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# Pretreatment of actual high-strength phenolic wastewater by manganese oxide method

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ABSTRACT

This paper deals with treating high phenol-concentrated wastewater from coal gasification by manganese oxide method. Mixed-phase manganese oxides of manganite and hausmannite were synthesized with industrial $MnSO_4$ and NaOH by air oxidation. The effects of sulfuric acid dosage, reaction time, temperature, manganese oxide grain size and concentration on removal efficiency of total phenols were studied with laboratory bench-scale experiments. The results indicated that the removal process was more effective under the experimental conditions, i.e. acidified media at pH < 4 and an excessive amount of fine particles with a long reaction time. Solution pH and manganese oxide concentration were two of the most important factors which should be well regulated to guarantee higher removal rate. The mixture of manganite and hausmannite showed improved activity for removal of total phenols, TOC and $COD_{Cr}$ as compared with $MnO_2$ (AR) but similar to cryptomelane and K-birnessite. Most of organic contaminants especially phenol which occupied absolute predominance in initial wastewater were removed to enhance the biodegradability for further biological treatment. This investigation will provide fundamental method for developing a pretreatment method of industrial phenolic wastewater with flexibility, simplicity and high activity.

## 1. Introduction

Phenolic wastewater is a typical kind of industrial effluents with high toxicity and poor biodegradability. Huge quantities of phenol-polluted waters are formed from many chemical operations including coking, coal gasification, oil refineries, plastics, pesticides, steel and phenolic resin production [1,2]. Phenolic compounds and their derivatives are considered preferred controlled pollutants in water since they can pose a severe health hazard as mutagens and carcinogens and cause serious damage to aquatic animals and microorganisms even at low concentrations [3–6]. Various species of phenolic pollutants at high concentrations from hundreds to thousands mg/L are identified in the industrial wastewaters especially from heavy chemical or petrochemical industries. Once released into the environment, they may have adverse effects on ecological health and represent a serious environmental problem [7]. Therefore, removal of phenolic compounds from wastewater becomes urgent in the field of practical industrial wastewater treatment.

At present, the common remediation methods to deal with phenolic compounds contain physical, chemical and biological processes. Removals of phenols at high concentrations are accomplished through physical or chemical processes, namely adsorption by activated carbon [8] or clays [9], solvent extraction [10], liquid membrane [11], coagulation [12], bubble [13]/wet air oxidation [14], ozonation [15], photocatalytic oxidation [16] and decomposition by Fenton reagents [17]. Although effective, some of these techniques present a number of disadvantages for example high cost and non-regenerant property of activated carbon material [18] or disposal of toxic residues in liquid–liquid extraction method [19].

Biodegradable approaches such as traditional activated sludge process, novel bioreactors [1,20] and bioaugmentation strategies [21], are the most widely used and economical alternative in phenolic wastewater treatment. Despite that biological treatment processes cannot treat phenolic wastewater at high concentrations successfully. It is ascribed to the inhibitory growth of microorganisms at a high concentration of phenolic wastewater, thus resulting in low biodegradability [22]. Biological techniques are feasible at intermediate concentrations ranging from 5 to 500 mg/L [23], preferably not more than 300 mg/L [24]. Therefore, it is necessary to pretreat phenolic wastewater to make biochemical treatment easier [25]. In practice solvent extraction, coagulation, agitation and even dilution are the most important techniques used in high phenol-concentrated wastewater pretreatment [25–27]. The effect of pretreatment process directly determines the stability and validity of following biodegradation.

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**Table 1**
Some water quality indices of phenolic wastewater from coal gasification.

| Water quality index | Original wastewater |
|---|---|
| pH | 7.25 |
| Total phenols (mg/L) | 969 |
| $COD_{Cr}$ (mg/L) | 5825 |
| TOC (mg/L) | 2295 |
| $BOD_5$ (mg/L) | 100 |
| $COD_{Cr}$/TOC | 2.54 |
| $BOD_5/COD_{Cr}$ | 0.017 |

Within the group of pretreatment processes, oxidation by manganese oxide minerals to remove phenols is put forward and gives good results in this study. Manganese oxides and hydrates are ubiquitous in soils and sediments and are some of the most redox reactive mineral constituents in environments [28]. They are efficient in accepting electrons from phenolic compounds, which have been proven to be utilized as oxidants or catalysts for removal of phenols and their derivatives with low concentration by oxidation [29–32]. However, little is known about the efficiency of manganese oxides on real wastewater. In this work we used the mixed minerals of manganite and hausmannite to treat phenolic wastewater from gasworks. The main goal of our work is to provide a more cost-effective and efficient pretreatment method to solve the puzzle of high phenol-concentrated wastewater treatment.

## 2. 2 Materials and methods

### 2.1. Materials

All chemicals, analytical grade, were supplied by Sinopharm Chemical Reagent Beijing Co., Ltd., China unless otherwise stated. Deionized water was used as the solvent and scour. Manganese sulfate for manganese oxide preparation was of industrial grade and provided by Guangxi Dameng Industry Co., Ltd., China. Dichloromethane of high performance liquid chromatography grade was purchased from DikmaPure Co., Ltd., USA.

Active manganese oxides mainly used in this work were synthesized with $MnSO_4$ and NaOH. In 10 L of reaction system, 0.2 M $MnSO_4$ solution with 0.4 M NaOH solution were mixed at room temperature. Air was bubbled through the mixture solution at flow rates of 120 and 100 L/min, respectively, for 3 h by two air compressors. The precipitate was separated from suspension, air-dried and then grinded to certain gain sizes. Powder X-ray diffraction results demonstrated that the presence of poorly crystalline minerals with mixed phases of manganite (β-MnOOH, mainly) and hausmannite ($Mn_3O_4$). The surface area was 71.8 $m^2$/g by B.E.T analysis of $N_2$ adsorption at 77 K. Other manganese oxides for comparison contained cryptomelane, K-birnessite synthesized in the optimal conditions as reported in the literature [33] and $MnO_2$ with analytical purity.

### 2.2. Phenol-polluted wastewater

A typical phenolic wastewater from the process of coal gasification was collected from Harbin gasification plant, China. The main characteristics are intensive violet-dark brown color, strong specific offensive smell, a large number of bubbles and high degree of organic pollution. Some relevant indices of water quality are shown in Table 1. $COD_{Cr}$/TOC ratio and $BOD_5/COD_{Cr}$ ratio have been chosen as biodegradability indicators. Both of them explain this aqueous water hardly biodegradable [34,35]. The chemical constituents of this coal-gasification wastewater are very complicated as shown in Fig. 1 and Table 2. Phenol accounts for the largest concentration among these organic compounds. Other phenolic pollutants contain phenol, 2,4-bis(1,1-dimethylethyl)- (No. 14) and 1,2-benzenediol (No. 21). Benzene series compounds, pyridinones, ketones, aldehydes, long-chain alkanes and organic acids present also contribute to $COD_{Cr}$ and TOC determinations, some of which show characteristics of POPs and/or EDCs.

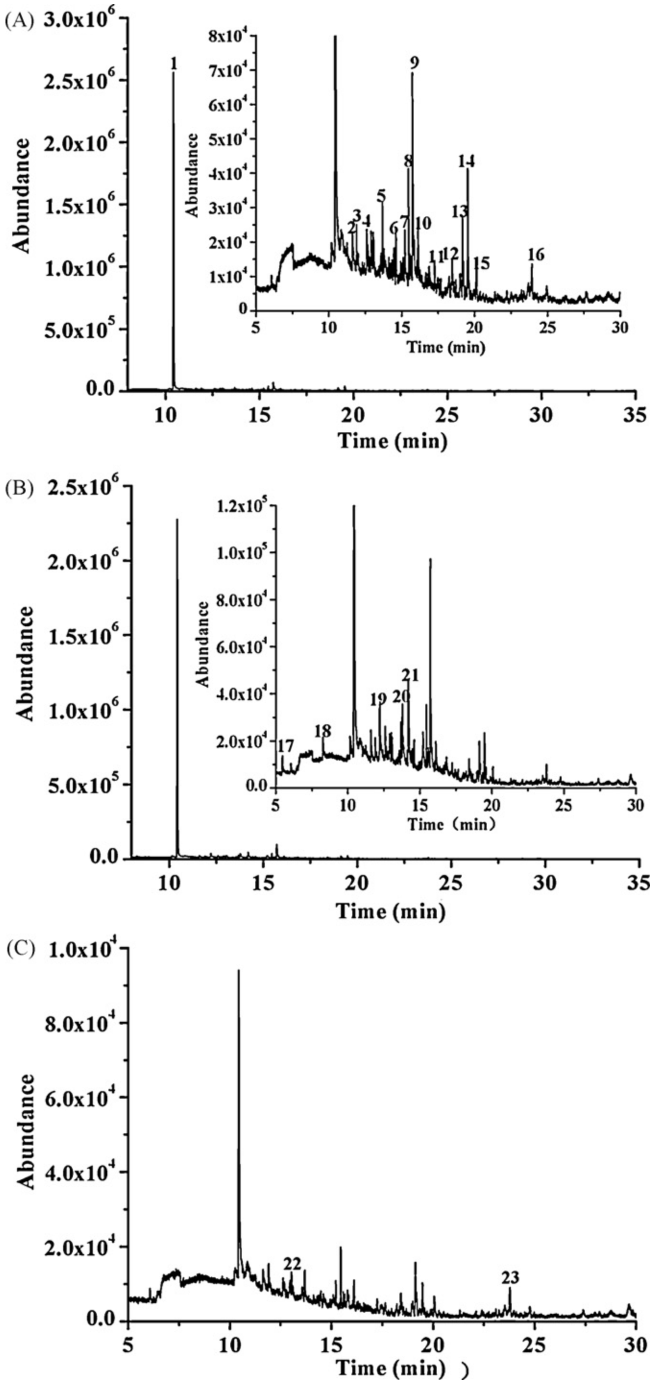

**Fig. 1.** The total ion chromatograms of original phenolic wastewater from coal gasification plant (A) pH 7, (B) pH 2, (C) pH 12.

### 2.3. Methods

Degradation of phenols in coal-gasification wastewater in the presence of a mixture of manganite and hausmannite was investigated. A weighed amount of manganese oxide powder with restricted grain size was first introduced into 50 mL phenolic

**Table 2**
Compositions of organic compounds in phenolic wastewater corresponding to Fig. 1.

| No. | Retention time (min) | $m/z$ | Integral area | Compound[a] |
|---|---|---|---|---|
| 1 | 10.437 | 94, 66 | 4,380,0191 | Phenol |
| 2 | 11.610 | 67, 110 | 350,233 | 2-Cyclopenten-1-one, 2,3-dimethyl- |
| 3 | 11.903 | 57, 71, 85 | 193,332 | 3-Ethyl-3-methylheptane |
| 4 | 12.602 | 67, 123 | 165,385 | 2(1H)-pyridinone, 1-ethyl- |
| 5 | 13.684 | 55, 75, 105 | 337,905 | Silane, cyclohexyldimethoxymethyl- |
| 6 | 14.604 | 71, 105, 133 | 334,819 | Benzaldehyde, 2,4-dimethyl- |
| 7 | 15.223 | 57, 71, 85 | 290,724 | 4,4-Dipropylheptane |
| 8 | 15.462 | 57, 71, 85 | 479,943 | Dodecane, 4-methyl |
| 9 | 15.734 | 202, 328 | 1,289,462 | Benzyl-chloro-mercury |
| 10 | 16.114 | 57, 71, 85 | 196,651 | Nonadecane |
| 11 | 17.265 | 57, 71,85 | 177,778 | Tetradecane |
| 12 | 18.460 | 57, 71, 85 | 170, 018 | Hexadecane,2,6,10,14-tetramethyl- |
| 13 | 19.173 | 57, 71, 85 | 595,846 | Tridecane,2-methyl- |
| 14 | 19.535 | 57, 191, 206 | 890,024 | Phenol, 2,4-bis(1,1-dimethylethyl)- |
| 15 | 20.129 | 57, 71, 85 | 206,161 | Heneicosane |
| 16 | 23.931 | 57, 71, 85 | 419,259 | Heptadecane, 2,6,10,15-tetramethyl- |
| 17 | 5.455 | 55, 60, 73 | 134,625 | Butanoic acid |
| 18 | 8.275 | 60, 73 | 156,274 | Pentanoic acid |
| 19 | 12.215 | 60, 73, 87 | 343,299 | Heptanoic acid |
| 20 | 13.790 | 73, 84, 101 | 947,798 | Octanoic Acid |
| 21 | 14.199 | 64, 110 | 938,946 | 1,2-Benzenediol |
| 22 | 13.033 | 119, 134 | 134,876 | Benzene, 1,2,3,4-tetramethyl- |
| 23 | 23.786 | 57, 71, 85 | 221,998 | Heptadecane |

[a] Possible compounds according to NIST standard spectra.

wastewater in a 100 mL Erlenmeyer flask. A known volume of sulfuric acid was also added into the flask. Two concentrations (1 and 5 M) of sulfuric acid were used to keep the errors of volume change in a range of 0–2.6%. After mixing, samples were incubated in a shaking water bath at a rate of 150 rpm and a temperature for a predetermined period of time. At the end of the experiment, the suspension was filtered through 30–50 μm qualitative filter paper. The pH value of the supernatant was measured, and an aliquot was sampled for total phenols determination. In the control tests, five series of experiments were carried out to determine the effects of acid dosage, reaction time, temperature, mineral concentration and grain size on the removal rate of phenolic compounds from the solution by the mixture of manganite and hausmannite. In general, a series of indexes of 40 g/L 58–74 μm manganese oxide powder, 0.1 mol/L sulfuric acid, room temperature (25 °C) and reaction for 2 h were assessed, respectively. One parameter was discussed while fixing others.

The capabilities of manganese oxide mineral compositions containing the mixture of manganite and hausmannite, cryptomelane, K-birnessite and $MnO_2$ (AR) were studied by fixing up above reaction conditions. The concentration of total phenols, $COD_{Cr}$, TOC, pH, dissolved Mn concentration and organic constituents of the filtrates were analyzed. At the same time, dissolved Mn in treated wastewaters were precipitated by adjusting the solutions' pH value to 9–10, and then after centrifugal sedimentation, $COD_{Cr}$ and TOC in the supernatant were determined again.

The concentration of total phenols was measured by bromide method commonly used in factories for water quality determination (EPA 320.1). An excessive bromide agent would react with the existing phenols and then iodometric method (EPA 345.1) was used to measure excessive bromide agent to help calculate the total phenols [25]. The presence of manganous ion was considered as a possible interference on phenol index. A known concentration phenol solution containing $Mn^{2+}$ was titrated by bromide method, and the result errors were −3.8%, −6.1% and −3.3% respectively in three repeated experiments. So this interference of manganous ion was neglected in phenol detection. The pH value in the wastewater was tested with a Sartorius PB-10 basic pH meter. $COD_{Cr}$ was measured by fast digestion spectrophotometric method (HJ/T 399-2007) using Model HATO CTL-12 COD rapid determination instrument. TOC and $BOD_5$ were examined by Shimadzu TOC-5000a instrument and WTW OxiTop IS 12-6 BOD instrument respectively. The Mn concentration was determined by potassium periodate spectrophotometric method (GB 11906-89). UV absorption scan was carried out by UV–visible spectrophotometer (Aglient 8453 UV spectrophotometer) after diluting 100 times. GC/MS research was used for organic constituents of wastewater analysis by Aglient 7890/5975C GC/MSD chemstation with a 30 m × 0.32 mm × 0.25 μm HP-5MS capillary column. A liquid–liquid extraction pretreatment using $CH_2Cl_2$ was conducted at acidic, neutral and alkaline conditions respectively [36]. The partial flow ratio was 1:10, and a temperature for the gasification compartment was maintained at 280 °C. The temperature control program registered initial 40 °C retaining for 9 min, then increasing to 150 °C with an increment of 10 °C/min; after maintaining 2 min, increasing to 280 °C with an increment of 5 °C/min; after retaining 3 min, continuing to increase to 300 °C with an increment of 10 °C/min, and maintaining for 10 min.

## 3. Results

### 3.1. Effect of acid dosage

It has been established that the pH has a considerable influence on the performance of phenol removal by manganese oxides [37]. In our work, the index of acid amount was used instead of initial pH value because the initial reaction rate (Section 3.2) was too rapid to measure the initial pH value. The sulfuric acid dosage vs the rate of phenolic removal is shown in Fig. 2. It was obvious that the efficiency of phenol removal increased evidently in more acidic aqueous suspensions. After 2 h' reaction, the concentration of total phenols was reduced to 82 mg/L and the removal efficiency was 92% when 0.16 mol/L sulfuric acid was added in (the initial pH value was roughly detected at about 2.3). It was much better than 729 mg/L at neutral conditions without the addition of acid. However, when sulfuric acid dosage exceeded 0.1 mol/L, the concentration of total phenols did not reduce obviously and remained at about 80–100 mg/L. Consequently, to cut down the treatment cost, it was proposed that a sulfuric acid dosage of 0.075–0.1 mol/L would be suitable and the effluent pH was at 4.7 at these conditions. There were close ties between effluent pH and initial sulfuric acid dosage. Increased pH explained an amount of $Mn^{2+}$ dissolved with

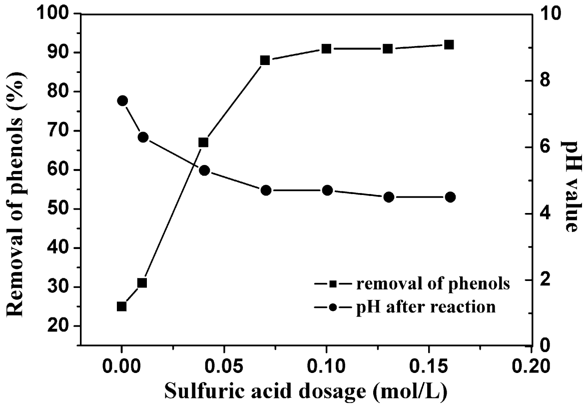

**Fig. 2.** The effect of sulfuric acid dosage on removal of phenols by the mixture of manganite and hausmannite and pH value of solution after reaction.

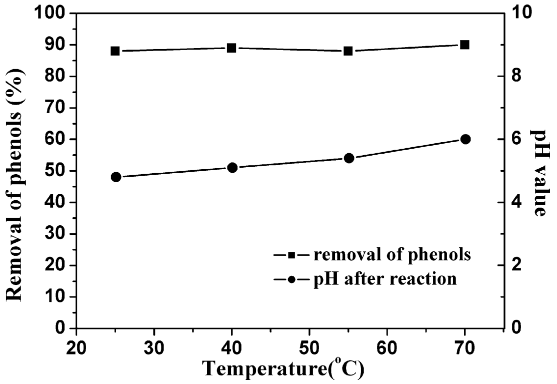

**Fig. 4.** The effect of temperature on removal of phenols by the mixture of manganite and hausmannite and pH value of solution after reaction.

phenols present in the suspensions. However, when acid dosage increased continuously even to 0.16 mol/L, effluent pH did not steadily decline but stabilized in the range of 4–5 at manganese oxide dosage of 40 g/L. This phenomenon was probably ascribed to surface acid–base characteristics and high adsorption capability of manganese oxides [38,39].

### 3.2. *Effect of reaction time*

The initial rate of phenol oxidation significantly depends on pH, soluble manganese, oxide: phenol ratio and redox potentials of manganese oxides [30]. Fig. 3 represents the relationship between the percentage of phenol removal and reaction time. The residual phenols decreased remarkably to 174 mg/L in just 10 min corresponding to 82% removal rate. After half of an hour, the rate of phenol removals slowed down quite markedly. All the phenols would be almost removed from water body and pH 5 till reacting for 6 h. The change trend of solution pH was in conformity with that of phenol removal rate. It illustrated that proton was involved into the process of oxidation of phenols by manganese oxides. However, it was observed although 84% phenols had been removed, pH was still at 2.8 after 20 min reaction time. Except by phenol oxidation, at pH < 3.5 manganese oxides would dissolve by oxidation of water as well [30].

### 3.3. *Effect of temperature*

Fig. 4 displays the phenol removal as a function of liquid temperature at 25, 40, 55 and 70 °C. It was found in our experiments that the effect of temperature on removal performance was limited. The concentration of total phenols in the wastewater was reduced from 969 to 99 mg/L at 70 °C which was close to 114 mg/L at 25 °C after 2 h reaction. By contrast the variation scope of pH at higher temperature during the same time reaction was larger than that at low temperature. Temperature might influence mineral surface chemistry properties such as intrinsic acidity constant and surface charge [40,41]. The few investigations into metal oxides/hydroxides indicate that $pH_{PZC}$ generally decreases with higher temperature [40]. Small temperature changes could also have a strong influence on the stability of surface complex [41]. However, so far there are no available data on the effect of temperature on the surface charge and $pH_{PZC}$ of manganese oxides. The role of temperature on phenol removal behavior by manganese oxide is uncertain, which is based on surface complexion reactions. More comprehensive study would be done on the variations in surface charge as a function of temperature. Besides, in consideration of industrial process and easily volatile problems of phenols, it is appropriate to set the reaction temperature at room temperature or actual temperature of influents.

### 3.4. *Effect of grain size*

A series of experiments were performed with five grades of manganese oxide particle size. In Fig. 5, it revealed that small particles resulted in a high removal efficiency of phenols. When the grain size was at >198 μm, 74–107 μm and <58 μm, 775 mg/L, 814 mg/L and 873 mg/L total phenols were removed, respectively. The solution pH increased from 3.2 to 4.6 with decreasing particle size. As is

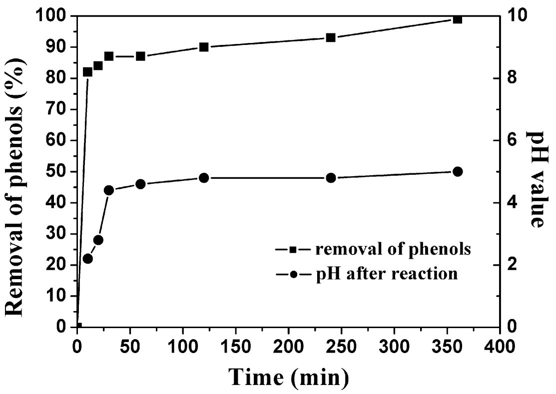

**Fig. 3.** The effect of reaction time on removal of phenols by the mixture of magnetite and hausmannite and pH value of solution after reaction.

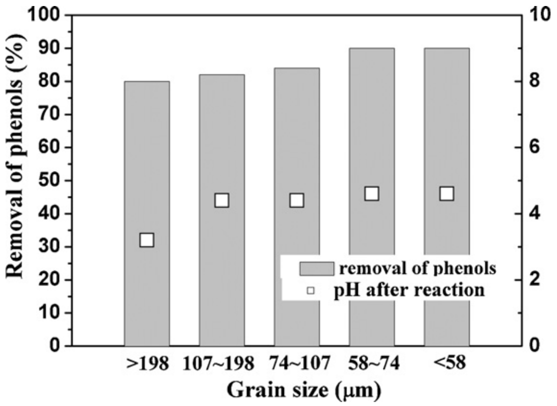

**Fig. 5.** The effect of grain size on removal of phenols by the mixture of manganite and hausmannite and pH value of solution after reaction.

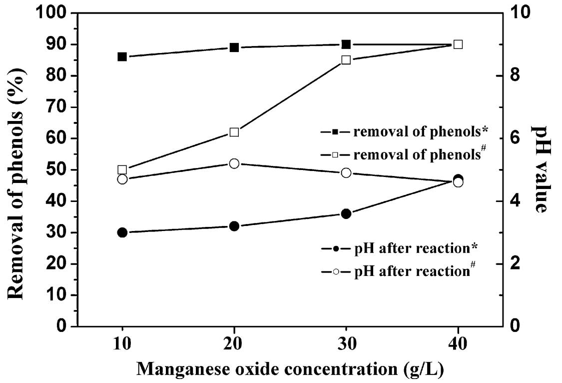

**Fig. 6.** The effect of oxide particle concentration on removal of phenols by the mixture of manganite and hausmannite and pH value of solution after reaction ((*) adding the same amount of 0.1 mol/L sulfuric acid at different initial pH; (#) adjusting the initial pH 3–3.5 with injections of different quantity of acid.).

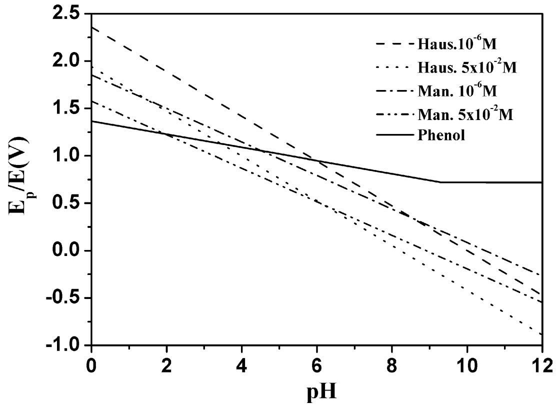

**Fig. 7.** Electrochemical peak potential (vs std. $H_2$ electrode) of phenol and reduction potential of manganite (Man.) and hausmannite (Haus.) at 25 °C at $10^{-6}$ M and $5 \times 10^{-2}$ M $Mn^{2+}$ activity, respectively, as a function of pH.

known, the specific surface area is inversely related with the manganese oxide particle size [42]. The surface adsorption process is necessary for further chemical reaction of phenols on manganese oxide particle interface to occur [43]. Larger surface area provides more adsorption sites which assist phenols and proton be quickly adsorbed onto the surface of manganese oxides to form complexes, and then accelerate the electron transfer rate. However, fine particles cause trouble in engineering for instance requiring long time for precipitation or more difficult to be separated from solution. So the optimal grain sizes would be controlled in the range of 75–150 μm.

### *3.5. Effect of manganese oxide concentration*

The effect of manganese oxide dosage on total phenol removal was analyzed in two ways: (1) adding the same amount of sulfuric acid (0.1 mol/L) at different initial pH or (2) adjusting the initial pH 3–3.5 with injections of different quantity of acid. High affinity for protons of manganese oxide surface indicates that the dosage of acid should be regulated according to the oxide concentration, so as to keep the initial pH value as consistent as possible. As shown in Fig. 6, the removal of total phenols is related positively to the amount of manganese oxide particle as a result of closely initial pH and changing trend in way (2). On the contrary, when sufficient protons are supplied in way (1), a high removal efficiency of 86% achieves at particle concentration of 10 g/L. There is no obvious enhancement with further increase of manganese oxide. These results show that manganese oxide oxidation process can effectively degrade most of phenols in gasification plant wastewater, but it is important to coordinate with the dosages of acid in order to guarantee good removal efficiency.

## 4. Discussions

Based on the above experimental results, the most important factors which affect the removal efficiency of total phenols are solution pH and manganese oxide concentration. The reactions of oxidation degradation of phenols attribute to the interfacial behavior on the manganese oxide particle [44]. Solution pH determines the protonation reactions and formation of surface complexes between phenols and manganese oxide [37]. Moreover, pH is of great importance in changing the thermodynamic redox potentials of manganese oxides and phenols [30]. For manganite and hausmannite used in our experiments, the redox potentials of them at two $Mn^{2+}$ activities as a function of pH are compared in Fig. 7 [45,46]. It is easy for manganite and hausmannite to degrade phenol when pH < 4.5 and pH < 6 respectively at low $Mn^{2+}$ activity of $10^{-6}$ M and this reaction is stronger at a more acidic environment. However, low pH may also facilitate the release of reduction product of Mn(II) or other oxidized organic substrate from manganese oxide surface into solution [37], which results in abundance of $Mn^{2+}$ activity. Released Mn(II) competes for the manganese oxide surface sorption sites [43] as well as reduces the reduction potentials of manganese oxides. With the diffusion of $Mn^{2+}$ products away from the surface, manganite and hausmannite can only oxidize phenol at pH < 2 and pH < 3.5 respectively when $Mn^{2+}$ activity increases to $5 \times 10^{-2}$ M. Suspension pH rises quickly with released Mn(II) which slows and finally prevents the reaction.

It is also suggested that there is a delicate relationship among phenol removal efficiency, manganese oxide and acid dosage. On one hand, abundant manganese oxide particles are needed to provide enough sorption sites for phenols, which results in high initial rates of phenol oxidation; on the other hand, too many protonated surface sites will increase solution pH, which is unfavorable to the reaction.

**Table 3**
Indexes of original and treated phenolic wastewater by four kinds of manganese oxides.

| Sample | Index | | | | | | |
|---|---|---|---|---|---|---|---|
| | Phenols (mg/L) | pH | Dissolved Mn (mg/L) | TOC (mg/L) | | COD (mg/L) | |
| | | | | Before removal of Mn | After removal of Mn | Before removal of Mn | After removal of Mn |
| Original wastewater | 969 | 7.25 | – | 2295 | – | 5825 | – |
| Treated by manganite and hausmmanite | 99 | 4.08 | 2298 | 1547 | 809 | 6592 | 3020 |
| Treated by cryptomelane | 45 | 3.12 | 2570 | 1487 | 972 | 5653 | 2859 |
| Treated by K-birnessite | 99 | 4.25 | 2839 | 1528 | 969 | 6146 | 2870 |
| Treated by $MnO_2$ (AR) | 846 | 1.39 | 151 | 2405 | 2200 | 6313 | 3996 |

(–): without detection.

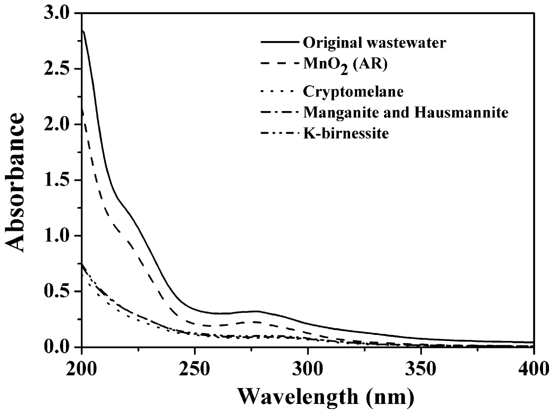

**Fig. 8.** The UV scan results of original and treated phenolic wastewaters by the mixture of manganite and hausmannite, cryptomelane, K-birnessite and $MnO_2$ (AR).

In addition, the compositions and structures of manganese oxides have effects on removal efficiency. The influence of four kinds of manganese oxides on the degradation efficiency of total phenols, $COD_{Cr}$ and TOC was studied in Table 3 with the mixture of manganite and hausmannite, cryptomelane, K-birnessite and $MnO_2$ (AR) respectively. Except $MnO_2$ (AR), almost 90% of total phenols and 40% of TOC could be degraded by other three kinds of manganese oxides after suspension reaction. The final pH also remains low at 1.39 in $MnO_2$ (AR)'s suspension because of its slow reaction rate. All of the mixture of manganite and hausmannite, cryptomelane and K-birnessite are similarly prepared with $MnSO_4$ and alkali by air oxidation. Well developed nano-scale crystals and variable valence of Mn content ($Mn^{3+}/Mn^{4+}$) give them good performance. Although pure $MnO_2$ in the form of pyrolusite has the similar crystal structure as manganite [47], it is considered as "inactive" for nonreactive nature of single Mn(IV). It is believed much more difficult to gain an electron by $Mn^{4+}$ which requires a change in spin state than by $Mn^{3+}$ [30].

As in Table 3, reduction product of Mn(II) from oxidation of phenols by manganese oxides makes contributions to $COD_{Cr}$ to a certain degree. After removal of Mn ions in solutions by alkali precipitation method, $COD_{Cr}$ decreased rapidly to half its original concentration. In the meantime, about 600–700 mg/L TOC diminished again. $Mn(OH)_2$ colloid formed from precipitation between the soluble $Mn^{2+}$ and $OH^-$ has amorphous particles and high adsorption capacity. Part of organic pollutants were absorbed on its surface and removed from wastewater by filtration process. If air bubbles are introduced into precipitation process of dissolved Mn (II), it can be collected in the form of manganese oxide and recycling used.

The constitutions of wastewater generate change and the concentration of contaminants decrease noticeably after treatment by manganese oxide method. In UV scan shown in Fig. 8, it is found that the contaminants which have strong absorption peaks between 200 and 350 nm are well removed by manganese oxide treatment. It is clear that the most of conjugated systems such as aromatic or heteroaromatic molecules are eliminated by this process [48]. The residual absorbency shows some organic contaminants cannot be removed. The intensities of these peaks of the effluents treated by the mixture of manganite and hausmannite, cryptomelane and K-birnessite are much lower than that by $MnO_2$ (AR). At the same time in GC-MS analysis, phenol which is extremely predominant in quantity in initial wastewater and 1,2-benzenediol are not detected in the effluents (Fig. 9A and C). Simultaneously, small peak of intermediate product of p-benzoquinone in phenol oxidation reaction is observed [37] (Fig. 9B). Although other organic pollutants still remain, the intensities of abundance peaks decrease markedly and the average removal rate achieve about 40–50%. Since the concentrations of organic compounds have been considerably reduced, the remaining compounds are much easier to be utilized by microorganism for further biological treatment, which results in increased $BOD_5/COD_{Cr}$ of 0.36.

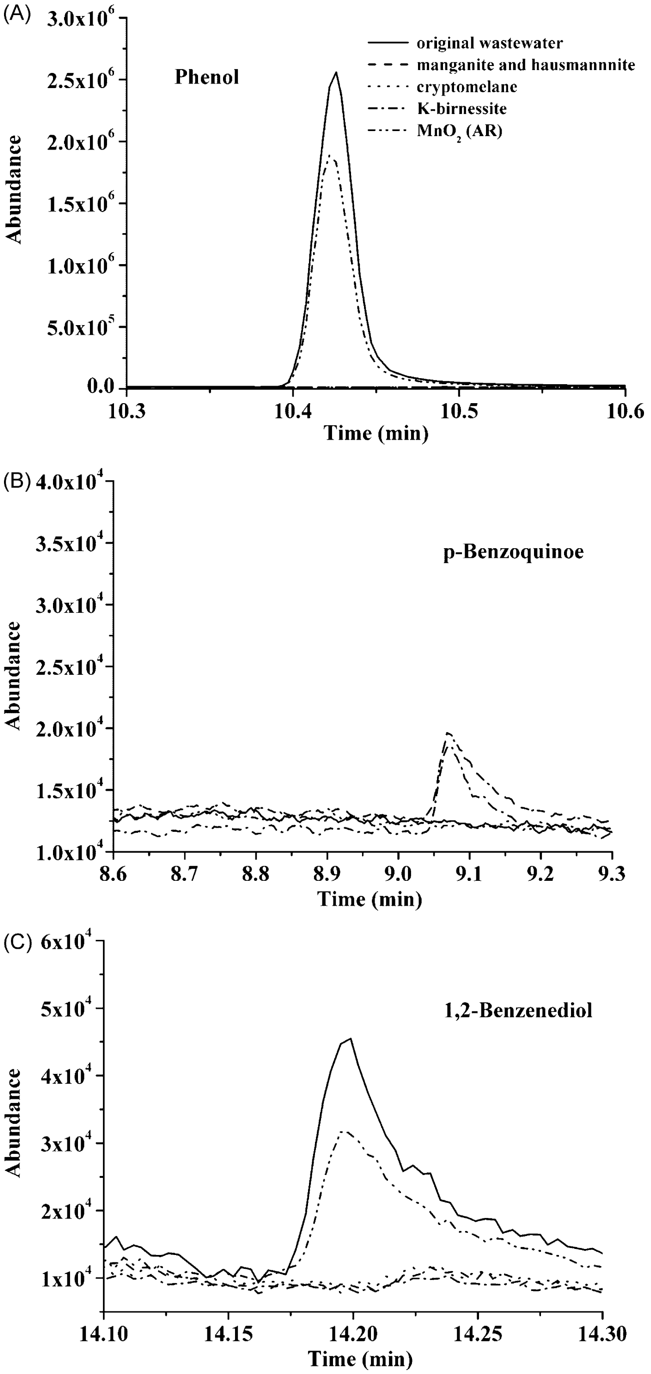

**Fig. 9.** The comparisons of (A) phenol, (B) p-benzoquinone, (C) 1,2-benzenediol in original and treated phenolic wastewaters by the mixture of manganite and hausmannite, cryptomelane, K-birnessite and $MnO_2$ (AR).

## 5. Conclusions

Manganese oxides with compositions of manganite and hausmannite were investigated for pretreatment of high concentration phenolic wastewater from coal gasification. According to the experimental results, the optimal operational parameters was confirmed as follows: after 40 g/L 58–74 μm active manganese oxide particles reacted with 969 mg/L phenolic wastewater and 0.1 mol/L $H_2SO_4$ in 25 °C water bath with 150 rpm oscillatory rate for 2 h, the removal efficiency of total phenols reached 90%. Solution pH and manganese oxide dosage are considered as the primary factors. The increase of acidity and manganese oxide concentration can improve the total phenol removal efficiency evidently. It has been proved to provide much better performance in removal of total phenols, TOC and $COD_{Cr}$ than $MnO_2$ (AR), but similar activity with cryptomelane and K-birnessite. After treatment, phenol which constitutes a extremely high proportion in the raw wastewater and 1,2-benzenediol cannot be detected out. Manganese oxide approach eliminates most of organic compounds and increases the biodegradability of the effluent. This method also offers several important advantages that no special equipments, costly chemicals and complex operations are required. Therefore, it will be designed as a feasible pretreatment process for industrial wastewater.

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