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pH-dependent mechanisms of methylene blue reacting with tunneled manganese oxide pyrolusite

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HIGHLIGHTS

- The mechanism of MB reacting with tunneled pyrolusite is significantly pH dependent.
- Pyrolusite being the oxidant at pH under the pH_{iep} (4.70) while playing as catalyst at pH over pH_{iep}.
- MB degradation followed N-demethylation; stepwise generated AB, AA, AC, and TH.
- TH is the alone compound adsorbed onto the pyrolusite surface.

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ABSTRACT

This study examined the reaction of methylene blue (MB) with tunneled manganese oxide pyrolusite regarding pH and reaction time. MB was cleaved through *N*-demethylation, in which reaction azure B (AB), azure A (AA), azure C (AC), and thionin (TH) were stepwise generated at all tested pH. Pyrolusite predominantly serves as the oxidant in the oxidative degradation of MB at a pH under the pH_{iep} of pyrolusite (4.70) while playing the role of the catalyst at pH higher than pH_{iep}. Among all oxidative products and original MB molecule, TH is the alone compound adsorbed onto the pyrolusite surface at all tested pH. However, the quantity of adsorbed TH increases with pH because of the stronger affinity between the cationic TH molecule and the more negatively charged surface of pyrolusite with pH increasing. Because the lattice oxygen and surface hydroxyl groups form excited oxygen firstly to cause the oxidation of MB, the tunneled pyrolusite with less constrained corner and edge oxygen catalytically promote the oxidation reaction at pH beyond pH_{iep}. The vacancy of the consumed lattice oxygen forms the active sites for the other oxidation and could be replenished by molecular oxygen to complete a catalytic cycle.

1. Introduction

Manganese oxides play a crucial role in soil and aqueous environments because of a narrow Eh-pH stability extent. With various oxidation states of manganese, manganese oxides serve as a potential oxidant and govern the mobility and toxicity of various inorganic and organic compounds [1,2]. Because of their excellent semiconductivity, porosity, and mixed-valent property, manganese oxides have also been used or synthesized recently as a catalyst via the re-oxidation of manganese from a lower valence to a higher valence in many technological applications [3,4]. Stone [5–7] also indicated that when oxygen is present under particular pH conditions, Mn^{2+} ions that are reductively dissolved from a manganese oxide solid are oxidized to regenerate manganese (III/IV) oxides. Under these situations, manganese may act as a catalyst for the oxidation of natural organic compounds using oxygen. Despite possessing the characteristics of both oxidants and catalysts, the exact role of manganese oxides has seldom been clearly distinguished in the process of contaminant removal. Stone [5] demonstrated that pH may exert substantial impact on the oxidation rate of organic compounds using manganese oxides by altering surface protonation–deprotonation and redox potential of manganese oxides. Therefore, the pH-dependent mechanism of organic removal must be systematically investigated and identified.

Generally, manganese oxides can be divided into layered and tunneled (also named as molecular sieve) structures, depending on the octahedral MnO_6^{x-} ions connected via edges and vertices, respectively, schematically showed as Fig. 1. Both layered and tunneled structures are commonly found in terrestrial deposits and ocean nodules [8]. Arising from a high surface charge density, layered manganese oxides, such as birnessite, have been widely used as a typical adsorbent/catalyst/oxidant for removing organic and inorganic pollutants [9] and being most identifiable in soils and sediment [10]. Recently, because of the distinct properties of molecular

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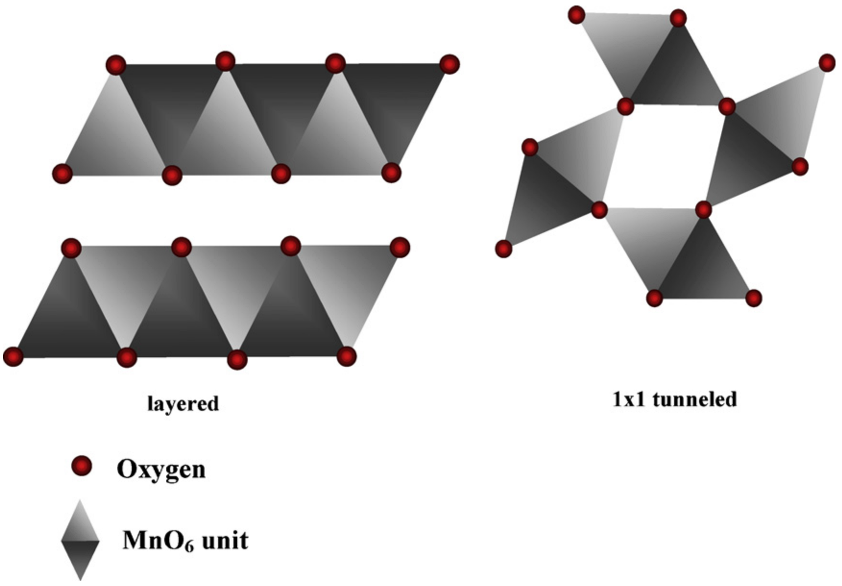

Fig. 1. Scheme showing structure of layered and tunneled manganese oxides.

sieve and reaction selectivity in tunneled manganese oxide, there has been considerable interest in using these materials in wide-ranging sectors including catalysis, sensing, electronics and photoelectronics [11,12]. However, the study of tunneled manganese oxides application onto pollutants control is still lack in literatures.

Methylene blue (MB), a type of thiazine dye, widely used as a photodynamic anti-microbial agent in biological materials, a photosensitizer commonly employed in solar cells, a surface modifier of semiconductor colloids, and a test compound in semiconductor photocatalysis [13]. Aside from a considerable amount of colorful wastewater generated from various industrial processes, the biodegradable resistance of MB suggests that physico-chemical treatments are necessary and abiotic reactions predominately govern the degradation of MB in natural environments [14,15]. Numerous studies have reported the photocatalytic decomposition of MB [16–18] or adsorption of MB onto various materials [19,20]. Few studies have focused on the oxidative degradation of MB using manganese oxide during a spontaneous reaction [21,22]. However, based on research, no previous study has described the pH-dependent degradation mechanisms or the application of tunneled manganese oxides in MB control.

This study used pyrolusite as a representative of tunneled manganese oxide for the model MB removal. The pH-dependent mechanism of MB removal was investigated and substantiated using MB removal by pyrolusite and pyrolusite surface-adsorbed compound desorption experiments. To identify the exact pH-dependent role of pyrolusite from its dual oxidant and catalyst natures, a complementary experiment of dissolved oxygen restricted was conducted.

2. Materials and methods

2.1. Materials

The used MnO_2 particles were purchased from the TOSOH Co. and were confirmed to be pyrolusite with a 1 × 1 tunneled (or molecular sieve) structure, using an X-ray diffractometer (XRD, Philips PANalytical X'pert PRO MPD) (data not shown). The physico-chemical properties of MnO_2 were measured using a specific surface area analyzer (Micrometrics ASAP 2010), porosity analyzer (Micrometrics ASAP 2010), and electrophoresis instrument (Malvern Nano-ZS90). The results are listed in Table 1. Methylene blue ($C_{16}H_{18}N_3SCl$, Riedel-deHaen) and thionin ($C_{12}H_{10}N_3SCl$, standard Fluka for microscopy) were used without further purification before the experiments. All chemicals used in this study were of AnalaR grade, and the solutions were prepared with ultra-pure water produced using a Milli-Q water purification system (Milli-Q-Academic, Millpen RIOS16).

2.2. Experimental procedures

Batch experiments of MB removal using MnO_2 were performed in 250 mL Erlenmeyer flasks. Before the batch experiments, the MnO_2 suspensions were aged at room temperature under a N_2 atmosphere overnight. The reaction volume of dye solution was 200 mL with 10 mg L^{-1} MB and the MnO_2 concentration was maintained at 2 g L^{-1}. The test solutions were adjusted to the desired pH (pH meter, HACH Sension 156) using dilute NaOH and HNO_3 solution. System pH was not controlled during the reaction proceeded because both inorganic and organic buffer agents might be oxidized, which could significantly influence MB degradation [23,24]. Because the surface of manganese oxide can proceed protonation and deprotonation reactions in solution, system was naturally buffered by pyrolusite suspension. The solution pH was almost unchanged during reaction. All experiments were conducted under natural room light irradiation, maintained at 25 °C by the water circulating temperature controller, and stirred at 150 rpm (Firstek

Table 1
The physicochemical properties of MnO_2.

Surface area	
S_{BET} (m^2/g)[a]	46
S_{ext} (m^2/g)[b]	32
S_{μ} (m^2/g)[c]	14
Pore volume	
V_p (cm^3/g)[d]	0.11
$V_{\mu p}$ (cm^3/g)[e]	0.007
Pore width (nm)[f]	9.23
pH_{iep}[g]	4.70

[a] BET surface area.
[b] External surface area.
[c] Micropore surface area.
[d] Total pore volume.
[e] Micropore volume obtained from *t*-plots.
[f] Adsorption average pore width (4 V/A by BET).
[g] Isoelectric point of pH.