

Treatment of coking wastewater by using manganese and magnesium ores

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ABSTRACT

This study investigated a wastewater treatment technique based on natural minerals. A two-step process using manganese (Mn) and magnesium (Mg) containing ores were tested to remove typical contaminants from coking wastewater. Under acidic conditions, a reactor packed with Mn ore demonstrated strong oxidizing capability and destroyed volatile phenols, chemical oxygen demand (COD), and sulfide from the coking wastewater. The effluent was further treated by using Mg ore to remove ammonium-nitrogen and phosphate in the form of magnesium ammonium phosphate (struvite) precipitates. When pH of the wastewater was adjusted to 1.2, the removal efficiencies for COD, volatile phenol and sulfide reached 70%, 99% and 100%, respectively. During the second step of precipitation, up to 94% of ammonium was removed from the aqueous phase, and precipitated in the form of struvite with phosphorus. The struvite crystals showed a needle-like structure. X-ray diffraction and transmission electron microscopy were used to characterize the crystallized products.

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1. Introduction

Coking wastewater is generated from coal coking, coal gas purification and by-product recovery processes of coke plants. The wastewater usually contains elevated amount of ammonia, sulfide, phenols and other organic compounds [1–3]. Phenolic compounds are one of the main contributors to the total chemical oxygen demand (COD) in coking wastewater [4]. Coking wastewater is considered hazardous and presenting a threat to environmental and human health [5,6].

Biological processes such as activated sludge, anoxic–oxic, anaerobic–anoxic–oxic and sequencing batch reactors are commonly used in industrial wastewater treatment. However, the presence of elevated concentrations of toxic, refractory and inhibitory compounds (e.g., phenols, sulfides) in the coking wastewater sometimes prohibits the performance of biological treatment, resulting in effluents containing high chemical oxygen demand (COD) and ammonium nitrogen (NH₄-N) [7,8]. Physical or chemical treatment processes are usually needed as a pre-treatment to improve the performance of biological systems [9]. Techniques such as chemical oxidation by Fenton's reagent [10],

ultrasonic irradiation [11], catalytic oxidation [12], and bottom ash adsorption [13] have been used or studied as pretreatment of coking wastewater prior to its treatment by biological systems.

Manganese oxide (MnO₂) has been used for removing COD from wastewaters, including oxidation of phenol and sulfide and conversion their final oxidation products of carbon dioxide and sulfate at low pH (<2.0) [14–17]. Another example of inorganic compound used in wastewater treatment is the precipitation of NH₃-N and phosphate (PO₄³⁻) in presence of magnesium, forming struvite precipitates as the product. This reaction has been used for removing nitrogen and phosphorus constituents from various sources of wastewaters, such as swine wastewater [18,19], agro-industrial effluents [20], landfill leachate [21], coke manufacturing waste stream [22], leather tanning [23] and anaerobic digester side streams [24,25]. The struvite crystal recovered can be used as a slow releasing fertilizer and soil conditioner [25,26].

Using pure inorganic compound in wastewater treatment is limited by the material cost. In a previous study, we explored the low cost raw manganese (Mn) containing ore as an alternative material in oxidizing phenols from wastewater [27]. In this study, we further extended that process by packaging both Mn- and Mg-containing ores in a two-step process to remove NH₄⁺, phenols, sulfide, and COD from coking wastewater. The contaminant removal efficiencies and reaction mechanisms of this mineral ore based treatment system were also investigated.

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2. Materials and methods

2.1. Materials

Wastewater used in this study was collected from a phenol cyanogen wastewater treatment plant (Hefei, China). Raw Mn containing ore was obtained from a mine in Qingyang (Anhui province, China). The ore was known to contain todorokite, rancieite and impure quartz. The Mn ore was grounded, air dried, and sieved to a particle size of 0.9–2.0 mm. Magnesium containing ore (magnesite) was obtained from Haicheng City (Liaoning Province, China). The Mg ore was calcined at 800 °C and the product was used for this study. Chemical reagents of analytical grade were purchased from the Shanghai Reagent Company (Shanghai, China), unless indicated otherwise.

2.2. Experimental methods

Crushed Mn ore (120 g) was packed in a glass column (10 mm diameter). The effective loading height was 1.10 m. The column openings were designed at <2 mm (diameter) to minimize fugitive volatilizations. Phosphoric acid (132 mL, 85%) was added to 10 L of coking wastewater to adjust the molar N/P ratio of 0.82. Based on N:P = 1:1 in MgNH_4PO_3 , we calculated 108 mL of phosphoric acid to be needed. We overdosed 24 mL of phosphoric acid (total 132 mL) to compensate for phosphate that was to be consumed by Mn. The overdosed amount was based on our previous experiments.

The resultant water had a pH of 2.1. Sulfuric acid (68 mL, 1:1) was added to further adjust the pH to 1.2, and the acidified wastewater was pumped into the reactor column. A peristaltic pump was used to maintain a flow rate of 2.65×10^{-4} m/s. The hydraulic retention time (HRT) was maintained at 70 min. The effluent from the reactor was monitored for pH, COD, Mn^{2+} and volatile phenols. The effluents were contained and used for the next step of experiment of magnesium ammonium phosphate precipitation.

Precipitation of NH_4^+ and PO_4^{3-} by MgO was performed in a conical flask (500 mL) with an airtight lid. The reactor was mixed by using magnetic stirrers at 25 °C. Acidic condition and the airtight container minimized the loss of ammonium in the form of ammonia gas. Different dosages of solid (magnesia)–liquid (wastewater) (S/L) ratios of 10, 14, 18, and 22 g/L and reaction times 0.5, 1, 2, 4, 6, 8, 12, 16, 20, and 24 h were established. Samples collected from the reactor at different intervals were centrifuged, and the supernatants were filtered through a 0.45 μm membrane filter. The filtrates were acidified with 1:1 nitric acid solution to stop the precipitation reaction and used for the analysis of NH_4^+ , PO_4^{3-} , and Mn^{2+} . Deposits were vacuum dried (40 °C), and the crystallized products were analyzed by X-ray diffraction (XRD) and transmission electron microscopy (TEM).

2.3. Analytical methods

The water samples were analyzed by following the standard methods specified in the Monitoring and Analytical Methods of Water and Wastewater [28]. The pH was measured by using the glass electrodes; volatile phenol was detected by using the 4-amino-antipyrine spectrophotometric method; COD by the potassium dichromate method; Mn^{2+} by the potassium periodate method; $\text{NH}_3\text{-N}$ by using Nessler's reagent spectrophotometry; S^{2-} by using iodometry; and P-PO_4^{3-} by using the molybdenum-antimony anti-spectrophotometric method. The BET surface area was determined by using nitrogen adsorption (SA3100TM surface area analyzer). The XRD analyses were performed by a D/max-RB powder diffractionmeter (Rigaku, Japan), with a Cu-target operated at 40 kV, 100 mA at a scan rate of 6°min^{-1} . Transmission electron

Table 1

Baseline characterization of the coking wastewater.

Parameter	Measured value	Unit
pH	10.5	
COD	3890	mg/L
Phenol	475	mg/L
Sulfide	32.0	mg/L
$\text{NH}_4\text{-N}$	2213	mg/L
$\text{PO}_4\text{-P}$	<0.01	mg/L
Mn^{2+}	<0.02	mg/L

microscopy studies were performed on a HITACHI H-800 electron microscopy (Hitachi Co., Tokyo, Japan).

3. Results and discussion

3.1. Baseline characterization of wastewater, Mn and Mg ore

Baseline parameters of the coking wastewater are listed in Table 1. Coking wastewater had a pH of 10.5, and elevated concentrations of COD and volatile phenols (quantified as phenol). Total nitrogen was detected at 2438 mg/L, with $\text{NH}_3\text{-N}$ dominating at 2213 mg/L. Manganese ore contained 26.62% of Mn and 46.4% of MnO_2 . The BET surface area of the Mn ore was determined to be 40.3 m^2/g . The magnesia used for the experiments was composed of 71.38% of MgO and 1.69% CaO. Also, quartz (3.07%) and talc (7.1%) were detected in the magnesia mixture. Loss of ignition of 13.61% during calcination indicates the presence of uncalcined magnesite and dolomite in the ore.

3.2. Oxidation of coking wastewater by Mn ore

Manganese ore was mixed in coking wastewater that was preacidified by phosphoric and sulfuric acids to oxidize phenol. Post-oxidation analysis of the wastewater indicated substantial decrease in phenol, sulfide, and COD (Table 2). Phenol decreased by 99.2% (from 475 to 4 mg/L), and COD decreased by 69.5% (from 3890 to 1185 mg/L); resulting in the removing efficiencies of 3.93 mg phenol/(Lg) Mn ore and 22.5 mg COD/(Lg) Mn ore. Sulfide was completely oxidized and no breakthrough was observed during the testing period. The resulting concentration of Mn^{2+} (2929 mg/L) in the post-reaction water indicated that approximately 47.4% of the MnO_2 were consumed in the reaction, although the exact amount could not be determined due to the possible sorption-desorption of the resultant Mn^{3+} and Mn^{2+} on the remaining MnO_2 . The presence of $\text{PO}_4^{3-}\text{-P}$ (6001 mg/L) was attributed to the excessive dose of the added phosphoric acid.

Acidic conditions (pH 1–2) favor the oxidizing activity of manganese ore. Stone [14] has investigated phenol oxidation by manganese oxides and found that lower pH favors phenoxenium ion formation and production of quinones over radical coupling. Ring cleavage of quinones to carboxylic acids and other aliphatic products occurs through further oxidation. Reactant manganese oxides are reduced to Mn^{3+} and Mn^{2+} , either dissolved in the solution or

Table 2

Characterization of coking wastewater after oxidation by Mn ore.

Parameter	Measured value	Unit
pH	1.8	
COD	1185	mg/L
Phenol	4.0	mg/L
Sulfide	<1.0	mg/L
$\text{NH}_4\text{-N}$	2213	mg/L
$\text{PO}_4\text{-P}$	6001	mg/L
Mn^{2+}	2929	mg/L

P concentration must be 6001 instead of 4900. Note: Mean concentration of $\text{NH}_4\text{-N}$ (2213 mg/L) was obtained from three measurements of 2196, 2191, and 2252 mg/L.

absorbed on the surface of manganese oxides [16]. This step of oxidation by Mn ore reactor also generated constituents of concern, including Mn^{2+} (2929 mg/L) and $\text{PO}_4^{3-}\text{-P}$ (6001 mg/L), which are to be addressed by the second step of the process.

The Mn ore was not able to oxidize $\text{NH}_4\text{-N}$, which was detected almost unchanged in concentration before and after the reaction (pre-reaction concentration of 2213 mg/L versus post-reaction concentrations of 2196, 2191, and 2252 mg/L with the mean of 2213 mg/L).

The reports of $\text{NH}_4\text{-N}$ oxidation by Mn were limited to the cases of extreme reaction conditions, for example, with $\text{MnO}_2/\text{CeO}_2$ serving as a catalyst under supercritical water condition with temperature $>400^\circ\text{C}$ and pressure of 27.6 MPa [29].

Volatilization of phenols might count toward minor fraction of the total phenol removal. However, the reactors had minimal openings (<2 mm diameter) to minimize volatilization. In addition, previous study of COD removal from phenol-dominated coking wastewater resulted in 69% and 68% decline in COD, respectively in fully sealed and open reactors similar to what used in this study. Therefore, although we cannot exclude trace volatilization of phenols, its contribution to phenol removal is presumed fractional.

3.3. Precipitation of ammonium and phosphate with magnesia

Phosphoric acid added during phenol oxidation resulted in a N:P molar ratio of 0.82. Considering that the molar ratio N:P:Mg to form struvite is 1:1:1, the theoretical minimum requirement of the magnesia used in this study would have been 8.8 g/L. However, the pH of the mixture must be 8–10 to favor form struvite formation [23,30,31] and remove Mn^{2+} by forming $\text{Mn}_3(\text{PO}_4)_2$, therefore, excess magnesia was used in this study.

Phosphate–phosphorus concentrations decreased from 6001 mg/L to 2.5 mg/L and 1.6 mg/L after 24 h in wastewater treated with 18 and 22 g magnesia/L (Fig. 1). Concentration of $\text{PO}_4\text{-P}$ decreased to 103 mg/L after 24 h in wastewater treated with 14 g magnesia/L, while wastewater treated with 10 g magnesia/L yielded a $\text{PO}_4\text{-P}$ decrease to 659 mg/L. Ammonium-nitrogen concentrations decreased from 2213 mg/L to 220 mg/L after 24 h in wastewater treated with 18 g magnesia/L (Fig. 2), while wastewater treated with 22 g magnesia/L yielded a $\text{NH}_3\text{-N}$ decrease to 186 mg/L. The values of pH as a function of magnesia added and reaction time are depicted in Fig. 3. Adding 18 g magnesia/L into coking wastewater treated by Mn ore with a reaction time of 24 h, the residual concentrations of $\text{NH}_3\text{-N}$, P-PO_4^{3-} and Mn^{2+} were 220 mg/L, 2.5 mg/L, and 4.9 mg/L, respectively. The value of pH increased to 9.39 (Table 2).

Removal efficiency of $\text{NH}_3\text{-N}$ reached 90.1% by struvite precipitation, while all NH_4^+ was recovered in the form of struvite. The

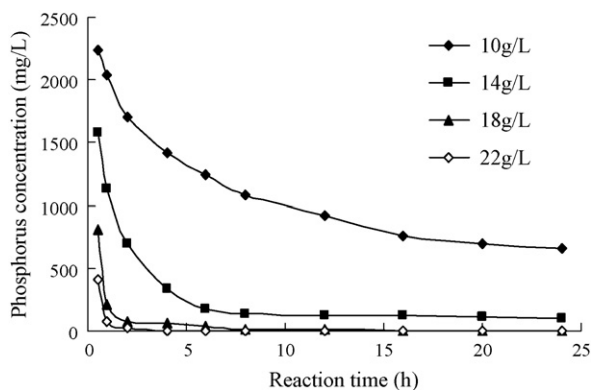


Fig. 1. Variation of the $\text{PO}_4\text{-P}$ concentration in the coking wastewater as a function of magnesia versus reaction time.

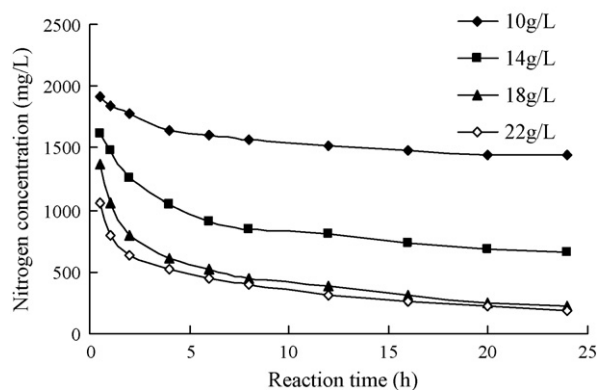
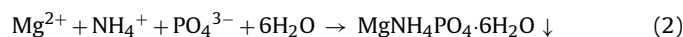


Fig. 2. Variation of nitrogen ($\text{NH}_3\text{-N}$) concentration in the coking wastewater as a function of magnesia versus reaction time.

removal of Mn^{2+} is due to $\text{Mn}_3(\text{PO}_4)_2$ compounds formation, which requires 18.3% $\text{PO}_4\text{-P}$. The residual concentration was decreased to 4.9 mg/L. The removal of P-PO_4^{3-} was higher than $\text{NH}_3\text{-N}$, because other Mg^{2+} and PO_4^{3-} minerals such as newberyite and bobierite could also form [32]. The pH increased near neutral range and the toxicity of high concentrations of phenol and NH_3 were eliminated by Mn ore oxidation and struvite precipitation. The residual concentrations of $\text{NH}_3\text{-N}$, P-PO_4^{3-} , Mn^{2+} may be removed by the follow-up biological treatment. In addition, the crystallized struvite product did not adsorb organic constituent, therefore stays harmless for crops when used as slow release fertilizer.

The reactions for struvite formation are:



Although magnesia used as source of magnesium produced showed a lower $\text{NH}_3\text{-N}$ removal efficiency when compared with pure magnesium salts such as $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ [21]; however, its cost is much lower and the postreaction ore remains impose minimal environment impact. In addition, magnesia has a high alkalinity that helps achieving neutral pH in the otherwise acidified wastewater streams during the first step of treatment.

The precipitates were used for the analysis of crystalline mineral phases. The XRD profiles were illustrated in Fig. 4, confirming that struvite was the main phase. Precipitates also contained unreacted periclase, magnesite, dolomite, talc, and quartz, which are all components in magnesia. No amorphous manganese phosphate or brucite were identified. Characteristic diffraction peaks of periclase appear to weaken gradually with reaction time. Fig. 4 only presents crystallized constituents. The formed compound of $\text{Mn}_3(\text{PO}_4)_2$ is

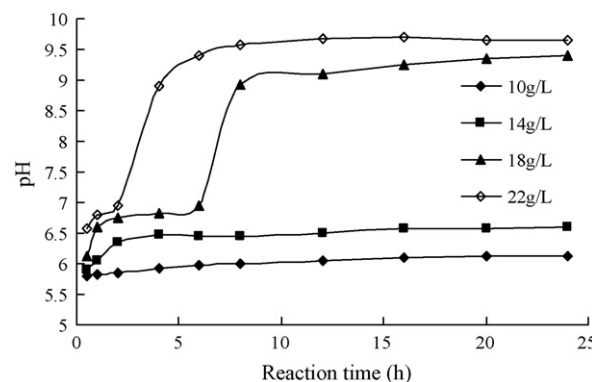


Fig. 3. pH values in the coking wastewater as a function of magnesia versus reaction time.

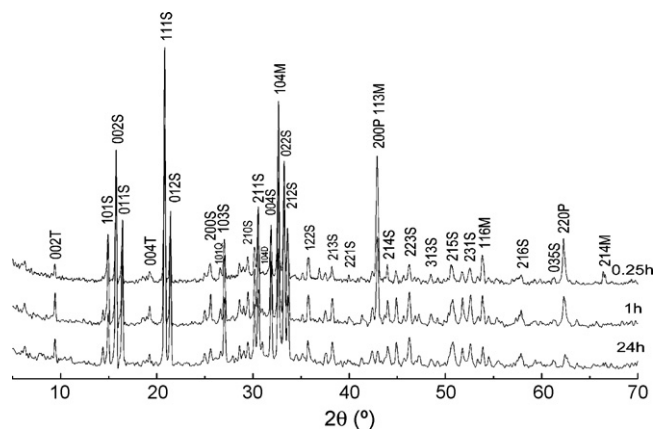


Fig. 4. XRD patterns of the reaction precipitates with 18 g magnesia/L at different reaction time. T: Talc; S: Struvite; M: Magnesite; Q: Quartz; D: Dolomite; P: Periclase.

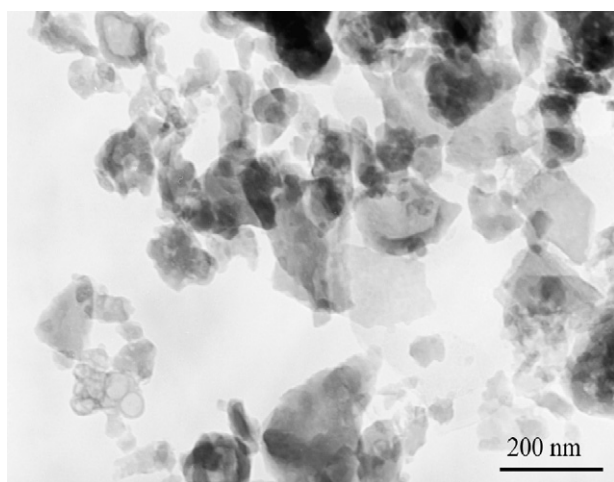


Fig. 5. TEM pattern of the reaction precipitate with 18 g magnesia/L at 1 h.

usually in amorphous form, therefore not shown in the XRD pattern. This was also supported by a separate experiment, in which KH_2PO_3 and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ based on their constitution in the wastewater were reacted, and white amorphous precipitates of $\text{Mn}_3(\text{PO}_4)_2$ were formed (unpublished data).

The TEM pattern of crystallized product with S/L concentration of 18 g/L and reaction time of 1 h was shown in Fig. 5. There was an obvious interface between the interior and exterior surfaces of the particle at reaction time of 1 h (Fig. 5). Combined with XRD analysis, this demonstrates that struvite formation did not take place in the bulk solution but on the surface of magnesia. Modified from Chimenos et al. [32], we proposed the mechanism of struvite formation as: (a) magnesia neutralizes protons, resulting in the increase of pH from 1.8 to 5–6 at the beginning of the reaction; (b) magnesia particles surface hydrolysis takes place and Nernst interface forms; (c) concentrations of magnesium ion and hydroxyl groups around the particles increase and diffuse to bulk solution, PO_4^{3-} and NH_4^+ in the solution diffuse into the interface at the same time; and (d) struvite crystal forms and grows on particles surface and hinders the diffusion of magnesium ions and hydroxyls. Though excess of magnesia was added, a decrease in the reaction rate was observed.

4. Conclusions

Results from this study suggest that the two-step process of using the low cost raw Mn- and Mg-containing ores as the pre-

treatment prior to biological systems can effectively remove volatile phenol, sulfide, and COD in general. The second step of struvite precipitation also removes NH_4^+ , PO_4^{3-} and Mn^{3+} , formed from the Mn oxidation process. The process can raise pH to near neutral range to facilitate the follow-up biological treatment, which can remove residual constituents left in the pretreatment effluent. Also observed from this study is that struvite formation takes place on the magnesia surface instead of in the bulk solution. This surface crystallization process does not incorporate hazardous organic constituents in the precipitates, enabling the resultant struvite to be used as a possible slow-release fertilizer.

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