Research on resourceful disposal of organosilicon wastewater containing magnesium

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ABSTRACT

In this paper, iron–carbon micro-electrolysis as well as Fenton oxidation are adopted to degrade the organism in wastewater containing magnesium. And then the generated Fe^{3+} was used to coprecipitate with Mg^{2+} in the wastewater to prepare layered double hydroxides (LDHs). The wastewater achieves a 73% decreasement in chemical oxygen demand (COD) under the optimum condition of pH = 2 and iron–carbon ratio = 1:3 through iron–carbon micro-electrolysis while a 77% decreasement in COD is achieved under the optimum condition of pH = 3 with 6 mL/L H_2O_2 and 2 g/L $FeSO_4·7H_2O$ via Fenton oxidation. After treatment, the wastewater containing magnesium with COD of 248 mg/L and removal efficiency of 93% meets the sewage drainage standard. Furthermore, the efficient resourceful utilization of magnesium can be achieved through synthesis of magnesium iron layered double hydroxides (MgFeCl-LDH).

Keywords: Wastewater containing magnesium; Iron–carbon micro-electrolysis; Fenton oxidation; Mg-based functional materials; Layered double hydroxides

1. Introduction

Methylsiloxane monomer can be obtained via simple reaction between silicon powder and chloromethane [1]. Techniques for preparation of organosilicons are in permanent revolution, for instance, requirement for other chlorine-containing alkyl monomers, such as triethylchlorosilane, triisopropylchlorosilane, triisopropylsilane and phenylchlorosilane, has increased sharply annually ascribe to the distinguishing performance between specific alkyl and methyl. Nevertheless, it is difficult to obtain these monomers from direct reaction, and the Grignard reaction has been adopted as a preferred method for industrial preparation of these monomers.

Grignard reagents, short from alkyl magnesium halides, have been widely applied in the synthesis of medicines, perfumes and special organosilicon monomers [2,3]. After

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Grignard reactions, alkyl magnesium halides transform into soluble magnesium halides, which lead to relatively acidic wastewater. Generally speaking, chlorine ions, unlike both bromine ions and iodine ions with recycling value, are discharged in industrial wastewater without any further treatment. Consequently, serious environmental pollution and severe wastage of magnesium resources are becoming big problems.

At present, reports about research on resourceful treatment of magnesium in Grignard wastewater are relatively rare and are mainly confined in condensation or precipitation. In order to recover magnesium, Li et al. [4] has condensed a great deal of wastewater and then added concentrated sulfuric acid to produce magnesium sulfate. This method results in high energy consumption and serious corrosion to equipment's. Similarly, Yang and Wang [5] has realized the recovery of magnesium through generation of hydrosoluble magnesium chloride. This method requires extremely high energy to evaporate wastewater. Furthermore, it is tough for the as-prepared magnesium chloride to reach high purity. On the other side, precipitation has been preferred by both Sun et al. [6] and Xiao et al. [7]. Sun adopts lime slurry as precipitant to obtain solution containing magnesium hydroxide and calcium chloride. However, the consumption of abundant energy to get calcium chloride from dilute solution leads to difficulty in industrial production. In order to avoid separation problem caused by magnesium hydroxide colloidal precipitation from the method of direct precipitation, Xiao has adjusted the pH of the wastewater by alkali metal, and then added carbonates to obtain light magnesium carbonate. However, this method consumes plenty of alkali. The salinity in wastewater after extraction of magnesium has not changed yet, therefore it is still difficult for the wastewater treatment. Meanwhile, the as-prepared light magnesium carbonate cannot be widely applied.

A further study on advanced treatment of organosilicon wastewater containing magnesium has been proposed in this paper. Industrial wastewater from production of triisopropylsilyl chloride and chlorotriethylsilane is adopted as raw material, iron–carbon micro-electrolysis as well as Fenton oxidation are utilized to degrade organic materials and introduce Fe^{3+}. After nucleation/crystallization isolation, Mg^{2+} and Fe^{3+} have quickly entered into layered double hydroxides (LDHs) to form crystal nucleus via accurate control of diffusion/mass transfer process. In a very short time, the concentration of ions in reaction has decreased to a value which is lower than precipitation threshold, consequently, so the formation of impurity as well as intermediary has been inhibited and the magnesium resource in wastewater has been maximized used. As a result, the quality of as-prepared magnesium-based functional materials is similar to that of commercial-available magnesium-based functional materials. At same time, the chemical oxygen demand (COD) of wastewater decreases to lower than 500 mg/L, which fits the emission requirement [8–11].

2. Experimental section

2.1. Raw materials

Silicone oil (AR), citric acid (AR) were purchased from Aladdin Bio-Chem Technology Co., Ltd., (Shanghai, China). Silver sulfate (Ag_2SO_4, AR), sodium hydroxide (NaOH, AR),

ferrous sulfate ($FeSO_4·7H_2O$, AR), ethylenediaminetetraacetic acid disodium salt (EDTA-2Na, AR), acetic acid (HAC, AR), ammonium acetate (CH_3COONH_4, AR), hydroxylamine hydrochloride ($HONH_2HCl$, AR) were obtained from Xilong Chemical Co., Ltd., (China). Triethanolamine ($C_6H_{15}NO_3$, AR), hydrogen peroxide (H_2O_2, AR), ammonia monohydrate ($NH_3·H_2O$, AR), hydrogen chloride (HCl, AR), sulfuric acid (H_2SO_4, AR) were purchased from Zhejiang Hannuo Chemical Technology Co., Ltd., (Zhejiang, China). Potassium dichromate ($K_2Cr_2O_7$, AR), o-phenanthroline were obtained from Tianjin Chemical Reagent Research Institute (Tianjin, China). Iron(III) chloride hexahydrate ($FeCl_3·6H_2O$, AR), calcium carbonate ($CaCO_3$, AR), iron powder were purchased from Sinopharm Chemical Reagent Co., Ltd., (China). Mercurous sulfate ($HgSO_4$, AR) were obtained from Shanghai Sihewei Chemical Co., Ltd., (Shanghai, China). Sodium carbonate (Na_2CO_3, AR) were purchased from Hangzhou Gaojing Chemical Co., Ltd., (Hangzhou, China). Eriochrome black T were obtained from Tianjin Damao Chemical Regent Factory (Tianjin, China) and organosilicon wastewater containing magnesium obtained from Zhejiang HuTu PharmChem Co., Ltd., (Zhejiang, China).

2.2. Instruments and equipment

The chemical composition of the samples was obtained by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher Scientific, USA) and X-ray diffractometer (XRD, D8 ADVANCE, Bruker, Germany). The Fourier-transform infrared spectroscopy (FT-IR) measurements were carried out on Nicolet 380 (USA) and observed the morphology by scanning electron microscope (Insect F50, FEI).

2.3. COD determination of wastewater containing magnesium

In this section, varieties of solution have been prepared to determine COD of wastewater containing magnesium. Standard solution of potassium dichromate was fixed to calibrate ammonium ferrous sulfate solution while ferroin indicator solution was prepared to indicate color change during the calibration. Afterwards, the calibrated ammonium ferrous sulfate solution was used to titrate wastewater containing magnesium for COD determination.

2.4. Determination of Mg^{2+} concentration in wastewater containing magnesium

Same as above, varieties of solutions need to be prepared in this section. Standard solution with Ca^{2+} concentration of 0.02 mol/L can be obtained by the method of the fixed volume.

In order to calibrate EDTA concentration, 25 mL standard solution with Ca^{2+} concentration of 0.02 mol/L was adjusted to of pH ≥ 12 by NaOH with concentration of 0.5 mol/L, solid calcium carboxylic acid was added as indicator.

Based on above experiment, 25 mL diluted sample was titrated by the calibrated EDTA concentration with black T as indicator for determination of Mg^{2+} concentration.

2.5. Iron–carbon aeration micro-electrolysis

In order to investigate the results of electrolysis influenced by different iron–carbon mass ratios under same pH,

we added 100 mL undiluted wastewater containing Mg^{2+} into 5 beakers and adjusted the pH to 4, respectively. Then we put iron–carbon powder with mass ratio of 1:3, 1:2, 1:1, 2:1, 3:1 into the 5 beakers and aerated for 18 h, respectively. After the aeration, the liquid precipitation was filtered, and the filtrate was diluted by a certain multiple for the determination of the COD value after the reaction.

The iron–carbon ratio for optimum removal efficiency has been determined from previous step, the influence of different pH values on the results of micro-electrolysis under same iron–carbon ratio was explored.

2.6. Fenton oxidation

The optimal ratio between hydrogen peroxide and ferrous sulfate can be determined through controlling of variables. The pH values of the wastewater were adjusted to 3. 0.1, 0.3, 0.5 and 0.7 g $FeSO_4 \cdot 7H_2O$ were added to the wastewater, respectively. Then 1 mL H_2O_2 was added to the mixture, respectively. After shaking for 40 min, the filtrate obtained from filtration was taken to determine the value of COD.

The optimum dosage of hydrogen peroxide and ferrous sulfate was determined by control of variables as well. The pH values of the wastewater were adjusted to 3. According to the optimal ratio determined by the previous step, dosages taken as 0.3, 0.5, 0.8, 1.0 and 1.3 times of the ratio were put for the test, respectively. Ferrous sulfate was added at first and hydrogen peroxide later. After shaking for 40 min, the filtrate obtained from filtration was taken to determine the value of COD.

From the combination of the final results of the first two steps, the optimum dosage ratio and input amount for Fenton oxidation have been determined. The pH value of wastewater from iron–carbon aeration was adjusted to 3. The optimal dosage of agents was added, after vibration for 40 min, the filtrate obtained from filtration was taken to determine the value of COD. Therefore, the optimal removal efficiency of COD by Fenton oxidation was obtained.

2.7. Determination of Fe^{3+} concentration

After treatment by iron–carbon reaction and Fenton oxidation, it is necessary to measure Fe^{3+} concentration in the wastewater for preparation of magnesium iron layered double hydroxides (MgFeCl-LDH) with magnesium iron ratio of 2:1, 3:1 and 4:1 through addition of appropriate ferric salt into the wastewater. In this section, we adopted o-phenanthroline spectrophotometry to measure Fe^{3+} in the wastewater.

Table 1 shows the dosages of iron working solution used in the experiment. Reagent solution without iron was set as reference solution. The absorbance was determined on the spectrophotometer, whose maximum absorption wavelength is 510 nm.

2.8. Preparation of MgFeCl-LDH

Table 2 exhibits the dosages of raw materials used in preparation of MgFeCl-LDH. According to Table 2, a certain amount of ferric salt was dissolved in wastewater containing Mg^{2+} to form a mixed salt solution A with the molar ratio of magnesium to iron of 2, 3 and 4, respectively. On the other hand, a certain amount of NaOH and Na_2CO_3 was taken to form an alkali solution B.

Two types of solution were simultaneously dropped into a four-port flask, which was filled with a small amount of distilled water and preheated to 65°C. At constant 65°C, the dropping speed was controlled at 200 mL/h and the pH was about 10 under intense stirring, which was continued for 30 min after dropping of liquid A and B. Then the slurry was taken out and crystallized for 10 h at 80°C. After filtration, the filter residue was washed until neutral. Subsequently, the residue was then dried and ground, sieved by 100-mesh sieve and stored in a dry environment for further characterization.

3. Results and discussion

3.1. COD determination of wastewater containing Mg^{2+}

From the experiment described in 2.3, the data was collected in Table 3. It can be learned that the concentration of as-prepared ammonium ferrous sulfate standard solution is 0.09981 mol/L. Table 4 shows the COD value of initial wastewater containing Mg^{2+}. It can be seen from Table 4

Table 1
Data for ferrous ion concentration standard curve

Number	Volume of iron working solution (mL)	Iron content in sample (μg/L)
1	0.5	10
2	1.0	20
3	2.0	40
4	3.0	60
5	4.0	80
6	5.0	100
7	6.0	120
8	7.0	140
9	8.0	160
10	9.0	180
11	10.0	200

Table 2
Dosages of raw materials used in preparation of MgFeCl-LDH

$n_{Mg}:n_{Fe}$	Reagents	Mg^{2+}		$FeCl_3 \cdot 6H_2O$		NaOH		Na_2CO_3	
		(mol)	(mL)	(mol)	(g)	(mol)	(g)	(mol)	(g)
2:1		0.0876	50.00	0.0438	10.387	0.1	4	0.0876	9.29
3:1		0.0876	50.00	0.0292	6.438	0.1	4	0.0584	6.19
4:1		0.0876	50.00	0.0219	4.463	0.1	4	0.0438	4.64

that the COD value of initial wastewater containing Mg^{2+} is 3.98×10^3 mg/L. Table 5 is the collection of COD values after iron–carbon reaction under different iron–carbon ratios but same pH. From Table 5, it can be learned that under the condition of pH = 4, the removal efficiency of COD is up to 61% when the mass ratio of iron to carbon is 1:3. The COD values after iron–carbon reaction under different pH conditions are exhibited in Table 6. Obviously, when the ratio of iron to carbon is 1:3, the removal efficiency of COD reaches the optimum of 70.8% at pH = 2.

After confirmation of the optimum conditions for removal of COD, Table 7 shows the determination of COD after iron–carbon reaction. It is clear that after 1 L wastewater containing Mg^{2+} is adjusted to pH = 2 and iron–carbon powder (20 g iron powder and 60 g activated carbon) with

mass ratio of 1:3 is put into the aeration, COD decreases from 3.98×10^3 mg/L to 1.08×10^3 mg/L. The removal efficiency is up to 72.9%, which is similar to the result of inquiry process.

Determination of COD after Fenton oxidation under different Fe^{2+} concentrations is shown in Table 8. Clearly, the highest removal efficiency of COD (64.2%) can be realized by combination of 0.3 g $FeSO_4$ and 1 mL H_2O_2 while the dosage of hydrogen peroxide remains at 1 mL/50 mL. Therefore, it is confirmed that $(0.3FeSO_4 + 1$ mL $H_2O_2)/50$ mL is the optimal ratio.

Table 9 gives the COD values after Fenton oxidation under different dosages of hydrogen peroxide and ferrous salt. According to data in Table 9, the removal efficiency of COD reaches the optimum value of 73.0% when the dosages of H_2O_2 and $FeSO_4$ are 0.3 times of the optimal ratio mentioned above. Hence, 6 mL/L H_2O_2 and 2 g/L $FeSO_4 \cdot 7H_2O$ are the optimal dosages.

After determination of the optimal dosages for Fenton oxidation, Table 10 exhibits the COD values after Fenton oxidation. After Fenton oxidation of 6 mL/L H_2O_2 and 2 g/L $FeSO_4 \cdot 7H_2O$, the COD of wastewater after iron–carbon aeration reduces from 1.08×10^3 mg/L to 247 mg/L with the removal efficiency of 77.1%.

In conclusion, after iron–carbon aeration and Fenton oxidation, the COD of wastewater containing Mg^{2+} has been reduced from original 3.98×10^3 mg/L to final 247 mg/L. The

Table 3
Calibration of ammonium ferrous sulfate standard solution

	1	2	3
$V_{consumedFe(NH_4)_2(SO_4)_2 \cdot 6H_2O}$ (mL)	25.18	25.11	24.86
$C_{Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O}$ (mol/L)	0.09928	0.09956	0.1006
$C_{averageFe(NH_4)_2(SO_4)_2 \cdot 6H_2O}$ (mol/L)	0.09981		

Table 4
Determination of chemical oxygen demand in initial wastewater containing Mg^{2+}

	Blank group	Parallel group 1	Parallel group 2	Parallel group 3
$V_{consumedFe(NH_4)_2(SO_4)_2 \cdot 6H_2O}$ (mL)	24.61	19.62	19.59	19.66
CODcr (mg/L)		3.98×10^3	4.01×10^3	3.95×10^3
CODcr average (mg/L)		3.98×10^3		

Dilution by a factor of 20.

Table 5
Determination of chemical oxygen demand under different iron–carbon ratio

	Blank group	$m_{Fe}:m_C$ 3:1	$m_{Fe}:m_C$ 2:1	$m_{Fe}:m_C$ 1:1	$m_{Fe}:m_C$ 1:2	$m_{Fe}:m_C$ 1:3
$V_{averageFe(NH_4)_2(SO_4)_2 \cdot 6H_2O}$ (mL)	24.35	20.11	21.16	21.80	21.76	22.40
CODcr (mg/L)		3,385	2,547	2,035	2,068	1,557
Removal efficiency (%)		15	34	49	48	61

pH = 4, dilution by a factor of 20.

Table 6
Determination of chemical oxygen demand under different pH conditions

	Blank group	pH = 1	pH = 2	pH = 3	pH = 4	pH = 5
$V_{averageFe(NH_4)_2(SO_4)_2 \cdot 6H_2O}$ (mL)	24.40	22.50	22.95	22.40	22.10	22.01
CODcr (mg/L)		1.52×10^3	1.16×10^3	1.60×10^3	1.84×10^3	1.91×10^3
Removal efficiency (%)		61.8	70.8	59.8	53.8	52.0

$m_{Fe}:m_C$ = 1:3, dilution by a factor of 20.

Table 7
Determination of chemical oxygen demand after iron–carbon reaction with optimum conditions

	Blank group	Parallel group 1	Parallel group 2	Parallel group 3
$V_{averageFe(NH_4)_2(SO_4)_2 \cdot 6H_2O}$ (mL)	24.60	23.21	23.28	23.26
CODcr (mg/L)		1.11×10^3	1.05×10^3	1.07×10^3
CODcr average (mg/L)		1.08×10^3		
Removal efficiency (%)		72.9		

pH = 2, m_{Fe}:m_C = 1:3, dilution by a factor of 20.

Table 8
Determination of chemical oxygen demand after Fenton oxidation under different Fe^{2+} concentrations

	Blank group	0.1 g FeSO$_4$	0.3 g FeSO$_4$	0.5 g FeSO$_4$	0.7 g FeSO$_4$
$V_{averageFe(NH_4)_2(SO_4)_2 \cdot 6H_2O}$ (mL)	25.40	22.79	23.46	23.19	23.30
CODcr (mg/L)		521	387	441	399
Removal efficiency (%)		51.8	64.2	59.2	63.0

Dilution by a factor of 5.

Table 9
Determination of chemical oxygen demand after Fenton oxidation with different dosages of H$_2$O$_2$ and FeSO$_4$

	Blank group	0.3x	0.5x	0.8x	1.0x	1.3x
$V_{averageFe(NH_4)_2(SO_4)_2 \cdot 6H_2O}$ (mL)	24.90	23.44	22.36	22.41	22.85	22.89
CODcr (mg/L)		291	507	494	409	401
Removal efficiency (%)		73.0	53.0	54.2	62.1	62.9

Dilution by a factor of 5.

Table 10
Determination of chemical oxygen demand after Fenton oxidation with optimum dosages

	Blank group	Parallel group 1	Parallel group 2	Parallel group 3
$V_{averageFe(NH_4)_2(SO_4)_2 \cdot 6H_2O}$ (mL)	24.90	23.35	23.31	23.40
CODcr (mg/L)		248	254	240
CODcr average (mg/L)		247		
Removal efficiency (%)		77.1		

6 mL/L H$_2$O$_2$, 2 g/L FeSO$_4$·7H$_2$O, dilution by a factor of 4.

ultimate removal efficiency of COD reaches 93.8%, which meets the requirements of nanotube discharge. It can be seen that the combination of iron–carbon micro-electrolysis with Fenton oxidation displays favorable effect on the treatment of organosilicon wastewater containing magnesium.

3.2. Determination of Mg^{2+} concentration in wastewater containing Mg^{2+}

According to the steps described in 2.4, the calibration results of EDTA standard are displayed in Table 11. From Table 11, it can be learned that the concentration of as-prepared EDTA standard solution is 0.0204 mol/L.

Table 12 shows the results of Mg^{2+} concentration in the initial wastewater. The concentration of Mg^{2+} is 3.70 mol/L. Table 13 exhibits the concentration of Mg^{2+} in the wastewater after treatment. The concentration of Mg^{2+} in the wastewater after iron–carbon aeration and Fenton oxidation is 1.75 mol/L.

3.3. Determination of total Fe^{3+} concentration in treated wastewater

According to procedure in 1.5, the standard curve of ferrous ion concentration was obtained. The absorbance of sample is 0.025, so Fe^{2+} concentration in the sample is

Table 11
Calibration of ethylenediaminetetraacetic acid standard solution

	Parallel group 1	Parallel group 2	Parallel group 3
$V_{consumedEDTA}$ (mL)	24.10	24.75	24.80
$V_{averageEDTA}$ (mL)	24.55		
c_{EDTA} (mol/L)	0.0204		

Table 12
Determination of Mg^{2+} concentration in the initial wastewater

	Parallel group 1	Parallel group 2	Parallel group 3
$V_{consumedEDTA}$ (mL)	11.29	11.35	11.36
$V_{averageEDTA}$ (mL)	11.33		
$C_{Mg^{2+}}$ (mol/L)	3.70		

Dilution by a factor of 400.

Table 13
Determination of Mg^{2+} concentration in the wastewater after treatment

	Parallel group 1	Parallel group 2	Parallel group 3
$V_{consumedEDTA}$ (mL)	5.36	5.33	5.40
$V_{averageEDTA}$ (mL)	5.36		
$C_{Mg^{2+}}$ (mol/L)	1.75		

Dilution by a factor of 400.

130 µg/L. The total Fe^{2+} concentration in the wastewater is 0.0058 mol/L due to 25,00 times dilution.

3.4. Characterization of MgFeCl-LDH

3.4.1. FT-IR analysis

The FT-IR spectra are exhibited in Fig. 1. Obviously, there is a broad and strong peak near 3,450 cm⁻¹, which indicates the stretching vibration of O–H with hydrogen bond association. The peak at 1,600 cm⁻¹ is bending vibration of O–H and the peak at 1,490 cm⁻¹ may be caused by the intercalation of untreated organic compound. The infrared spectra prove that the as-prepared material has the structural characteristics of LDHs.

3.4.2. XRD analysis

Fig. 2 displays the XRD spectra of MgFeCl-LDH. It can be learned that the crystal structure of LDHs with different molar ratios of Mg to Fe is basically the same, with regular layered structure and high crystallinity. The positions and patterns of the diffraction peaks of the three ratios are almost the same, which indicates that different Mg/Fe ratios
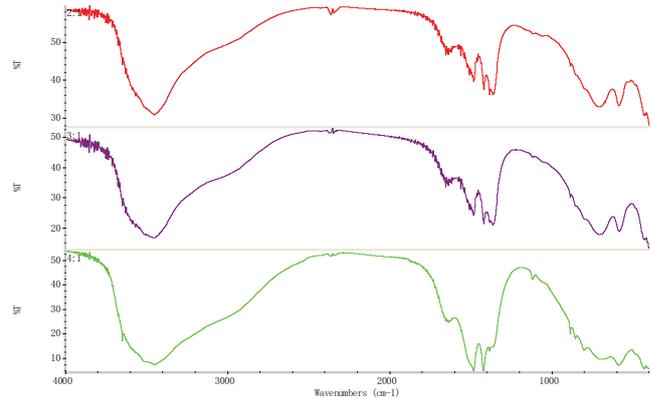
Fig. 1. Fourier-transform infrared spectra of as-prepared MgFeCl-LDH.
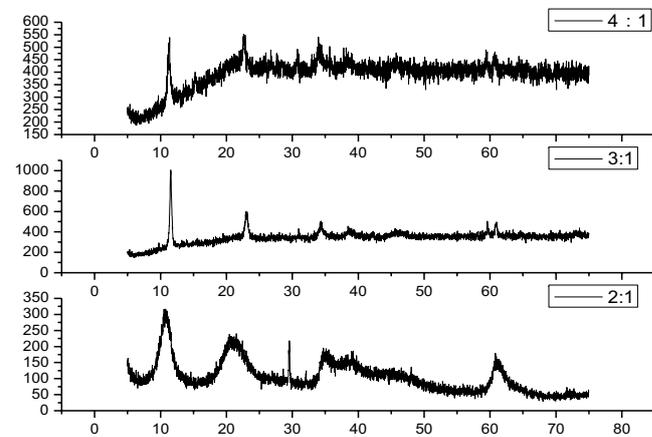
Fig. 2. X-ray diffraction spectra of as-prepared MgFeCl-LDH.

have no effect on the lamellar structure and composition. The MgFeCl-LDH prepared in the experiment shows typical layered structure and characteristic diffraction peak of hydrotalcite.

4. Conclusion

The organic compounds in wastewater containing magnesium were degraded by iron–carbon micro-electrolysis and Fenton oxidation, then three types of MgFeCl-LDH were prepared through coprecipitation of Fe^{3+} and Mg^{2+} in wastewater. The results show that the optimal conditions of iron–carbon micro-electrolysis are pH = 2, Fe/C ratio = 1:3. Under the conditions, the COD of wastewater can be reduced by 73%. The optimal conditions of Fenton oxidation reaction are pH = 3, dosage of 6 mL/L H_2O_2 and 2 g/L $FeSO_4·7H_2O$. Under the conditions, the COD of wastewater after iron–carbon reaction is reduced by 77%. After treatment, the COD of wastewater containing Mg^{2+} is reduced to 248 mg/L and the removal efficiency is 93%, which meets the requirements of discharge by nanotube. According to the concentration of Mg^{2+} and Fe^{3+} in wastewater, a certain amount of ferric salt is added to prepare MgFeCl-LDH with the ratio of 4:1, 3:1 and 2:1, so efficient utilization of magnesium is realized.

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