Electric Double-Layer Effects Induce Separation of Aqueous Metal Ions

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ABSTRACT Metal ion separation is crucial to environmental decontamination, chromatography, and metal recovery and recycling. Theoretical studies have suggested that the ion distributions in the electric double-layer (EDL) region depend on the nature of the ions and the characteristics of the charged electrode surface. We believe that rational design of the electrode material and device structure will enable EDL-based devices to be utilized in the separation of aqueous metal ions. On the basis of this concept, we fabricate an EDL separation (EDLS) device based on sandwich-structured N-functionalized graphene sheets (CN-GS) for selective separation of aqueous toxic heavy metal ions. We demonstrate that the EDLS enables randomly distributed soluble ions to form a coordination-driven layer and electrostatic-driven layer in the interfacial region of the CN-GS/solution. Through tuning the surface potential of the CN-GS, the effective separation of heavy metal ions (coordination-driven layer) from alkali or alkaline earth metal ions (electrostatic-driven layer) can be achieved.

KEYWORDS: electric double layer · metal ions separation · water purification · electrochemistry · graphene

Modern industrial production processes generate huge amounts of metal-containing wastes, which present great ecotoxicity challenges that need to be addressed.1–3 Although the safe disposal of these wastes can immobilize most of these hazardous elements, there may still be small amounts of metals that migrate into groundwater or surface waters.4,5 These disposed nondegradable wastes, which are considered “ecological time-bombs”, continue to be environmental risks. Recently, there has been a growing recognition that metals recovery and recycling can contribute to sustainable development by reducing the exploitation of virgin ores and is crucial in preventing hazardous metals from entering the environment.6–8 In particular, the recovery of heavy metal ions from dilute solutions is a key issue because of the lack of economic viability. To deal with this problem, a concentration process is often needed. On the other hand, metal ion separation is of fundamental importance in metal recovery and recycling,9–12 because metal-containing industrial discharges often contain large amounts of common elements (e.g., Na, K, Ca, and Mg) that are unworthy of recovery. However, achieving high selectivity and efficient separation and concentration of heavy metal ions from a diverse mix of elements remains a challenge.

The electric double layer (EDL) is an important feature in a variety of electrochemical applications, such as batteries,13,14 supercapacitors,15 fuel cells,16 solar cells,17 electrocatalysis,18 and chemical sensors.19,20 EDLs represent the interfacial region of an electrode/electrolyte solution, which governs adsorption phenomena and influences charge transfer and electrochemical reaction.21 Recently, it was realized that electrostatic adsorption can be used for removal of charged species from aqueous solutions. On the basis of the above phenomena, capacitive deionization was developed and has been widely explored for water desalination.22 When a porous electrode is charged by an external power supply, the EDL will be formed at the electrode–solution interface, where ions are electrostatically adsorbed. Charged ionic species can be removed from aqueous solutions using capacitive deionization. The successful utilization of EDL in capacitive deionization...
pushed fundamental researchers to study the principles related to the EDL, through which other innovative applications could be developed.

In a typical aqueous EDL, the organization of the ions is described by the Gouy–Chapman–Stern model,23,24 which proposed that the EDL in the interfacial region could be divided into the inner Helmholtz layer, the outer Helmholtz layer, and the Gouy–Chapman diffuse layer. Preferentially adsorbed ions adhere to the electrode surface on fixed sites, giving the inner Helmholtz layer. This preferential adsorption is mainly caused by short-range interactions (e.g., specific-ion effects,25,26 hydrogen bonding,27 and coordination effects28) between the electrode surface and ions in the electrolyte.29 Other co-ions or counterions driven by electrostatic interactions (long-range interactions) constitute the outer Helmholtz layer and the Gouy–Chapman diffuse layer. The ion distributions in the EDL depend on the nature of ions and the characteristics of the charged electrode surface. Therefore, preferentially adsorbed ions and electrostatically adsorbed ions would be separated during the EDL formation process. This theory inspired us to develop EDL-based ion separation technology.

Herein, we demonstrate an EDL separation method (EDLS) for selective separation of aqueous metal ions. As noted above, an electrode with tailor-made functionalities can selectively interact with certain metal ions. Once the electrode is charged, these certain metal ions (e.g., precious metals or toxic heavy metal ions) will preferentially be captured in the inner Helmholtz layer through reversible coordination reactions with surface functional groups on the electrode. The alkali or alkaline earth metal ions, which have weak binding affinity with the electrode surface functional groups, are electrostatically captured in the outer Helmholtz layer or the Gouy–Chapman diffuse layer. In this study, we constructed a sandwich-structured EDLS device based on a N-functionalized graphene sheet hydrogel (GS). The successful separation of heavy metal ions (coordination-driven layer) from alkali or alkaline earth metal ions (electrostatic-driven layer) was achieved by tuning the surface potential of the N-functionalized GS (CN-GS). The EDLS device exhibits high separation performance under a variety of conditions and operates at low voltage with an extremely low energy demand and long-term cycle stability. This work presents a new application of EDL effects in ionic separation technology.

RESULTS AND DISCUSSION

Characteristics of the EDL on the CN-GS. Theoretically, the three-dimensional hierarchical structures of GS are beneficial toward ion capture. The interconnected macropores can serve as fast diffusion paths for ion capture and release.30 To enhance the coordination ability toward heavy metal ions, the GS was functionalized by carbon nitride (CN) through a hydrothermal treatment of melamine with graphene oxide, and the product was denoted as CN-GS (see Experimental Section). Melamine is rich in amino and triazine groups, which provides CN-GS with a high nitrogen content (7.77% by weight) and effective nitrogen species to provide pseudocapacitance, such as pyridinic-N, pyrrolic-N, and graphitic-N groups, which also are widely known to bind heavy metals.31 Derived from the EDL theory discussed above, Figure 1a illustrates the hypothetical transformation of the EDL in the CN-GS/electrolyte interface. The applied bias dramatically affects the formation of the EDL and subsequently influences the ion concentration in the bulk electrolyte.

To study the transformation of the EDL on the CN-GS, Na(I) ions were selected as electrostatic-driven ions because of their lack of short-range interaction with the CN-GS, such as by specific-ion effects or coordination effects; as a typical toxic heavy metal, Pb(II) ions were used as coordination-driven ions. A 200 mg CN-GS thin-film electrode (50 mm × 60 mm, Pt mesh as current collector) as the working electrode and graphite (50 mm × 60 mm) as counter electrode were immersed in a mixture of 150 mL of Na(I) (0.5 mM) and Pb(II) (25 μM) solution (see the experimental setup in Figure S2). The variations of Na(I) and Pb(II) concentration in the electrolyte solution were recorded. The randomly distributed ions (stage 1) were driven to the surface of the CN-GS by a negative bias (−0.8 V). Pb(II) ions were preferentially captured in the inner Helmholtz layer through coordination reactions with N-containing groups,24 while Na(I) ions would be electrostatically adsorbed in the outer Helmholtz layer or diffuse layer (stage 2). As a result, the Na(I) and Pb(II) concentrations in the solution decreased to 0.08 mM and 1.9 μM, respectively (Figure 1b). Once the negative bias was removed (0 V), Na(I) released to the solution resulted in an increase of Na(I) concentration to 0.48 mM (96% recovery), while the Pb(II) concentration only slightly increased to 3.9 μM (stage 3). After the application of a positive bias (1.2 V), we found that Pb(II) ions were rapidly released to the bulk solution, giving a final concentration of 24.5 μM (98% recovery) (stage 4).

In situ Raman spectroscopy was performed to probe the interaction of CN-GS with Pb(II) during the capture and release processes (Figure 1c). The CN-GS G band (E_g mode) (∼1601 cm⁻¹) (stage 1) downshifts to ∼1592 cm⁻¹ after capturing Pb(II) (−0.8 V applied, stage 2), probably associated with the formation of a metal–organic complex.32 The peaks located at 1350–1650 cm⁻¹ are sensitive to C–N bonding.33,34 Two weak peaks at ∼1452 and ∼1500 cm⁻¹ disappear, while a new peak emerges at ∼1471 cm⁻¹ (stages 2 and 3), which is indicative of changes in the structure and the environment of the C–N bond that are
probably due to the coordination reaction of Pb(II) with N-containing groups at \(-0.8\) and \(0\) V. Importantly, the peak changes are reversed upon release of Pb(II), as the peaks (\(\sim 1601, \sim 1452, \text{ and } \sim 1500\) cm\(^{-1}\)) are recovered when a \(1.2\) V positive bias is applied (stage 4).

Surface elemental analyses by X-ray photoelectron spectroscopy (XPS) show the Pb 4f peak of the CN-GS at different stages (Figure 1d). The Pb 4f spectrum of CN-GS after capture of Pb(II) shows doublet peaks (4f\(^{7/2}\) and 4f\(^{5/2}\)) at \(\sim 139.0\) and \(\sim 143.7\) eV, associated with divalent lead compounds,\(^{35}\) which indicates that there is no valence changes of Pb(II) in the interfacial reactions. Furthermore, the peak intensities reflect the amount of Pb(II) on the CN-GS, which is consistent with the variations in ion concentration shown in Figure 1b.

The capture of Pb(II) was attributed to its coordination reaction with CN-GS, through which a metal complex was generated. The \(1.2\) V positive bias induced the production of electron depletion on the CN-GS, and an EDL was formed through electrostatic accumulation of anions on the CN-GS. Due to the nanometer scale of the EDL, extremely strong local electric fields (\(\sim 10^9\) V m\(^{-1}\)) can be generated in the electrode–electrolyte interface upon polarization.\(^{36}\) This strong local electric field was capable of perturbing the intrinsic electronic structure of the electrode, which can theoretically influence the chemical stability of metal complexes.\(^{37}\) Experimentally, the Pb-chelate complex was decomposed and released Pb(II) to the electrolyte upon \(1.2\) V positive bias. This result revealed that the coordination reaction of heavy metal ions with CN-GS is reversible and could be achieved under applied positive bias. The above discussion clearly demonstrates that bias-induced electron accumulation/depletion on the CN-GS electrode not only can electrostatically accumulate charged species in the interfacial region of the electrode–electrolyte but also can influence the behavior of ions that can chemically interact with the electrode. As the behavior of ions relies on the transformation of the EDL, the above finding provides a foundation for the application of EDL effects in separation technology.

**EDLS Device Fabrication and Applicability for Ion Separation.** To implement the concept of EDL in aqueous metal ion separation, an EDLS device was fabricated. Figure 2 illustrates the structure of the EDLS device, which was assembled in a cell consisting of a GS layer and a CN-GS layer sandwiching a thin nonconductive porous separator (Figure 2a). This architecture allows the EDLS device to work in a flow-through mode, which can enhance the mass transfer and improve the separation efficiency (Figure 2b).\(^{38,39}\) The CN-GS possesses a highly interconnected 3D network of pores ranging from tens to hundreds of nanometers and displays an open porous morphology (Figure 2c). The macroscopically lamellar structure enables dissolved ions to interact with the CN-GS electrode sufficiently through an interconnected 2D nanofluidic network (Figure 2d).

Figure 2e presents a top-view scanning electron microscopy (SEM) image of the CN-GS layer, which shows the macroporous structure that was suitable for constructing high-flux capacity and low pressure drop flow-through electrodes.
The ionic separation experiments were carried out using the EDLS device shown in Figure 2b. An aqueous solution containing a mixture of Na(I), K(I), Pb(II), and Cd(II) ions was injected into the device, and the effluent was collected at regular intervals. Different voltages were applied to control the EDL transformation, which allowed the capture and release of ions. Figure 3 displays the ion concentration profiles in the effluent during the capture/release cycles. The concentrations of Pb(II) and Cd(II) in the effluent decrease during the capture process ($V_{ca} = -0.8$ V), while increasing during the release process ($V_{re} = 1.2$ V), indicating that the Pb(II) and Cd(II) were successfully captured and recovered through the capture/release procedures. Interestingly, the concentration profiles of Na(I) and K(I) show opposite tendencies to those of Pb(II) and Cd(II) during the operation cycles. This remarkable unprecedented phenomenon implies that this design of the EDLS device enables the successful separation of heavy metal ions from alkali metal ions in aqueous solution.

As discussed earlier, heavy metal ions tend to be captured in the inner Helmholtz layer, while alkali metal ions reside in the outer Helmholtz layer. Accordingly, the EDL was in equilibrium: heavy metal and alkali metal ions constituted the inner and outer Helmholtz layers, respectively (Figure 4 state I). No electric field existed between the GS and CN-GS layers, and excess ions were driven out by the bulk flow ($u_b$). Switching the applied voltage ($V_{ca}$ to $V_{re}$) resulted in disequilibrium, and an electrical field was generated before the establishment of a new equilibrium. Alkali metal ions in the outer Helmholtz layer (electrostatic-driven) were released to the bulk solution (Figure 4 state II). These ions would subsequently migrate toward the GS layer (counter electrode) driven by the electric field ($u_e$) and finally be electrostatically adsorbed on the GS/solution interface. It is noteworthy that $V_{re}$ (1.2 V) is higher than $V_{ca}$ (0.8 V), which means that more ions can be electrostatically adsorbed on the electrode. This result led to the decrease of alkali metal ions.
concentrations in the effluent (Figure 3). Simultaneously, anions were driven to and quickly adsorbed on the CN-GS and sharply weakened the electric field strength between the CN and CN-GS layer. The heavy metal-chelate complexes on the CN-GS decomposed and released heavy metal ions to the bulk solution upon the formation of electron depletion on the electrode, as illustrated in Figure 1 (stage 4). The increase in heavy metal ion concentration in the effluent indicated that the heavy metals released from the CN-GS were driven out by the bulk flow. Moreover, the result indicated that the driving force of the weakening electric field ($\omega_a$) between the GS and CN-GS layers was much weaker than that of the bulk flow ($\omega_b$), leading to very little influence on the migration of ions. As expected, ion separation between heavy metals and alkali metals was achieved.

The basis for ionic separation in the EDLS device is the two types of interaction (coordination and electrostatic) of ions with CN-GS in the interfacial region. We cannot neglect the fact that the two types of interaction simultaneously occur between heavy metal ions and the charged CN-GS electrode. Suppose that the amount of chelating sites on the CN-GS is insufficient for binding a large excess of heavy metal ions. Accordingly, the electrostatic interaction may play a major role in accumulating heavy metal ions at high concentration (Figure 5a). Figure 5b shows the performance of the EDLS device in removing Cd(II) ions at a series of initial concentrations (0.025 to 2 mM). With increasing Cd(II) concentration, the profiles of Cd(II) exhibit a shift from coordination-driven to electrostatic-driven behavior. Furthermore, Na(I) ion (0.025 to 2 mM) and Cd(II) ion (0.1 mM, in the presence of 0.025 to 2 mM Pb(II) ions) variations are shown in Figure 5c and d. Since Na(I) ions have weak affinity in binding with chelating sites on the CN-GS, the driving force for Na(I) in the EDLS device was electrostatic only. As a result, the variation of Na(I) concentration was not affected by Pb(II) concentration (Figure 5c). A competitive coordination reaction would occur between Cd(II) and Pb(II) with chelating sites on the CN-GS. Pb(II), with its powerful binding ability, could occupy a large proportion of chelating sites. With increasing concentration of Pb(II), the amount of free chelating sites will decrease. Accordingly, the profiles

Figure 5. Influence of heavy metal ion concentrations on the performance of the EDLS. (a) Schematic diagram of interaction type of a negatively charged CN-GS surface with heavy metal ions at low and high concentrations. (b) Variations of Cd(II) concentrations during capture and release cycles with different initial concentration. (c) Variations of Na(I) concentrations during capture and release cycles with different Pb(II) concentrations. (c) Variations of Cd(II) concentrations during capture and release cycles with different Pb(II) concentrations. The fluxes were 100 L h$^{-1}$ m$^{-2}$ for capture and 500 L h$^{-1}$ m$^{-2}$ for release. The capture and release times were 120 min ($V_{ca} = -0.8$ V) and 6 min ($V_{re} = 1.2$ V) for each cycle, respectively (initial pH = 5.0, temperature = 25 °C).
of Cd(II) concentration shift from coordination-driven to electrostatic-driven mode (Figure 5d). These results show that Na(I) ions are electrostatic-driven at various initial concentrations, while the behavior of Cd(II) depends on its initial concentration and on that of other competing coordinating ions. Considering the fact that the major challenge of metal separation and recycling in practical applications is in concentrating dilute resources,1,42 we expect that this EDLS method has the potential for effective separation of heavy metal ions from water.

**Performance of the EDLS Device for Selective Separation of Toxic Heavy Metals.** The concept of EDL effects induced separation opens new possibilities in utilizing the EDLS device for separation of aqueous toxic heavy metals. The EDLS is applicable for use with a variety of trace heavy metal contaminants in water for effectively reducing the level of heavy metal concentration, while leaving alkali and alkaline earth metal ions in solution. Separation tests were performed with the EDLS in a solution containing Pb(II), Cd(II), Hg(II), Na(I), K(I), Ca(II), and Mg(II) ions (Table 1). The EDLS can substantially remove the highly toxic heavy metal ions Pb(II), Cd(II), and Hg(II) at various voltages. In contrast, the alkali and alkaline earth metal ions such as Na(I), K(I), Ca(II), and Mg(II) remain in the water. The chelating anchors on the CN-GS could selectively capture transition metal ions, while having weak affinity for binding alkali and alkaline earth metal ions. Kinetic experiments showed that the highest k value (kinetic constants) could be achieved at $V_{ca} = -0.8$ V for Pb(II), Cd(II), and Hg(II) ions (Figure S3). Additionally, metal ions showed different k values even at the same voltage, probably due to the different binding constants.43 The heavy metal ion removal efficiency increased as the $V_{ca}$ was switched from 0 to $-0.8$ V. The increases in removal efficiency are attributed to changes in the chemistry of the chelating sites on the CN-GS when a voltage is applied.13 However, the removal efficiency decreased when the higher voltage of $V_{ca} = −1.2$ V was applied, and this should be attributed to the accumulation of relatively high concentrations of alkali or alkaline earth metal ions at the interface, which will inhibit the diffusion of heavy metal ions to the chelating anchors on the CN-GS. Nevertheless, the higher Pb(II) removal efficiency observed in the adsorption isotherms with high initial Pb(II) concentration at $V_{ca} = −1.2$ V is likely due to the electrostatic-driven effect discussed above (Figure 5a). Since the ion capture is mainly driven by the electrostatic force at higher concentration, increasing the $V_{ca}$ (from 0 to $-1.2$ V) will result in a higher amount of captured Pb(II). Fitting of the experimental data with the Langmuir model shows a $q_{max}$ of 136.11 mg g$^{-1}$ ($V_{ca} = −1.2$ V) for the CN-GS (Table S1).

The ability to withstand a variety of conditions is highly desirable for methods of separating heavy metals from aqueous solution in practical applications.44,45 Therefore, the applicability of the EDLS under various conditions was evaluated. The pH studies showed that the EDLS is effective for Pb(II) removal over a range of pH values (Figure 6a). After the treatment by the EDLS, the residual Pb(II) in the effluent was reduced from 100 ppb to 13.43, 5.00, and 4.51 ppb, at pH 2, 5, and 11, respectively. This result represents an advantage of the EDLS compared with other traditional adsorption-based methods, whose performance tends to be highly affected by pH value.44 The separation tests were also performed at various ionic strengths, a well-known factor that could greatly affect the electrochemical process (Figure 6b). However, the EDLS could still decrease Pb(II) to 8.14, 5.00, and 6.14 ppb at ionic strengths of 1, 10, and 100 mM NaNO$_3$, respectively. The coexistence of organic matters can greatly influence the performance of traditional adsorption methods. In particular, N-containing and O-containing functional groups on organic molecules may act as ligands to bind heavy metal ions.46 Regarding this issue, we studied the influence of ethylenediaminetetraacetic acid (EDTA), which can bind with heavy metal ions to form a metal–EDTA complex.45 However, in the case of the EDLS, the removal efficiencies of Pb(II) remained as high as 88.2%, 87.9%, 85.1%, and 83.3% with Pb(II):EDTA molar ratios of 2:1, 1:1, 1:2, and 1:5, respectively, demonstrating the applicability of the EDLS in aqueous solutions containing complexing ligands (Figure 6c).

Continuous separation experiments were carried out to evaluate the capture and recovery performance of the EDLS (Figure 6d). The Pb(II) concentrations were reduced to <6 ppb at various $V_{ca}$. The profiles of Pb(II) concentration indicate that the EDLS successfully captured and released Pb(II) ions with highly reproducible efficiency in each cycle. It is worth noting that

**TABLE 1. Concentrations of Metal Ions before and after the EDLS Treatments**

<table>
<thead>
<tr>
<th>Metal Ions</th>
<th>Pb(II) (ppb)</th>
<th>Cd(II) (ppb)</th>
<th>Hg(II) (ppb)</th>
<th>Na(I) (ppm)</th>
<th>K(I) (ppm)</th>
<th>Ca(II) (ppm)</th>
<th>Mg(II) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial concentration</td>
<td>107.8</td>
<td>67.17</td>
<td>61.33</td>
<td>53.57</td>
<td>77.57</td>
<td>72.25</td>
<td>50.88</td>
</tr>
<tr>
<td>0 V</td>
<td>7.03</td>
<td>4.99</td>
<td>1.58</td>
<td>52.62</td>
<td>77.64</td>
<td>71.21</td>
<td>51.33</td>
</tr>
<tr>
<td>$-0.4$ V</td>
<td>6.51</td>
<td>3.04</td>
<td>1.27</td>
<td>53.19</td>
<td>77.64</td>
<td>70.73</td>
<td>51.16</td>
</tr>
<tr>
<td>$-0.8$ V</td>
<td>5.44</td>
<td>2.46</td>
<td>0.82</td>
<td>53.61</td>
<td>77.46</td>
<td>70.47</td>
<td>50.67</td>
</tr>
<tr>
<td>$-1.2$ V</td>
<td>7.31</td>
<td>3.82</td>
<td>1.91</td>
<td>53.03</td>
<td>77.23</td>
<td>70.94</td>
<td>51.07</td>
</tr>
</tbody>
</table>

$^{a}$ 50 mL of metal ion solution was fed into the EDLS device with the effluent recycled for 12 h (temperature = 25 °C, pH = 5.0).
the steady-state operating current density is approximately 1 A m$^{-2}$ ($V_{ca} = -0.8$ V) (Figure 6e), based on which the energy demand is calculated to be just 16 mWh L$^{-1}$. The sandwich-structured EDLS works like a supercapacitor: it stores energy once charged. Therefore, the EDLS can maintain a stable voltage during the capture period. It follows that the EDLS maintains low energy consumption through usage of stored energy rather than consuming energy during the selective capture of heavy metal ions.

In addition to its high selectivity and energy efficiency, the EDLS exhibited remarkable durability throughout capture and release operations. We cycled the device for a duration of 3000 capture ($V_{ca} = -0.8$ V) and release ($V_{re} = 1.2$ V) cycles. For the traditional adsorption method, regeneration of adsorbents (treatment with strong acid or alkali) can cause substantial loss of binding affinity because of the destruction of active functional groups.$^{47,48}$ These harsh conditions dramatically influence the cycling performance of the absorbents, whose capacity can sharply decrease after only a limited number of regeneration cycles, leading to poor recyclability (Table S2).$^{49-51}$ In contrast, the performance of the EDLS had no significant decrease (98% retention) after about 3000 cycles, which is 2 orders of magnitude longer than traditional adsorption-based methods (Figure 6f). Fourier transform infrared (FT-IR) spectra in Figure 6f (inset) and SEM images in Figure S5 show that the microstructure and active functional groups maintained good stability after cycling.

The outstanding durability is ascribed to the relatively low voltage operating conditions (no higher than 1.2 V). This mild condition greatly preserved the active functional groups, consequently improving the cycle stability and energy conservation performance of the EDLS.

**CONCLUSIONS**

Inspired by the EDL theory, we developed a novel EDLS device for separation and concentration of aqueous metal ions. We have demonstrated that the EDL effect can control the ion distribution in the interfacial region of the electrode/solution, which opens a new possibility for ionic separation using a novel EDLS device. Separation tests suggest that the EDLS method can be used for separation of heavy metal ions from alkali and alkaline earth metal ions. The EDLS not only has significant selectivity but also can withstand broad pH ranges, various ionic strengths, and strong competing ligands with stable separation performance. Also, the EDLS exhibits high separation performance under a variety of conditions and operates at 1.2 V with the extremely low energy demand of 16 mWh L$^{-1}$. Moreover, the EDLS shows long-term cycle stability, retaining 98% of its performance after 3000 cycles. Specifically, this study highlights the advantages of the EDL effect in separation technology, including high selectivity, low energy consumption, and continuous separation operation. This innovative separation method, initially developed for separation of heavy metal ions in aqueous...
solution, has potential for broader applications in other areas such as rare earth and precious metal recovery, analysis, biomolecule separation, and chromatography systems.

**EXPERIMENTAL SECTION**

**Materials.** Synthetich graphite powder (<20 μm) was purchased from Sigma-Aldrich. P2O5, K2S2O8, KMnO4, NaNO3, KNO3, Mn(NO3)2, Ca(NO3)2, Pb(NO3)2, and Cd(NO3)2 of analytical grade and a 98% H2SO4 and 30% H2O2 aqueous solution were purchased from Sinopharm Chemical Reagents Beijing Co., Ltd., and were used directly as received. All solutions were prepared using ultrapure water (18.2 MΩ·cm) (Milli-Q, Merck Millipore, Germany).

**Syntheses of GS and CN-GS.** GO was synthesized using the modified Hummers’ method (see details in the Supporting Information). GS was prepared through a hydrothermal process. Typically, 30 mL of a 1.5 mg mL−1 homogeneous GO aqueous solution was sealed in a 50 mL Teflon-lined stainless steel autoclave and maintained at 180 °C for 12 h. Then the autoclave was cooled to room temperature. The as-prepared GS was taken out and washed with water. For the synthesis of the CN-GS, 20 mg of melamine was added to 30 mL of a 1.5 mg mL−1 GO aqueous solution followed by ultrasonication for 30 min. The subsequent steps are the same for GS preparation.

**Materials Characterization.** In situ Raman spectra were performed using a confocal Raman microscope (inVia-Reflex, Germany). A linearly polarized He–Ne laser Spectra Physics model 127 (λ = 532 nm, nominally 60 mW output) was used as the excitation source. XPS data were obtained with an ESCALAB 250XI X-ray photoelectron spectrometer microprobe (Thermo Scientific, USA). Field-emission SEM was carried out in an SU 8020 instrument (Hitachi, Japan). FT-IR spectra were obtained with a TENSOR 27 (Bruker, Germany) spectrometer in the range 400–4000 cm−1. Ion concentrations were measured by inductively coupled plasma mass spectrometry (ICP-MS) (ICAP Q, Thermo Scientific, USA) for a concentrations range of 0–200 ppb and inductively coupled plasma optical emission spectrometry (ICP-OES) (710, Agilent Technologies, USA) for ion concentrations of >200 ppb.

**Fabrication of the EDLS Test Cell.** The GS or CN-GS layer was prepared by a direct compression method under a pressure of ~0.2 MPa to form a 25 mm × 25 mm thin film electrode without any binder or conductive additives. The device contained 30 mg of the CN-GS, 20 mg of melamine was added to 30 mL of a 1.5 mg mL−1 GO aqueous solution followed by ultrasonication for 30 min. The subsequent steps are the same for GS preparation.

**Continual Capture and Release Test.** Voltage (Vca and Vre) adjustment was required before ion separation tests. A peristaltic pump was employed to pump solution to the EDLS test cell. The flow rate of the pump was calculated by eq 1:

\[ Q = j \times A \]  \hspace{1cm} (1)

where \( Q \) (L h−1 m−2) is the flux required for the EDLS device and \( A \) (m²) is the area of the EDLS.

The capture and release cycles were repeated several times before performing the measurement of the EDLS. The test cell was at steady state. An automatic fraction collector was used to collect the effluent. The capture and release cycles were repeated several times before performing the measurement of the EDLS. The test cell was at steady state. An automatic fraction collector was used to collect the effluent.

**Influence of pH, EDTA, and Ionic Strength.** Several cycles were repeated before performing the pH effect, ionic strength, EDTA influence, and adsorption isotherm experiments. The test cell was fed from a plastic beaker storing solution to which the effluent was recycled. The solutions were withdrawn from the test cell at regular intervals and filtered through a 0.22 μm membrane filter before analyzing the solution. Solutions were stirred throughout the experiments. The solution pH was adjusted to different values using hydrochloric acid and sodium hydroxide. For the ionic strength, EDTA influence and adsorption isotherm experiments, the solution pH was kept at 5.0 ± 0.1.

The amount of Pb(II) captured by the EDLS device was taken as the difference between the initial and equilibrium Pb(II) concentrations. The Pb(II) capture capacity of the EDLS was obtained from eq 2:

\[ q_e = \frac{(C_i - C_e)V}{w} \]  \hspace{1cm} (2)

where \( C_i \) is initial concentration (ppm), \( C_e \) is equilibrium concentration (ppm), \( V \) is the volume of the solution (L), and \( q_e \) is the captured capacity (mg g⁻¹).

**Pb(II) Adsorption Isotherm Experiments.** Adsorption isotherm experiments for the EDLS were carried out with initial Pb(II) concentrations of 0.005, 0.01, 0.02, 0.1, 0.2, 0.5, and 1 mM at 25 °C. The solution pH was kept at 5.0 ± 0.1. The adsorption isotherm data were fitted with the Langmuir model as presented in eq 3:

\[ q_e = \frac{q_{\text{max}}bC_i}{1 + bC_i} \]  \hspace{1cm} (3)

where \( C_i \) is the equilibrium concentration (mg L⁻¹), \( q_{\text{max}} \) is the maximum adsorption capacity (mg g⁻¹), and \( b \) is a measure of the energy of adsorption.

**Long-Time Cycling Performance Test.** A 200 ppb Pb(II) solution (10 mM NaNO3) in a 10 L plastic container was fed into the test cell by a peristaltic pump. A time relay was employed to switch the applied voltage (between −0.8 V and +1.2 V) at regular intervals (Vca for 360 s and Vre for 240 s). The capacity of the EDLS was measured every 200 cycles as described by eq 2.

The capacity retention \( R \) was calculated by eq 4:

\[ R = \frac{q_e}{q_{\text{max}}} \]  \hspace{1cm} (4)

where \( q_e \) is the capacity after cycling (mg g⁻¹) and \( q_{\text{max}} \) is the initial capacity (mg g⁻¹).

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**REFERENCES AND NOTES**

3. de Vries, W.; Römkens, P. A. M.; Schütze, G. Critical Soil Influences, and Adsorption Isotherm Experiments. The test cell was fed from a plastic beaker storing solution to which the effluent was recycled. The samples were withdrawn from the test cell at regular intervals and filtered through a 0.22 μm membrane filter before analyzing the solution. Solutions were stirred throughout the experiments. The solution pH was adjusted to different values using hydrochloric acid and sodium hydroxide. For the ionic strength, EDTA influence and adsorption isotherm experiments, the solution pH was kept at 5.0 ± 0.1.
