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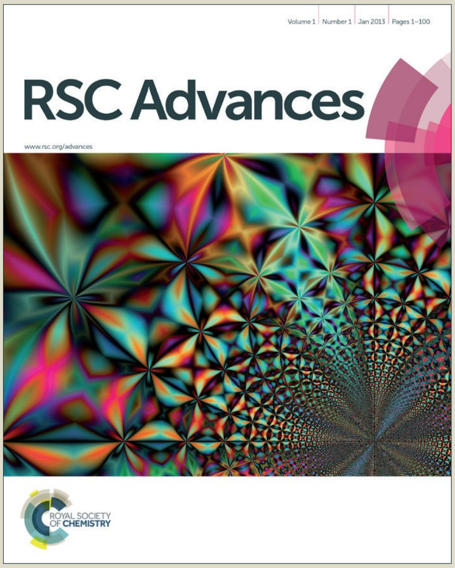

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Separation of Cd(II) and Ni(II) in a binary mixture through competitive adsorption and acid leaching

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ABSTRACT

Different heavy metals present simultaneously in aqueous solutions should be separated to promote environmental protection. In this study, the biosorbent, succinylated maize straw, was used to separate and recover Cd(II) and Ni(II) ions from a binary mixture. The effects of various factors, such as contact time, pH, multi-metal isotherms, and adsorbent dose on the simultaneous removal of the two metal ions were investigated; a separation factor was introduced to evaluate this separation behavior. A separation process was proposed on the basis of the competitive adsorption results to separate metal ions from the binary system. This technique was then successfully employed to separate Cd(II) and Ni(II) ions from the simulated leach liquor of spent Ni–Cd batteries. Approximately 90 % of the adsorbed Cd(II) ions were recovered, and the resulting solution contained <0.7 wt% of Cd(II) and >99 wt% of Ni(II).

Keywords: Maize straw, Competitive adsorption, Separation, Recovery, Ni–Cd batteries

1. Introduction

Spent Ni–Cd batteries are classified as hazardous wastes because their components, namely, Ni and Cd, are heavy metals and suspected carcinogens [1].Cd, a toxic heavy metal, together with Pb and Hg, has been listed as one of the “Big Three” most toxic heavy metals with the greatest potential hazard to humans and the environment [2].Approximately 3% Ni is used to manufacture batteries [3]. Therefore, recycling of Ni–Cd batteries is considerably needed in terms of economic and environmental perspectives. Pyrometallurgical and hydrometallurgical processes are commonly employed to separate and recover Cd(II) and Ni(II) in industrial production, however, these methods require complex procedures, cause secondary pollution, and entail expensive and risky processes [4]. Hence, eco-friendly and low-cost methods must be developed to separate and recycle the two metals from spent Ni–Cd batteries.

Biosorption, a process that utilizes inexpensive biomass to sequester toxic heavy metals, is used to remove contaminants from industrial effluents. In contrast to conventional methods, such as precipitation, chemical oxidation or reduction, and membrane separation, biosorption is an environment-friendly method that requires low operating costs and renewable raw materials [5]. In our previous study [6], maize straw, a major agricultural waste in China, is successfully modified with succinic anhydride (succinylated maize straw, S–MS) and treated with Na_2CO_3 to obtain sodium carboxylate salts (NaS–MS). NaS–MS is a biosorbent utilized to adsorb Cd(II) from an aqueous solution efficiently. Approximately 97% of the adsorbed Cd(II) can be recovered in the form of oxides.

As a continuation of our previous studies, the biosorbent, NaS–MS, was initially used to investigate the competitive adsorption behavior of Cd(II) and Ni(II) in a binary system. Thus far, only a few biosorbents have been used to simultaneously adsorb the two metal ions in binary mixtures [7, 8]. However, these biosorbents were mainly used to treat the wastewater containing < 100 mg/L heavy metals. To the best of our knowledge, no information available in literatures on the separation Cd(II) and Ni(II) from mixed solution containing high concentrations by biosorbents.

This study aimed to establish a method to separate Cd(II) and Ni(II) from binary mixtures by using NaS–MS. It is imperative to study the competitive adsorption behavior to understand the selectivity of each metal onto the biosorbent. The optimum separation conditions were then obtained. A potential separation procedure was also proposed to recover pure Cd(II) and Ni(II) from a binary mixture with various molar ratios of Ni(II) to Cd(II). The process was successfully applied to separate and recover Cd(II) and Ni(II) ions from the simulated leach liquor of spent Ni–Cd batteries.

2. Experimental Procedure

2.1. Materials

S–MS was prepared and characterized in accordance with the methods described in our previous work [6]. After free carboxylic acid groups in a Na_2CO_3 solution were deprotonated, NaS–MS was successfully obtained and passed through a 0.5 mm sieve. All chemicals used in this study were of analytical grade and used without further treatment or purification. Stock solutions of Cd(II) and Ni(II) were prepared by dissolving an exact amount of $CdCl_2 \cdot 2.5H_2O$ and $NiCl_2 \cdot 6H_2O$ in distilled water, respectively. The pH of the tested solution was adjusted to the desired value by adding sodium hydroxide (0.1~1 M) or hydrochloride solution (0.1~1 M).

2.2 Adsorption experiments

The competitive adsorption of Cd(II) and Ni(II) onto NaS–MS was carried out by performing batch experiments in 250 mL Erlenmeyer flasks; the following variables were examined: contact time, pH, multi-metal isotherms, and adsorbent dose. After the flasks were agitated with magnetic stirrers, the samples were filtered through a 0.45 μm membrane filter. The concentrations of the metal ions in the filtrate were determined using a flame atomic adsorption spectrophotometer (FAAS HITACHI 180−80, Japan) equipped with air-acetylene flames at wavelengths of 228.8 and 232 nm for Cd(II) and Ni(II), respectively. The equilibrium adsorption capacity (Q_e) and adsorption yield (*Ad* %) can be calculated by the following equations:

$$Q_e = \frac{(C_0 - C_e)V}{W} \qquad (1)$$

$$Ad_i(\%) = \frac{C_0 - C_e}{C_0} * 100 \qquad (2)$$

where C_0 and C_e are the initial and equilibrium concentrations of solutions containing metal ions (mmol/L), respectively. *V* (L) is the volume of the solution, and *W* (g) is the weight of the used adsorbent.

The preference of the adsorbent for one of the two ions in the binary system is expressed by a separation factor $(SF_{A/B})$, which is a selectivity index [9] in Eq.3:

$$SF_{A/B} = \frac{Q_{eA} * C_{eB}}{C_{eA} * Q_{eB}} \qquad (3)$$

$SF_{\mathrm{A/B}}$ is predicted as dependent on the concentration and coexisting species. $SF_{\mathrm{A/B}}$ is greater than unity if ion *A* is preferred; by contrast, $\mathrm{SF}_{\mathrm{A/B}}$ is smaller than unity if ion *B* is preferred.

2.3 Separation experiments of Cd(II) and Ni(II) from the binary mixture

NaS–MS was stirred with binary mixtures at the optimum separation condition to recover Cd(II) and Ni(II) in proportion. Residue I was collected through filtration and then placed in a muffle furnace. After residue I was heated for 5 h at 723 K, CdO and NiO mixture was obtained. The CdO and NiO mixture was dissolved in 0.3 M HCl solution and filtered to obtain filtrate II and residue II. For Cd(II) recycling, the adsorbent was stirred with filtrate II and residue III was calcined at a 723 K for 5 h to produce CdO. Residue II was dissolved in 6 M HCl at 353 K to obtain a light-green solution. The light-green solution was subsequently stirred with NaS-MS for 1.5 h to obtain filtrate IV. Fig. 1 illustrates the separation of Cd(II) and Ni(II) from the binary solutions through competitive adsorption and acid-leaching experiments.

(Fig. 1.)

3. Results and discussion

3.1 Binary competitive adsorption

Adsorption in multi-metal systems is complicated because of the possible interactions among the solutes. To confirm the competitive adsorption interactions between heavy metals, we conducted batch experiments and determined the uptake rate and the time required to reach equilibrium at various metal concentrations. In the first stage, the initial Ni(II) concentrations were maintained at 0, 0.45, 1.07 mmol/L; the initial Cd(II) concentration was fixed at 1.0 mmol/L. In the second stage, the initial Cd(II) concentration was altered and the Ni(II) concentration was kept constant at 1.0 mmol/L.

The adsorption yield in the binary system is lower than that in the single system of either Cd(II) or Ni(II) as a result of the competitive adsorption (Fig. 2). Furthermore, the adsorption rate of Ni(II) decreases to a greater extent than that of Cd(II), which is inferred that Cd(II) exhibits a greater antagonistic effect than Ni(II) during competitive adsorption [10].

Fig. 2A illustrates the plot of Cd(II) adsorption yields versus contact time with various initial Ni(II) concentrations. The adsorption processes of Cd(II) from both single- and binary- adsorbates show the same pattern, the adsorption yields increases rapidly during starting stage of adsorption and then increase slowly until equilibrium is reached at 90 min.

(Fig. 2.)

The fate of Ni(II) is completely differs from that of Cd(II) (Fig. 2B). At an initial Cd(II) concentration of 0.48 mmol/L, the percentage removal efficiency of Ni(II) is increased as time is prolonged; then the percentage removal efficiency of Ni(II) reaches a plateau similar to that in the single system. At an initial Cd(II) concentration of 1.0 mmol/L, the adsorption yield of Ni(II) increases initially and then reduces gradually after the maximum yield is obtained. Similar phenomena were documented in earlier literatures [11, 12]. An optimum agitation period of approximately 90 min is chosen as the contact time in subsequent experiments

Fig. 3 depicts the possible cause of the difference in behavior between the two metals. Cd(II) and Ni(II) are adsorbed simultaneously at the beginning when numerous vacant adsorption sites are available. However, the constantly adsorbed Ni(II) is practically displaced from the active sites as the initial Cd(II) concentration increases because of the higher affinity of the adsorbent to Cd(II) than to Ni(II). The desorption behavior results in a decreasing uptake rate of Ni(II) ions in the succeding stage.

(Fig. 3.)

3.2 Effect of pH on the competitive adsorption process

The initial pH (pH_i) of the mixed system is a highly important parameter affecting adsorption efficiency. The separation factors of Cd(II)/Ni(II) and adsorption yield at different pH_i values by NaS–MS in the Cd(II)/Ni(II) solutions were determined to evaluate the effect of pH_i (Fig. 4). As pH_i increases, the separation factor of Cd(II)/Ni(II) ($SF_{Cd(II)/Ni(II)}$) increases and reaches the maximum value (5.41) at pH 5.0 and decreases slightly as the pH_i increases from 5.0 to 6.0. Cd(II) or Ni(II) ions are considered as the only ionic species present in the solution at pH ≤ 6 [8]. In our previous study, ion exchange is the main mechanism of the adsorption of cationic metal ions on NaS–MS [6]. pH_{pzc} of NaS–MS is 5.4, which idicates that the adsorbent surface is negatively charged when pH > 5.4 and favors the adsorption of cations. The final pH (pH_f) of sorption should be measured. At $pH_i \geq 4$, pH_f is higher than its pH_{pzc}; this finding suggests that the adsorbent will carry negatively charged functional groups to bind to Cd(II) and Ni(II) ions favorably. Therefore, the pH range for the optimal simultaneous removal of the two metal ions is 4.0–6.0.

(Fig. 4.)

3.3. Non-linear adsorption isotherms of Cd(II) and Ni(II) ions

Equilibrium adsorption isotherms are necessary to establish predictive models to analyze and design adsorption systems. The non-linear adsorption isotherms are given in Fig. 5, for single component adsorption, for Cd(II) adsorption in presence of Ni(II) (Fig. 5A); and for Ni(II) adsorption in presence of Cd(II) (Fig. 5B), respectively. These graphs show that the inhibitory effect enhances with increasing concentrations of the competing metal ions. Fig. 5A shows that the Cd(II) adsorption capacity of NaS–MS is slightly affected by the presence of Ni(II). However, Fig. 5B reveals that the equilibrium uptake of the adsorbed Ni(II) decreases from 1.20 mmol/g to 0.12 mmol/g as the initial Cd(II) concentration increases from 0 to 1.61 mmol/L at an equilibrium concentration of 0.6 mmol/L Ni(II). This finding demonstrates that the Ni(II) adsorption capacity of NaS–MS is decreased by nine orders of magnitude because of the competition with Cd(II). Hence, NaS–MS is more selective to Cd(II) than to Ni(II) in the binary solution. This finding is consistent with that described in Section 3.1.

(Fig. 5.)

The metal affinity sequence onto the same adsorbent is associated with the metal physicochemical properties (Table 1).

(Table. 1.)

Hydration number (N) and hydrated radius (R_H) were considered to explain the metal affinity of adsorbents in a previous study [13]. Metals with low N/R_H exert high Coulumbic forces toward amorphous oxide surfaces [14]. Table 1 reveals that N/R_H of Cd(II) is lower than that of Ni(II); hence, Cd(II) ions could exhibit a higher affinity to the maize straw surface, which also displays amorphous features [15].

Additionally, covalent index, which was devised by Nieboer and McBryde [16], can also verify the conclusion. The covalent index can be expressed as Eq. 4:

$$\text{Covalent Index} = X_m^2 \times r \qquad (4)$$

where X_m represtents the electronegativity of the metal ion and r is the cationic crystal radius. The metal adsorption capacity is positively correlated with the covalent index [17]. From Table 1, it can be calculated that the covalent index value of Cd(II) is higher than that of Ni(II). Likewise, the affinity of Cd(II) to NaS–MS is higher than that of Ni(II).

3.4. Application of multi-metal adsorption isotherm models to equilibrium data

The adsorption equilibrium data of a single-component system can be normally interpreted by the Langmuir and Freundlich isotherm models In Langmuir isotherm model, a mono-molecular layer is formed through adsorption, and no interaction exists between adsorbed molecules [18]. Freundlich isotherm model is often used to describe non-ideal adsorption that involves heterogeneous surface energy systems[19].These models are mathematically represented as follows:

Langmuir: $$\frac{C_e}{Q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{Q_{\max} K} \qquad (5)$$

Freundlich: $$Q_e = K_F C_e^{1/n} \qquad (6)$$

where C_e is the equilibrium concentration of the adsorbate (mmol/L), Q_e is the amount of the adsorbate adsorbed per unit mass of the adsorbent at equilibrium (mmol/g), Q_{max} is the theoretical maximum monolayer adsorption capacity of the adsorbent (mmol/g), K is the Langmuir isotherm constant related to the adsorption energy (L/mmol), K_F (mmol/L) is Freundlich adsorption constant, and $1/n$ is a measure of the adsorption intensity, which determines whether the adsorption intensity and the type of isotherm are favorable ($0.1 < 1/n < 0.5$) or unfavorable ($1/n > 2$).

The parameters predicted with Langmuir and Freundlich isotherm models are presented in Table S1. Langmuir model could accurately predict the experimental data with a satisfactory correlation coefficient ($R^2 > 0.99$). The affinity of NaS–MS to Cd(II) is slightly higher than that of the affinity of NaS–MS to Ni(II); this finding indicates that the carboxyl groups of succinate are equivalent to Cd(II) or Ni(II) in the single solution.

Interference and competition in adsorption sites occur and lead to a complex mathematical formulation of the equilibrium when several components are present in a system. The isotherm parameters of single-component models may not accurately define the multi-metal adsorption behavior of mixtures [20]. Hence, various multi-metal isotherm equations derived from single systems have been developed.

In this study, the adsorption data of the binary system are simulated with two isotherm models. These models are derived from Langmuir isotherm because the adsorption behavior of the investigated metal species in the single system follows Langmuir isotherm model.

The modified Langmuir multi-metal isotherm is expressed as follows [21]:

$$Q_{e,i} = \frac{Q_{\max,i} K_i (C_{e,i} / \eta_i)}{1 + K_i (C_{e,i} / \eta_i) + K_j (C_{e,j} / \eta_j)} \qquad (7)$$

where $C_{e,i}$ and $C_{e,j}$ are the equilibrium concentrations of the metal ions (mmol/L), $Q_{max,i}$ is the maximum capacity, K_i, and K_j are Langmuir adsorption constants determined from the corresponding individual Langmuir isotherm, while η_i and η_j are the correction parameters for the first and secondary metals respectively. These parameters are estimated from the binary adsorption data.

The extended Langmuir multi-metal isotherms are shown as follows [22]:

$$Q_{e,i} = \frac{Q_{\max,i}K_{EL,i}C_{e,i}}{1 + K_{EL,i}C_{e,i} + K_{EL,j}C_{e,j}} \qquad (8)$$

where $K_{EL,\,i}$ and $K_{EL,\,j}$ are the sorption constants representing adsorption affinity (L/mmol).

The adsorption equilibrium is modeled using non-linear least-squares technique to determine the deviations between the experimental and calculated values because some errors derived from non-linear models are inherent. The isotherm parameters of the multi-metal models are determined by the sum of the squares of the errors (ERRSQ) [23]:

$$\mathrm{ERRSQ} = \sum_{i=1}^{n} (q_{e,\exp} - q_{e,cal})_i^{\;2} \qquad (9)$$

where n is the number of experimental data points, $q_{e,\,exp}$ and $q_{e,\,cal}$ are the experimental and the calculated equilibrium concentrations, respectively. A low ERRSQ value indicates that the better multi-metal model can effectively describe the experimental values.

Table 2 lists the parametric values of the multi-metal adsorption models and ERRSQ. In the extended Langmuir isotherm model, Q_{max} and $K_{EL,\,i}$, are irrespective of those derived from the individual isotherm. $K_{EL,\,i}$ reveal the affinity of the adsorbent toward the adsorbates [24].For example, $K_{EL,\,i}$ of Cd ions is higher than that of Ni ions; hence, Cd(II) ions present a higher affinity to NaS–MS than Ni(II) ions. The same conclusion can be obtained from the modified Langmuir isotherm. In the modified Langmuir isotherm model, the high interaction coefficient, η may result in a minor inhibitory effect of metal ions on the adsorption of the other species [5]. Table 2 also shows that η of Ni(II) is higher than that of Cd(II), which indicates that Ni(II) exerts less inhibitory effect on the Cd(II) adsorption. Therefore, the adsorbent exhibits a stronger affinity to Cd(II) than to Ni(II) during competitive adsorption.

(Table. 2.)

The experimental and calculated q_e from these models are compared and presented in Figs. S1 and S2. Most of the data points are distributed around the 45° line; this result implies that the multi-metal isotherm models can represent the experimental adsorption data of the binary systems with varied degrees of fitness [8]. The ERRSQ values of both isotherm models were compared. The result demonstrates that the modified Langmuir model accurately fits the experimental data of the adsorption of Cd(II) and Ni(II) ions from the binary systems onto NaS–MS.

3.5 Effect of adsorbent dose on the separation of Cd(II)/Ni(II) by NaS-MS

$SF_{Cd(II)/Ni(II)}$ and adsorption capacity of NaS-MS of Cd(II) and Ni(II) were investigated in aqueous solutions at various adsorbent doses ranging from 0.4 to 1.2 g/L (Fig. 6). The equilibrium adsorption capacity of Cd(II) decreases as the adsorbent dosage increases. This result is possible because a high amount of adsorbent corresponds to a small amount of ions per unit weight of the adsorbents.

By contrast, the amount of adsorbed Ni(II) increases as the adsorbent concentration increases. It can be explained that with increasing the dosage of NaS–MS the number of availability adsorption sites and surface area are both increased and the inhibitory effects of Cd(II) on Ni (II) are decreased.

(Fig. 6.)

As the amount of the adsorbent increases, the separation factor of Cd(II)/Ni(II) ($SF_{Cd(II)/Ni(II)}$) also increases and reaches the maximum value of 8.59 at 0.6 g/L. After the critical dosage of 0.6 g/L is reached, $SF_{Cd(II)/Ni(II)}$ decreases continuously because the amount of the adsorbed Cd(II) decreases; conversely, the amount of the adsorbed Ni(II) increases. Operational costs and separation efficiencies must be considered to apply adsorbents in industrial separation procedures. A dose of 0.6 g/L meets the two conditions. Hence, 0.6 g/L is applied in all of the separation experiments discussed in this paper.

3.6 Separation of Cd(II) and Ni(II) from the binary mixture

NaS–MS presents a high affinity to Cd(II) but a low affinity to Ni(II); hence, this biosorbent could be used to separate mixed solutions containing high concentrations of the two metals. The separation factor of Cd(II)/Ni(II) reaches as high as 8.59 after 1.5 h of contact time at pH 4–6 with an adsorbent dose of 0.6 g/L when the initial concentration of both Cd(II) and Ni(II) is 1 mM at 303 K.

Another study was conducted, in which the initial Ni(II) concentration was maintained at 0.90 mmol/L and the initial Cd(II) concentration was increased from 0 mmol/L to 3.89 mmol/L. In Fig. 7A, the uptake capacity of Ni(II) drastically decreases as the initial Cd(II) concentration increases. Interestingly, nearly no interaction exists between the adsorbent and Ni(II) ions when the initial concentration of Cd(II) is 3.27 times higher than that of Ni(II). After the mixture was filtered, the filtered residue was collected and calcined at high temperatures to obtain CdO [6]. The adsorbed Cd(II) could then be recovered in the form of oxides. By contrast, the uptake capacity of Cd(II) slightly decreases at high background metal concentrations when the initial Ni(II) concentration increases and the Cd(II) concentration is maintained at the same concentration range. The uptake of Cd(II) only decreases by 33 % when the initial concentration molar ratio of Ni (II) to Cd(II) is 3.7 (Fig. 7B). Thus, the adsorbed Cd(II) cannot be recovered from the binary mixture by using the biosorbent only when the initial molar ratio of Cd(II) to Ni(II) is ≤ 3.27.

(Fig. 7.)

Adsorbents, which are modified carbohydrate polymers, can disintegrate at high temperatures to release the mixture of the oxides of the adsorbed heavy metals. The solubilities of Cd(II) and Ni(II) oxides differ in acid solutions because of the differences in the activity of these oxides[25] (Fig. 8), which inspires us to prepare aqueous solutions containing the two metals at high molar ratio. A procedure could be designed to separate and recover Cd(II) and Ni(II) through competitive adsorption and acid leaching from binary mixtures.

(Fig. 8.)

Residue I is the adsorbent containing the adsorbed Cd(II) and Ni(II) (Fig. 1). After residue I was calcinated for 5 h at 723 K in a porcelain crucible, the mixture of CdO and NiO (Fig. S3) kept in the crucible. CdO easily dissolved in the solution and NiO remained (residue II) when the mixture was dissolved in 0.3 M HCl at 303 K. In filtrate II, the concentration of Cd(II) was much higher than that of Ni(II) and the molar ratio of Cd(II) to Ni(II) was higher than 3.27. The adsorbent unlikely adsorbed Ni(II) ions when the adsorbent was stirred and mixed with filtrate II. The adsorbent could be collected (residue III) and calcined to obtain reddish-brown powder, which comprises pure cadmium oxide; the corresponding structure was confirmed through XRD (Fig. S4). Residue II was dissolved in 6 M HCl at 353 K to obtain a light-green solution, which contained a notebly higher amount of Ni(II) than Cd(II). The presence of Ni(II) could not affect the adsorption of Cd(II). After the solution was treated with NaS–MS, the solution contained lower amounts of Cd(II) than Ni(II), which could be recovered as a salt or precipitated as a hydroxide of Ni(II). The concentrations of Cd(II) and Ni(II) under various initial concentrations in the separation procedure are summarized in Table S2. A maximum of 98.4 % adsorbed Cd(II) ions can be recovered, and the streams containing the coexisting of Cd(II) at a minimum (0.2 *wt.*%) and > 99% *wt.* Ni(II) are obtained (filtrate IV). Therefore, the procedure can be potentially used to acquire pure metals from Cd(II) and Ni(II) mixture solutions to produce valuable commercial products from real effluents.

3.7 Separation of Cd (II) and Ni (II) from the simulated leach solution of spent Ni-Cd batteries

Considering that NaS–MS shows an excellent separation ability in the binary mixture of Cd(II) and Ni(II) ions, we propose that this biosorbent can be potentially applied to separate and recover Cd(II) and Ni(II) in the leach liquor of spent Ni–Cd batteries.

A synthetic aqueous solution containing 7.31 g/L Cd(II) and 12.45 g/L Ni(II) was prepared by dissolving appropriate amounts of chloride salts in double deionized water. This mixture simulated the leach liquor of waste Ni–Cd batteries [26]. Cd(II) and

Ni(II) were separated and recovered in accordance with the procedures illustrated in Fig. 1. The Cd(II) and Ni(II) concentrations during the separation are presented in Table 3. Approximately 90 % of the adsorbed Cd(II) ions can be recovered. The solution contained only < 0.7 % *wt*.% of Cd(II) and > 99 % *wt*.% of Ni(II) (filtrate IV).

(Table. 3.)

4. Conclusion

In this study, an efficient approach to separate and recover Cd(II) and Ni(II) from a binary aqueous solution was established on the basis of competitive adsorption behavior and acid-leaching experiments. A non-toxic and low-cost biosorbent named NaS–MS was used to adsorb Cd(II) and Ni(II) simultaneously. After the adsorbent was stirred into the binary aqueous solution for 1.5 h, the optimum separation results could be obtained at pH 4.0–6.0 and an adsorbent dose of 0.6 g/L. The separation factors and the modified Langmuir model showed that the adsorbent displayed higher selectivity to Cd(II) in the two-metal systems than to Ni(II). The CdO and NiO mixture was obtained after the biosorbent was stirred with the binary mixture and calcined in a muffle furnace. The dissolution rates of the mixture differed at varying HCl concentrations. Competitive adsorption could be applied to acid-leaching solutions. Therefore, a separation and recovery scheme of Cd(II) and Ni(II) was proposed and successfully performed to separate Cd(II) and Ni(II) from the simulated leach liquor of spent Ni–Cd batteries. The results demonstrated the feasibility of separating and recycling heavy metals by using environment-friendly biosorbents from industrial mixtures. The proposed method can also be used to ameliorate environment-related issues.

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Supporting Information

Supporting Information include: comparison of the experimental and calculated Q_e values of cadmium(II) ions in a binary mixture of Cadmium(II) and Nickel(II) ions; comparison of the experimental and calculated Q_e values of nickel (II) ions in a binary mixture of cadmium(II) and nickel(II) ions; XRD spectra for the mixture of the oxides of Cd(II) and Ni(II); XRD spectra for the recovered cadmium oxide; Adsorption isotherm parameters for Cd(II) and Ni(II) onto NaS-MS in single-component system; Summary of the concentration of heavy metals during the separation process and the recovery of Cd(II).

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Figure captions:

Fig.1. Procedure for the separation of Cd(II) and Ni(II) from their binary mixture

Fig.2. Comparison of adsorption yield of Cd(II) and Ni(II) ions in the presence of increasing concentration of coexistence ions (original pH 6.0, adsorbent dose = 1 g/L, T=303 K, t =1.5 h)

Fig.3. Schematic illustration for the displacement mechanism between Cd(II) and Ni(II)

Fig. 4. The dependence of the separation factor of Cd(II) / Ni(II) (blue circles) and the adsorption yield of Cd(II) (black squares) and Ni(II) (blank black squares) on the pH values in the Cd(II) / Ni(II) mixture solutions ($C_{0,\mathrm{Cd(II)}} \approx 1.0$ mM, $C_{0,\mathrm{Ni(II)}} \approx 1.0$ mM, adsorbent dose = 1 g/L, T=303 K, t =1.5 h)

Fig.5. Comparison of non-linearized adsorption isotherms of Cd(II) and Ni(II) ions in the presence of increasing concentration of coexistence ions (original pH 6.0, adsorbent dose = 1 g/L, T=303 K, t =1.5 h)

Fig. 6 Separation factor of Cd(II) / Ni(II) (blue circles) and adsorption quantities of Cd(II) (black squares) and Ni(II) (blank black squares) by NaS-MS versus the various concentration of the adsorbent in the Cd(II) / Ni(II) mixture solutions ($C_{0,\mathrm{Cd(II)}} \approx 1.0$ mM, $C_{0,\mathrm{Ni(II)}} \approx 1.0$ mM, pH = 4~6, T=303 K, t =1.5 h)

Fig.7. Comparison of the uptake capacity of Ni(II) or Cd(II) in the presence of increasing initial concentration of the coexistence ions (original pH 4.0~6.0, adsorbent dose = 0.6 g/L, T=303 K, t =1.5 h)

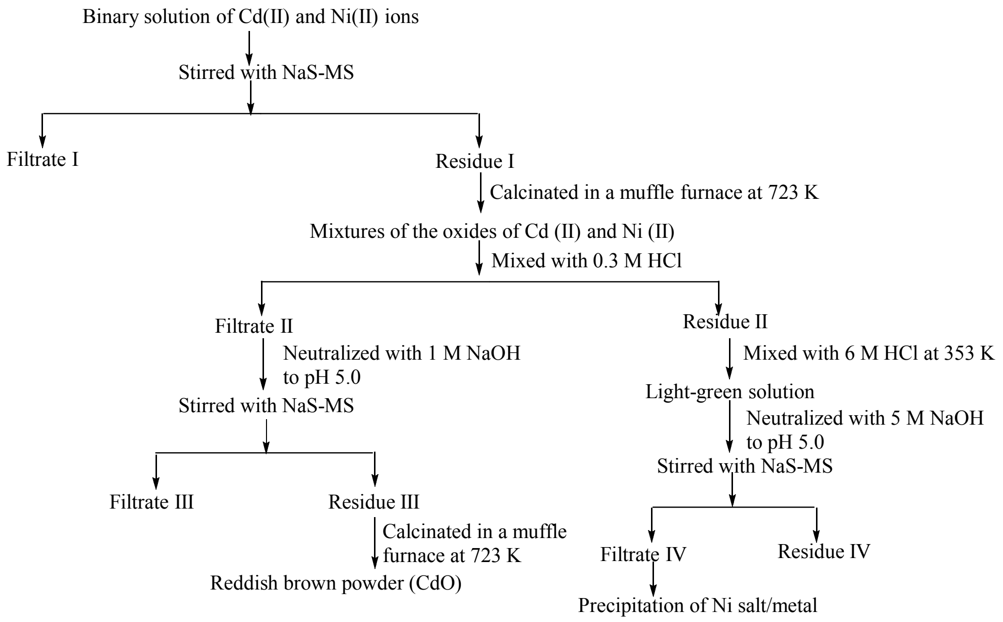
Fig. 8. (a) Dissolution rates of CdO and NiO with various concentrations of HCl at

303 K; (b) Dissolution rate of NiO with various concentrations of HCl at 353 K; (c) Dissolution rates of NiO with different temperatures

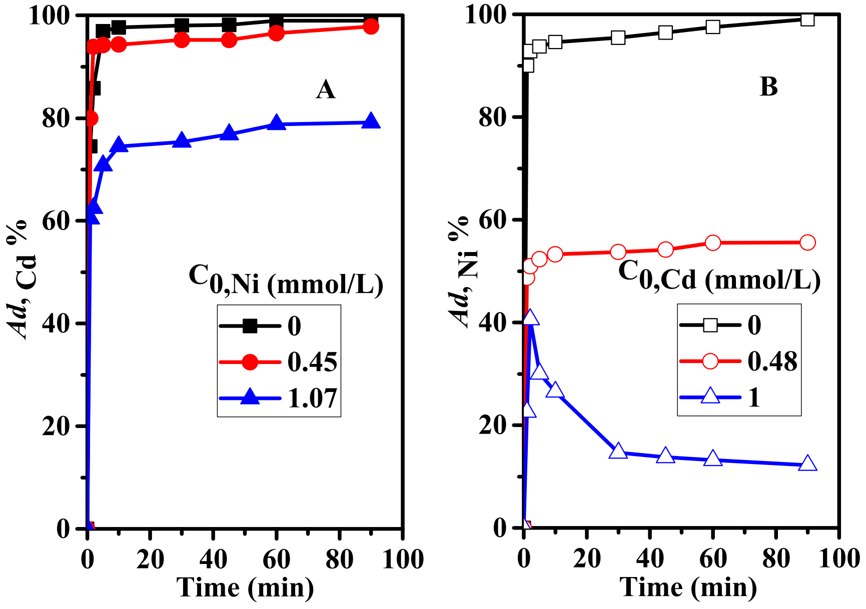
Table 1. The physicochemical properties of Cd(II) and Ni(II)

Table 2 Binary-component isotherm models parameters for the adsorption of cadmium(II) and nickel(II) (original pH 6.0, adsorbent dose = 1 g L^{-1}, T=303 K, t =1.5 h)

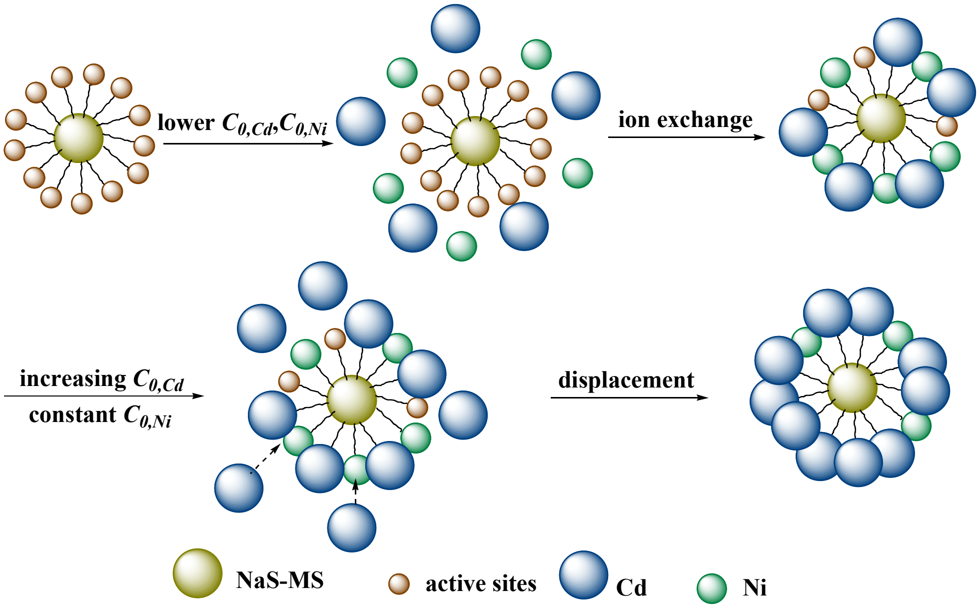
Table 3 Summary of the concentration of Cd(II) and Ni(II) during the separation process onto the simulated leach liquor of spent Ni-Cd batteries


Binary solution of Cd(II) and Ni(II) ions
Stirred with NaS-MS
Filtrate I
Residue I
Calcinated in a muffle furnace at 723 K
Mixtures of the oxides of Cd (II) and Ni (II)
Mixed with 0.3 M HCl
Filtrate II
Neutralized with 1 M NaOH to pH 5.0
Stirred with NaS-MS
Filtrate III
Residue III
Calcinated in a muffle furnace at 723 K
Reddish brown powder (CdO)
Residue II
Mixed with 6 M HCl at 353 K
Light-green solution
Neutralized with 5 M NaOH to pH 5.0
Stirred with NaS-MS
Filtrate IV
Residue IV
Precipitation of Ni salt/metal

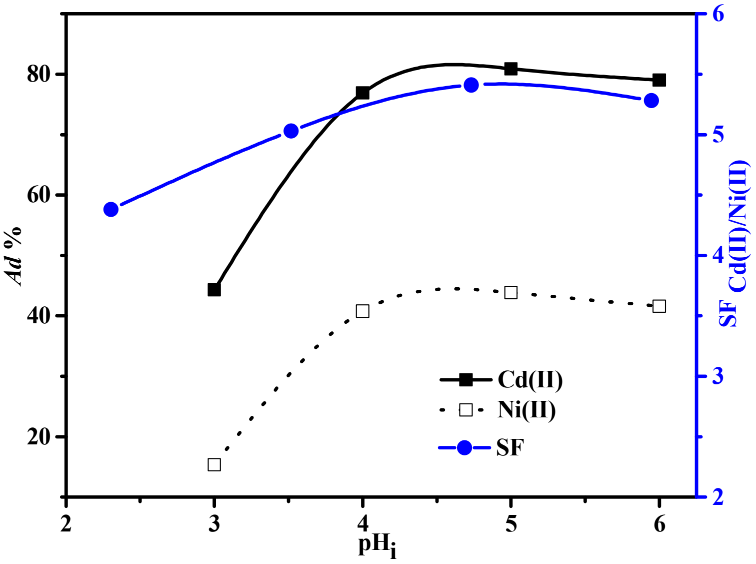
(Fig. 1.)


A
B
Ad, Cd %
Ad, Ni %
Time (min)
Time (min)
$C_{0,Ni}$ (mmol/L)
0
0.45
1.07
$C_{0,Cd}$ (mmol/L)
0
0.48
1
0
20
40
60
80
100

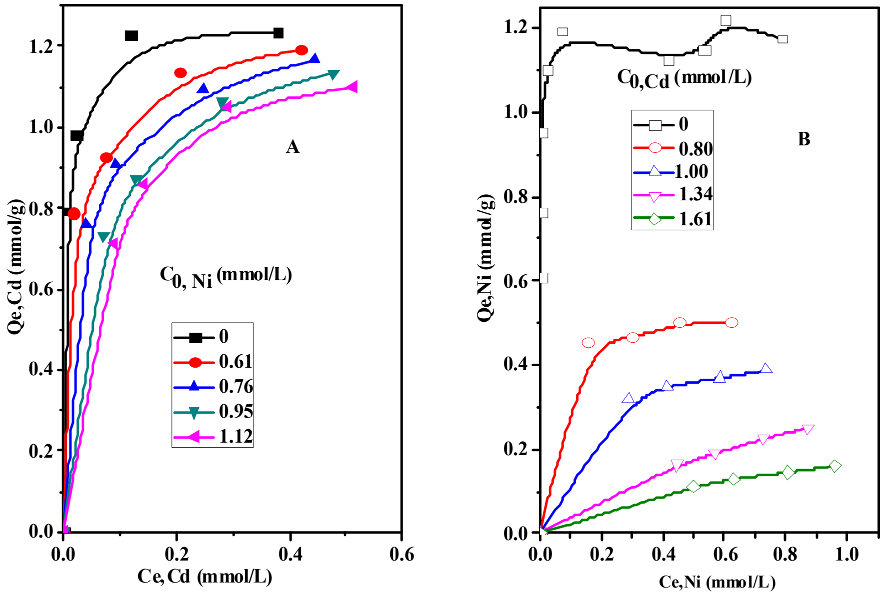
(Fig. 2.)


lower $C_{0,Cd}$,$C_{0,Ni}$
ion exchange
increasing $C_{0,Cd}$
constant $C_{0,Ni}$
displacement
NaS-MS
active sites
Cd
Ni

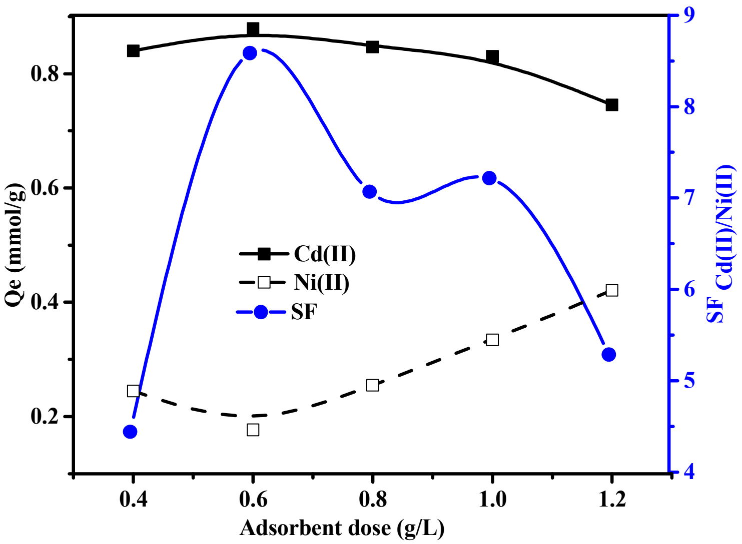
(Fig. 3.)



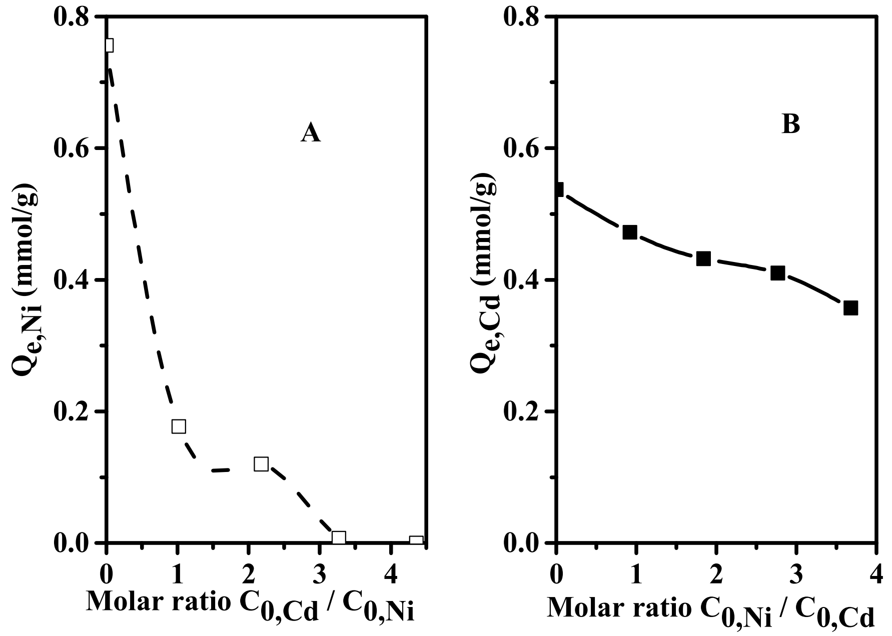
(Fig. 4.)


A
Qe,Cd (mmol/g)
Ce,Cd (mmol/L)
$C_{0,\,Ni}$ (mmol/L)
0
0.61
0.76
0.95
1.12
0.0
0.2
0.4
0.6
0.8
1.0
1.2
B
Qe,Ni (mmol/g)
Ce,Ni (mmol/L)
$C_{0,Cd}$ (mmol/L)
0
0.80
1.00
1.34
1.61
0.0
0.2
0.4
0.6
0.8
1.0
1.2

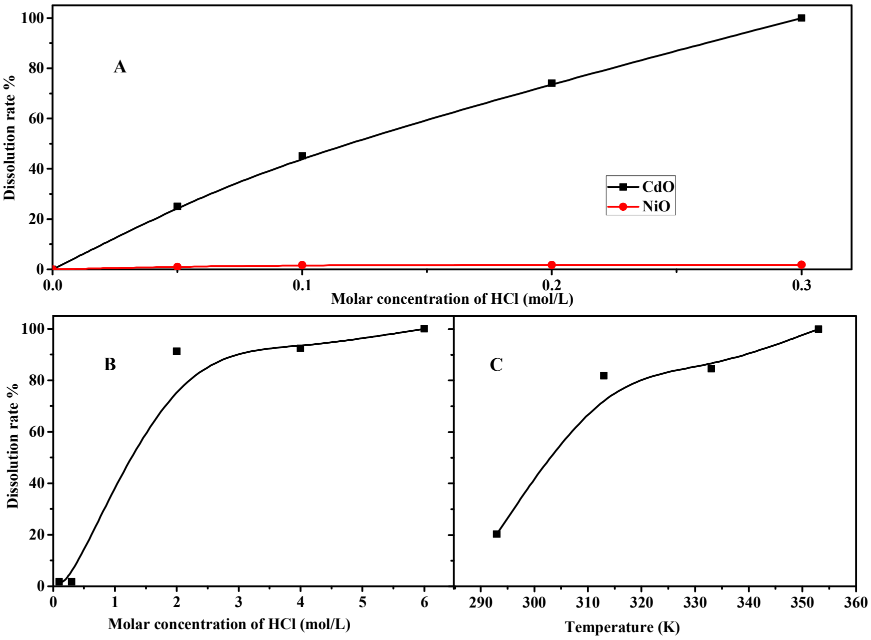
(Fig. 5.)


Qe (mmol/g)
0.2
0.4
0.6
0.8
SF Cd(II)/Ni(II)
4
5
6
7
8
9
0.4
0.6
0.8
1.0
1.2
Adsorbent dose (g/L)
■ Cd(II)
□ Ni(II)
● SF

(Fig. 6.)


A
B
$Q_{e,Ni}$ (mmol/g)
$Q_{e,Cd}$ (mmol/g)
0.0
0.2
0.4
0.6
0.8
0
1
2
3
4
Molar ratio $C_{0,Cd}$ / $C_{0,Ni}$
Molar ratio $C_{0,Ni}$ / $C_{0,Cd}$

(Fig. 7.)


A
B
C
Dissolution rate %
Molar concentration of HCl (mol/L)
Temperature (K)
CdO
NiO
0
20
40
60
80
100
0.0
0.1
0.2
0.3
0
1
2
3
4
5
6
290
300
310
320
330
340
350
360

(Fig. 8.)

Table 1. The physicochemical properties of Cd(II) and Ni(II)

Properties	Cd(II)	Ni(II)
Electronegativity (X_m)	1.61	1.91
Ionic radium, Å (r)	0.97	0.69
Hydration number (N)	6.0	6.6
Hydrated radium (R_H)	2.28	2.06

Table 2

Binary-component isotherm models parameters for the adsorption of cadmium(II) and nickel(II) (original pH 6.0, adsorbent dose = 1 g L^{-1}, T=303 K, t =1.5 h)

Components	Modified Langmuir		Extended Langmuir	
	η	ERRSQ	K_L	ERRSQ
Cd(II)	0.713	0.0598	46620.621	0.0601
Ni(II)	1.093	0.0328	15.299	0.0340

Table 3 Summary of the concentration of Cd(II) and Ni(II) during the separation process onto the simulated leach liquor of spent Ni-Cd batteries

Solutions	C_{Cd} (mg/L)	C_{Ni} (mg/L)
Filtrate I	4240	8603
Filtrate II	1135.15	18.75
Filtrate III	32.28	18.75
Light-green solution	88.85	1437.25
Filtrate IV	8.24	1130.5
Recovery of Cd(II)	90 %	