



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 $\text{pH} < 4$ 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.

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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. 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 MnSO₄ and NaOH. In 10 L of reaction system, 0.2 M MnSO₄ 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 grain sizes. Powder X-ray diffraction results demonstrated that the presence of poorly crystalline minerals with mixed phases of manganite (β-MnOOH, mainly) and hausmannite (Mn₃O₄). The surface area was 71.8 m²/g by B.E.T analysis of N₂ 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 MnO₂ 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 BOD₅/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

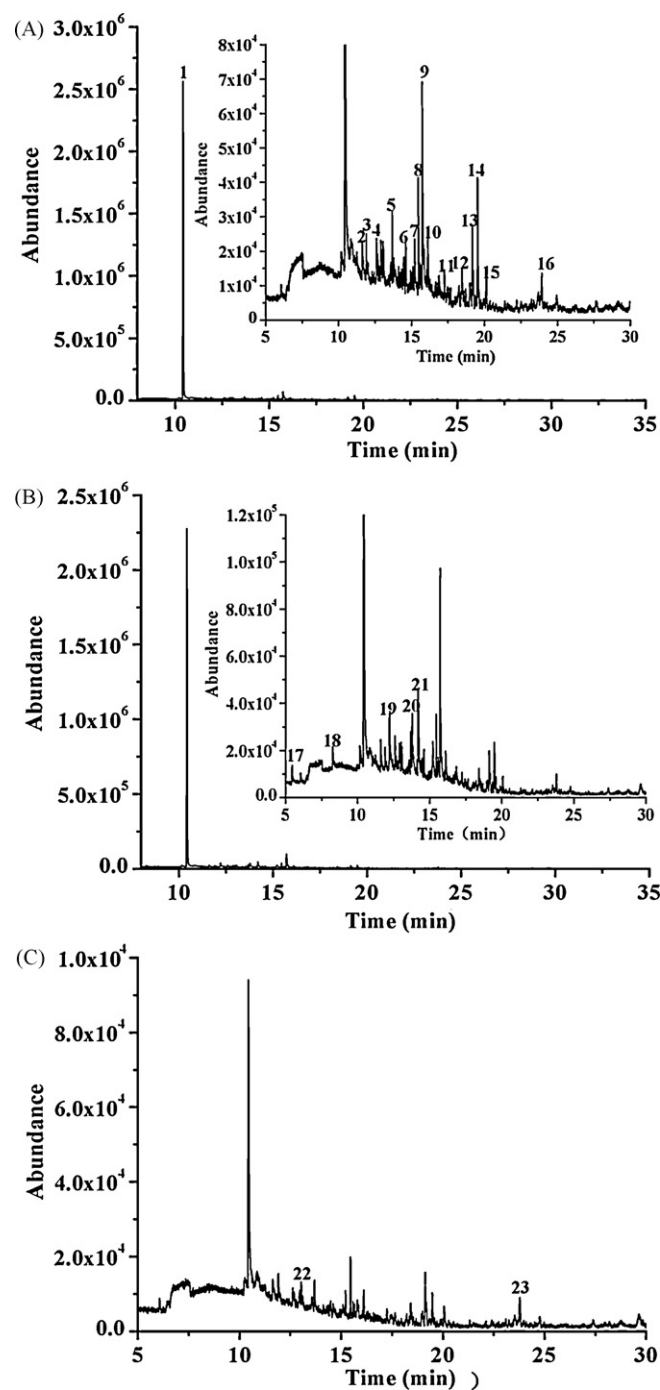


Fig. 1. The total ion chromatograms of original phenolic wastewater from coal gasification plant (A) pH 7, (B) pH 2, (C) pH 12.

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.

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

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