Enhanced removal of $I^-$ on hierarchically structured layered double hydroxides by in suit growth of Cu/Cu$_2$O

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Abstract

To further improve the removal ability of layered double hydroxide (LDH) for iodide ($I^-$) anions from wastewater, we prepared hierarchically porous Cu$_5$Mg$_{10}$Al$_5$-LDH and used as a matrix for in suit growth of Cu/Cu$_2$O on its surface, forming Cu/Cu$_2$O-LDH, which was characterized and applied as an adsorbent. Results displayed high $I^-$ saturation uptake capability (137.8 mg/g) of Cu/Cu$_2$O-LDH compared with Cu$_5$Mg$_{10}$Al$_5$-LDH (26.4 mg/g) even thermal activated LDH (76.1 mg/g). Thermodynamic analysis showed that the reaction between $I^-$ anions and Cu/Cu$_2$O-LDH is a spontaneous and exothermic. Uptake kinetics analysis exhibited that adsorption equilibrium can be reached after 265 min. Additionally, the adsorbent showed satisfactory selectivity in the presence of competitive anions (e.g., SO$_4^{2-}$), and could achieve good adsorption performance in a wide pH range of 3–8. A cooperative adsorption mechanism was proposed on the basis of the following two aspects: (1) ion exchange between iodide and interlayer anions; (2) the adsorption performance of Cu, Cu(II) and Cu$_2$O for $I^-$. Meanwhile, the difference between the adsorption mechanism of Cu/Cu$_2$O-LDH, Cu$_5$Mg$_{10}$Al$_5$-LDH and Cu$_5$Mg$_{10}$Al$_5$-CLDH adsorbents was also elaborated and verified.

Keywords: Layered double hydroxide, Cu/Cu$_2$O, Iodide adsorption, Hierarchical structure, In suit growth

Introduction

Environmental deterioration and energy shortage have increased the demand for green energy and contamination control technologies. Nuclear energy, a reliable and green resource, is becoming increasingly important for electricity generation. However, the concern on nuclear waste mainly generated by nuclear fuel reprocessing and nuclear accidents (e.g., Chernobyl and Fukushima) has drawn increasing attention (Zhang et al., 2018). Radioactive iodine (especially $^{131}$I and $^{129}$I) is an inevitable by-product of nuclear fission and, because of its long half-life, poses a major risk to health and the...
ecosystem (Liu et al., 2014; Mao et al., 2016). Generally, radioactive iodine is present in the form of iodide (I\(^{-}\), I\(^{\text{O}_{3}^{-}}\) and organic iodide (ROIs, e.g., methyl iodide and ethyl iodide) in aqueous solution. I\(^{-}\) is the dominant species in highly oxidizing water media (Hoskins et al., 2002; Hansen et al., 2011; Choung et al., 2014; Liu et al., 2014). For instance, in Fukushima nuclear leakage, radioactive iodine was mainly present as I\(^{-}\), with only a small part being discharged as other iodine species (Nakayama et al., 2015; Zhang et al., 2017b). In addition to nuclear power plant emissions, radioactive iodine is also released from several medical institutions due to the application of its to treatment of thyroid cancer (Rose et al., 2017; Liang et al., 2017b). Therefore, the effectively removal of radiiodine waste is of great inevitability. However, selectively iodine uptake with high adsorption capacity and environmentally friendly is toujours a grim challenge.

Several technologies have been applied to treatment of radioactive I\(^{-}\), such as membrane separation (Gryta, 2013), photodegradation (Liu et al., 2015) and adsorption (Saleh and Gupta, 2012). Notably, surface adsorption has been extensively studied due to its cost-effectiveness and efficient method for the I\(^{-}\) anions removal from wastewater (Li et al., 2017b; Zhang et al., 2017b; Chen et al., 2019). To develop high efficiency adsorbent is the priority in this field (Chen et al., 2017, 2019). In recent years, functional adsorbents, such as silver-based materials (Liu et al., 2015; Mao et al., 2016), copper oxide (Vance et al., 2018; Zhang et al., 2018; Wang et al., 2019) and heavy metal (Hg\(^{2+}\), Pb\(^{2+}\)) compounds (Mailen and Horner, 1977; Sazarashi, 1994) for capturing I\(^{-}\) have gained increasing attention. However, silver-based adsorbents are relatively costly and greatly difficult to split the thin Agl component from solid-liquid media, while copper oxide exhibits low uptake capacity and a slow adsorption rate due to its smaller specific surface area. As for heavy metal compounds, it generates secondary pollutants. Therefore, the development of effective, inexpensive material with excellent adsorbing capacity to remove I\(^{-}\) is of great urgency.

Several kinds of materials have been extensively studied as possible adsorbents, such as activated carbons (Zhang et al., 2018) and metal-organic frameworks (Chen et al., 2019). Besides, recently, some reports have been found regarding the use of layered double hydroxides (LDHs) (Kentjono et al., 2010; Theiss et al., 2016a, 2016b). LDHs are clay-like minerals with potential application in radioactive waste removal (Kentjono et al., 2010; Li et al., 2017b). They comprise cationic brucite-like layers and exchangeable interlayer anions. Their general formula is \([\text{M}^{2+}_{x}M^{3+}_{y}(\text{OH})_{z}]^{x-}\times n\text{H}_{2}\text{O}\), in which M\(^{2+}\) and M\(^{3+}\) are divalent and trivalent cations respectively; A\(^{n-}\) is an exchangeable anion or oxo-anionic complex (inorganic or organic). Various LDH-based compounds with different chemical compositions have been reported as candidates for capturing I\(^{-}\) (Kentjono et al., 2010; Theiss et al., 2016b). However, the process involves anion exchange, which results in undesirable adsorption capacity (Theiss et al., 2016a, 2017). Additionally, native LDHs have a relatively small surface area and no adsorption sites (Zhang et al., 2017a, 2013). To improve the removal efficiency of I\(^{-}\) anions by LDHs from wastewater, further research on the structure and the composition of LDHs have been carried out by many groups (Theiss et al., 2016a; Vaccari, 2002). For example, thermally activated (TA) LDHs display a feature described as reformation or “Memory Effect” (Mascolo and Mascolo, 2015; Theiss et al., 2016a). When calcined LDHs (CLDHs) are applied to the wastewater, a new structure LDHs are formed. Research have suggested that the reformed LDHs have significantly enhanced I\(^{-}\) adsorption capacity (Mascolo and Mascolo, 2015). Nevertheless, some challenges still need to be tackled. Typically, LDHs exhibit high affinity toward interfering anions and high sensitivity to pH. Therefore, to achieve desirable adsorption performance, it is necessary to further modify native LDHs.

Cuprous ions (Cu\(^{+}\)) have potential for capturing I\(^{-}\) because of the strong affinity between Cu\(^{+}\) and I\(^{-}\) and the relatively low toxicity and low cost of Cu\(^{+}\) (Lefèvre et al., 2003; Mao et al., 2017b; Zhang et al., 2017b). However, Cu\(^{2+}\)O shows relatively low adsorption capacity and slow adsorption kinetics due to the limited surface area and the oxidation of Cu\(^{+}\) to Cu\(^{2+}\) by dissolved oxygen. To deal with these challenges, researchers used Na\(_{2}\)SO\(_{3}\) as an oxygen scavenger to remove dissolved oxygen (Liu et al., 2016b), but this process is impracticable to apply in practice. In addition, Mao et al. (2016, 2017a, 2017b) adulterated metal Cu and Ag into Cu\(_{2}\)O adsorbents and applied as adsorbent to adsorb I\(^{-}\) anions. The results revealed that Cu\(_{2}\)O is generated by the reaction between metallic Ag or Cu and CuO, and the uptake capacity is enhanced. Compared with pure metallic@Cu\(_{2}\)O, the immobilization of nanoscale Cu/Cu\(_{2}\)O on a substrate could increase the surface area and the number of active adsorption sites, thereby increase the wastewater treatment efficiency (Zhang et al., 2017b). Therefore, considering the potential application of Cu/Cu\(_{2}\)O and LDH for I\(^{-}\) removal, studies used LDHs as substrate for Cu/Cu\(_{2}\)O loading. This not only increased the amount of adsorption sites for LDHs but also provided substrates for preparing nanoscale Cu/Cu\(_{2}\)O. For preparing of nanoscale Cu/Cu\(_{2}\)O on the surface of LDHs, in situ growth is undoubtedly an effective method (Liu et al., 2016a). So it becomes necessary to use Cu as an integral part of the synthesized LDH, as shown by Marcu et al. (2009) and Răciulete et al. (2017), who synthesized mesoporous Cu-Mg-Al LDHs. In addition, the Cu-based LDHs can be potential precursors for in situ growth of Cu/Cu\(_{2}\)O by Cu\(^{2+}\) reduction. To the best of our knowledge, I\(^{-}\) uptake from wastewater using porous Cu/Cu\(_{2}\)O-LDHs has rarely been investigated.

In this study, we fabricated a novel material that could efficiently adsorb I\(^{-}\) anions from aqueous and is promising for the removal of radioactive I\(^{-}\). We utilized porous Cu\(_{2}\)Mg\(_{2}\)Al\(_{5}\)-LDH as a matrix for the in situ growth Cu/Cu\(_{2}\)O nanoparticles. The morphology, crystallized phases, valence analysis and surface areas of as-prepared adsorbents were characterized. Subsequently, the as-synthesized adsorbents were applied to study the adsorption kinetics, isotherms and thermodynamic of I\(^{-}\) capture. The effect of pH and competitive ions on I\(^{-}\) capture were also examined.

1. Materials and methods
1.1. Materials
All chemicals used in this work were of analytical grade and were all purchased from Sinopharm Group Chemical Reagent Co., Ltd., China., including magnesium chloride hexahydrate (MgCl\(_{2}\)-6H\(_{2}\)O), copper chloride hexahydrate (CuCl\(_{2}\)-2H\(_{2}\)O),...
aluminum chloride hexahydrate (AlCl₃·6H₂O), sodium carbonate (Na₂CO₃), sodium hydroxide (NaOH), sodium iodide (NaI), ascorbic acid (C₆H₈O₆), sodium chloride (NaCl), sodium sulfate anhydrous (Na₂SO₄), absolute alcohol (C₂H₆O). The 5000 mg/L of iodide stock solution was prepared by dissolving sodium iodide in deionized water.

1.2. Adsorbent preparation

Cu₅Mg₁₀Al₅-LDH with a Cu:Mg:Al molar ratio of 5:10:5 was prepared as described previously (Guo et al., 2013; Ma et al., 2015). A mixture solution (75 mL) consisting of 300 mmol/L magnesium chloride hexahydrate, 150 mmol/L copper chloride hexahydrate and 150 mmol/L aluminum chloride hexahydrate were slowly dropped into a vigorously stirred sodium carbonate solution (250 mmol/L, 75 mL). The pH of the mixed solution was adjusted to 9.5 ± 0.2 by adding 2 mol/L sodium hydroxide solution. After the reaction, the resultant blue suspensions were aged at 65°C for 24 hr. The final product was collected, rinsed thoroughly with deionized water several times, and dried at 65°C. The power obtained was labeled as Cu₅Mg₁₀Al₅-LDH. A portion of the power was thermally activated by calcination in air at 400°C in a tube furnace, and the product obtained was denoted as Cu₅Mg₁₀Al₅-CLDH.

To prepare Cu/Cu₂O-LDH, some ascorbic acid was added to 40 mL of deionized water. 1.2 g of Cu₅Mg₁₀Al₅-LDH composite was dispersed into the solution and stirred for 3 hr. The resulting product was separated and washed with deionized water and absolute alcohol. Lastly, the solid obtained was dried overnight in vacuum at 65°C. The product obtained was denoted as Cu/Cu₂O-LDH.

1.3. Characterization

The morphology of the as-synthesized materials was examined using scanning electron microscope (SEM, FEI Quanta 250FEG, USA) and transmission electron microscopy (TEM, FEI Tecnai 20, USA). The phase purity and crystal structure were characterized by X-ray diffraction (XRD, Bruker D8 Advance, Cu Kα radiation). The XPS spectra were measured by using a PHI Quantera II electron spectrometer with a monochromatic Al Kα radiation. Fourier-transform infra-red spectra (FT-IR) were collected on a Thermal Scientific Instruments LLC using KBr pellets. N₂ adsorption/desorption isotherms were tested on a Thermal Scientific Instruments LLC using the Barrett-Emmett-Teller (BET) approach.

1.4. I⁻ adsorption

Considering the high radiation dose and toxicity of ¹³¹I, the I⁻ capture experiments were performed with ¹²⁷I (NaI) as substitution. The usage amount of the adsorbent in the following experiment was 1 g/L. Previous reports have pointed out that iodide could be transformed into other species, such as iodine, iodate, and triiodide in water solutions (Kireev and Shnyrev, 2015; Tauanov and Inglezakis, 2019). Therefore, we studied the whole UV spectra by using an ultraviolet spectrophotometer (UV-Vis) for the identification of iodine species in the adsorbed solution. As shown in Appendix A Fig. S1, whether in acidic, alkaline or deionized water samples, only iodide peak was detected at around 227 nm, indicating that no iodine form transition occurred during the adsorption process.

Batch equilibrium isotherm studies were carried out at room temperature (25°C) in capped polyethylene centrifuge tubes (50 mL) with I⁻ concentrations ranging from 0 to 240 mg/L. Next, 20 mg of the as-made Cu₅Mg₁₀Al₅-LDH, Cu₅Mg₁₀Al₅-CLDH, and Cu/Cu₂O-LDH were immersed into 20 mL of iodine solution. The solid-liquid media was shaken at 180 r/min in a shaker for 12 hr, and the supernatants were collected by centrifugation and filtration using a 0.22-μm PES filter. The remaining I⁻ concentration in the solution was determined by UV-Vis at a wavelength of 227 nm.

Thermodynamic analysis of Cu/Cu₂O-LDH was conducted at I⁻ concentrations from 0 to 240 mg/L. The solid-liquid media was stirred for 12 hr at 298, 308, 318 K, respectively. Afterward, the I⁻ concentrations left in the solution was measured.

Iodide uptake kinetic experiments were performed using iodide concentrations of 210 mg/L at room temperature. The mixtures were stirred and sampled 1.5 mL suspensions at specified time intervals. The clear supernatants were collected quickly through a 0.22-μm PES filter and measured as described earlier.

The I⁻ uptake performance of Cu/Cu₂O-LDH as a function of the solution pH ranging from 3 to 9 was conducted by aligning the acidity and alkalinity with dilute HNO₃ and ammonia solution. In addition, the competing effect of interfering ions (e.g., Cl⁻, CO₃²⁻, SO₄²⁻) on iodine uptake capacity was also investigated, with the interfering anions to I⁻ molar ratio reaching 100:1. All I⁻ anions removal tests were conducted at I⁻ concentration of 210 mg/L with stirring for 12 hr.

2. Results and discussion

2.1. Characterization of the synthesized samples

SEM images of the synthesized Cu₅Mg₁₀Al₅-LDH, Cu₅Mg₁₀Al₅-CLDH, and Cu/Cu₂O-LDH are presented in Fig. 1. Cu₅Mg₁₀Al₅-LDH shows the highly interconnected nanoplatelet-like structures (Fig. 1a). After thermal activation, the platelet-like structures were maintained well and less agglomerated compared to pure Cu₅Mg₁₀Al₅-LDH (Fig. 1b). The microstructure of fabricated Cu/Cu₂O-LDH (Fig. 1c-d) revealed that platelet-like hierarchical porous structures still remain, even after multistep treatment. The TEM pattern of Cu/Cu₂O-LDH (Fig. 1f) shows many fine particles with an average size of 5–10 nm covering the Cu–Mg–Al LDH nanoplatelet surfaces compared with the pure Cu₅Mg₁₀Al₅-LDH (Fig. 1e), indicating the successful growth of Cu/Cu₂O on the Cu₅Mg₁₀Al₅-LDH surface. Results obtained by the SEM and TEM measurements were highly consistent with the results determined by XRD characterization, described in the following sections.

Crystalline phase of the synthesized Cu₅Mg₁₀Al₅-LDH, Cu₅Mg₁₀Al₅-CLDH, and Cu/Cu₂O-LDH were examined by XRD analyses. The XRD pattern of the Cu₅Mg₁₀Al₅-LDH (Fig. 2a)
shows high-intensity peaks at 2θ = 11.6°, 22.3° and 34.9°, which were fitted to Cu–Mg–Al LDH with reflection of (003), (006) and (009), respectively (Barrault et al., 2004; Xu and Lu, 2005). Compared to Cu5Mg10Al5-LDH, the peaks of calcined composite (Cu5Mg10Al5-CLDH) became broader and the intensity low. Almost no phases of copper- and magnesium-containing compounds observed, implying that MgO and CuO are uniformly dispersed in Al2O3. The Cu/Cu2O-LDH peaks at 2θ = 36.7°, 42.4°, 61.6° could be assigned to Cu2O (JCPDS 65–3288), and the peaks corresponding to metallic Cu (JCPDS 65–9743) at 2θ = 43.5°, 56.7°, 74.3° were also observed. In addition, Cu/Cu2O-LDH showed peaks of the original precursor Cu5Mg10Al5-LDH despite Cu/Cu2O in suit growth, spreading the peaks and decreasing crystallinity. Therefore, XRD characterization results clearly revealed that metallic Cu and Cu2O are successfully formed on the surface of Cu5Mg10Al5-LDH, which was also validated by XPS, as described in the following sections.

Fig. 1 – SEM images of adsorbents: (a) Cu5Mg10Al5-LDH, (b) Cu5Mg10Al5-CLDH, (c–d) Cu/Cu2O-LDH at low (c) and higher (d) magnification. TEM images of adsorbents: (e) Cu5Mg10Al5-LDH, (f) Cu/Cu2O-LDH. The inset: magnified images of the corresponding products.

Fig. 2 – XRD patterns of the as-synthesized samples before (a) and after (b) adsorption I– anions.
Fig. 3a illustrates the XPS survey spectra of Cu/Cu$_2$O-LDH, which revealed the existence of C, O, Cu, Mg and Al. High-resolution Cu 2p XPS spectra (Fig. 3b) show individual peaks at 933.9 and 954.6 eV, corresponding with Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$, respectively, and two satellite peaks at 942.8 and 961.9 eV (Hsieh et al., 2014); peaks at binding energies of 932.5 and 952.4 eV corresponded with Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ from Cu$_2$O/Cu, respectively (Zhang et al., 2017b). It was difficult to differentiate between Cu$_2$O (Cu$^+$) and metallic Cu through the XPS due to the small chemical shifts of Cu$^0$ and Cu$_2$O (only 0.1–0.2 eV) (Wu et al., 2006; Mao et al., 2017b). Nevertheless, above-mentioned XRD patterns fully affirmed the concomitance of Cu and Cu$_2$O. Additionally, two satellite peaks and the peaks at 934.2, 935.2, 954.4 eV confirmed the presence of Cu(II) (Pedersen et al., 2008; Ai et al., 2009). Here, Cu(II) may be found on the surface of adsorbents owing to the oxidization of trace amount of Cu$_2$O. However, the most likely form was divalent metal cations to form the cationic brucite-like layers of the LDH.

Fig. 4 shows the FT-IR spectra of the as-prepared materials. Obviously, all the adsorbents exhibited a weak, broad band around 3310-3623 cm$^{-1}$ assigned as O–H stretching, which corresponded with the interlayer water molecular and metal-hydroxyl groups (Guo et al., 2013; Li et al., 2017b). The bands at 1629 and 1646 cm$^{-1}$ were attributed to the deformation vibration of H–O–H ($\delta$H$_2$O) of adsorbed water molecules (Ji et al., 2017). As expected, the stretching vibration of H–O–H was almost disappeared after calcination owing to the loss of water molecules. The absorbance peak at 1360 cm$^{-1}$ was $\nu_3$ (asymmetric stretching) of the carbonate ($\nu$CO$_3$) in the interlayer (Guo et al., 2013). The bands observed in the range of 400–1000 cm$^{-1}$ were ascribed to metal-hydrogen or metal-oxygen bonds (Ji et al., 2017). These results illustrated that in situ growth of Cu/Cu$_2$O does not destroyed the structure of LDH, as evidence by the XRD curves.

The specific surface area and pore structure are crucial parameters affecting the adsorption performance of porous materials, and thus the nitrogen adsorption-desorption isothermal analysis of sample is necessary. Fig. 5 shows nitrogen adsorption-desorption isotherms of the synthesized adsorbents. The isothermal curves exhibited a type IV isotherm shape with H3-type hysteresis loops, indicating that there were mesoporous existed in adsorbents. H3 and H4 hysteresis are generally found in solids comprising aggregates or agglomerates of particles forming slit-shaped pores with uniform (type H4) or non-uniform (type H3) size and/or shape (Chen et al., 2017; Leofanti et al., 1998), further validating that all materials in this study were hierarchically structured. Based on the pore size distribution curves, the diameters of Cu$_5$Mg$_{10}$Al$_5$-LDH, Cu$_5$Mg$_{10}$Al$_5$-CLDH and Cu/Cu$_2$O-LDH were 11.4, 15.7 and 40.7 nm respectively, which were sufficiently for loading the active ingredient to purify wastewater (Li et al., 2017a). As shown in Fig. 5 and Table 1, the thermal activated LDH and in situ growth of Cu/Cu$_2$O-LDH samples would lead to an increase in the BET surface area from 44.29 to 98.62 m$^2$/g and 57.64 m$^2$/g for Cu$_5$Mg$_{10}$Al$_5$-CLDH and Cu/Cu$_2$O-LDH, respectively. Optimization of the BET surface area and total pore volume of LDH materials might improve I$^-$ removal (Zhang et al., 2017a), which can be confirmed by subsequent iodine removal studies.

2.2. Adsorption tests

2.2.1. Uptake isotherm and thermodynamic analyses

To determine the distribution of I$^-$ between adsorbent and adsorbate at equilibrium, the uptake isotherms were investigated. Fig. 6a revealed the I$^-$ anions adsorption capacity of all adsorbents increased with increasing iodide concentration. Compared with Cu$_5$Mg$_{10}$Al$_5$-LDH and Cu$_5$Mg$_{10}$Al$_5$-CLDH, the
maximum iodide adsorption capacity of Cu/Cu2O-LDH composite increased from 26.4 mg/g to 137.8 mg/g and 76.1 mg/g to 137.8 mg/g, respectively. The higher \( I^- \) adsorption capacity of Cu/Cu2O-LDH could be attributed to synergistic effects of the adsorption ability of LDH and Cu/Cu2O. Additionally, the high surface area provided sufficient binding sites and accessible diffusion pathways for \( I^- \), which also increased adsorption capacity (Ji et al., 2017). Compared with the adsorbents already reported in other literatures (Table 2), the removal performance of the adsorbent synthesized in this work was considerably higher than or comparable.

The adsorption isotherm data were further analyzed by Langmuir and Freundlich isotherm models to understand the adsorption process. The expressions were represented by:

\[
q_e = \frac{K_L \cdot q_m \cdot C_e}{1 + K_L \cdot C_e} \quad (1)
\]

\[
q_e = \frac{K_F \cdot C_e^{1/n}}{1 + C_e^{1/n}} \quad (2)
\]

where \( q_e \) (mg/g) is the equilibrium adsorption capacity, \( C_e \) (mg/L) is the equilibrium concentration of \( I^- \), \( q_m \) (mg/g) is the maximum uptake quantity of \( I^- \) adsorbed. \( K_L \), \( K_F \) and \( n \) are the Langmuir and Freundlich constants, respectively. As depicted in Fig. 6a and Appendix A Table S1, experimental data were satisfactorily fitted by the Langmuir isotherm model with greater correlation coefficients \( R^2 \) compared to the Freundlich model. The Langmuir adsorption model was based on the assumption that monolayer adsorption occurs at the specific homogeneous adsorption sites without interactions between the adsorbed anions (Manzoor et al., 2013; Ullah et al., 2013), while the Freundlich isotherm tries to simulate the effects of heterogeneous surface on sorption. Thus, it was concluded that the \( I^- \) uptake proceeds by all adsorbents could be described as monolayer adsorption.

Generally, the adsorption intensity of adsorbents can be described by the dimensionless coefficient \( R_L \) (Eq. (3)):

\[
R_L = \frac{1}{1 + K_L C_0}
\]

where \( C_0 \) (mg/L) represents the initial iodide concentration. \( R_L \) determines the appearance of isotherm and can be applied to categorize as irreversible \((R_L = 0)\), favorable \((0 < R_L < 1)\), linear \((R_L = 1)\) or unfavorable \((R_L > 1)\) (Gupta et al., 2010). The values of \( R_L \) in this work between 0 and 1 for all samples (Appendix A Table S1), indicating the \( I^- \) removal was favorable.

To understand inherent energetic changes involved in adsorption, thermodynamic analysis was performed at 298, 308, and 318 K. As shown in Fig. 6b, temperature significantly affected \( I^- \) removal. The equilibrium uptake capacity of Cu/Cu2O-LDH decreased when the temperature changed from 298 to 318 K, indicating the exothermic nature of adsorption between adsorbate and adsorbent. The experimental data were fitted using Langmuir and Freundlich isotherm models, with the Langmuir isotherm model fitting the data better (Fig. 6b). Therefore, the Langmuir constant \( (K_L) \) can be used to calculate thermodynamic parameters. Variation in thermodynamic parameters \((\Delta G^0, \Delta H^0, \Delta S^0)\) were determined as follows:

\[
\Delta G^0 = -R \cdot T \cdot \ln K_L
\]

\[
\ln K = \frac{-\Delta H^0}{R \cdot T} + \frac{\Delta S^0}{R}
\]

where \( \Delta G^0 \) (kJ/mol), \( \Delta H^0 \) (kJ/mol) and \( \Delta S^0 \) (J/mol/K) are the standard Gibbs free energy, enthalpy and entropy change, respectively; \( R \) (8.314 J/mol/K) is the universal gas constant; and \( T \) (K) is the absolute temperature. The \( \Delta G^0, \Delta H^0 \) and \( \Delta S^0 \) values for \( I^- \) anions removal by Cu/Cu2O-LDH are given in Appendix A Table S2. \( \Delta G^0 \) was ~18.82, ~18.49, ~18.31 kJ/mol at 298, 308 and 318 K, respectively. \( \Delta G^0 \) values suggested that the reaction is spontaneous. The negative value of \( \Delta H^0 \) (~25.96 J/mol) was expected for adsorption because it indicated the decreased randomness at the solid-liquid interface during \( I^- \) removal by Cu/Cu2O-LDH (Gopal and Elango, 2007; Chen et al., 2019). The negative \( \Delta H^0 \) value showed that \( I^- \) adsorption is exothermic, which explains why an increase in temperature inhibits adsorption. Additionally, \( \Delta H^0 \) can be used to distinguish between chemical and physical sorption (Gopal and Elango, 2007; Chen et al., 2019). Therefore, on the basis of the \( \Delta H^0 \) (Appendix A Table S2), combined with results of previously studies, we concluded that chemisorption occurs during \( I^- \) removal.

### 2.2.2. Kinetic adsorption

To evaluate the performance of as-prepared samples for \( I^- \) anions removal, the adsorption capacity as a function of time was recorded. As shown in Fig. 7, Cu/Cu2O-LDH quickly removed 108.8 mg/g of \( I^- \) anions within 85 min and reached to its saturation uptake capacity of 142.4 mg/g of \( I^- \) by 265 min. The relatively high increasing trend of uptake capacity within
85 min could be attributed to the abundance of adsorbates and active sites on the adsorbents, and a fairly large amount of iodide from solution transported easily to the adsorbent active sites. The benchmark materials (Cu5Mg10Al5-LDH), even the Cu5Mg10Al5-CLDH, used for I\(^{-}\) removal under the same conditions exhibited I\(^{-}\) saturation uptake capacity of 21.2 and 72.4 mg/g by 85 and 205 min respectively. These results indicated that although the adsorption capacity of Cu/Cu2O-LDH increased, its adsorption rate was relatively slow. In addition to adsorption kinetics profiles, the kinetic data were further analyzed by pseudo-first-order and pseudo-second-order kinetic models, which can be described as Eqs. (4) and (5):

\[ q_t = q_e \left(1 - \exp(-k_1 t) \right) \]  
\[ q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \]

where \( q_e \) (mg/g) and \( q_t \) (mg/g) represent the equilibrium uptake capacity and adsorption amount in time \( t \) (min), respectively. \( k_1 \) (g/mg/min) and \( k_2 \) (g/mg/min) are the rate constants of pseudo-first-order and pseudo-second-order, respectively.

The plot \( q_t \) versus \( t \) for adsorbents is shown in Fig. 7. \( R^2 \) of different adsorbents fitted by the pseudo-second-order rate model was at least 0.995 and \( q_e \) was 25.2, 95.7, 172.4 mg/g for Cu5Mg10Al5-LDH, Cu5Mg10Al5-CLDH, Cu/Cu2O-LDH, respectively (Appendix A Table S3). These findings were in agreement with experimental data, and indicated that the pseudo-second-order model better describes kinetics data. Previous research (Ho and Mckay, 1999) has suggested that the hypothesis that the uptake process might be chemisorption or chemical sorption. Thus, chemisorption or chemical adsorption dominates the iodine anions adsorption process.

2.2.3. Effect of initial pH and interfering ions on I\(^{-}\) trapped

The capacity and efficiency of Cu/Cu2O-LDH to uptake and remove I\(^{-}\) as a function of initial pH are displayed in Fig. 8a. The removal efficiency first decreased and then increased with increasing pH in the range of 3–9. As pH decreased from 5 to 3, the adsorption efficiency increased from 49.48% to 76.9%, which would be attributed to the release of Cu2+ and Cu+ from the superficial CuO and inner Cu2O at low pH (Lefèvre et al., 1999; Mao et al., 2017b; Zhang et al., 2017b). Consequently, CuI precipitate yield on adsorbent surface. Moreover, Cu2+ could also trap I\(^{-}\) to yield CuI in the presence of metallic Cu. With increasing the pH from 5 to 7, the removal efficiency increased from 49.5% to 60.7%. According to the literature, neutral pH 7.0 is considered optimum for LDHs to adsorb I\(^{-}\) anions (Ji et al., 2017; Zhang et al., 2017a). Thus, improvement of the removal ability can be ascribed to the level-off effect of Cu5Mg10Al5-LDH. With further increased in pH, metallic Cu and Cu2O were oxidized into Cu(OH)2 or CuO, which did not exhibit affinity for I\(^{-}\). Additionally, more hydroxide ions released to the solution as pH increases resulted in a reduction of the adsorption amounts due to the competitive effect of hydroxides (Ji et al., 2017).

The industrial wastewater usually coexist some other cations and anions apart from the iodine ions. These other anions might compete with I\(^{-}\) for active sites on adsorbents owning to the electrostatic interaction between the anions and materials, which would influence the adsorption capacity of the adsorbent to adsorb I\(^{-}\). Hence, the uptake test in the

### Table 2 – A comparison of the Cu/Cu2O-LDH adsorbent in this work with previously reported adsorbents for I\(^{-}\) adsorption.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>( C_0 ) (mg/L)</th>
<th>Adsorbent dose (g/L)</th>
<th>Adsorption capacity (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-Al (NO3) LDH</td>
<td>342.3</td>
<td>20</td>
<td>10.1</td>
<td>Kentjono et al. (2010)</td>
</tr>
<tr>
<td>Zn/Al LDH</td>
<td>1000</td>
<td>50</td>
<td>200</td>
<td>Theiss et al. (2016a)</td>
</tr>
<tr>
<td>BiI2/LDHs</td>
<td>20–200</td>
<td>1</td>
<td>101.9</td>
<td>Zhang et al. (2017a)</td>
</tr>
<tr>
<td>Cu2O</td>
<td>16.5</td>
<td>50</td>
<td>0.3</td>
<td>Lefèvre et al. (2000)</td>
</tr>
<tr>
<td>1%Ag/Cu2O</td>
<td>0–38.1</td>
<td>1</td>
<td>25.4</td>
<td>Mao et al. (2016)</td>
</tr>
<tr>
<td>Cu/Cu2O</td>
<td>0–38.1</td>
<td>1</td>
<td>22.9</td>
<td>Mao et al. (2017b)</td>
</tr>
<tr>
<td>Nano Cu/Cu2O–C</td>
<td>1–30</td>
<td>1</td>
<td>41.2</td>
<td>Zhang et al. (2017b)</td>
</tr>
<tr>
<td>Cu/Cu2O-LDH</td>
<td>0–240</td>
<td>1</td>
<td>137.8</td>
<td>This work</td>
</tr>
</tbody>
</table>

Fig. 6 – (a) The uptake isotherm of as-made materials for I\(^{-}\) trapped over 12 hr; (b) Sorption isotherm investigations of Cu/Cu2O-LDH at different temperatures.
presence of Cl\textsuperscript{−}, SO\textsubscript{4}\textsuperscript{2−} and CO\textsubscript{3}\textsuperscript{2−} was conducted, and the result showed in Fig. 8b. It was observed that CO\textsubscript{3}\textsuperscript{2−} and Cl\textsuperscript{−} exhibited a strong inhibitory effect on I\textsuperscript{−} adsorption, only 16.4% and 35.6% of I\textsuperscript{−} removal percentage were obtained. The reason was the high ionic potential of CO\textsubscript{3}\textsuperscript{2−}, which was easier adsorbed by LDH compared with I\textsuperscript{−} anions (Ji et al., 2017; Zhang et al., 2017a). Additionally, because CO\textsubscript{3}\textsuperscript{2−} was assigned to weak acid, their presence was unfavorable to adsorb I\textsuperscript{−} for Cu/Cu\textsubscript{2}O (Mao et al., 2017b). The adverse effect of Cl\textsuperscript{−} could be attributed to the lower hydration energy of Cl\textsuperscript{−} (Forano, 2004) and the CuCl formed in the medium containing excessive Cl\textsuperscript{−} (Mao et al., 2017b). In contrast, in the presence of SO\textsubscript{4}\textsuperscript{2−}, 67.8% of I\textsuperscript{−} anions removal efficiency was obtained. The reason for SO\textsubscript{4}\textsuperscript{2−} exhibiting favorable on I\textsuperscript{−} removal was primarily due to the strong acid anions of SO\textsubscript{4}\textsuperscript{2−} (Mao et al., 2017b). From what has been illustrated in Fig. 8a, acidic environment was more favorable for I\textsuperscript{−} anions uptake.

2.3. Adsorption mechanism

As stated in adsorption behavior section, Cu/Cu\textsubscript{2}O-LDH exhibited excellent I\textsuperscript{−} adsorption. However, the Cu\textsubscript{5}Mg\textsubscript{10}Al\textsubscript{5}LDH without Cu/Cu\textsubscript{2}O displayed relatively poor adsorption capacity. We believe that Cu/Cu\textsubscript{2}O may activate and enhance the uptake capacity of the adsorbent. Generally, Cu/Cu\textsubscript{2}O is considered to be the best candidate for capturing I\textsuperscript{−} due to their strong affinity between Cu\textsuperscript{+} and I\textsuperscript{−}.

To understand the adsorption mechanism more clearly, several characterizations analyses were conducted. The XRD spectrum (Fig. 2b) of I-Cu\textsubscript{5}Mg\textsubscript{10}Al\textsubscript{5}-LDH revealed no difference before and after uptake of I\textsuperscript{−}, except for the change of the d spacing of (003) reflection from 0.756 to 0.769 nm, which was mainly attributed to the weaker interaction between the iodine and LDHs compared to CO\textsubscript{3}\textsuperscript{2−}. Therefore, only a portion of iodine anions were adsorbed through ion exchange (the corresponding reaction processes was given in Eq. (8)). Hence, the removals precede might also combination of surface complex formation (Jiang et al., 2007; Theiss et al., 2016b). For calcined LDH, characteristic peaks of LDH appeared, while weak reflections of the mixed oxide disappeared after uptake of I\textsuperscript{−} anions (Fig. 2b and Appendix A Fig. S2), indicating that a reconstruction of the layered structure in Cu\textsubscript{5}Mg\textsubscript{10}Al\textsubscript{5}-CLDH occurs during adsorption. During this process, I\textsuperscript{−} anions and water molecules as interlayer anions are incorporated into interlayer galleries. The reconstruction of CLDH is hypothesized by Eqs. 9 and 10. Therefore, the enhanced adsorption by Cu\textsubscript{5}Mg\textsubscript{10}Al\textsubscript{5}-CLDH may be ascribed to the reconstruction mechanism (Iglesias et al., 2014). As illustrated in the XRD spectra of Cu/Cu\textsubscript{2}O-LDH before and after adsorption (Fig. 2b), several distinct characteristic peaks assigned to CuI were found at 2θ = 25.7°, 29.7°, 42.4°, 50.1° and 64.5° (JCPDS No. 06–0246). Nevertheless, the peaks ascribed to metallic Cu disappeared, while Cu\textsubscript{2}O peaks become slightly distinct, indicating that metallic Cu plays a dominant role in I\textsuperscript{−} removal. In addition, the LDH still maintained characteristic peaks of Cu\textsubscript{5}Mg\textsubscript{10}Al\textsubscript{5}-LDH after adsorption, although the intensity of the peaks was somewhat weakened, indicating the structure of the material was not destroyed after adsorption of I\textsuperscript{−}. XPS spectra were also obtained to verify the structural information about Cu/Cu\textsubscript{2}O-LDH after adsorption. The Cu 2p XPS spectra of I-Cu/Cu\textsubscript{2}O-LDH showed that peaks at 635.2 eV (assigned as Cu(II)) and 952.4 eV (ascribed to Cu/Cu\textsubscript{2}O) disappeared, implying that Cu/Cu\textsubscript{2}O and Cu(II) participate in I\textsuperscript{−} uptake, while the binding energy at 932.7 eV could be assigned to Cu of CuI (Mao et al., 2017b). According to the XRD results of I-Cu/Cu\textsubscript{2}O-LDH, the disappeared peak at 952.4 eV may be mainly metallic Cu. The I 3d peaks appeared at binding energies around 631.0 eV (I 3d\textsubscript{3/2}) and 619.2 eV (I 3d\textsubscript{5/2}) (Fig. 3b and Appendix A Fig. S3) after adsorption. The I 3d\textsubscript{3/2} could be considered to be the best candidate for capturing I\textsuperscript{−} due to their strong affinity between Cu\textsuperscript{+} and I\textsuperscript{−}.
The uptake data of Cu/Cu2O-LDH appeared to influence the work reported in this paper.

Acknowledgments

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Appendix A. Supplementary data

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REFERENCES


