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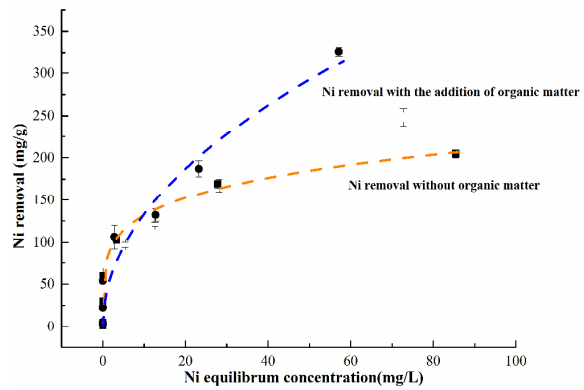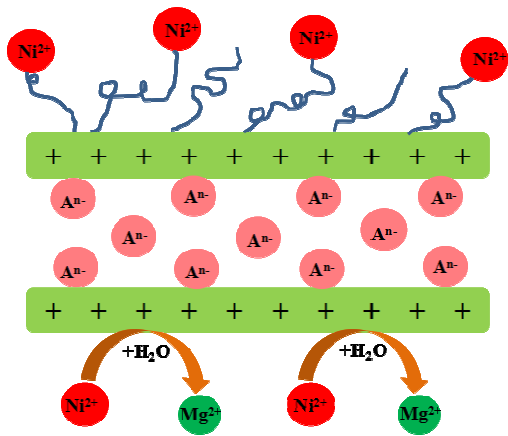
ARTICLE

Synergistic effect of humic and fulvic acids on Ni removal by the calcined Mg/Al layered double hydroxide

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Discharge of Ni(II) containing wastewater to terrestrial environment can lead to serious pollution issues. This study presents a facile, cost-effective and high efficient method to rapidly remove Ni(II) in wastewater by using a calcined Mg/Al layered double hydroxide (LDH), which is a pioneering investigation of using the calcined LDH to remove the positively charged Ni(II) ions. The kinetic studies show that the removal of Ni (II) is very rapid with a pseudo first order k of up to 3.6 ± 0.5 h^{-1}, and maximum removal of Ni (II) is up to 204.2 ± 10.6 mg/g. In addition, our results reveal that both humic (HA) and fulvic acids (FA) can strongly bind to the surface of the LDH, which demonstrates that the calcined LDH can effectively remove both cationic and anionic pollutants in a single process. With the increase of pH up to 7.5, the removal of Ni, HA and FA by the calcined LDH are all drastically enhanced. Our study also demonstrates a strong synergetic effect of FA and HA on the Ni(II) removal by the calcined LDH, with a maximum Ni(II) removal of 290.6 ± 16.4 mg/g and 480.4 ± 21.3 mg/g at pH 7, respectively. The possible mechanism of the Ni(II) removal can be due to the incorporation of Ni into the layered structure by replacing the leached Mg in the layers of the LDH during the process of rehydration of the calcined LDH. The HA or FA bound on the surface of the rehydrated LDH can induce an additional Ni(II)-HA or -FA complexation, consequently, leading to the enhancement of the Ni removal. The trial of treating a high Ni-containing wastewater in practice, indicates that the calcined LDH is an promising material for metal containing wastewater treatment.

Introduction

As one of most notorious metallic elements, nickel (Ni) containing wastewater mainly originates from weathering of soil minerals, deposition of nickel batteries, use of alloys and disposal of municipal sewage sludge [1]. Ni mostly presents as bi-charged Ni(II) species in wastewater. Hence, discharge of Ni to the terrestrial environment can constantly lead to the elevation of Ni (II) ions in the aquatic environment, and causing serious soil and water pollution. Even though trace amount of Ni is beneficial to human, the excessive presence of Ni can threat aqueous animals and human health; it is well known that Ni poses acute neurotoxic, embryotoxic and carcinogenic effects [2]. The threshold concentration of Ni should not exceed 2.0 mg/L for short-term effluent reuse and 0.2 mg/L for long-term effluent reuse According to US EPA guideline [3]. To match those criteria for Ni controlling, technologies based on processes such as precipitation, membrane filtration, reverse osmosis, electrolytic coagulation and adsorption have been developed to remove the Ni substances from effluents before discharge into the environment [2, 4, 5]. Although precipitation is considered an efficient approach, relatively high pH condition is commonly required by adding large amount of base such as NaOH or Ca(OH)$_2$. Adsorption is a very attractive process to remove Ni and other metallic elements. Many adsorbents have been developed and applied in practice, such as carbonaceous materials [6, 7], chitosan [8], diatomite[9], and solid humic acid [10]. However, limitations such as high cost, demanding synthesis condition, poor stability of sorbents, and lack of reproducibility, consequently, hinder those materials to be used in large scale.

Layered double hydroxide (LDH) such as hydrotalcite (HT; Mg$_6$Al$_2$(CO$_3$)(OH)$_{16}$·4(H$_2$O) belongs to a class of anionic clays with a "sandwich"-like structure [11]. In comparison to other materials, LDHs can be simply synthesized by coprecipitation of desired two or three different sorts of cations in an appropriate ratio, with which method can be easily scaled up [12, 13]. The structure of LDHs provides high anion exchange capacity depending on features of intercalated anions. Many studies have reported that LDHs can be used for removing a variety of oxyanions such as phosphate, arsenate, chromate and dissociable organic dyes [14-17]. However, this unique character limits its application for removal of cationic metallic elements, because the key mechanism to uptake those oxyanions is through a surface complexation. Perez and co-workers reported that to Zn/Al LDH intercalated with chelating agents such as ethylenediaminetetraacetic acid (EDTA) showed potential for removal of Cu(II), Pd(II) and Cd(II) via complexation of the cationic elements with the intercalated polyprotic anions [18]. The drawback of this approach is the introduction of toxic organic ligands such as EDTA in the LDH interlayers. On the other hand, previous studies have demonstrated that the carbonate intercalated LDHs can transfer to mixed metal oxides after the calcination at the elevated temperatures (e.g. 500 °C), and will undertake hydrolysis process of reassembling to LDH form by incorporating targeted anions into the interlayers when presenting in water [19]. Several studies have been taking this advantage of this so-called "structure memory effect", to obtain elevated removal efficiency for various targeted oxyanions [12, 20]. During the rehydration process it is likely that also metal cations in solution can be incorporated into metal hydroxide layers, whereas, this has hardly being explored. To our knowledge, no study has been taken on the removal of cationic metallic elements particularly Ni(II) by using the calcined LDHs.

We aim to investigate the removal efficiency of Ni(II) by using the calcined LDH at different experimental conditions such as pH and temperature. Besides, the effect of coexisting natural organic matters (NOMs) such as humic and fulvic acids on Ni(II) removal is further systematically examined. The possible removal mechanism of Ni(II) is also discussed in virtue of x-ray diffraction (XRD) and x-ray photoelectron spectroscopy (XPS) technologies. In final, the calcined LDH is then applied for cleaning a real wastewater sampled from a stainless steel manufactory to examine its performance in practice.

Experimental

Reagents and solutions

Ni(II) stock solution with 1000 mg/L was prepared from nickel nitrate hexahydrate (Ni(NO$_3$)$_2$ ·6H$_2$O; puriss grade) salt which was purchased from Sinopharm Co. Ltd (Beijing, China). Laboratory grade humic acid (HA) obtained from Sigma Aldrich was dissolved in water at pH 9, and then filtrated through 0.45µm mixed cellulose ester membrane prior to use. Fulvic acid (FA) from Nanjing Chemlin chemical industry Co., ltd (Nanjing, China), was used without further purification. All chemicals were analytical grade, MilliQ water (> 18.2 MΩ·cm) was used throughout this study.

The elemental composition of the HA and FA samples was determined on a Vario EL III CHN analyzer (Elementar, Germany). The functional groups in the HA and FA samples were determined by potentiometric titration using a Metrohm iTouch 916 (Metrohm Inc, USA) under argon flushing. The molecular weight distributions (MWDs) of the HA and FA in the test water samples were obtained using HPSEC (high-performance size-exclusion chromatography) method (see the supplemental document S1).

Preparation of the calcined LDH

Nanocrystalline LDH intercalated with carbonate was synthesized by fast coprecipitation of 0.06 mole Mg(NO$_3$)$_2$ and 0.02 mole Al(NO$_3$)$_3$ solutions with 0.13 mole of NaOH in the presence of 0.4 mole Na$_2$CO$_3$ solution. Total 200 mL of mixture was then vigorously stirred for half hour, and then subject to repeating centrifugation at 4000 g and washing several times with MilliQ water. Subsequently, the solid was dispersed in 200 mL of MilliQ water before hydrothermal treatment in a stainless steel autoclave at 100 °C [21]. The as-prepared LDH underwent freeze-drying, and calcined in muffle furnace at 500 °C for 8 hours. The resulting product was cooled and stored in a desiccator for further use in this study.

Ni(II) removal experiments by using the calcined LDH

The Experiments to study the kinetics of Ni(II) removal by the calcined LDH in the presence and absence of 30 mg-C/L HA or FA were performed, respectively, by dosing 10 mg calcined LDH samples into 50 mL of 30 mg/L Ni(II) aqueous solutions and shaking for a period up to 48 h at pH 7 and room temperature (25 ± 1 °C). At each selected time, three parallel sample tubes were taken out for analyses. For marking adsorption isotherms, 10 mg calcined LDH powders were dispersed in solutions with initial concentrations of Ni(II) ranging from 0.2 to 120 mg/L in the presence or absence of 35 mg-C/L HA or FA. The pH value of the solutions was adjusted to 7 by using 0.1 M HNO$_3$ or NaOH. Finally, the mixtures were equilibrated for 24 h at 25 °C in a thermostatic shaker.

The effect of pH on Ni(II) removal without the addition of the NOMs was studied in the pH range between 4.0 and 7.5 where no significant Ni(II) precipitation was observed. The influence of HA and FA on uptake of 35 mg /L Ni(II) was investigated at a HA or FA initial concentrations up to 120 mg-C/L at 25 °C. In order to evaluate

the reusability of the product, the processes of Ni removal and calcination of the solid after reaction were performed for five cycles at pH 7 by repeatedly adding 1 g of the calcined solids into 1 L of 100 mg/L Ni(II) solution. In addition, the calcined LDH was finally applied to examine its performance on treating a real Ni-containing wastewater.

All experiments were carried out in triplicates. The samples after reaction were centrifuged at 4000 g for 10 min. The concentrations of Ni(II), magnesium (Mg) and aluminium (Al) were analysed by using an Optima 8300 inductive coupled plasma optical emission spectrometer (ICP-OES; PerkinElmer, USA).

The species distribution of Ni in the aqueous solution as a function of pH was simulated by means of Visual MINTEQ ver. 3.0. The Ni species distribution against pH was given in Fig. S1.

Characterizations

The freshly prepared LDH, its calcined form before and after reacting with Ni(II) were analyzed on a X'Pert PRO MRD diffractometer (PANalytical, Netherlands) coupled with monochromatic Cu Kα radiation (λ = 0.15405 nm) at 40 keV and 40 mA. Fourier transformation infrared spectroscopy (FT-IR) spectra for the samples were obtained by using a Nicolet 8700 (Thermo scientific, USA), over a range from 400 to 4000 cm^{-1}. The morphologies of the LDH particles before and after calcination and the reaction with Ni (II) were pictured on Hitachi SU8000 ultra high resolution field emission scanning electron microscope (FE-SEM; Hitachi, Japan) at beam energy of 15 kV. The X-ray photoelectron spectroscopy (XPS) measurements were performed in an EscaLab 250Xi (Thermo Scientific, USA) equipped with two ultrahigh vacuum (UHV) chamber to study the surface elemental compositions and the states of Ni, Mg and Al on the calcined LDH before and after reaction with Ni (II).

The elemental compositions of LDH and its calcined from before and after reaction with Ni(II) were analyzed by using ICP-OES. Zeta potential of the LDH as a function of pH from 4 to 12 was monitored by using a Zetasizer Nano ZS (Malvern, England) (see the supplemental document S2).

Results and discussion

Characteristics of the as-synthesized LDH and its calcined form

Fig. 1a shows that the diffraction peaks for the as-synthesized LDH are rather shape and narrow, indicating its high crystallinity. The calculated basal spacing (d_{003}) of the LDH is 0.78 nm, which is consistent with previous reports for the carbonate form of LDH [22, 23]. The fast coprecipitation following hydrothermal treatment method generates a narrow particle size distribution (average value is about 100 nm) and few aggregates as shown in Fig. 2a, in contrast to conventional coprecipitation methods [24]. FT-IR analysis shows strong hydroxyl stretching at about 3490 cm^{-1} and 1630 cm^{-1} which is ascribed to hydroxyl groups bound to Mg, Al and water molecules presented within the interlayers (Fig. 3a). The strong band at 1360 cm^{-1} (Fig. 3a) is assigned to C-O asymmetric stretching of CO$_3^{2-}$ ions located at interlayers in LDH [16]. Zeta potential of the as-synthesized LDH at pH range of 4 to 12 is constantly positive with a potential of 25 to 50 mV (Fig. S2), which is in agreement with the principle of positive layered structure and electric double layer on the solid surface [25]. It can further conclude that the point of zero charge (pH$_{pzc}$) of the LDH is > pH 12 according to the estimation by Fig. S2.

The freshly prepared LDH was subject to calcination. As illustrated in Fig. 1b, the XRD pattern of the calcined LDH at 500 °C

significantly changes from its precursor, showing two characteristic peaks at 2θ of 43° and 62° in analogous with periclase (MgO). This indicates the destruction of the hydrotalcite-like structure after calcination, consequently leading to a mixture of crystalline magnesium oxide and amorphous aluminium oxide. The SEM image for the calcined LDH differs from its precursor, showing that the layers break down into pieces, leading to aggregation of the fragments (Fig. 2b). This is due to the loss of water molecules and carbonate anions from LDH during sinterization [26]. The FT-IR spectrum of the calcined LDH reveals that the shoulders at the band of about 3490 cm^{-1} and 1635 cm^{-1} due to hydroxyl vibration have almost vanished, which demonstrates that water molecules within layers and hydroxyl groups are removed at the elevated temperature (Fig. 3b). Additionally, the band of 1360 cm^{-1} due to C-O asymmetric stretching disappears as a result of carbonate ions removal from interlayers (Fig. 3b)[12].
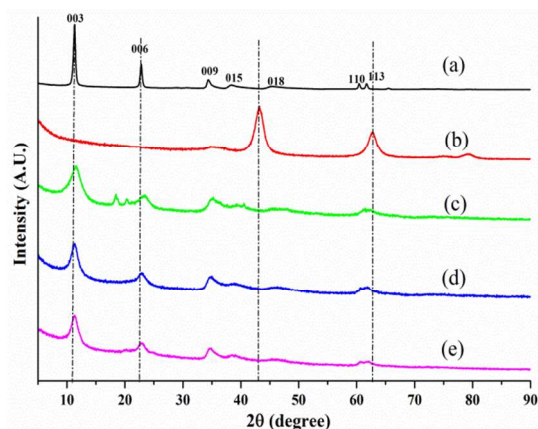

Fig. 1. XRD patterns for (a) the as-synthesized Mg/Al LDH, (b) the calcined LDH at 500°C, (c) the calcinced LDH after reaction with Ni(II), (d & e) the calcined LDH after reaction with Ni(II) in the presence of fulvic (FA) and humic acids (HA).
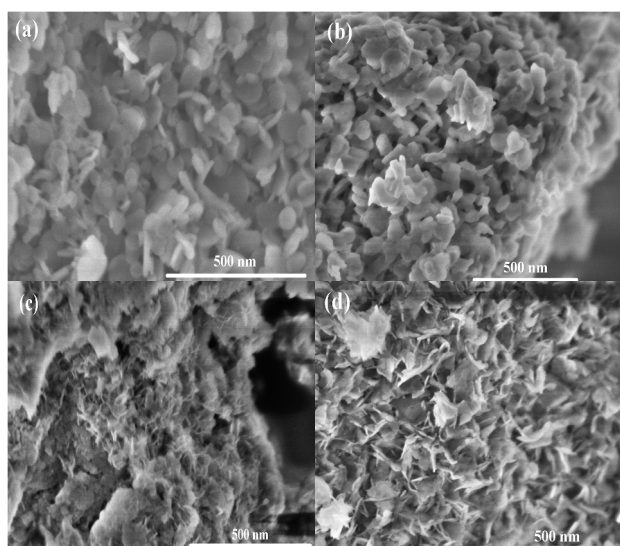

Fig. 2. SEM micrographs for (a) the as-synthesized Mg/Al LDH, (b) the calcined LDH, (c, d & e) the calcined LDH after reaction with 30 mg/L of Ni in the absence and presence of 35 mg-C/L of humic (HA), respectively.
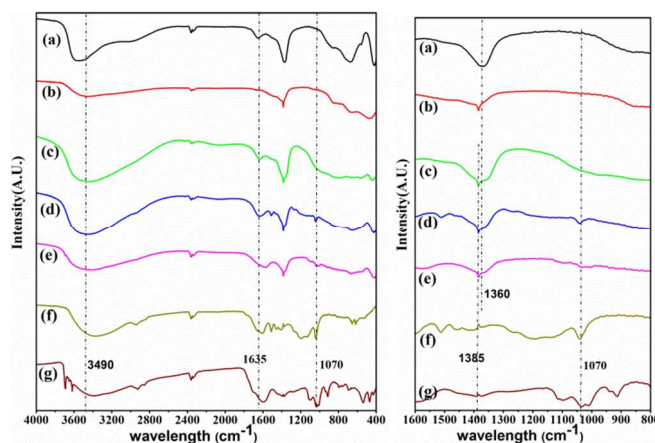

Fig. 3. FT-IR spectra of (a) the as-synthesized LDH, (b) the calcined LDH at 500°C, (c) the calcined LDH after reaction with Ni(II) solution at pH 7 in the absence, (d & e) the presence of 35 mg-C/L fulvic (FA) or humic acids (HA), respectively, FA (f) and HA (g).

Kinetic studies

Kinetic data of Ni(II) removal by the calcined LDH in the absence and presence of organic matter were fitted with Lagergren pseudo first order model (Eq.1).

$$q_t = q_e(1 - e^{-k_1 t}) \tag{1}$$

where q_t (mg/g) and q_e (mg/g) are the amount of removed Ni at equilibrium and at time t, and k_1 (h[-1]) represents the pseudo first order Ni removal constant. As shown in Table 1 and Fig. 4a, pseudo first order model can well describe Ni removal kinetics by the calcined LDH (R^2 values range from 0.942 to 0.997). The results show that the removal of Ni(II) rapidly accomplishes and reaches a plateau of 147 mg/g loading within the first one hour at neutral pH condition. The Ni(II) removal reaches approximately 100% when the dosage of the calcined LDH is 0.2 g/L for the initial Ni concentration of 10 mg/L. This explicitly indicates that the calcined LDH is an efficient material for removing Ni ions. A similar kinetic constant of closing to 3.6 h^{-1} is also observed for the uptake of HA or FA by the calcined LDH (data not shown), in agreement with previous studies of organic matters removal by an iron containing LDH [27]. The presence of HA or FA in media leads to the significant decrease of k_1 value to 1.0 or 0.6 from 3.6 h^{-1}, which implies suppression of the reaction rate and probably different/additional Ni uptake mechanisms (Table 1). The fast equilibrium of Ni with the calcined LDH shows comparably kinetic constant with the previous findings of using calcined LDH to remove those anionic pollutants such as fluoride [23] and arsenic [28].

Table 1 The parameters of pseudo first order model for Ni removal by the calcined LDH in the absence and presence of humic (HA) and fulvic (FA) acids.

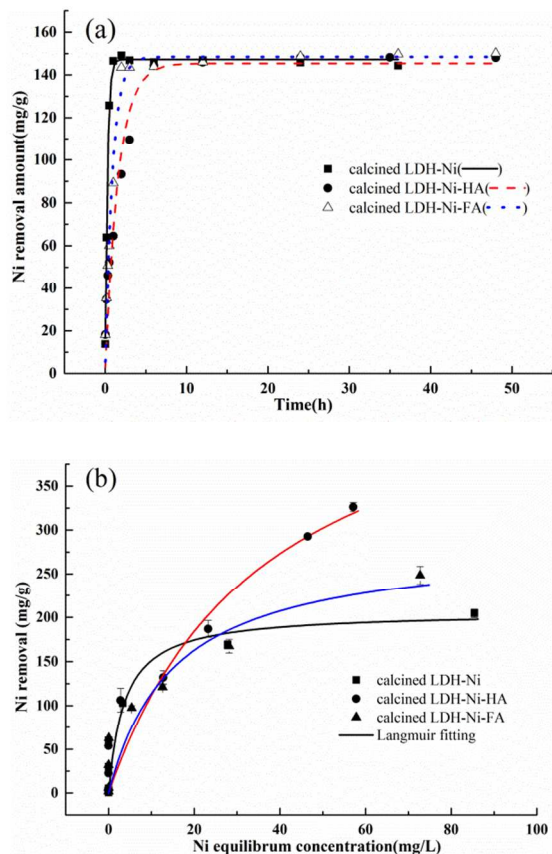| Samples	Pseudo-first order parameters		
	q_e (mg/g)	k_1 (h[-1])	R^2
Calcined LDH-Ni	147 ± 2.6	3.6 ± 0.5	0.997
Calcined LDH-Ni-HA	145 ± 1.3	0.6 ± 0.1	0.942
Calcined LDH-Ni-FA	148 ± 2.0	1.0 ± 0.1	0.970

Fig. 4. Pseudo first order of (a) the Ni removal kinetics by the calcined LDH in the absence and presence of 30 mg-C/L of humic (HA) or fulvic acids (FA) at pH 7. The initial concentration of Ni(II) is 35 mg/L. (b) the Ni removal isotherms by the calcined LDH in the absence and presence of 30 mg-C/L of HA or FA at pH 7.

Equilibrium isotherm studies

The Ni removal was further evaluated by equilibrium isotherms study, and the results were modeled by both Langmuir and Freundlich models given as Eq.s (2) and (3).

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \qquad (2)$$

$$q_e = K_F C_e^{1/n} \qquad (3)$$

where q_e (mg/g) is the amount of the removed Ni in the solid phase, and C_e (mg/L) is the equilibrium concentration of Ni in the solution phase. Q_m (mg/g) and K_L (L/mg) represent removal capacity of Ni by the calcined LDH and the Langmuir equilibrium constant. K_F (mg^{1-n} L^n /g) and n is considered as an indicator of removal capacity and affinity for Ni uptake, respectively.

The modelling shows that both Langmuir and Freundlich isotherms can give good descriptions for the removal of Ni by the calcined LDH. The maximum removal of Ni by the caclined LDH at pH 7 is 204 mg/g, which is remarkably higher than the maximum Ni removal by its precursor LDH (27.5 mg/g; Fig. S3), and Mg$_2$Al LDH in previous study [29]. Meanwhile, the Ni removal efficiency in this study is also substantially stronger than other sorbents activated carbons (74 to 141 mg/g) [2], paddy straw based sorbents (12 mg/g) [30],

and oxidized carbon nanotubes (10 mg/g) [6]. This evidence strongly demonstrates that the calcined LDH is a very efficient material for removing Ni from wastewater. The Freundlich constant n for Ni removal by the calcined LDH is 0.2 within the range of 0.1 to 1, representing a favourable removal process. Moreover, with the presence of 30 mg-C/L FA or HA in the media the removal of Ni significantly increases to a maximum Ni removal capacity of 290.6 ± 16.4 mg/g and 480.4 ± 21.3 mg/g, respectively (Fig. 4b; Table 2), which reveals that FA and HA can apparently improve the removal capacity of the calcined LDH for Ni.

Though negligible difference on physicochemical properties (e.g. molecular weights and functional groups) is observed between HA and FA (Fig. S4; Table S1), the presence of HA shows profound synergistic effect on enhancing the removal of Ni (Table 2). This can be ascribed to the stronger complexation of HA with Ni(II) than that by FA [31]. Besides, the Freundlich constant (n) for Ni removal increase to 0.4 and 0.5 after the addition of FA or HA which may imply a stronger affinity of Ni towards the calcined LDH (Table 2). On the basis of the comparison of correlation coefficients R^2s, the Langmuir isotherm is relatively suitable for description the Ni removal in this study, especially for the cases of organic matters presented (Table 2).
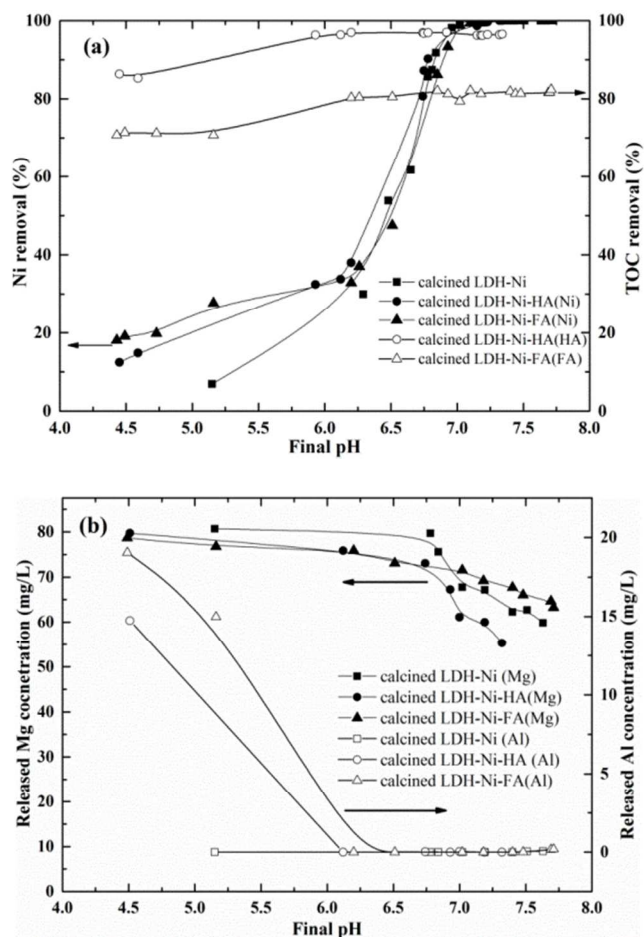

Fig. 5. (a) pH envelope experiment of the Ni removal by the calcined LDH in the absence/ presence of 10 mg-C/L of humic (HA) or fulvic acids (FA); (b) The release of Mg and Al from the calcined LDH after reaction with Ni in the absence and presence of 10 mg-C/L of FA or HA at pH ranging from 4 to 8. The initial concentration of Ni(II) is 10 mg/L.

Table 2 The Langmuir and Freundlich parameters of the Ni removal isotherms by the calcined LDH in the presence and absence of humic (HA) and fulvic acids (FA)

Parameters	Langmuir fitting			Freundlich fitting		
	Q_{max}(mg/g)	K_L(L/mg)	R^2	K_F (mg/g)	$1/n$ (mg^{1-n} L^n /g)	R^2
Calcined LDH-Ni(pH=7)	204.2 ± 10.6	3.7 ± 0.1	0.977	82.2 ± 1.2	5.0 ± 0.2	0.912
Calcined LDH-Ni(pH=5)	2.1 ± 0.4	2.2 ± 0.1	0.906	0.5 ± 0.2	2.5 ± 0.1	0.852
Calcined LDH-Ni-HA(pH=7)	480.4 ± 21.3	29.3 ± 0.5	0.976	47.8 ± 2.1	2.2 ± 0.3	0.924
Calcined LDH-Ni-HA(pH=5)	20.9 ± 1.0	33.7 ± 0.7	0.949	0.7 ± 0.1	1.2 ± 0.1	0.939
Calcined LDH-Ni-FA(pH=7)	290.6 ± 16.4	16.0 ± 0.1	0.960	46.7 ± 3.2	2.7 ± 0.3	0.903
Calcined LDH-Ni-FA(pH=5)	33.1 ± 4.2	11.6 ± 0.1	0.987	3.0 ± 0.1	1.4 ± 0.2	0.979

Effects of pH and NOMs

The effects of pH and NOMs (*i.e.* FA and HA) on Ni removal by the calcined LDH are depicted in Fig. 5a and 6, respectively. As illustrated in Fig. 5a, the removal of Ni is strongly dependent on pH; with increasing pH from 4 to 6.3 the enhancement of Ni removal is rather gentle, whereas, at pH > 6.3 the removal of Ni increases dramatically and almost 100% of Ni has been removed with a calcined LDH dosage of 0.2 g/L (Fig. 5a). This indicates that pH appears to be critical to the Ni removal by the calcined LDH. According to the Ni species distribution depicted in Fig. S1, Ni mainly presents as bi-charged species Ni(II) in our system (pH ≤ 7.5). There is no apparent Ni precipitation within the studied pH range in this work, which is also confirmed in our preliminary tests. Zhao and coworkers reported similar observation where the removals of Pb (II) and radionickel by Mg$_2$Al LDH also increased with the rise of pH [29, 32]. This can be due to the favourable formation of Ni containing LDH (Details will be discussed in the section 3.6). Meanwhile, the results also show that almost 100% of HA and over 80% of FA are removed by the calcined LDH with increasing pH to 7.5, exhibiting the similar trend with the case of Ni removal without the addition of HA or FA (Figure 5a). This explicitly demonstrates that the calcined LDH can efficiently and simultaneously remove both positively charged Ni(II) and organic matters. The release of Mg and Al ions from the calcined LDH into aqueous phase is shown as a function of pH in Fig. 5b. These data show that about 80 mg/L of Mg were detected in the aqueous phase at pH < 6.8, indicating that about 50% of the Mg ions are dissolved from the solid phase according to theoretical calculation. This is also further confirmed by the solid analysis by using ICP-OES (Table S2)

The presence of NOMs shows insignificant influence on the Mg release. By increasing pH to about 7.5, the release of Mg decreases to about 55 to 65 mg/L. Meanwhile, negligible amounts of Al release from the solid phase at pH 5 when no NOMs is presented in the reactor. The presence of equivalent content of FA or HA to that of Ni results in the dissolution of Al up to 20 mg/L at pH < 6.3, but barely releasing at higher pHs (Fig. 5b). The higher release of Mg than Al ions can be due to the corresponding larger solubility constant (K_{sp}) for Mg(OH)$_2$ than Al(OH)$_3$ [33], which is also analogue to the case of Mg$_2$Fe LDH [34].

Fig. 6 displays the effects of the FA and HA (normalized as C content) to the removal of Ni by the calcinced LDH. Our study shows that the removal of Ni slightly increases when the concentration of FA or HA increases from 0 to 70 mg-C/L (mass ratio of FA or HA as carbon to Ni: 0 to 2) at pH 7. At pH above 2, organic matters normally are negatively charged due to deprotonation of the abounding carboxylic and phenolic groups at pH > 2 (Table S1) [32]. Thus FA or HA can be strongly adsorbed on the positively charged surface of the rehydrated LDH as also

confirmed by zeta potential determination (Fig. S2), subsequently, the further potential complexation of FA or HA with Ni can lead to the enhancement of the Ni removal due to the increasing adsorption of FA or HA by the rehydrated LDH [35]. Our findings show a high removal rate of FA or HA by the calcined LDH (Fig. 5a). However, it shows that the negatively charged organic matter appears not being intercalated in the layers of the LDH (Fig. 1), which is in accordance with the findings from previous studies [27, 36].
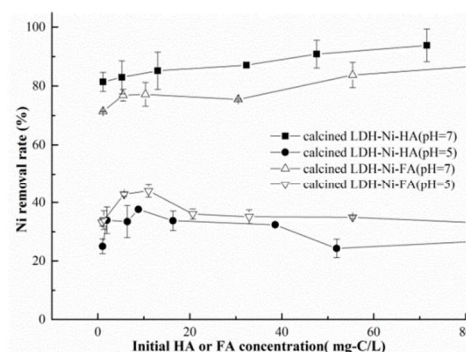

Fig. 6. Influence of humic (HA) or fulvic acids (FA) on the Ni removal by the calcined LDH at different pHs. The initial concentration of Ni(II) at pH 7 and 5 is 35 mg/L and 10 mg/L, respectively.
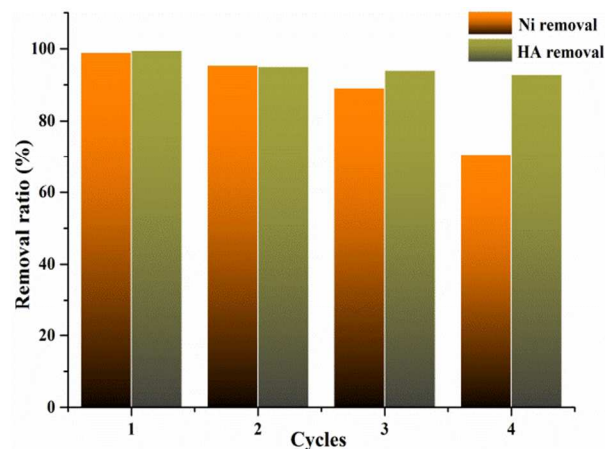

Fig. 7. Ni and HA removal and calcination cycles. The dosage of the calcined LDH was 1 g/L, the initial concentration of Ni (II) was 100 mg/L. The pH was remained at pH 7.

Reusability of the calcined LDH

The reusability of the calcined LDH for removing Ni and HA was carried out in a repeating sorption and calcination processes. The performance of the calcined LDH for removing Ni is found gradually decreased after four sorption and calcination cycles at pH 7 as given in Fig. 7. This is due to the fact that the metallic element Ni still remains in the calcined LDH after calcination process, consequently, the function of Ni removal by the calcined LDH will vanish as soon as the removed Ni reaches plateau. In opposite, the removal ratio of HA remains constantly at above 95% (Fig. 7), which is attributed to high adsorption capacity of HA by the calcined LDH (data not shown), and regeneration of adsorption sites on the LDH during decomposition of adsorbed HA to CO_2 in the process of calcination in air [37].

Possible Ni removal mechanism

As stated in the introduction, reconstruction of the calcined LDHs from the calcined form is an efficient way to remove anionic pollutants from aqueous solution as anions are incorporated into interlayers of the LDH [12]. However, in the case of Ni(II) where the dominant species in aqueous solution is Ni^{2+} (~ 100%) at pH < 8.0 (Fig. S1) [2], therefore, its incorporation into the interlayer is not expected to take place. Several approaches have been adopted to further interpret the possible Ni removal mechanism.
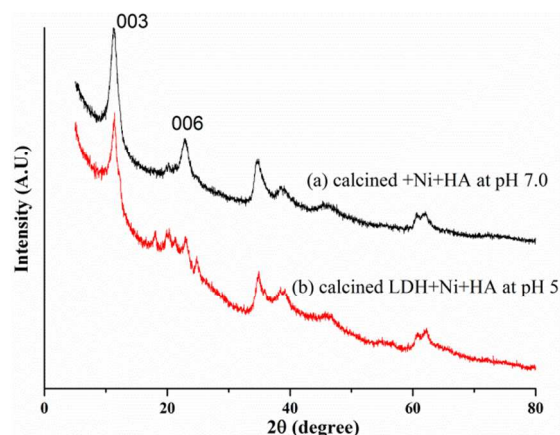

Fig. 8. XRD patterns of the calcined LDH after reaction with Ni (II) at, (a) pH 7 and pH 5, respectively.

Fig. 1 displays that XRD analysis of the calcined LDH after reacting with Ni ions shows the two broad peaks assigning to MgO disappearance, instead, similar basal peaks reflections (d_{003} = 0.77 nm) as seen for the non-calcined LDH precursor (d_{003} = 0.78 nm) show up and are significantly different from those for $Ni(OH)_2$ [38], which indicates there is no $Ni(OH)_2$ precipitates present in the solid. This strongly demonstrates that the removal of Ni is not a simple process of nickel precipitation, but probably related to the incorporation of Ni ions into the layered structure. This hypothesis is supported by the SEM images of the collected solids after reaction with Ni, where aggregates with plate-like structure are clearly observed in analogous with that of Mg/Al LDHs (Fig. 2). The morphology of the regenerated LDHs shows poor crystallinity in comparison to the original LDH as shown in Fig. 2c, which is also in agreement with the relatively broad XRD diffraction patterns (Fig. 1) of the regenerated LDHs [19]. The XRD survey of the calcined LDH

after reaction with Ni(II) shows intact diffraction peaks for that collected at pH 7, while the secondary peak (006) disappears for the sample obtained at pH 5 (Fig. 8). This confirms that the significant enhancement of the Ni(II) removal with increasing pH is strongly ascribed to the regeneration of intact LDH. The FT-IR spectrum of the calcined LDH after rehydration and reaction with Ni show significant bands at 3490 cm^{-1} and 1635 cm^{-1} due to hydroxyl vibration (Fig. 3), and the shift of band from 1360 cm^{-1} for LDH to 1385 cm^{-1} after reaction with Ni may be ascribed to the reconstruction of the layered materials and the presence of NO_3^- ions between interlayers [27, 39], which are introduced from the background ions.

The XPS elemental survey spectra further confirm the presence of Ni 2p peaks in the samples (Fig. 9a). Noticeable decrease of Mg 1s peak for the calcined LDH after reaction with Ni is observed, while Al 2p peaks almost remain consistent (Fig. 9b & c), in agreement with the evidence observed in Fig. 5b. This indicates that the incorporation Ni into layered structure leads to the dissociation of Mg from the calcined LDH throughout the whole studied pH range [40]. The elemental analysis of the calcined LDH reacted with Ni(II) is given in Table S2, which shows that the molar content of Al almost remains constantly before and after reaction, however, the molar content of Ni within the Ni saturated solid is very close to that of Mg released into aqueous phase. This evidence further supports the above assumption of a possible Ni isomorphic substitution process, consequently forming Ni containing LDH [41].

Previous studies have demonstrated that NOMs can associate with Ni ions to form organic matter-Ni complexes [31, 42]. Hence, the enhancement of the Ni removal in the presence of the NOM can be due to the additional removal mechanism of Ni by surface complexation of LDH-adsorbed organic matter with free Ni ions in solutions [43]. The strong intensity of C 1s peak when NOMs is present in solution confirms the association of the NOMs with the reconstructed LDH (Fig. 8a), subsequently leading to the possible complex of organic matter with Ni. On the other hand, the Ni 2p binding energy of the calcined LDH after reaction with Ni is found at 856.1 eV, while slightly shifting to 857.2 eV after the addition of HA at pH 7 (Fig. 8d). This may be due to the strong interaction of Ni with oxygen containing groups on HA [6, 42].

Real wastewater test

The performance of the calcined LDH in practical application was further tested. The wastewater was sampled in effluent of the 2nd sedimentation tank (before the coagulation tank) of the wastewater treatment plant from one of the Word largest stainless steel manufactory locating in Shiyan, Hubei province in China. The major composition of the wastewater was given in Table S3, which consists of 530 mg/L of Ni. The high content of Ni is mainly due to the high content of 8% of Ni used in stainless steel releasing from the surface during washing and cold rolling processes. As shown in Fig. 10, the applying a dosage of 4 g/L of the calcined LDH can dissipate the Ni content in aqueous phase lower than 0.1 mg/L which satisfies the requirement of 1 mg/L of threshold for Ni discharge according to Chinese industrial wastewater standard (GB8789-96). The addition of 5 mg/L HA and only a dosage of 2g/L the calcined LDH is sufficient to meet the standard for the discharge of wastewater, which is consistent with our lab-scale investigations (Fig. 10). This real wastewater test demonstrates that the calcined LDH can be considered as a useful material in cleaning Ni contaminated wastewater in practice.
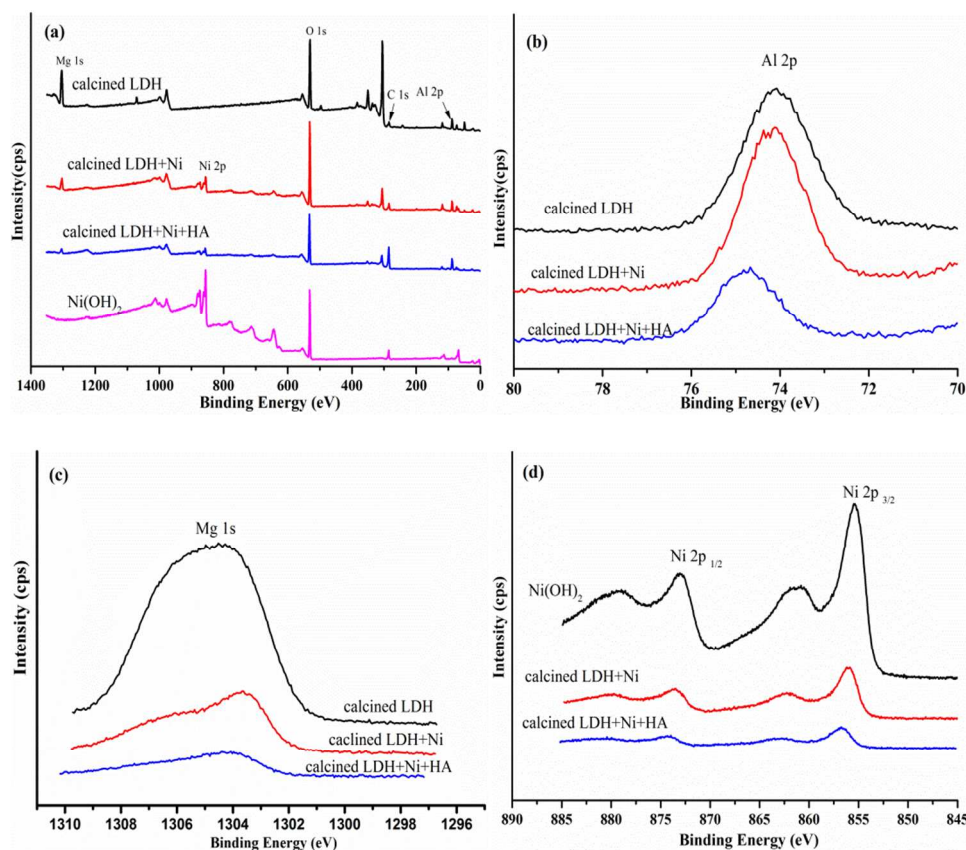
Fig. 9. XPS spectra of (a) element survey, (b) Al 2p, (c) Mg 1s, and (d) Ni 2p of the calcined LDH before and after reaction with Ni(II) in the presence and absence of organic matters.
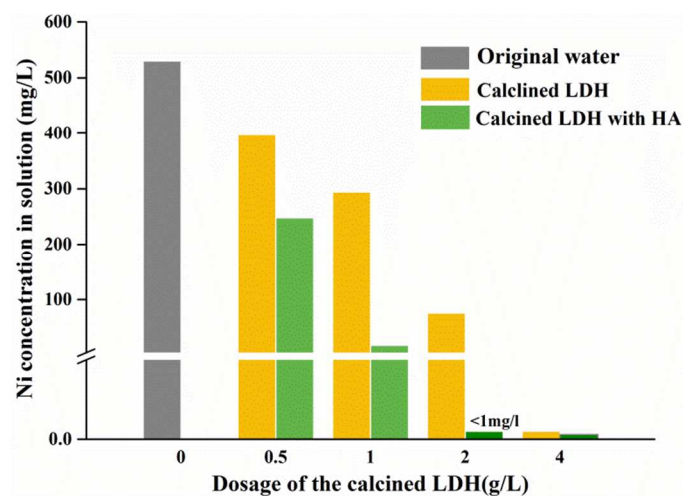

Fig. 10. Ni removal from a real stainless steel wastewater by using with different dosages of the calcined LDH at pH 7.5. The concentration of spiked HA is 5 mg-C/L. Experiments at each dosage were in triplicates.

Conclusions

In this study, the calcined LDH was used to remove metallic element Ni in the presence and absence of HA and FA. Our results show that the calcined LDH can strongly remove Ni with a maximum removal capacity up to 204.2 ± 10.6 mg/g at pH 7. The kinetic study indicates that the Ni removal is very rapid with a first order constant k_1 value ranging from 1.0 to 3.6 h^{-1}. Our study demonstrates that the Ni removal is highly pH dependent; with the increase of pH, the Ni removal dramatically increases at pH > 6.3 and reaches plateau at pH 7 where Ni ions are incorporated into the layered structure to form Ni/Al LDH as a result of Mg release. The presence of HA and FA leads to a significantly further increase of the Ni removal by the caclined LDH; a mass ratio of 2 for FA or HA as C to Ni is found to be optimal for the removal of Ni. Several evidences demonstrate that the enhancement of the Ni removal is attributed to the additional surface complexation of the reconstructed LDH adsorbed HA or FA with the free Ni ions from solutions. Our study is further well verified by applying the calcined LDH to clean up Ni containing wastewater sampled from a stainless steel manufactory. This work expands a new insight into the application of LDHs and its calcined forms to remove both anionic and cationic pollutants.

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†Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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