Chemical precipitation of heavy metals from wastewater by using the synthetical magnesium hydroxy carbonate
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ABSTRACT
Heavy metal pollution has become one of the most serious environmental problems today. The preparation of magnesium hydroxy carbonate from low-grade magnesite, and the chemical precipitation of heavy metal wastewater with magnesium hydroxy carbonate as precipitating agent were undertaken. The removal efficiencies of heavy metals were improved by increasing the dose of magnesium hydroxy carbonate, and the applicable dose of magnesium hydroxy carbonate was 0.30 g for 50 mL of the wastewater (6,000 mg/L). The precipitation reactions proceeded thoroughly within 20 min. At this time, the removal efficiencies of heavy metals were above 99.9%. The final pH value was 7.1, the residual VO$_2^+$, Cr$_3^+$ and Fe$_3^+$ concentrations were 0.01, 0.05 and 1.12 mg/L, respectively, which conformed to the limit of discharge set by China (0.5–2.0 mg/L, GB 8978–1996). The precipitate was mainly composed of Fe$_2$O$_3$, V$_2$O$_5$ and Cr$_2$O$_3$, which can be recycled as secondary raw material for metallurgical industry. The treatment of the heavy metal wastewater with magnesium hydroxy carbonate was successful in decreasing the concentrations of VO$_2^+$, Cr$_3^+$ and Fe$_3^+$ in wastewater.

Key words | heavy metals, low-grade magnesite, magnesium hydroxy carbonate, precipitation, removal, wastewater

HIGHLIGHTS
- Heavy metal pollution has become one of the most serious environmental problems today.
- The preparation of magnesium hydroxy carbonate from low-grade magnesite, and the chemical precipitation of heavy metal wastewater with magnesium hydroxy carbonate as precipitating agent were undertaken.
- The final pH value of wastewater was 7.1 and the residual VO$_2^+$, Cr$_3^+$ and Fe$_3^+$ concentrations conformed to the limit of discharge. The precipitate can be recycled as secondary raw material.

GRAPHICAL ABSTRACT
INTRODUCTION

Low-grade magnesite is a by-product that is generated during the mining of magnesite (MgCO₃), and the major composition is CaMg(CO₃)₂. It has caused the waste of valuable resources and environmental pollution. Therefore, the treatment and utilization of low-grade magnesite on an industrial scale have been a technical problem to be solved urgently (Zhu et al. 2015). On the other hand, magnesium hydroxy carbonate has several useful applications. It can be used in pharmaceuticals as an inert vehicle and an adsorbent; it is also used as a reinforcing agent in the rubber industry, as an extender for titanium dioxide in adsorbent; it is also used as a precursor for other magnesium-based chemicals (Botha & Strydom 2001).

With the rapid development of industries such as mining and smelting operations, metal plating facilities, metallic material manufactures, battery manufactures, pigment industries, etc., heavy metals are discharged into the aquatic environment increasingly (Nemade et al. 2009; Vyrides & Stuckey 2011). Because of their toxicity, carcinogenicity and non-biodegradability, the heavy metals have a detrimental effect on biological environment and human health. Heavy metal pollution has become one of the most serious environmental problems today (Su et al. 2019). Therefore, the treatment of heavy metal wastewater is important for protection of human health and the environment.

Current treatment technologies for the heavy metal wastewater include solvent extraction, ion exchange, membrane filtration, emulsion liquid membrane, coagulation–flocculation, electrochemical treatment, photocatalysis, reduction, chemical precipitation, biosorption and common adsorption (Sengupta et al. 2006; David & Edmund 2010; Yang & Xu 2015; Zhang & Wang 2017; Ayele et al. 2018).

Ion exchange is widely used to wipe off heavy metals from wastewater because of its advantages, such as high removal efficiency and fast kinetics, however, the process is costly, and not suitable for the industries located in countries suffering from economic recession. Furthermore, the regeneration process of ion exchange resins not only wastes chemical reagents, but also causes secondary pollution.

Membrane filtration has excellent efficiency in the treatment of heavy metal wastewater. Nevertheless, the cost of the process is high, especially when treating a large amount of wastewater. The reverse cleaning of the membrane is complex, and prone to causing secondary pollution, which limited the application of the method.

While biosorption and common adsorption combine simplicity, greenness and reliability with low capital and maintenance cost, there is limited adsorption capacity. Besides, the desorption of the heavy metals retained by adsorption material need to be carefully disposed.

Coagulation–flocculation is one of conventional methods for removal of heavy metals from wastewater, the produced chemical sludge has good settling and dewatering characteristics. But this technology involves chemical coagulants and flocculants consumption, in addition, it often must be used with other treatment methods in order to improve the removal efficiency.

Photocatalysis has significant limitations and it is only attractive for certain types of wastewater, the most common application is treatment of wastewater containing dichromate. Dichromate can be converted into less toxic Cr³⁺ via the photocatalysis process, but the Cr⁵⁺ ion cannot be removed from wastewater.

In general, heavy metal ions such as Cu²⁺, Ni²⁺ and Pb²⁺ can be removed from solution with metallic iron by reduction method. However, this method wastes a valuable iron resource, and thus it is difficult to realize an industrial scale.

Electrochemical treatment has a wide range of applications, but the process involves relatively large capital investment, expensive electric energy requirement and toxic sludge.

Most of the technologies are incapable of meeting the discharge standard limits (0.1–3 mg/L) for heavy metals.

Chemical precipitation is a useful and simple technology for the treatment of heavy metal wastewater. Traditionally, strong alkaline reagents, such as ammonia, lime, sodium hydroxide, sodium carbonate and sodium sulfide, are used to increase the pH of wastewater so that soluble heavy metal ions convert to their insoluble hydroxide, carbonate or sulfide forms and precipitate in an alkaline environment. Nevertheless, the traditional reagents have several disadvantages: (1) most of the heavy metal ions exist in acidic solution and sulfide reagents in acidic solution can form toxic hydrogen sulfide gas, which has detrimental effect on human health and environment, (2) the sulfide of heavy metal formed is difficult to filter due to its small particle size, (3) the insoluble hydroxide of amphoteric metals, such as copper and chromium, tend to form water-soluble coordination compounds as the pH rises beyond the optimal range, (4) the strong alkaline precipitating agents have corrosive effect on the equipment (Chen et al. 2009; Fu & Wang 2011). This has led the experts to search for weak alkaline, lower cost and non-corrosive reagent. In recent years,
magnesium hydroxide is used as alkalescent reagent for the chemical treatment of heavy metal wastewater. However, the resultant precipitate often contains unreacted magnesium hydroxide, which has small particle size that cause some problems in the filtration and separation processes (Jiang et al. 2003; Du & Wang 2008). Therefore, more efficient, less problematic and new precipitants still need to be found.

Magnesium hydroxy carbonate was employed as a precipitating agent in this work due to its excellent filtration properties. There is no literature on the removal of heavy metals from wastewater with magnesium hydroxy carbonate as the precipitating agent. Consequently, in the present work, the preparation of magnesium hydroxy carbonate as well as calcium carbonate from low-grade magnesite, and the chemical precipitation of heavy metals from wastewater with magnesium hydroxy carbonate were carried out through the experiment for the first time, which overcame the disadvantages of the technologies and reagents mentioned previously. And at the same time, waste recycling solved environmental pollution.

**MATERIALS AND Methods**

**Raw materials**

The low-grade magnesite collected from Yingkou city of China was milled to 80 μm. The chemical composition of low-grade magnesite is shown in Table 1 and the molecular formula is CaMg(CO₃)₂.

The chemical composition of the heavy metal wastewater produced in a metallic smelter is shown in Table 2. The pH value of the wastewater was 1.33, and the metals in wastewater were existed in the form of sulphate.

**Preparation of magnesium hydroxy carbonate**

The mixture of magnesium chloride hexahydrate and low-grade magnesite powder with a mass ratio of 1:100 was calcined in muffle furnace at 650 °C for 120 min to obtain a calcined product, which was mainly composed of calcium carbonate and magnesium oxide (Shan et al. 2015). The presence of magnesium chloride hexahydrate accelerated the decomposition reaction of low-grade magnesite by decreasing the pressure of carbon dioxide. Then 5 g of calcined product was cooled to room temperature, added into 36 mL of ammonium chloride solution (2.5 mol/L) and the mixture was stirred at 80 °C for 60 min through a magnetic stirrer to obtain calcium carbonate and magnesium chloride solution. Finally, magnesium hydroxy carbonate was precipitated from the magnesium chloride solution with ammonium carbonate solution at 60 °C. When the temperature was lower, a large amount of nesquehonite formed. The reactions during the process are present as follows:

\[
\begin{align*}
\text{MgCO}_3 \cdot \text{CaCO}_3 &= \text{CaCO}_3 + \text{MgO} + \text{CO}_2 \uparrow \quad (1) \\
\text{MgO} + 2\text{NH}_4\text{Cl} &= \text{MgCl}_2 + \text{H}_2\text{O} + 2\text{NH}_3 \uparrow \quad (2) \\
5\text{MgCl}_2 + 5(\text{NH}_4)_2\text{CO}_3 + 5\text{H}_2\text{O} &= \text{Mg}_5(\text{OH})_2(\text{CO}_3)_4 \cdot 4\text{H}_2\text{O} \downarrow + 10\text{NH}_4\text{Cl} + \text{CO}_2 \uparrow \quad (3) \\
4\text{MgCl}_2 + 4(\text{NH}_4)_2\text{CO}_3 + 4\text{H}_2\text{O} &= \text{Mg}_4(\text{OH})_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O} \downarrow + 8\text{NH}_4\text{Cl} + \text{CO}_2 \uparrow \quad (4)
\end{align*}
\]

The magnesium hydroxy carbonate was solid material, the yield was 2.5 g, and the mass fraction of Mg element was 25%.

**Treatment of heavy metal wastewater**

The synthetical magnesium hydroxy carbonate was added into 50 mL of the wastewater and the mixture was stirred through a magnetic stirrer at room temperature. After this, the liquid was filtered to obtain filtrate and precipitate.

Magnesium hydroxy carbonate reacted with acid and heavy metals in the wastewater due to its chemical characters. Magnesium hydroxy carbonate was slightly

| Chemical composition of low-grade magnesite (mass fraction, %) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| MgO             | CaO             | SiO₂            | Fe₂O₃           | Al₂O₃           | MnO₂            | P₂O₅            | K₂O             | SO₃             | SrO             |
| 21.95           | 30.42           | 0.435           | 0.219           | 0.194           | 0.142           | 0.069           | 0.025           | 0.017           | 0.012           |

| Chemical composition of the heavy metal wastewater (g/L) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| VO₂             | Cr³⁺            | Fe³⁺            | Mg²⁺            | TiO²⁻           |
| 0.21            | 0.04            | 1.04            | 0.21            | 0.01            |
soluble in water, while Fe(OH)₃, Cr(OH)₃ and VO₂OH were hardly soluble in water, so according to the principle of inorganic chemistry, the precipitation reactions proceeded spontaneously.

The reactions during the process are present as follows:

\[ 3\text{Mg}_5\text{(OH)}_2\text{(CO}_3\text{)}_4\cdot 4\text{H}_2\text{O} + 5\text{Fe}_2\text{(SO}_4\text{)}_3 = 15\text{MgSO}_4 + 10\text{Fe(OH)}_3 + 12\text{CO}_2 \uparrow \]  
(5)

\[ 3\text{Mg}_4\text{(OH)}_2\text{(CO}_3\text{)}_3\cdot 3\text{H}_2\text{O} + 4\text{Fe}_2\text{(SO}_4\text{)}_3 = 12\text{MgSO}_4 + 8\text{Fe(OH)}_3 + 9\text{CO}_2 \uparrow \]  
(6)

\[ 3\text{Mg}_5\text{(OH)}_2\text{(CO}_3\text{)}_4\cdot 4\text{H}_2\text{O} + 5\text{Cr}_2\text{(SO}_4\text{)}_3 = 15\text{MgSO}_4 + 10\text{Cr(OH)}_3 + 12\text{CO}_2 \uparrow \]  
(7)

\[ 3\text{Mg}_4\text{(OH)}_2\text{(CO}_3\text{)}_3\cdot 3\text{H}_2\text{O} + 4\text{Cr}_2\text{(SO}_4\text{)}_3 = 12\text{MgSO}_4 + 8\text{Cr(OH)}_3 + 9\text{CO}_2 \uparrow \]  
(8)

\[ \text{Mg}_5\text{(OH)}_2\text{(CO}_3\text{)}_4\cdot 4\text{H}_2\text{O} + 5\text{(VO}_2\text{)}_2\text{SO}_4 = 5\text{MgSO}_4 + 10\text{VO}_2\text{OH} + 4\text{CO}_2 \uparrow \]  
(9)

\[ \text{Mg}_4\text{(OH)}_2\text{(CO}_3\text{)}_3\cdot 3\text{H}_2\text{O} + 4\text{(VO}_2\text{)}_2\text{SO}_4 = 4\text{MgSO}_4 + 8\text{VO}_2\text{OH} + 3\text{CO}_2 \uparrow \]  
(10)

\[ \text{Mg}_5\text{(OH)}_2\text{(CO}_3\text{)}_4\cdot 4\text{H}_2\text{O} + 5\text{H}_2\text{SO}_4 = 5\text{MgSO}_4 + 10\text{H}_2\text{O} + 4\text{CO}_2 \uparrow \]  
(11)

\[ \text{Mg}_4\text{(OH)}_2\text{(CO}_3\text{)}_3\cdot 3\text{H}_2\text{O} + 4\text{H}_2\text{SO}_4 = 4\text{MgSO}_4 + 8\text{H}_2\text{O} + 3\text{CO}_2 \uparrow \]  
(12)

**Analytical methods**

The phase identification of the synthetical magnesium hydroxy carbonate was conducted by X-ray powder diffraction (XRD). The pH value of the filtrate was measured by pH3-3 pH meter. The residual heavy metal ion concentrations in the filtrate were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES), and the removal efficiencies were calculated. The precipitate was calcined in a muffle furnace at 800 °C for 120 min to remove the moisture, and the chemical composition was analyzed by X-ray fluorescence (XRF).

**RESULTS AND DISCUSSION**

**Preparation of magnesium hydroxy carbonate**

The XRD pattern of the sample is shown in Figure 1. The major compositions were Mg₅(OH)₂(CO₃)₄·4H₂O and Mg₄(OH)₂(CO₃)₃·3H₂O, with a small amount of MgCO₃·3H₂O and MgCO₃·5H₂O. The presence of MgCO₃·3H₂O and MgCO₃·5H₂O was due to the reactions (13) and (14).

\[ \text{MgCl}_2 + (\text{NH}_4)_2\text{CO}_3 + 3\text{H}_2\text{O} = \text{MgCO}_3\cdot 3\text{H}_2\text{O} \downarrow + 2\text{NH}_4\text{Cl} \]  
(13)

\[ \text{MgCl}_2 + (\text{NH}_4)_2\text{CO}_3 + 5\text{H}_2\text{O} = \text{MgCO}_3\cdot 5\text{H}_2\text{O} \downarrow + 2\text{NH}_4\text{Cl} \]  
(14)

**Removal efficiencies of heavy metals from wastewater**

When the reaction time was 20 min, the effects of the addition of magnesium hydroxy carbonate on removal efficiencies of heavy metals are shown in Figure 2. The results in Figure 2 indicated that the removal efficiencies increased rapidly with the increase of the dose of magnesium hydroxy carbonate from 0.14 g to 0.20 g, while it increased slightly from 0.20 g to 0.30 g. The reason for this is that the actions of magnesium hydroxy carbonate are neutralizing acid and precipitating heavy metals in the wastewater via the reactions (11)–(12) and (5)–(10), respectively. The precipitation reactions occur under neutral or alkaline conditions. According to the chemical equilibrium, the concentration of OH⁻ ion in the wastewater increases with the increasing the dose of magnesium hydroxy carbonate, which in turn enhances the precipitation reaction of the heavy metals. On the other hand, magnesium hydroxy carbonate is the reactant for the precipitation reaction of the heavy metals, the sufficient amount of magnesium hydroxy carbonate
enhances this reaction. Therefore, the applicable addition of magnesium hydroxy carbonate was 0.30 g, when the dose was more than 0.30 g, the removal efficiencies would not increase, and it would lead to the waste of magnesium hydroxy carbonate.

When the addition of magnesium hydroxy carbonate was 0.30 g, the effects of reaction time on removal efficiencies of heavy metals are shown in Figure 3. The results showed that the removal efficiencies increased rapidly with the increase of reaction time from 0 to 3 min, while increased slightly from 3 to 20 min. According to the chemical kinetics, the reaction rate depends on the concentration of reactant. The initial faster reaction rates may be explained by the high concentrations of heavy metals and magnesium hydroxy carbonate. As most of the heavy metals and magnesium hydroxy carbonate were exhausted, the reaction rates became slower. In addition, the precipitation reactions had proceeded thoroughly within 20 min, which indicated that the reactions has fast kinetics.

The final pH value was 7.1, the residual VO$_2^+$, Cr$^{3+}$ and Fe$^{3+}$ concentrations were 0.01, 0.05 and 1.12 mg/L, respectively, which met with the limit of discharge set by China (0.5–2.0 mg/L, GB 8978-1996). Based on this, the precipitated amounts of VO$_2^+$, Cr$^{3+}$ and Fe$^{3+}$ by using magnesium hydroxy carbonate were 0.7, 0.133 and 3.47 g/g, respectively, which displayed a good precipitation performance of magnesium hydroxy carbonate.

It is well known that the strong alkaline precipitating agents such as sodium hydroxide are easily dissolved in water, and it lead to the sharp rise of pH (pH > 9) and corrosive effect on the equipment after the reaction. The situation is quite different in the present paper, where magnesium hydroxy carbonate is employed. This result may be explained by the weak alkaline and slight solubility of magnesium hydroxy carbonate.

**Chemical composition of precipitate**

The chemical composition of the precipitate is shown in Table 3. It can be seen that the precipitate was mainly
 composed of Fe₂O₃, V₂O₅ and Cr₂O₃. As may be expected, Fe₂O₃, V₂O₅ and Cr₂O₃ gathered via Equations (5)–(10). The precipitate contains large amounts of metal elements, and can be reused as secondary raw material for metallurgical industry. The technology not only remove the heavy metals from wastewater, but also recovery the metal resources.

On the basis of the experimental results, a process is proposed for transferring the laboratory results to real industrial applications. At room temperature, the wastewater is pumped to a treatment tank, and magnesium hydroxy carbonate is stirred into the wastewater to react with the heavy metal ions. The formed mixture is subsequently filtrated by filter, yielding the effluent and precipitate. The precipitate is sold to metallurgical plants to offset the process cost. The process require pump, treatment tank, stirrer and filter, which is the common equipment for chemical and metallurgical industries. Compared to the other techniques, the recommended method is more favorable due to lower cost, higher controllability and performance. This method is thus promising for heavy metal wastewater treatment plants, particularly for ones located in the regions rich in magnesium resource.

While the presented paper provided proof of concept and demonstrated promising results for the application of magnesium hydroxy carbonate in heavy metal wastewater treatment, some relative aspects need further studies, for example, the feasibility of the method for heavy metal wastewater containing dichromate or complexing agents.

**CONCLUSIONS**

The preparation of magnesium hydroxy carbonate with low-grade magnesite as a raw material was carried out, and the major compositions of magnesium hydroxy carbonate were Mg₅(OH)₂(CO₃)₄·4H₂O and Mg₄(OH)₂(CO₃)₃·3H₂O.

The treatment of the heavy metal wastewater with magnesium hydroxy carbonate was successful in decreasing the concentrations of VO₂⁺, Cr³⁺ and Fe³⁺ in wastewater. The precipitation reactions had proceeded thoroughly within 20 min, the dose of magnesium hydroxy carbonate was 0.30 g for 50 mL of wastewater. At this time, the final pH value was 7.1, the residual VO₂⁺, Cr³⁺ and Fe³⁺ concentrations were 0.01, 0.05 and 1.12 mg/L, respectively, which conformed to the limit of discharge set by China (0.5–2.0 mg/L, GB 8978-1996). The precipitated amounts of VO₂⁺, Cr³⁺ and Fe³⁺ using magnesium hydroxy carbonate were 0.7, 0.133 and 3.47 g/g, respectively.

The precipitate was mainly composed of Fe₂O₃, V₂O₅ and Cr₂O₃, which can be reused as secondary raw material for metallurgical industry.

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