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The integration of ozonation catalyzed with MgO nanocrystals and the biodegradation for the removal of phenol from saline wastewater

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ABSTRACT

Efficient treatment of saline wastewaters, particularly those containing inhibitory and toxic compounds, has been a challenge in recent years. This study proposed and investigated an efficient option for treating such streams. An MgO nanocrystal mesoporous powder was prepared from natural magnesite, and its potential to serve as a catalyst for degradation and chemical oxygen demand (COD) removal of phenol from saline wastewater was evaluated. The influence of several parameters including pH, dose of MgO nanocrystals, and NaCl concentration was investigated on the catalytic ozonation process (COP) of phenol in saline wastewater. The concentration of NaCl had no adverse influences on the phenol degradation. The results indicated that 96% of the phenol and 70% of the COD were removed in the COP (initial phenol concentration was 1100 mg/L and initial COD was 2500 mg/L) under optimum experimental conditions of pH 7 and a 4 g/L catalyst dose after an 80 min reaction time. A synergistic influence of about 39% was observed for phenol degradation in the COP. The effluent from the COP obtained from the aforementioned conditions was efficiently post-treated in a batch biological reactor, such that after 10 h of aeration, the COD was reduced to around 20 mg/L. In contrast, it took 50 h for reduction of COD to below 100 mg/L when adding raw phenol wastewater into the bioreactor. Therefore, the prepared powder was found to be an efficient and promising catalyst for ozonation, and coupling the developed COP with a biological process might be an attractive treatment option for saline wastewaters containing high concentrations of toxic compounds.

1. Introduction

As a result of the increasing number of industries throughout the world, the generation of industrial effluents having different contaminants is thereby increasing, which has become a main concern from the viewpoints of sustainable development and environmental protection. One of the most ubiquitous industrial wastewater contaminants is phenol [1], which is present in high levels in the effluent from numerous industries including chemical, petrochemical, pharmaceutical, refineries, oil field activities, coal processing, olive oil production, etc. [1–3]. Phenol is toxic to humans and causes headaches, fainting, vertigo and mental disturbances. Additionally, it can cause several severe ecological and environmental problems in receiving environments [4]. Wastewater generated in many of the above-mentioned industries commonly contains high concentrations of phenol and dissolved solids in particular chloride salts [5,6], which render its handling very difficult. Indeed, salts in high concentrations can inhibit the performance of biological processes [7,8].

Several physical, chemical and biological methods or combinations thereof are available for removing the organic compounds, such as phenolic compounds, from the wastewaters. Biological processes are commonly adopted as the first option for treating wastewater containing biodegradable contaminants due to their efficacy, cost-effectiveness, operation simplicity and environmental compatibility advantages; however, they are not appropriate techniques for removing biorecacitrant compounds [2]. The phenolic compounds are known to be refractory and resistant to biodegradation and are thus biorecalcitrant due to their aromatic structure [9–11]. Therefore, they can inhibit the biodegradation reaction at concentrations above 50 mg/L [12].

Physical methods are only phase-changing unit operations that simply transfer the contaminants into another phase like that attained in adsorption, and they still elicit environmental concerns. Therefore, using chemical processes in particular as a pretreatment option for partial oxidation of resistant organics and converting those products into simple and biodegradable intermediates are highly necessary [13,14] and have recently been the subject of significant attention.

Due to their high capability in destroying organic compounds, the advanced oxidation processes (AOPs) are among the chemical processes most attractive for treating wastewater containing

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inhibitory and toxic contaminants [15]. The main feature of an AOP is the generation of very reactive radicals [15], mainly •OH, at ambient temperature and pressure, which non-selectively degrades the organic molecules they come into contact with [16,17]. COPs are the recently emerged and attractive types of AOPs in which a material such as a homogenous or heterogeneous catalyst is accompanied with the ozone to generate highly powerful oxidative radicals [18,19]. Heterogeneous COP has recently attained much attention as the most attractive and preferred option due to its ease of catalyst retrieval [20], higher degradation efficiency [21], simplicity of operation, non-residual catalyst in the treated wastewater [22,23] and lower cost [24].

Although several works have been published so far on using COP for the degradation of different contaminants, investigation of this process in terms of removal of contaminants from saline media is very rare. Furthermore, although the catalytic capabilities of several materials including activated carbon, metal ions and oxides, natural zeolites and ores, and impregnated materials have been studied in COPs [20], finding an active and stable material for use as a catalyst to achieve an optimized COP for oxidation of organic contaminants in liquid streams has remained a challenge [25]. In this regard, the research on COPs in recent years has been focused on the synthesis and study of nano-sized metal oxides as catalysts [e.g., 24,26–29], and it seems that efficient and suitable alternatives are continuing to be found.

We have recently shown that MgO nanocrystals are efficient catalysts in the catalytic ozonation of dye [22] and formaldehyde [30]. In effect, MgO contains surface basic sites [31], and it has a destructive adsorbance [32], high surface reactivity, high adsorption capacity, high specific surface area [33], and it is hard and almost non-soluble in water. Moreover, if leached into the liquid under treatment, magnesium is not toxic and would not cause water pollution. These properties present MgO as a very suitable and deserving candidate for use in the catalytic ozonation context, particularly in saline media where the radical scavenging species interfere with the oxidation reaction and compete with the target compounds in utilizing the oxidative radicals [34–36]. Although MgO has been previously used as a catalyst in the catalytic ozonation of phenol [37] and dyes [22] giving a high catalytic activity, no report could be found either on the preparation of nanocrystal MgO from natural magnesite or on catalytic ozonation of the saline wastewaters.

Despite their high degradation efficiencies, the intermediates produced during organic degradation in an AOP are generally smaller and thus more difficult to mineralize, and they are generally more biodegradable than the original molecules [38]. Hence, using AOPs for complete mineralization of the toxic organics requires extensive operating conditions [39]; consequently, cost is generally expensive, and it is not affordable to use AOPs as the stand-alone treatment process for mineralization of organic compounds [40]. Hence, there is a great advantageous potential of coupling an AOP with a biological process to attain a more efficient and cost-effective technology for treating low biodegradable or toxic compounds [20,41,42].

Based on the above introduction, combining COP with the biological process for phenol removal in saline wastewater provides a possibility for overcoming the inhibitory influences of phenol to microorganisms' activity through its partial degradation in COP into simple and low molecular organic acids [42], which would be easily mineralized in a subsequent biological process. Accordingly, the evaluation of the performance of MgO nanocrystal-based COP for phenol degradation in saline wastewater is required to find its optimum operational conditions and capability in treating such difficult-to-treat streams. Also, an investigation to determine the effectiveness of the biological post-treatment process as a post-treatment option in the removal of intermediates generated in the COP stage of phenol oxidation in saline wastewater is still required. The availability of huge mines of very high-quality magnesite in Iran provides a low-cost and natural-based mineral material for preparation of nanocrystal MgO for application in COPs.

The novelty of the present investigation is as follows: (1) the preparation of MgO nanocrystal powder from the natural mineral of magnesite, (2) the comparison of the prepared MgO nanocrystals to the raw magnesite in their use as catalysts for catalytic ozonation of phenol in saline wastewater, and (3) the evaluation of the integrated nano-MgO-based COP/biological process for degradation and COD removal of phenol in saline wastewater. In COP experiments, the influence of several important factors such as solution pH, concentration of NaCl, and catalyst dose on phenol degradation in saline wastewater was tested. The mechanism of phenol degradation was also investigated. For the post-treatment phase, the effluent from catalytic ozonation experiments under the optimum experimental conditions was treated in a batch biological process with suspended biomass.

2. Materials and methods

2.1. Preparation of catalyst

MgO nanocrystal powder was prepared from natural mineral magnesite obtained from West Azerbaijan, Iran. The natural magnesite ore was first crushed into fine particles, washed with distilled water, and then dried. The MgO was made using the calcination method [43]. For preparation of the catalyst, the natural magnesite particles were first grinded and then washed with distilled water (soaked in acid for 2 h) to remove the surface impurities. The water was then poured out, and the powder was allowed to dry at 100 °C in a dryer for 24 h. The dried powder was then calcined in a furnace at 700 °C for 2 h. Finally, the prepared catalyst was manually powdered in a mortar, and this powder was characterized and used in the COP as a catalyst.

2.2. Catalytic ozonation experiments

The catalytic potential of the prepared MgO nanocrystals was assessed by degradation of phenol in saline media using COP, compared with single ozonation and catalytic ozonation with natural magnesite powder. The experiments were carried out in a batch cylindrical glass reactor as detailed elsewhere [19]. The influences of several parameters including solution pH, NaCl concentration, dose of catalyst, and the reaction time were investigated on the phenol degradation using catalytic ozonation with the prepared MgO nanocrystals. The ozonation rate was constant at 0.25 g/h throughout the experiment. The phases of experiments along with the experimental conditions are given in Table 1. For each test, 200 mL of 1100 mg/L phenol solution prepared in distilled water were poured into the reactor. The desired conditions (Table 1) were regulated, and the solution was ozonated for the given time. The contents in the reactor were then centrifuged at 10,000 × *g* for 10 min, and the clear solution was analyzed for residual phenol and chemical oxygen demand (COD) to determine the efficacy of the COP. The phenol degradation degree in COP under optimum conditions was calculated from the total COD of the solution before and after the reaction.

2.3. Biological post-treatment experiments

After evaluating the catalytic ozonation of phenol in saline wastewater, the conditions at which the phenol concentration was decreased to below 100 mg/L were selected as optimum conditions for heterogeneous catalytic ozonation of phenol in saline wastewater using the prepared MgO nanocrystals. This level of