of dendritic fibrous nano-silica functionalized by cysteine and its application as advanced adsorbent

Nilufar Khantana, Nasrin Shadjoua, Mohammad Hasanzadeh

Department of Nanochemistry, Nanotechnology Research Center, Uremia University, Uremia, Iran;
Pharmaceutical Analysis Research Center, Tabriz University of Medicinal Science, Tabriz, Iran

ABSTRACT

L-Cysteine-modified dendritic fibrous nanosilica grafted by amine groups (Cys-DFNS-NH₂) have been synthesized by a novel hydrothermal method. The N₂ adsorption–desorption isotherms analysis on the Cys-DFNS-NH₂ show that the average pore volume and surface area of the prepared fibrous Cys-DFNS-NH₂ were 2.2 cm³/g and 205 m²/g, respectively, while the average pore size is 6.06 nm. Adsorption behavior of the Cys-DFNS-NH₂ for Cd²⁺, Cu²⁺, Ag⁺, and Pb²⁺ was investigated by electrochemical methods. The results show that Cys-DFNS-NH₂ can selectively adsorb Cd²⁺, Ag⁺, and Pb²⁺ in different potentials. Finally, the application of the engineered adsorbent for the removal of Cd²⁺, Ag⁺, and Pb²⁺ from contaminated water samples was examined. This work provides a new platform to the synthesis of Cys-DFNS-NH₂ with high specific surface area for efficient adsorbent of specific metal ions.

GRAPHICAL ABSTRACT

CONTACT

Nasrin Shadjou N.shadjou@urmia.ac.ir
Department of Nanochemistry, Nanotechnology Research Center, Uremia University, Uremia, Iran;
M. Hasanzadeh mhmmd_hasanzadeh@yahoo.com; hasanzadehm@tbzmed.ac.ir
Pharmaceutical Analysis Research Center, Tabriz University of Medicinal Science, Tabriz, Iran

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Introduction

Water polluted by toxic compounds is an important environmental issue. Recently, there has been a growing interest in materials capable of removing toxic compounds and ions from contaminated water. The removal of toxic metal ions, polyaromatic hydrocarbons, phosphorus, etc., from water is a critical environmental concern. Recently, there is a growing demand for the application of superadsorbents for the removal of metals ions and organic pollutants such as oil, dyes, and volatile organic compounds from contaminated water [1–6].

Among different methods, adsorption suggest many advantages such as simple and stable operation, easy handling of waste, absence of toxic reagents, compact facilities, and generally lowers operation cost [7,8]. Adsorption is a fundamental process involving the enrichment of guest species at the interface of a certain adsorbent [9–11]. Such a process provides one of the most efficient ways to dramatically reduce release of contaminations [12,13]. Therefore, one of the most efficient routes for removal of metal ions is adsorption-based processes. The fundamental and great challenge is developing highly efficient adsorbents. An important requirement for an excellent adsorbent is a large substrate [7]. Mesoporous nanomaterials with large pore volume and uniform mesopores show a fast removal of contaminations with high efficiency. Traditionally, functionalized mesoporous silica materials are widely adopted as adsorbents [7]. Due to their high porosity, mesoporous silica nanomaterials with more sophisticated functions are of great interest for adsorption processes and separation of contaminations from waste waters [7]. Dendritic fibrous nano-silica is one of the recently introduced nanomaterials by Polshettiwar and coworkers [14,15] which showed excellent potential in energy storage, sensor technology, catalysis, gas capture, solar energy harvesting, and biomedical applications. According to the fibrous morphology of these materials, they are named fibrous nano-silica (KCC-1) [14]. However, the fibers are more like thin sheets of 3.5 to 5.2 nm thickness (like petals of flowers) rather than sharp needle shaped rods, and hence several other names have been used in the literature, such as fibrous, wrinkled, nanoflower, dendritic, dandelion, lamellar, etc.

The uniqueness of DFNS is mainly due to its dendritic fibrous morphology, which is in principle accessible from all sides (as compared to the tubular pores of MCM-41 and SBA-15). This improved accessibility allowed for increased loading of active sites (such as metals, metal oxides, organometallics, organic molecules, etc.) onto the silica surface without blocking the pores (channels) and, lead to an increment in accessibility of these generated active sites. The surface area of DFNS can be differ from 450 m² g⁻¹ to 1244 m² g⁻¹ again font size by tuning their particle size (from 40 to 1120 nm) and fiber density (number of fibers within one sphere) [15]. Importantly, unlike the tiny pore size distribution in conventional silica materials, DFNS possesses radially oriented pores (fibrous channels), the size of which increase from the center of the sphere to its outer surface. Control over the fiber density of DFNS allowed for tunable pore size and pore volume. Therefore, its tunable pore size (from 3.7 to 25 nm) allowed for tailor-made pores to fit specific guest molecules with various sizes, while its tunable pore volume (up to 2.18 cm³/g) allowed for high loadings of these guests. Guests can be organometallic complexes, organic molecules, metals, metal oxides, peptides, inorganic salts, proteins, enzymes, polymers, carbon, etc. DFNS also show excellent stability (chemical, mechanical, thermal, and hydrothermal), which is of key importance in conventional mesoporous materials due to their silica walls. Interestingly, these materials have low toxicity and are biocompatible. Control over the particle size allows for the fine tuning of the dispersion, uptake, and toxicity of these nanospheres.

Interestingly, Huang and coworkers, applied lanthanum (La)-doped DFNS for the adsorption of phosphorus [16]. Also, Xie et al., grafted DFNS with cyano groups and used these for the removal of some ions (Fe³⁺, Cu²⁺, and Pb²⁺) from waste contaminated solution [17]. Also, Yan and coworker used multifunctional and magnetic DFNS for both the removal of Zn²⁺ ions and their detection (sensing probe) [18].

Amine functionalized mesoporous silica [19–22] have been used as super-adsorbent for metal cations, phosphate and nitrate anions, and chromate and arsenat oxyanions [23–25]. Application of these materials for the removal of metals cations has been the subject of extensive research recently, while our knowledge of the adsorption of cations using silica-based mesoporous materials is, comparatively, incomplete. Following our work on synthesis of new modified mesoporous sorbents [26] in this work, the synthesis of amino-functionalized DNFS functionalized by l-Cysteine (l-Cys), its properties and sorption behavior for some cations from water samples using electrochemical methods was investigated.

Experimental

Materials

Tetraethyl orthosilicate (TEOS, 98%), (3-aminopropyl)triethoxysilane (APTES, 99%), N-hydroxysuccinimide (NHS, 98.0%), and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC, 98.0%) were purchased from Sigma-Aldrich Co. (USA).
Cyclohexane, toluene, hexanol, dimethylsulfoxide (DMSO), and cetyltrimethylammonium bromide (CTAB) were obtained from Merck (Germany).

**Instruments**

Electrochemical cyclic voltammetry (CV), differential pulse voltammetry (DPV), and square wave voltammetry (SWV) measurements were carried out using a potentiostat/glavanostat system AUTOLAB system with PGSTAT302N boards (Eco Chemie, Utrecht, Netherlands) at room temperature, using a standard electrochemical cell with three-electrodes. A conventional three-electrode electrochemical cell comprising glassy carbon electrode (GCE), Ag/AgCl/KCl (saturated) and platinum wire were used as working, reference, and auxiliary electrodes, respectively. The system was controlled by a PC with GPES operating software.

**Characterization**

X-ray diffraction (XRD) patterns of KCC-1-based materials were recorded on a Siemens D 5000 X-Ray diffractometer (Texas, USA) with a Cu Kα anode (λ = 1.54 Å) operating at 40 kV and 30 mA. TEM analysis was conducted on a Carl Zeiss LEO 906 electron microscope operated at 100 kV (Oberkochen, Germany). Fourier transform infrared (FTIR) spectra were measured using a Shimadzu model FTIR prestige 21 spectrophotometer (Tokyo, Japan) using KBr discs. Brunauer–Emmett–Teller (BET) was recorded on a Micromeritics NOVA 2000 apparatus at 77 K using nitrogen as the adsorption gas (Florida, USA). The surface morphology of the KCC-1, KCC-1-NH₂, and KCC-1-NH₂-Cys modified GCE electrodes and the porous nanoparticles and energy dispersive X-ray (EDX) spectroscopy were evaluated with a FESEM analysis, which was conducted on TESCAN system of FEG-SEM MIRA3 TESCAN (Brno, Czech Republic). The particle size distribution and zeta potential values were determined using Malvern particle size analyzer (Malvern, UK).

**Synthesis**

**Preparation of KCC-1 and KCC-1-NH₂, KCC-1-NH₂-Cys**

KCC-1 was synthesized according to the methods which was reported by Bayal and coworkers [27]. Briefly, 1 g CTAB was added to 10 cc distilled water and after addition of 0.6 g urea, the mixture was stirred for about 3 h at room temperature. Then, the mixture of 2 g TEOS, 30 cc cyclohexane, and 1.5 cc hexanol was added to the flask and sonicated for 30 min. Afterwards, the mixture was refluxed at 120 °C for 4 h and subsequently refluxed at 80 °C for 24 h. Next, the mixture was cooled to room temperature and centrifuged to collect the KCC-1 as white sediment. The collected KCC-1 was washed several times with ethanol and dried in a vacuum oven at 60 °C for 24 h.

**Scheme 1. Synthesized procedure of KCC-1-NH₂-Cys.**
times with water and ethanol and dried at 60 °C for 24 h. Finally, the as-synthesized KCC-1 was calcinated at 550 °C for 6 h to remove the CTAB as templating agent. As mechanism of the KCC-1 synthesis, urea was used to hydrolyze the TEOS to produce negatively charged (SiO4)−4 silicate. Using of CTAB induce the silicate molecules to form self-assembled linear structures where the CTAB help to the aggregating of the silicates [14,28].

To functionalize the KCC-1 surface with NH2 moieties, 0.02 g of KCC-1 was dispersed on 1.2 mL dried toluene and sonicated for 30 min. Then 50 µL 3-aminopropyltriethoxysilane (APTES) was added to the mixture and refluxed for 20 h at 80 °C. Then the mixture was separated and washed with toluene several times and dried at 80 °C for at least 24 h. Finally, Cys was conjugated to the dendritic fibers of KCC-1-NH2 by EDC/NHS chemistry which provides the attaching of the Cys molecules at room temperature. Scheme 1 summarized all of the synthesizing procedures (Scheme 1).

Characterization of KCC-1, KCC-1-NH2, and KCC-1-NH2-Cys

TEM was used for the further characterization of the KCC-1, KCC-1-NH2, and KCC-1- NH2-Cys (Figure 1). The TEM images revealed the fibrous, porous, and dendritic shape of the nanomaterials, of which the fibrous form is the result of using the CTAB for templating. Also, the particle sizes of KCC-1, KCC-1-NH2, and KCC-1-NH2-Cys were about 167, 188, and 216 nm, respectively.

Supporting information Figure S1 (see supporting information), show the morphological features of the KCC-1, KCC-1-NH2, and KCC-1-NH2-Cys using FE-SEM. The fibrous-sphere indicates that the formation of KCC-1-based materials, which the functionalization have not any effect on the morphology of the KCC-1. EDX results reveal the atomic composition of the KCC-based materials where the KCC-1 is composed only with O and Si. However, the carbon is arising from the FE-SEM grid and the templating agent (Supporting information Figure S2 (see supporting information)).
Upon functionalization with APTES, the weight percent of N, O, and C are increased which implies the effective surface modification of KCC-1 with APTES.

FTIR was applied to approve the proper functionalization of the KCC-1 with $\text{–NH}_2$. As shown in Supporting information Figure S3 (see supporting information), the characteristic peaks of the silica-based materials could be observed in the range of 1020 to 1110 cm$^{-1}$ representing the Si–O–Si asymmetric stretching while a Si–OH peak is observed at 960 cm$^{-1}$, which represents the stretching vibration and asymmetric bending.

The BET and BJH analyses of the KCC-1, KCC-1-NH$_2$, and KCC-1-NH$_2$-Cys were used to determine the pore volume of the KCC-1, KCC-1-NH$_2$, and KCC-1-NH$_2$-Cys. Supporting information Table S1 (see supporting information) lists the average pore size, surface area, and pore volume of KCC-1, KCC-1-NH$_2$, and KCC-1-NH$_2$-Cys. The BJH pore volumes were changed from 1.52 to 1.1 and 2.2 cm$^3$/g for KCC-1, KCC-1-NH$_2$, and KCC-1-NH$_2$-Cys, respectively, where the surface area of KCC-1 changed from 617 m$^2$/g to 367 and 205 m$^2$/g for KCC-1-NH$_2$, and KCC-1-NH$_2$-Cys, respectively. Mean pore diameter distribution of the materials were 9.9, 11.9, and 6.09 for KCC-1, KCC-1-NH$_2$, and KCC-1-NH$_2$-Cys, respectively (Supporting information Figure S4 (see supporting information)). The pore size, pore volumes, and surface area of KCC-1, KCC-1-NH$_2$, and KCC-1-NH$_2$-Cys are obviously approved by the reported results [27,29].

Figure 2. (A-C) CVs, DPVs, and LSVs of GCE in the presence of Cd$^{2+}$ (2.5 mM) before and after incubation with KCC-1-NH$_2$-Cys (0.02 g). Sweep rate of CV is 50 mV/s. Sweep rate of CV is 100 mV/s. Sweep rate of LSV is 100 mV/s. Modulation time = 0.05, Interval time = 0.25, Modulation amplitude = 0.025.
Zeta potentials of KCC-1, KCC-1-NH₂, and KCC-1-NH₂-Cys were checked at pH 7.5 to determine the surface charge to identify the possible surface modification. The KCC-1 bare fibrous nanomaterials display negative charge at pH 7.5 which could be the result of Si-OH functional groups. However, the zeta potential of the KCC-1-NH₂, and KCC-1-NH₂-Cys show positive charges which confirms the anchoring amine and -SH groups on the surface of the fibrous materials, respective. DLS results of the KCC-1, KCC-1-NH₂, and KCC-1-NH₂-Cys also show an increase in the hydrodynamic diameter of the nanomaterials from KCC-1 to KCC-1-NH₂-Cys which supports again the surface functionalization with NH₂ and FA groups. The XRD patterns of KCC-1, KCC-1-NH₂, and KCC-1-NH₂-Cys were performed from 3.0° (2θ) to 70.0° (2θ) (Supporting information Figure S5 (see supporting information)) to test the crystallinity of the produced KCC-1-based nanomaterials where two major peaks could be observed, indicating that the crystallinity increased from KCC-1 to KCC-1-NH₂-Cys. The broad peak at 20° and 30° is assigned to the amorphous silica [30]. Also, compared to the KCC-1, the KCC-1-NH₂ and KCC-1-NH₂-Cys patterns were shifted to the higher 2θ values which are again an indication of the surface functionalization of KCC-1.

Results and discussion

For the investigation of functionalized DNFS adsorbent capacity for the removal of metal ions, some electrochemical techniques such as cyclic voltammetry (CV), linear sweep voltammetry (LSV), and differential pulse voltammetry (DPV) were used. For this purpose, 0.02 g of KCC-1-NH₂-Cys was incubated with some of the metal ions. Then CVs, LSV, and DPVs of Cd²⁺, Cu²⁺, Ag⁺, and Pb²⁺ ions were recorded before and after incubation.
with synthesized adsorbent (Cys-DFNS-NH₂) using GCE as working electrode.

As can be seen in Figure 2, the peak current of the GCE was reduced after incubation of Cd²⁺ with synthesized adsorbent in the 25 °C. It is found that the peak location of CVs, LSV, and DPVs was about −0.9 V. Also, it is found that the redox peak potentials of Cd²⁺ appeared at −0.9 V vs. Ag/AgCl (Figure 3(A)) before incubation with Cys-DFNS-NH₂ using CV technique and GCE as working electrode. Interestingly, after incubation of this metal ion with a concentration of 2.5 mM with synthesized absorbent, the oxidation peak potential was reduced and reached −0.83 V vs. Ag/AgCl. These results were confirmed by other techniques (DPV and LSV) which are shown in Figure 2(B and C). Therefore, Cd²⁺ was strongly captured by Cys-DFNS-NH₂. In other words, Cys-DFNS-NH₂ has excellent capacity for entrapment of Cd²⁺ ions and its efficient removal from aqueous solution.

The second approach is based on the idea of interaction of Cys-DFNS-NH₂ and Cd²⁺ as an example of electroactive metal ions at different incubation times. Correlated electrochemical responses shown in Figure 3 indicate that by increasing the time of incubation between adsorbent and Cd²⁺, the electrochemical peak currents also decreased. This demonstrates that as incubation time increases, the interaction between Cys-DFNS-NH₂ and Pb²⁺ gets tighter and bolstered. Nevertheless, the influence of the incubation time on the electrochemical measurements of Cd²⁺ could not be extended for other ions.

Combining two approaches, it can be concluded that the interaction of Cys-DFNS-NH₂ and Cd²⁺ can be verified via electrochemical procedures while
also the strength of the interaction can be checked through electrochemical techniques.

Scheme 2 shows the removal mechanism of Pb$^{2+}$ KCC-1-NH$_2$-Cys as a model.

Incubation time of Cd$^{2+}$ with synthesized adsorbent was evaluated by CV, DPV, and LSV, techniques. For this purpose, 0.02 g of KCC-1-NH$_2$-Cys was incubated with 2.5 mM of Cd$^{2+}$ ions at vigorous stirring for different times (15, 30, 45, 60 min). Then, the homogeneous solution was centrifuged. At the final step, super-naturated solution was collected and above mentioned voltammograms were recorded. As can be seen in Figure 3(A), different incubation times lead to a 4 fold decrease in peak current. As can be seen, after 60 min incubation of Cd$^{2+}$ with 0.02 g of KCC-1-NH$_2$-Cys, the peak current reaches about 1 $\mu$A. According to the obtained results, it is found that the candidate adsorbent saturated by 2.5 mM of Cd$^{2+}$. On the other hand, a change of peak potential of GCE after incubation at various times (15–60 min) confirmed the excellent interaction of the suggested adsorbent with this heavy metal ion. These results were confirmed by other techniques (DPV and LSV) which are shown in Figure 3(B and C).

Finally, we need to investigate the concentration profile of the adsorbent using a sensitive technique. For this purpose, DPVs of GCE were recorded for different concentrations of metal ions incubated with KCC-1-NH$_2$-Cys (Figure 4). As can be seen, the peak current of GCE was decreased with decrease of Cd$^{2+}$ concentration. According to the obtained results, a linear relation was obtained between peak current of GCE and Cd$^{2+}$ concentration using the DPV technique.

Similar investigations were applied for the removal of Pb$^{2+}$ ions from aqueous solution using KCC-1-NH$_2$-Cys. In contrast to Cd$^{2+}$, the oxidation potential of Pb$^{2+}$ ions appeared at −0.65 V vs. Ag/AgCl and few changes in oxidation potential were observed after incubation with KCC-1-NH$_2$-Cys. However, similar to Pb$^{2+}$ ions, peak currents were decreased after incubation of the Pb$^{2+}$ with KCC-1-NH$_2$-Cys. Therefore, this adsorbent can be used for the removal of Pb$^{2+}$ at the potential of −0.65 V vs. Ag/AgCl (Supporting information Figure S6 (see supporting information)).

CV technique was used for the evaluation and optimization of incubation time of Pb$^{2+}$ with KCC-1-NH$_2$-Cys. For this purpose 2.5 mM of Pb$^{2+}$ was incubated with KCC-1-NH$_2$-Cys in different times (15, 30, 45 min) and DPVs, LSVs were recorded. As can be seen in Supporting information Figure S7 (see supporting information), an increment of incubation time lead to a decrement of peak current while peak potential was not changed. These results show that, KCC-1-NH$_2$-Cys has excellent capacity for the removal of Pb$^{2+}$ from aqueous solution.

Finally, we need to investigate the concentration profile of the adsorbent using a sensitive technique. For this purpose, DPVs of GCE were recorded in different concentrations of metal ions incubated with KCC-1-NH$_2$-Cys (Supporting information Figure S8 (see supporting information)). As can be seen, peak current of GCE were decreased with decrement of metal ion concentration. According to obtained results, a linear relation was obtained between peak current of GCE and Pb$^{2+}$ concentration using DPV technique.

CV, DPV, and LSV techniques were applied for the investigation of Ag$^+$ ions removal from aqueous solution using KCC-1-NH$_2$-Cys. Interestingly, the oxidation potential of Ag$^+$ ions appeared in the more positive potentials (0.1 V vs. Ag/AgCl) and few changes in oxidation potential were observed after incubation with KCC-1-NH$_2$-Cys. But, similar to Pb$^{2+}$ and Cd$^{2+}$ ions, peak currents were decreased after incubation of the Ag$^+$ with KCC-1-NH$_2$-Cys. Therefore, this adsorbent can be used to removal of Ag$^+$ from aqueous solution in the potential of +0.1 V vs. Ag/AgCl (Supporting information Figure S9 (see supporting information)).

The effect of incubation time of Ag$^+$ (2.5 mM) on the efficient removal of this ion by KCC-1-NH$_2$-Cys was investigated using CV, DPV, and LSV techniques. As can be seen in (Supporting information Figure S10 (see supporting information)), increment of incubation time lead to decrement of peak current while peak potential was not changed approximately. These results show that, KCC-1-NH$_2$-Cys has excellent capacity for the removal of Ag$^+$ from aqueous solution. Also, surface of KCC-1-NH$_2$-Cys was saturated by 2.5 mM of Ag$^+$ after 60 min.

Similar to previous parts, the concentration profile of the candidate adsorbent for the removal of Ag$^+$ was investigated by a sensitive technique (DPV). For this purpose, DPVs of GCE were recorded in different concentrations of metal ions incubated with KCC-1-NH$_2$-Cys (Supporting information Figure S11 (see supporting information)). As can be seen, peak current of GCE were decreased with decrement of metal ion concentration. According to obtained results, a linear relation was obtained between peak current of GCE and Ag$^+$ concentration using DPV technique. This approach related to high affinity of

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**Table 1. Amount of ions in river-water and local natural ground water samples analyzed by proposed method.**

| Sample                                    | Found  | Sample                                    | Found  |
|-------------------------------------------|--------|-------------------------------------------|--------|
| Pb$^{2+}$                   |        | Cd$^{2+}$                   |        |
| River-water (near of ground water)        | 0.5 $\mu$M | Local natural ground water               | 0.8 $\mu$M |
| KCC-1-NH$_2$-Cys                |        | KCC-1-NH$_2$-Cys                |        |
| River-water (near of ground water)        | 0.06 $\mu$M | Local natural ground water               | 0.01 $\mu$M |
| Ag$^+$                                    |        | Ag$^+$                                    |        |
| River-water (near of ground water)        | 1 $\mu$M   | Local natural ground water               | 1.1 $\mu$M  |
Ag\(^{+}\) to –SH functionalized group of candidate adsorbent. Another idea is high and strong interaction of Ag\(^{+}\) with –NH and –SH groups which lead to saturation of proposed adsorbent by this ion.

Interestingly, in the case of Cu\(^{2+}\) ion, different behavior was observed. At the first part and in contrast to previous ions (Cd\(^{2+}\), Pb\(^{2+}\), and Ag\(^{+}\)), peak current of CVs, LSVs, and DPVs were not changed after incubation of Cu\(^{2+}\) with KCC-1-NH\(_2\)-Cys (Supporting information Figure S12 (see supporting information)). Also, the effect of incubation time on the performance of adsorbent show new and different results. As can be seen in Supporting information Figure S13 (see supporting information), with increment of incubation times (15 and 60 min), peak current was not changed. These results indicated that, DNFS was not sensitive for this ion.

Finally, it is found that KCC-1-NH\(_2\)-Cys is very effective in removing candidate ions from ground natural water with low ions concentrations as most cases in the natural environment. The method was also applied to the analysis of local natural ground water samples. Table 1 gives the possibility for accurate analysis of low concentration of Pb\(^{2+}\), Cd\(^{2+}\), and Ag\(^{+}\), and Cu\(^{2+}\) in natural ground water and river samples by electrochemical methods and based on the proposed adsorbent.

Conclusion

In summary, KCC-1-NH\(_2\)-Cys was found to be a new and efficient adsorbent for the removal of some ions (Pb\(^{2+}\), Cd\(^{2+}\), and Ag\(^{+}\)) from water samples. Also, it showed high efficiency in the removal of selected cations from aqueous samples to improve the quality of water samples. The results show that Cys-DNFS-NH\(_2\) can selectively adsorb Pb\(^{2+}\), Cd\(^{2+}\), and Ag\(^{+}\) in different potentials. This work introduced novel methods to prepare Cys functionalized DNFS-NH\(_2\) with high specific surface area and total pore volumes, which have the potential to be applied as an efficient adsorbent for specific metal ions. In addition, KCC-1-NH\(_2\)-Cys can be potentially employed as an excellent adsorbent in large-scale plants for contaminated water treatment due to their easy, efficient separation and high adsorption capacity.

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Disclosure statement

There is no conflict of interest.
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