



Determination of potassium permanganate demand variation with depth for oxidation–remediation of soils from a PAHs-contaminated coking plant

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ABSTRACT

Bench-scale experiments were conducted to investigate the potassium permanganate demand, a key parameter for in situ chemical oxidation (ISCO) system design, and its variation with depth in PAHs-contaminated site of a coking plant. The concentrations of permanganate decreased rapidly during the first 8 d of the reaction process. The reaction follows first order kinetics, with rate constant ranging from 0.01 to 0.3/h. The total oxidant demand (TOD) is significantly higher for clayey silt fill than for soils of other lithology. The typical TOD is about 50 g MnO₄⁻/kg soil for clayey silt fill, 20–40 g MnO₄⁻/kg soil for silt, silty clay and 1–7 g MnO₄⁻/kg soil for fine sand. Statistical analysis revealed that TOD was positively correlated with total organic carbon (TOC) content, clay content and PAHs concentrations, besides sand content, meanwhile TOC was the parameter with the strongest influence on oxidant demand. After 32 d duration of oxidation, PAHs in all tested soils were effectively removed, with total removal percent ranging from 78% to 99%, and small molecular weight PAHs were removed to a greater extent than high molecular weight PAHs. Parameters obtained in this study, combined with soil bulk density, soil porosity and soil moisture, can be used for full-scale ISCO system design and application in coking contaminated site.

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1. Introduction

Chemical oxidation has been used for removing organic contaminants from industrial wastewater and water disinfection since 1930s. In the past decade, this technique has been rapidly developed for the remediation of contaminated groundwater and soil. Currently, chemical oxidation is used in remedying sites contaminated by chlorinated organic solvents or petroleum hydrocarbons because of its various advantages, such as high removal efficiency, short remediation period, low sensitivity to contaminant species, and low environmental risk [1,2]. It was reported that, chemical oxidation accounted for 3% of the source remedy projects at Superfund sites in the USA between 1982 and 2004, and increased to 5% for projects between 2005 and 2008 [3].

Potassium permanganate is a common oxidant for chemical oxidation–remediation. It has high redox potential and slow rate of decomposition, and can also be easily monitored, therefore, it has been used for the treatment of a variety of organic contaminants [4]. A survey of 135 in situ chemical oxidation (ISCO) remediation projects showed that more than 65% of the projects

used potassium permanganate as oxidant [5]. A critical success factor for chemical oxidation–remediation is the application of accurate amount of oxidant. It is vital not only for the most effective remediation at the lowest cost, but also for avoiding potential environmental risks associated with inappropriate use of oxidants [1,2,5–7]. The rebound of contaminant concentrations after chemical oxidation–remediation has been reported in numerous research and engineering projects [5,7,8]. This is primarily because of underestimating the oxidant demand, contaminant and oxidant mass transfer and mass transport limitations [2], and consequently the incomplete removal of contaminant of all fractions (e.g. dissolved, adsorbed, non-aqueous phase liquids (NAPL)). Clearly, accurate determination of the total oxidant demand (TOD) is essential for effectively preventing rebound of contaminant concentrations.

Most oxidants used for chemical oxidation–remediation are non-selective. The target contaminants were oxidized as well as other non-target compounds, mainly some reductive substances naturally present in soil. Thus oxidants were partly consumed by these organic substances and reduced inorganic reactants (e.g. ferrous, manganous, arsenic, sulfidic species) [1,2,9–11]. Correspondingly, the natural oxidant demand (NOD) of a soil is defined as the amount of oxidant required to oxidize the naturally occurring organic and inorganic reactive species in soil. The NOD have been measured in many soils, especially sand [12–14], and values varied

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Table 1
Depth, lithology, soil particle size distribution, TOC content and PAHs concentrations of soil samples.

Depth(m)	Lithology	Location of Sample	soil particle size distribution (%)			TOC (%)	PAHs conc. (mg/kg)
			0.02-2mm	0.002-0.02mm	<0.002mm		
0.4	Clayey silt fill (black)	●	43.2	41.7	15.2	1.32	114.52
1.5	Clayey silt fill (brown)						
3.4	Clayey silt fill (gray)	●	78.3	16.5	5.2	0.86	226.22
4	Silt (gray)	●	83.4	12.4	4.2	0.31	13.58
6	Sandy silt (gray)						
8.4	Silt (brown)	●	92.8	5.8	1.4	0.56	307.28
		●	87.3	9.6	3.1	0.02	76.28
8.7	Silty clay (sallow)	●	91.2	7.8	1	0.48	145.78
		●	79	15.8	5.2	0.37	124.18
9.5	Clayey silt (brown)	●	60.8	25.7	13.6	0.31	59.87
10	Fine sand (yellow gray)	●	82.3	13.5	4.2	0.08	3.24
13.3	Fine sand (gray)	●	97	2.6	0.4	0	8.05
		●	95.7	3.6	0.8	0.06	15.07

substantially. The total oxidant demand refers to the amount of oxidant required to oxidize all reactive species in that soil, including the target contaminants. Naturally, the TOD of a soil is greater than the NOD [13], and TOD is more meaningful than NOD for determining the amount of oxidant required for soil remediation. The TOD of soil contaminated by chlorinated solvents has been more investigated previously [13,15], however, TODs of soil contaminated by PAHs have not been intensively studied.

Industrial site contamination is typically characterized by shallow and deep contamination zones, and significant variability in contaminant concentrations and soil/aquifer lithology. Successful remediation of such sites is generally based on treating soils at different depth with different quantities of oxidant according to their TOD. However, oxidant demand for soils at different depth has been rarely studied. It has been confirmed that soils of 0–12 m below the surface in a coking plant of Beijing have been severely contaminated by PAHs. In a previous study [16], the effects of various chemical oxidants were compared (hydrogen peroxide, potassium permanganate, sodium persulfate) and potassium permanganate showed the highest percent of PAHs removal (>96%). This paper reports an experimental study on TOD of representative contaminated soils from the coking plant site. In this study, the reaction pattern and process of permanganate with different depths of soil was investigated. In addition, factors influencing the TOD were quantified for studying scientific model of TOD prediction.

2. Experimental

2.1. Contaminated soil

Soil was collected from a coking plant in Beijing, China where coal was used as the raw material for producing coke, coke oven gas, tar, pitch, benzene, and naphthalene. Eleven soil samples were collected 1–12 m below the ground surface (Table 1). The contaminant concentrations, soil particle size, and TOC were measured in well-mixed air-dried soil samples that passed through a 20-mesh wire screen.

2.2. Experiment design

Soil (10 g) collected from each depth was transferred to a VOC vial in triplicate and mixed with potassium permanganate (35 mL; 15 g/L). The vial was capped, thoroughly shaken, and placed in the dark for different periods (1, 2, 4, 8, 16, and 32 d). Subsequently, a liquid (50 μ L) sample was collected from each vial, diluted (0.05 mL, 50 mL) and tested for potassium permanganate concentration. After each sample, the reactor was immediately capped and shaken.

The TOD was calculated based on the changes in permanganate concentration by: $TOD = V_p \times (C_t - C_0) / m_s$. V_p : volume of potassium permanganate; C_t : final permanganate concentration; C_0 : Initial permanganate concentration; m_s : soil mass.

2.3. Analysis

2.3.1. PAHs concentrations

The soil sample was freeze dried and a sub-sample (2 g) was weighed and mixed with dichloromethane (10 mL). The mixture was ultrasonic extracted (1 h) and centrifuged. The supernatant (2 mL) was collected and added to a silica gel column extraction cell for purification (10 g of 200–300 mesh silicone, with anhydrous sodium sulphate placed on top of the silicone), and eluted with n-hexane/dichloromethane (1:1, v/v). The purified extract was condensed to approximately 0.5 mL using a rotary evaporator (RE-52AA, Shanghai) and adjusted to 1 mL with n-hexane for analysis. PAHs concentrations were analyzed by gas chromatography (Agilent 7890A) under the following conditions: HP-5MS 30 m \times 0.25 mm capillary column, helium as carrier gas, inlet pressure 0.03 MPa, linear velocity 37 cm/s, inlet temperature 300 $^{\circ}$ C, start temperature 60 $^{\circ}$ C, programmed to 300 $^{\circ}$ C at the rate of 5 $^{\circ}$ C/min, retained for 20 min until complete elution of all species.

2.3.2. Potassium permanganate concentration

Permanganate ion (MnO_4^-) absorbance was determined at 525 nm using a UV-Vis spectrophotometer (2800 UV/Vis

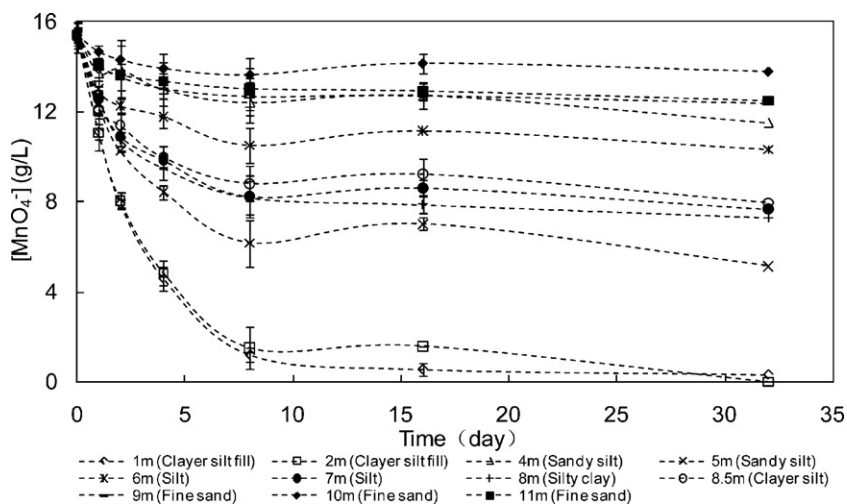


Fig. 1. Permanganate concentrations as a function of time for the tested soils from different depth.

Spectrophotometer, Shanghai). A five-point calibration curve ($r^2 = 0.999$) was used to estimate the MnO_4^- concentration.

2.3.3. TOC

TOC was analyzed with an automatic TOC analyzer (TOC-5000A, Shimadzu Corporation) by the following procedures. First, calibration curves of total carbon (TC) and inorganic carbon (IC) were established with corresponding standards (glucose for TC and Na_2CO_3 for IC). Then, soil samples were ground and sieved with a 140-mesh wire screen. 20 mg of samples were weighed for TC measurement and 60 mg for IC. TOC was calculated by:

$$TOC = TC - IC.$$

2.3.4. Soil particle size distribution

The particle size distributions of soil samples were analyzed with a laser particle size analyzer (HORIBA LA-950, Japan).

2.4. Data analysis

Significance test and Pearson’s correlation analysis of the data were performed using Statistic Analysis System (SAS) and Statistical Product and Service Solutions (SPSS). A p-value of less than 0.05

was considered statistically significant. Partial least squares (PLS) regression was performed using SIMCA-P software.

3. Results

3.1. Kinetics of permanganate consumption by soil samples from different depth

The changes of permanganate concentration during reaction with the soil samples collected from different depths are shown in Fig. 1. The $[MnO_4^-]$ declined rapidly in samples collected 1–3 m below ground surface (bgs). The concentration declined by 50% after 2 d, approximately 90% after 8 d, and permanganate was nearly completely reacted after 32 d. In contrast, $[MnO_4^-]$ in 5–9 m bgs samples declined 30–60% after 8 d reaction time and the 4 m and 9–12 m bgs samples consumed even less, and $[MnO_4^-]$ decreased slightly or essentially maintained stable after 8 d.

The consumption of MnO_4^- cannot be described by a single rate expression for the entire duration of the experiment. A semi-log plot of normalized concentration versus time (t) revealed that during the first 8 d, the consumption of MnO_4^- by all soil from different depths follow first-order kinetics (Fig. 2).

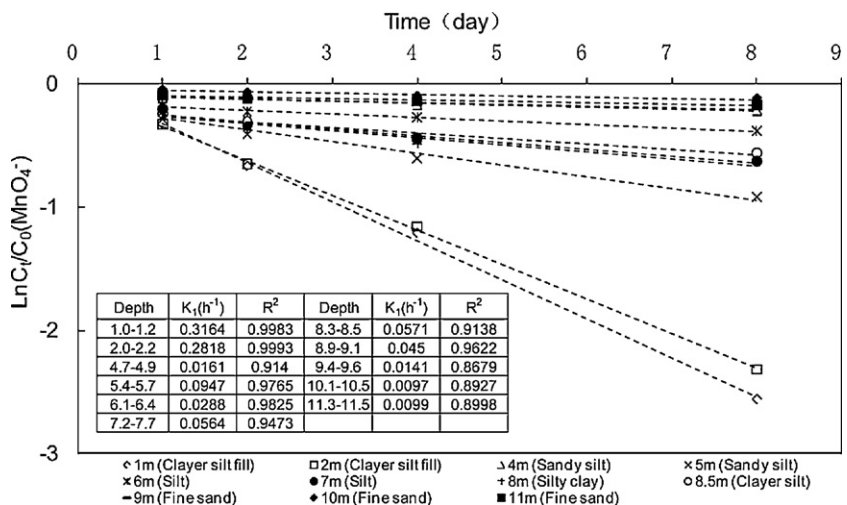


Fig. 2. The natural logarithm of normalized concentration of MnO_4^- over time for tested soil samples of different depth. Also shown (dotted line) are the fits to the experimental data made using the first order expression. The first order reaction rate (K_1), equal to the slope of the fitting line, and regression coefficient (R^2) for each sample are shown in the attached table.

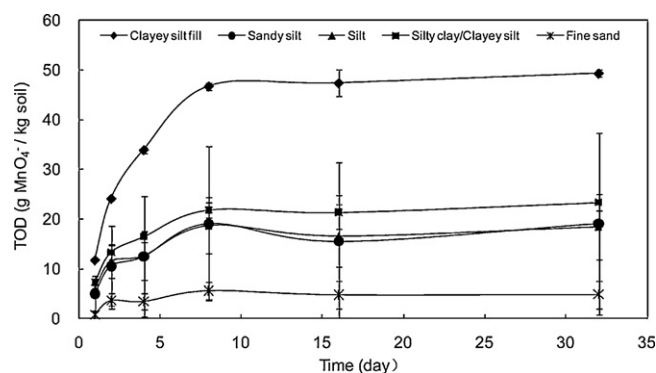


Fig. 3. Changes of TODs with reaction time for soil samples of different lithology.

Samples from 1 to 3 m bgs consumed permanganate most rapidly (0.3/h), followed by 5 m and 7–9 m bgs samples (0.04–0.1/h). The samples from 9 to 12 m bgs reacted slowest with permanganate (0.02/h).

3.2. PAHs removed by permanganate

After reaction with permanganate for 32 d, significant PAHs removal (78–99%) was measured in all samples (Table 2). The total PAHs concentration of all samples reduced to ≤ 10 mg/kg. The low molecular weight PAHs were greatly removed and percent of the medium to high molecular weight PAHs removal ranged from 60% to 100%, except for samples collected at 1 m, 10 m, and 11 m bgs. PAHs removal in the clayey silt fill, silt, and clayey silt/silty clay was all greater than 90%, and large variation in total PAHs removal was observed for sandy silt and fine sand. The sandy silt samples from 4 m and fine sand samples from 10–12 m bgs showed comparatively low PAHs removal, probably due to their relatively low initial total PAHs concentrations.

3.3. Total oxidant demand

The TOD increased with time of reaction (Fig. 3). Within the first 8 d after the addition of permanganate, the TOD of all soil samples rapidly increased. The TOD of clayey silt fill increased fastest (indicated by a 400% increase in TOD from day 1 to day 8), followed sequentially by silty clay/clayey silt, silt, sandy silt, and finally fine sand. After 8 d reaction, the TODs of the clayey silt fill and silty clay/clayey silt continued to increase slightly; in comparison, TODs of other soil remained generally constant in this period. TOD of all tested soil reached maximum after 32 d reaction, consequently TOD of 32 d was determined as the final TOD.

Table 2
Residual PAHs concentration and PAHs removal (%) in soil samples of different depth and different lithology.

Depth (m)	Lithology	Residual PAHs conc. (mg/kg)	PAHs removal (%)			
			Total PAHs	PAHs with 2–3 rings	PAHs with 4 rings	PAHs with 5–6 rings
1.0	Clayey silt fill	8.19	93	94	–173 ^a	–121 ^a
2.0	Clayey silt fill	5.81	97	97	95	100
4.0	Sandy silt	2.64	81	87	86	84
5.0	Sandy silt	4.63	98	99	88	98
6.0	Silt	2.00	97	98	91	80
7.0	Silt	10.31	93	94	73	83
8.0	Silty clay	1.15	99	99	99	94
8.5	Clayey silt	4.93	92	92	95	94
9.0	Fine sand	0.04	99	99	99	69
10.0	Fine sand	1.77	78	83	69	–21 ^a
11.0	Fine sand	1.68	89	95	93	–46 ^a

^a Concentration of PAHs increased after treatment with permanganate, consequently PAHs removal (%) was negative.

All TODs mentioned below in this paper refer to TODs after 32 d reaction.

Soil collected from different depths showed widely different TODs and generally fell into five categories (Fig. 4). For the shallow samples (1–3 m bgs), the TOD was approximately 50 g MnO₄[–]/kg soil and was consistently greater than the TOD measured in deeper soil samples. The TOD in the next layer (4–7 m bgs) showed great variation, ranging from 9 to 32 g MnO₄[–]/kg soil, yet the TOD in samples from 7 to 9 m bgs clustered over a narrow interval (22–25 g MnO₄[–]/kg soil). The TOD in the deepest soil samples (9–12 m bgs) was the lowest (1–7 g MnO₄[–]/kg soil), especially from about 10 m bgs.

Statistical analysis revealed that clayey silt fill had a significantly higher mean TOD (49.3 g MnO₄[–]/kg soil) than other soils, and the mean TOD of fine sand (4.2 g MnO₄[–]/kg soil) was significantly lower than other soils. Moreover, the mean TODs of silt (19.5 g MnO₄[–]/kg soil), sandy silt and silty clay/clayey silt (23 g MnO₄[–]/kg soil) were similar.

3.4. Factors affecting soil TOD

The relationships between TOD and the physico-chemical properties and contaminant concentrations of soil samples were analyzed by Pearson's correlation. Physico-chemical properties analyzed included TOC, sand particle content (*sand*), clay particle content (*clay*), total PAHs concentration (*PAHs*), concentration of low molecular weight (ring number: 2–3) PAHs (*IPAHs*), concentration of medium molecular weight (4 rings) (*mPAHs*), and the reduction of total PAHs concentration (*SPAHS*). Results (Table 3) revealed that TOD was significantly correlated with several factors, including TOC, *sand*, *PAHs*, *IPAHs*, *mPAHs*, and *SPAHS*. Noticeably, although TOD was highly correlated with TOC (coefficient of correlation > 0.9), oxidation of organic substances alone could not explain the total consumption of permanganate. Other reductive reactants must have also contributed to the permanganate consumption.

We further evaluated the correlation using PLS between TOD and the following factors: TOC, *sand*, *clay*, *PAHs*, *IPAHs*, *mPAHs*, and *SPAHS*. Mathematically, PLS can quantify the correlation between a dependent variable and its independent variables without being complicated by the inter-correlation among the independent variables themselves. With PLS analysis, three principal PLS components were selected based on cross-validity and an optimal regression model was determined.

The loading plot (Fig. 5) of the principal components suggested that sand content was negatively correlated with TOD. All other factors were positively correlated with TOD; TOC and *mPAHs* were the most important factors affecting TOD, followed by *clay*, *IPAHs*,

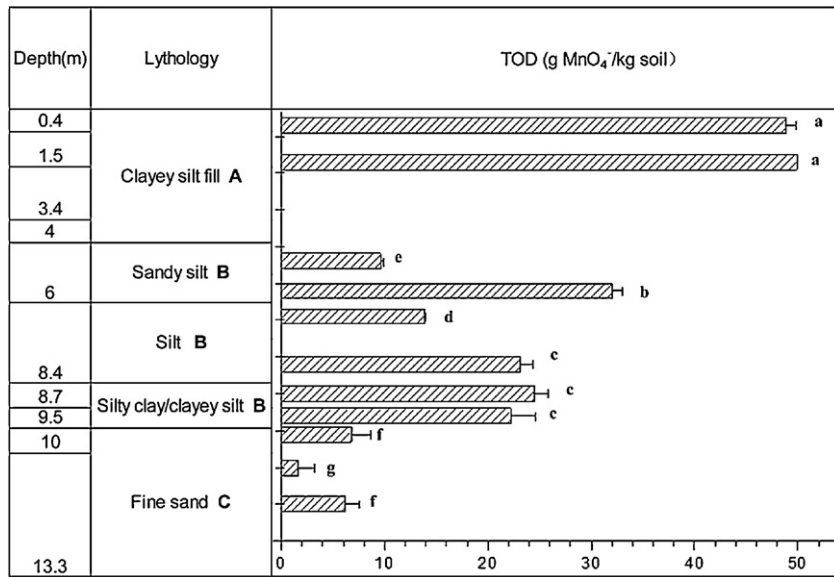


Fig. 4. TOD variation with depth and lithology (letters in lower case indicate statistical significance between samples of different depths, capital letters indicate statistical significance between samples of different lithology; data pairs with the different letter are significantly different ($P \leq 0.05$), and pairs with same letters are not significantly different).

Table 3
Simple correlation coefficients of TOD with soil properties and simple correlation coefficients between every two soil properties acquired by bivariate correlation analysis using SPSS (*indicate significant correlation existed between the two parameters, **indicate highly significant correlation existed between the two parameters).

	TOD	PAHs	SPAHS	Sand	Clay	TOC	IPAHS	mPAHs
TOD	1	0.744**	0.734*	-0.609*		0.927**	0.722*	0.612*
PAHs		1	1.000**				0.996**	0.731*
SPAHS			1				0.996**	0.733*
Sand				1	-0.981**	-0.703*		
Clay					1			
TOC						1		
IPAHS							1	0.673*
mPAHs								1

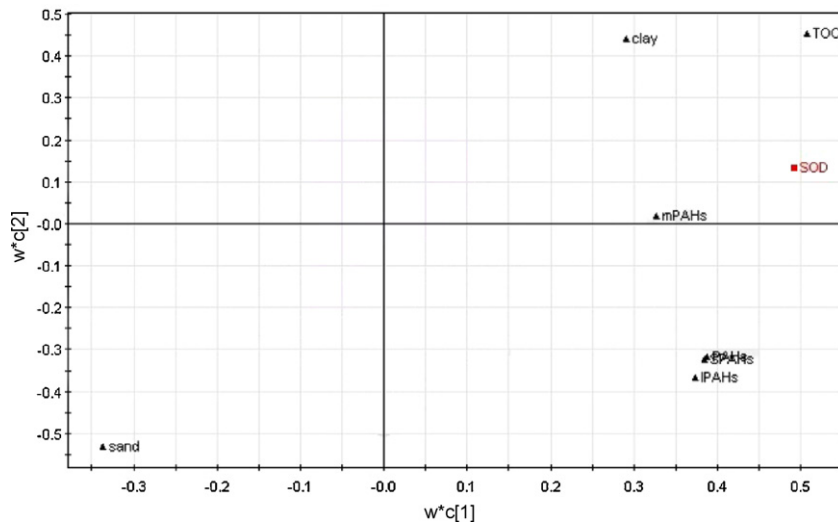


Fig. 5. Loading plot of PLS principal components, showing the influence of soil physico-chemical properties (including TOC, sand, clay, PAHs, SPAHs, IPAHS, mPAHs) on TOD. The PLS calculations resulted in three principal components, explaining 84.7% of the variation in the data and a predictability (Q^2) of 98%.

PAHs, and SPAHs. The regression model was determined to be:

$$\begin{aligned} \text{TOD} = & -0.2366 \times \text{sand} + 0.2021 \times \text{clay} + 0.3104 \times \text{TOC}(\%) \\ & + 0.1351 \times \text{IPAHS} + 0.1633 \times \text{mPAHS} + 0.1485 \times \text{PAHS} \\ & + 0.1469 \times \text{SPAHS}. \end{aligned}$$

4. Discussion

4.1. PAHs removal by potassium permanganate

Results showed that potassium permanganate could effectively remove PAHs from the soil of the coking plant, with a mean PAHs removal percent of 92%. Furthermore, potassium permanganate was effective for removing PAHs from soils of various lithologies (e.g. silt, fine sand, and clayey silt/silty clay) and most effective for low molecular weight PAHs than high molecular weight PAHs. Ferrarese et al. [17] found that potassium permanganate could remove 96% of total PAHs from certain sediments and low molecular weight PAHs in the sediments were also more readily reactive with permanganate than high molecular weight PAHs. The various removal percent for different PAHs were suggested to be attributed to their differences in electronic structures [18]. The concentration of PAHs with medium to high molecular weight in some soil samples increased after treatment. The elevation of concentration may be due to the changes of properties and concentrations of soil organic substances during oxidation, consequently desorption of PAHs was enhanced [19]. Kawahara et al. [20] and Yan and Sun [21] found that oxidation could reduce the concentrations of organic substances in soil, particularly humic acid, which considerably influenced the adsorption behavior of PAHs and decreased their partition coefficients in the soil.

4.2. Kinetics of permanganate consumption

The reaction of permanganate with contaminants and other organic and inorganic substances in all soils collected from all depths mainly took place in the first 8 d and was described by first-order kinetics. In a similar study, the NOD increased rapidly within the first 12 h of reaction, and 50% of permanganate consumption occurred during this time frame. The permanganate consumption followed first-order kinetics within the first 8 h, and then gradually slowed and became stable after 3 weeks [13]. Urynowicz et al. studied permanganate oxidation of soils containing more than one contaminant, and found that the NOD increased rapidly within the first 48 h. Subsequently, the reaction slowed and did not reach equilibrium even after 6 weeks [14]. Additionally, Mumford et al. [12] investigated the kinetics of permanganate oxidation of contaminants in sands, and found that the NOD increased rapidly in the first 2 weeks and then gradually stabilized. These studies indicated that oxidation reactions of contaminants in different soils exhibited different reaction kinetics and oxidation time frames. Specifically, our results indicated that permanganate reaction in soils of different lithologies proceeded at substantially different kinetics: fastest in clayey silt fill (rate constant: 0.3 h^{-1}), followed by silty clay/clayey silt, sandy silt, silt, and finally fine sand (rate constant: 0.01 h^{-1}). In addition to the permeability of soil and aquifer materials, factors influencing the timing and rate of oxidant injection include reaction kinetics of oxidant consumption, and lithology of soil.

4.3. TOD variation with depth and lithology

Previous studies have shown that soil TODs of different lithologies varied widely. Generally, clayey soils consumed more oxidant

than sandy soils. The current study showed that the TOD decreased with the depth of soil, being highest for shallow subsurface soil (1–3 m bgs; $\text{TOD} = 50 \text{ g MnO}_4^-/\text{kg soil}$), followed by soils 5–6 m and 7–9 m bgs ($\text{TOD} = 20\text{--}40 \text{ g MnO}_4^-/\text{kg soil}$), and finally soils 9–12 m bgs ($\text{TOD} = 1\text{--}7 \text{ g MnO}_4^-/\text{kg soil}$). The TOD of soil from different depth was a key parameter in ISCO and could be referenced for the design of oxidant amount for different soil layers.

Existing studies indicate NODs/TODs of different soil varied significantly and a general trend of NODs/TODs: peat soil > clayey silt/silty clay > sandy silt > silt > fine sand. The NOD was reported to be $20 \text{ g MnO}_4^-/\text{kg soil}$ for calcareous karst aquifers, $10.8 \text{ g MnO}_4^-/\text{kg soil}$ for silty clay and $0.15\text{--}5 \text{ g MnO}_4^-/\text{kg soil}$ for sandy aquifer sediments or soil [12,13,22–25], compared with $2.5\text{--}5.6 \text{ g/kg}$ for aerobic sediments [26]. Hønning et al. [13] found that clayey tills contaminated by chlorinated organic solvents had TODs of $5\text{--}20 \text{ g MnO}_4^-/\text{kg soil}$, compared with $1\text{--}8 \text{ g MnO}_4^-/\text{kg soil}$ for sandy tills. An EPA report listed extraordinarily high TODs of $104.7 \text{ g MnO}_4^-/\text{kg soil}$ and 146.9 g/kg for two peat soils at a Superfund site; $1.8\text{--}5.6 \text{ g MnO}_4^-/\text{kg soil}$ for the silt and $4.6\text{--}21.0 \text{ g MnO}_4^-/\text{kg soil}$ for the sandy soil at the site [15]. In this study, we recorded TODs of up to $50 \text{ g MnO}_4^-/\text{kg soil}$ for the clayey silt fill, $>20 \text{ g MnO}_4^-/\text{kg soil}$ for the silt, sandy silt, and clayey silt/silty clay, and $1\text{--}7 \text{ g MnO}_4^-/\text{kg soil}$ for the fine sand. For the ISCO remediation at a site with wide and disperse contaminant distribution, different amounts of oxidant will be required for each soil layers, according to their soil characteristics and levels of contamination.

4.4. Factors affecting TOD

Correlation analysis showed that there were multiple factors affecting TOD. A negative correlation existed between TOD and sand particle content, and positive correlations existed between TOD and clayey particle content and, particularly, TOC and total PAHs concentration. Previous studies have found significant correlations between TOC of uncontaminated soils and the NOD, indicating that organic substances (especially humic acid) in these soils were chiefly responsible for the consumption of permanganate [11,12]. In comparison, for the soils containing both high concentrations of organic substances and contaminants, the TODs were not significantly correlated with the TOCs. For these soils, TOCs alone could not completely account for the total permanganate consumption and, instead, the contaminants contribute considerably to the consumption of permanganate [13]. PLS regression in this study provided a reliable model for the relation fitting of TOD and some independent variables. The model could be used to estimate the TOD of other soils in this site, as well provide reference for TOD determination for soils from other sources.

5. Conclusions

Potassium permanganate effectively removed PAHs in various types of soil from coking plants (including clayey silt fill, silty clay/clayey silt, silt, sandy silt, and fine sand), and is a favourable oxidant for ISCO remediation of coking plant site. Reactions between permanganate and soils from different depths occurred primarily within the first 8 d of treatment and followed first order kinetics, the corresponding rate constants ranging from 0.0097 h^{-1} to 0.3164 h^{-1} . TOD of soils at different depth followed the order of clayey silt fill > silty clay/clayey silt > sandy silt > silt > fine sand. The TOC and total PAHs concentration were the main factors positively correlated with TOD, while a negative correlation existed between sand content and TOD. The study had important practical significance and could provide guidance for the determination of oxidant amount during ISCO remediation of industrial contaminated sites.

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