



Treatability assessment of polycyclic aromatic hydrocarbons contaminated marine sediments using permanganate, persulfate and Fenton oxidation processes



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HIGHLIGHTS

- Treatability of PAH contaminated marine sediment was assessed by chemical oxidations.
- KMnO_4 was better on PAH degradation than $\text{Na}_2\text{S}_2\text{O}_8$ and Fenton chemicals.
- Citrate chelated Fe(II) efficiently catalyzed $\text{Na}_2\text{S}_2\text{O}_8$ and Fenton oxidation of PAH.
- Correlation between degradability and physicochemical properties of PAH was evaluated.
- Removal of PAH was affected more by the reactivity than by the hydrophobicity.

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ABSTRACT

Various chemical oxidation techniques, such as potassium permanganate (KMnO_4), sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$), Fenton ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$), and the modified persulfate and Fenton reagents (activated by ferrous complexes), were carried out to treat marine sediments that were contaminated with polycyclic aromatic hydrocarbons (PAHs) and dredged from Kaohsiung Harbor in Taiwan. Experimental results revealed that KMnO_4 was the most effective of the tested oxidants in PAH degradation. Owing to the high organic matter content in the sediment that reduced the efficiencies of $\text{Na}_2\text{S}_2\text{O}_8$ and regular Fenton reactions, a large excess of oxidant was required. Nevertheless, KH_2PO_4 , $\text{Na}_4\text{P}_2\text{O}_7$ and four chelating agents (EDTA, sodium citrate, oxalic acid, and sodium oxalate) were utilized to stabilize Fe(II) in activating the $\text{Na}_2\text{S}_2\text{O}_8$ and Fenton oxidations, while Fe(II)-citrate remarkably promoted the PAH degradation. Increasing the molecular weight and number of rings of PAH did not affect the overall removal efficiencies. The correlation between the effectiveness of the oxidation processes and the physicochemical properties of individual PAH was statistically analyzed. The data implied that the reactivity of PAH (electron affinity and ionization potential) affected its treatability more than did its hydrophobicity (K_{ow} , K_{oc} and S_w), particularly using experimental conditions under which PAHs could be effectively oxidized.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of persistent organic pollutants widely identified in aquatic environments; they comprise two to six benzene rings and are highly toxic, carcinogenic, and environmentally persistent. PAHs are ubiquitous contaminants in aquatic environments and most are from anthropogenic sources (Nouira et al., 2013). Owing to their

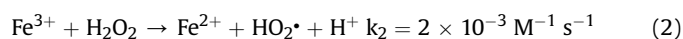
hydrophobic nature and poor solubility in water, PAHs rapidly sorb to particulate matter and thus accumulate in soils and sediments. Sediments may act as a source of organic pollutants and lead to bioaccumulation in aquatic organisms and biomagnification in the food chain. Approximately 130 PAHs have been identified, of which the most essential are 16 that have been listed by the U.S. Environmental Protection Agency (US EPA) as priority contaminants (Rubio-Clemente et al., 2014; Zhou et al., 2015). Accordingly, Canadian interim sediment quality guidelines (ISQGs) has been developed to evaluate the degree to which adverse biological effects are likely to occur as a result of exposure to PAHs in marine sediments (the concentrations of specific PAHs are as listed in

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Table S1) (CEQG, 1999). Kaohsiung Harbor is the largest international port in Taiwan and its container traffic volume ranks the sixth globally. The port region receives flowing water from four rivers, which run through Kaohsiung city, which has a population of over 1.5 million. Domestic, agricultural and industrial wastewaters directly contribute to the critical level of accumulated PAHs in sediments. Earlier studies have previously found that the total concentration of carcinogenic PAHs can vary in a range of 10^2 – 10^5 ng g⁻¹ dw in the sediments from Kaohsiung Harbor, depending on the sampling site (Chen et al., 2013). Annual dredging from Kaohsiung Harbor has been steadily increasing in volume for years (from 4.5×10^5 m³ in 2005 to 9.6×10^5 m³ in 2015 (Table S2, TIPC, 2015)). The need for the development of feasible *ex-situ* methods for remediating PAH-contaminated sediments before further disposal is urgent.

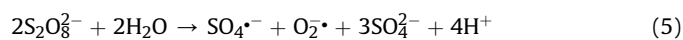
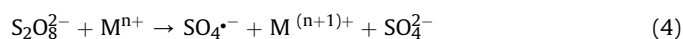
Advanced oxidation processes (AOPs) are chemical treatments for removing organic and sometimes inorganic materials using highly reactive radicals that are generated from various combinations of reactants, such as O₃/UV, TiO₂/UV, H₂O₂/O₃ and transition metal/H₂O₂ (Bokare and Choi, 2014; Sievers, 2011). Among AOPs, those that involve Fenton's reagent and activated persulfate have been the most powerful for treating polluted wastewaters in the last decade. A typical Fenton process uses ferrous ions (Fe²⁺) to catalyze hydrogen peroxide (H₂O₂), generating hydroxyl radicals (HO•), which are strong nonspecific oxidants that are highly reactive and capable of decomposing organic compounds at high diffusion-controlled rates (10^7 – 10^{10} M⁻¹ s⁻¹) (Brillas et al., 2009). The primary Fenton reactions include the following (Venny et al., 2012a).



Typically, hydrogen peroxide reduces the ferric species (Fe(III)) in catalytic reactions. The rates of ferrous consumption and regeneration (k_1 and k_2) differ substantially. The rapidly exhausted ferrous ions terminate the Fenton reaction and shorten the period of efficient degradation of the target compounds. Persulfate, as an emerging oxidizing agent for removing a broad range of organic contaminants, has gained much attention owing to some of its important characteristics (Cuypers et al., 2000; Long et al., 2013). Persulfate salts dissociate in water to S₂O₈²⁻ anions, which slowly remove most of contaminants (Ferrarese et al., 2008), even though powerful as oxidants of the peroxy-family ($E^0 = 2.1$ V). Persulfate can be further activated by UV irradiation and heat, by homolysis of the peroxide bond in the persulfate molecule,



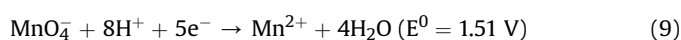
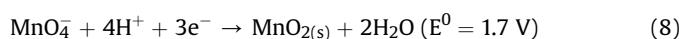
or by charge transfer with metal ions or a base.



Persulfate activation results in the formation of the sulfate radical (SO₄•⁻, $E^0 = 2.6$ V) (Neta et al., 1977). Another strong, non-specific oxidant, the hydroxyl radical (OH•, $E^0 = 2.8$ V), is also formed during persulfate propagation reactions under neutral to alkaline conditions (Tsitonaki et al., 2010):



In contrary to Fenton oxidation, sulfate radicals prevent the treatment from producing large quantities of slurry. The activation of persulfate by ferrous ions is known to be effective in PAH removal. The use of activated persulfate for PAH oxidation can be effective for up to 24 h (Cuypers et al., 2000; Zhao et al., 2013). Iron is the typical candidate transition metal for environmental applications, but ferric ions are easily precipitated as iron hydroxides at neutral pH (Pignatello et al., 2006). High buffer capacity of clay and sediment limit the ability to maintain a low pH in a solution of ferrous ions. Therefore, many chelating agents have been employed to maximize the catalytic activity of ferrous ions by preventing the loss of iron (II) by binding it with the hydrophilic sites of natural organic matter (NOM) (Kang and Hua, 2006; Rastogi et al., 2009; Venny et al., 2012a). Potassium permanganate (KMnO₄) is a favored oxidant in breaking the carbon–carbon double bonds of a PAH structure, because it is effective over a wide range of pH values (Brown et al., 2003; Rauscher et al., 2012). KMnO₄ has also been successfully used; the high oxidation state (+7) of manganese atoms in KMnO₄ degrades pollutants without forming radical species:



For the practical treatment of marine sediments, organic matters complicate the use of chemical oxidation processes, as they scavenge considerable amounts of nonselective oxidants and sequester PAH into hydrophobic pores of particles. This investigation demonstrates various chemical routes, including those based on KMnO₄, Na₂S₂O₈, the regular Fenton reagent, modified Na₂S₂O₈ and the Fenton reagent with chelated-Fe(II) catalysts, for remediating contaminated sediments. Experimental parameters that affect the efficiency of removal of 16 PAHs include the type and doses of oxidants and chelating agents. Several chemicals, including sodium pyrophosphate (Pp), sodium oxalate (Ox), ethylene diamine tetraacetic acid (EDTA), oxalic acid (OA), sodium citrate (Ct) and potassium dihydrogen phosphate (DP), were used to modify Na₂S₂O₈ and Fenton reagents (MP and MF) in the oxidation of PAHs. These chelating agents and stabilizers are often adopted for complexing ferrous ions, and thus enhance the production of radicals at circumneutral pH (Kakarla and Watts, 1997; Wang and Brusseau, 1998; Rastogi et al., 2009; Xue et al., 2009; Vicente et al., 2011). The correlation between degradation efficiency and the chemical and physical properties of individual PAH (including the standard reduction potential, E^0 , solubility, S_w , octanol/water and octanol/carbon partition coefficients, K_{ow} and K_{oc} , potential of ionization, I_p and electron affinity, E_a) is evaluated to determine key factors that may influence the oxidation of aromatic compounds.

2. Materials and methods

2.1. Sediment sample

Contaminated sediments were collected from the industrial port of southern Kaohsiung, Taiwan (the location of contaminated site was as provided in authors' earlier work (Dong et al., 2012)). This area receives from a steel refinery effluent that is polluted by organic and inorganic compounds. After collection (using an Ekman Dredge Grab Sampler (6'' × 6'' × 6''), from Jae Sung International Co., Taiwan), samples were immediately transferred into glass bottles that had been pre-rinsed with *n*-hexane, and stored in a refrigerator (–20 °C) until they were used. Around 3 kg of sediments were homogenized by a tumbling mixer and then dried in a freeze-drier for 72 h. Before oxidation treatment, the samples were

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