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Contaminated Soil Remediation with Hydrogen Peroxide Oxidation

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Abstract**—**The hydrogen peroxide treatment was able to remediate chlorophenols, polycyclic aromatic hydrocarbons, diesel and transformer oil contaminated soil. Chemical treatment of contaminants adsorbed in peat resulted in lower contaminants' removal and required higher addition of chemicals than the treatment of contaminants in sand. The hydrogen peroxide treatment was found to be feasible for soil remediation at natural soil pH. Contaminants in soil could degrade with the addition of hydrogen peroxide only indicating the ability of transition metals ions and minerals of these metals presented in soil to catalyse the reaction of hydrogen peroxide decomposition.

Keywords**—**Hydrogen peroxide, oxidation, soil treatment, decontamination.

I. INTRODUCTION

SOIL contamination is a serious world-wide problem. It is driven by human activity such as inadequate agriculture, construction works, industrial and military activities, etc. It has been estimated that 3.5 million sites only in the European Union may be potentially contaminated, with 0.5 million sites being really contaminated and needing remediation [1].

Chlorophenols have been extensively used as fungicides, insecticides and bactericides. Chlorophenols are also applied as drilling mud, preservatives in paints, hides and leathers, photographic solutions and textiles. They appear as undesirable by-products of many industrial processes that involve organic material and chlorine. Thus, a wide-spread contamination of soil with chlorophenols is caused by leaching of these chemicals from dumping sites or following accidental spill from industry.

Polycyclic aromatic hydrocarbons (PAH) are the products of thermal decomposition, formed during incomplete combustion of organic materials and geochemical formation of fossil fuels. PAH have been identified in many emission sources, such as vehicle exhausts, power plants, and chemical, coke, oil-shale industries. Primary natural sources are forest fires and volcanic activity. Accumulation of PAH in soil is also believed to result from atmospheric deposition after long-range transport.

Soil contamination with diesel is caused mainly by leakage of underground storage tanks and accidental spills during transportation and disposal. Transformer oil may enter the environment during salvage operations, as it is dumped, spilled, or leaks from used transformers into the ground. Diesel and transformer oil can migrate to deeper layers through leaching, and surface flow pose a substantial threat of release of aromatic (polychlorinated biphenyls, PAH and phenols) and aliphatic compounds. A considerable amount of these contaminants can be held in soil in the form of residual saturation and lead to long-term contamination of groundwater.

Thus, due to the great number of sources and environmentally hazardous chemical composition of these contaminants, implementation of innovative treatment processes for contaminated soil remediation is a matter of pressing concern.

Chemical oxidation is a promising innovative process for degrading an extensive variety of hazardous compounds in remediation of soil at waste disposal and spill sites. Chemical oxidation has been used for organic contaminants degradation over 100 years in water and wastewater industries. What is still new is the utilization of chemical oxidation for the destruction of contaminants in soil. Chemical oxidation can be applied both *in situ* (to soil in place) and *ex situ* (after soil excavation). Matching the remedial oxidant and technology of delivery to the contaminant of concern and site conditions is an extremely important step in the successful remediation of contaminated soil.

Hydrogen peroxide is one of the most successfully used remedial chemical for contaminated soil remediation. Oxidation with hydrogen peroxide can be direct and/or through the generation of free radicals (hydroxyl radicals $OH^{\bullet}$). The latter relies on the decomposition of hydrogen peroxide catalysed by most ions of transition metals (Fe, Cu, Zn, etc.) and by natural minerals of those metals (hematite, goethite, etc.) present in soil. The basic reaction is:

$$H_2O_2 + Fe^{2+} \rightarrow OH^- + OH^{\bullet} + Fe^{3+} \qquad (1)$$

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Superoxide anion ($O_2^{\bullet -}$), hydroperoxyl radical ($HO_2^{\bullet}$) and hydroperoxide anion (HO_2^-) can also act as desorbing oxidizing agents in soil remediation. These species are created during the propagation reactions with high (≥ 2%) H_2O_2 concentrations [2]:

$$HO_2^{\bullet} \rightarrow H^+ + O_2^{\bullet -} \quad (2)$$

$$HO_2^{\bullet} + O_2^{\bullet -} \rightarrow HO_2^- + O_2 \quad (3)$$

Treatment with hydrogen peroxide has several advantages over other soil remediation methods. Hydrogen peroxide oxidation is relatively fast, taking only days or weeks. The contaminants are treated *in situ*, converted to innocuous and/or natural occurring compounds (e.g. H_2O, CO_2, O_2, halide ions). By acting/reacting up on the contaminant in place, the reagent serves to eliminate the possibility of contaminant vertical movement other than resulting from the act of vertical injection itself, which is often a concern in other remediation technologies [3]. As a side advantage, aerobic biodegradation of contaminants can benefit from the presence of oxygen released during H_2O_2 decomposition, if large quantities of chemical needed to be applied. Hydrogen peroxide can be electrochemically generated on site, which may further increase the economic feasibility and effectiveness of this process for treated contaminated sites [3]. Natural iron oxide minerals (hematite α-Fe_2O_3, goethite α-FeOOH, magnetite Fe_3O_4 and ferrihydrite) present in soil can catalyse hydrogen peroxide oxidation of organic compounds [4-6]. Thus, the treatment of contaminated soil would require no addition of soluble iron catalyst.

Disadvantages include the need for pH control in some cases and difficulties controlling *in situ* heat and gas production [7]. The efficacy of hydrogen peroxide oxidation may be limited by low soil permeability, incomplete site delineation, subsurface heterogeneities, and highly alkaline soil where carbonate ions are free radical scavengers [3].

In the present study hydrogen peroxide treatment was applied for remediation of soil contaminated with chlorophenols, PAH, diesel and transformer oil. The influence of hydrogen peroxide dosage, ferrous iron catalyst addition and a manner of hydrogen peroxide application on the removal of the contaminants in soil was investigated. The assessment of natural organic matter content impact on the feasibility of chemical treatment was performed.

II. MATERIALS AND METHODS

Current study was carried out with artificially spiked samples at 20 ± 1°C in a laboratory scale. Preliminary dried (40°C) soil was artificially spiked with contaminant by adding a contaminant-acetone solution. The acetone was evaporated to dryness under continuous mixing to ensure contaminant distribution homogeneity and, hence, a better reproducibility in repeated experiments. Initial concentrations of contaminants were verified by the analysis of at least four replicates.

The initial concentration of chlorophenols in soil was 5.35 g kg^{-1}. The mixture of chlorophenols consisted of 2-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol. Soil contained 13 g kg^{-1} total iron and 2.0 g kg^{-1} ion-exchangeable Fe(II). The pH of untreated soil was 5.2. The organic carbon content of soil was 460 ± 30 mg kg^{-1}. Total concentrations of PAH were 52.46 and 357.8 mg kg^{-1} in sand and peat, respectively. The mixture of PAH consisted of phenanthrene, anthracene, fluoranthene, pyrene, triphenylene, benz(a)anthracene, chrysene, benzo(e)pyrene, perylene, benzo(a)pyrene and benzo(ghi)perylene. The initial concentrations of diesel were 12.5 ± 0.4 and 10.4 ± 0.3 g kg^{-1} in peat and sand, respectively. The initial concentration of transformer oil was 17.4 ± 0.1 g kg^{-1} in sand and 19.0 ± 0.1 g kg^{-1} in peat. The pH of untreated sand and peat was 6.7 and 6.4, respectively. Sand contained 4.5 g kg^{-1} total iron and 0.3 g kg^{-1} ion-exchangeable Fe(II). Peat contained 2.6 g kg^{-1} total iron and 0.2 g kg^{-1} ion-exchangeable Fe(II). Sand represented a mineral part of soil, while peat was chosen as a model of organic-rich soil.

The degradation of contaminants in slurry during the treatment was examined under batch conditions. The standard procedure was that slurry of soil and liquid (H_2O_2 solution) were treated in a cylindrical glass reactor with 0.2 L of volume under a vigorous magnetic-stirring during 24 or 72 h. Various manner of hydrogen peroxide addition (the addition of H_2O_2 all at once or stepwise addition) was used in these experiments. The reaction was stopped by adding 10-20% aqueous solution of Na_2SO_3. The contaminated soil was treated without pH adjustment and at pH 3.0. Some experiments on the soil treatment by hydrogen peroxide oxidation process were also performed with the addition of iron catalyst (Fe^{2+}). The $FeSO_4$ x $7H_2O$ salt was used as a source of Fe^{2+}.

After the treatment the samples were dried with anhydrous sodium sulphate prior extraction. Dry soil samples were extracted with hexane. Dry matter of soil samples was determined by oven-drying at 105ºC. Chlorophenols were measured with GC-FID. PAH were measured with HPLC-FLD. Diesel and transformer oil were measured with GC-MS.

III. RESULTS AND DISCUSSIONS

The contaminant removal in soil with the hydrogen peroxide oxidation was found to be dependent on H_2O_2/soil weight (w/w) ratios, treatment time and a manner of hydrogen peroxide addition. The influence of these treatment conditions was quite different for various types of contaminants (chlorophenols, PAH, diesel and transformer oil).

A. Chlorophenols Removal

Chlorophenols degraded with the addition of hydrogen peroxide only (Fig. 1) indicating the ability of transition metals ions and minerals of these metals presented in soil to catalyse the reaction at natural soil pH.

Chlorophenols degradation in soil was dependent on the dosage of hydrogen peroxide applied. The 31% of chlorophenols removal was obtained when the (w/w) ratio of H_2O_2/chlorophenols=0.5:1 was used. A six-fold increase of

H_2O_2/chlorophenol ratio to 3:1 enhanced the degradation and resulted in 62% removal of chlorophenols in soil.

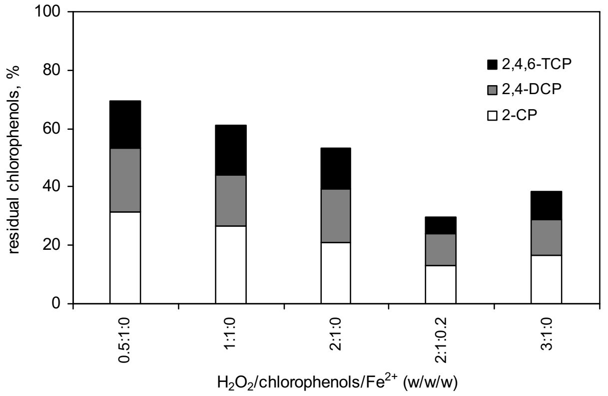

Fig. 1 Residual chlorophenols in soil after a 24-h hydrogen peroxide treatment with different w/w ratios of H_2O_2/chlorophenols

In spite of higher hydrogen peroxide doses may result in more effective chlorophenols reduction it makes the treatment less cost-effective and more destructive for the microbial community. The addition of iron (Fe^{2+}) catalyst was able to improve the degradation that allowed applying moderate dosages of hydrogen peroxide for chlorophenols contaminated soil remediation (Fig. 1).

B. PAH Removal

Similar to chlorophenols degradation in soil PAH could degrade in sand and peat with the addition of hydrogen peroxide only (Fig. 2).

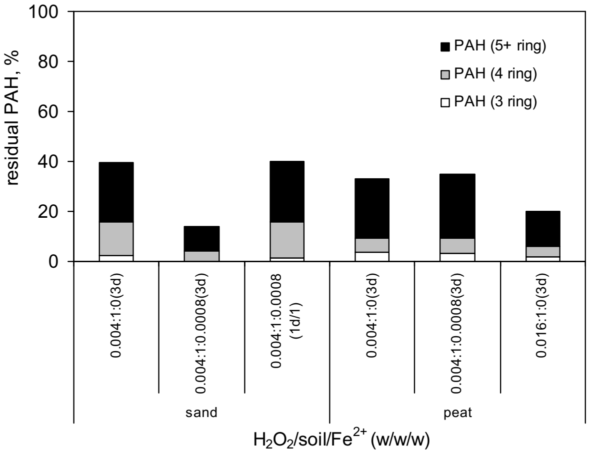

Fig. 2 Degradation of PAH in sand and peat with the hydrogen peroxide treatment at different w/w ratios of H_2O_2/sand or peat (pH 3.0), where 1d/1 – 1 day treatment (24 h) and a single-step addition of H_2O_2; 3d – 3 days treatment (72 h) and a 1-step addition of H_2O_2 per day

In the experiments with the catalyst addition PAH degradation in sand depended on the treatment time and a manner of hydrogen peroxide application. A stepwise addition of H_2O_2 and the increasing of the treatment time to 3 days (72 h 1 addition per day, 3d) was more effective for the removal of PAH in sand than the addition of H_2O_2 all at once and a 24-h treatment time (1d/1). A slow addition of H_2O_2 to the system with excess iron provides conditions that minimise quenching of OH radicals [8]. Thus, a 3-step addition of hydrogen peroxide in the presence of the extra catalyst during a 72-h treatment (3d) may be recommended for the remediation of PAH contaminated sand.

The addition of catalyst (Fe^{2+}) did not improve the degradation of PAH in peat resulting the same PAH removal as with the addition of H_2O_2 only (Fig. 2). A four-fold increase of H_2O_2/peat (w/w) ratio from 0.004:1 to 0.016:1 slightly enhanced PAH degradation in peat by the hydrogen peroxide treatment (Fig. 2).

C. Diesel Removal

The degradation of diesel in sand increased with the increasing of H_2O_2/diesel (w/w) ratio until it reached 93% removal of contaminant (Fig. 3). Further increasing of H_2O_2/diesel to 5:1 did not improve the contaminant degradation in sand resulting in similar diesel removal.

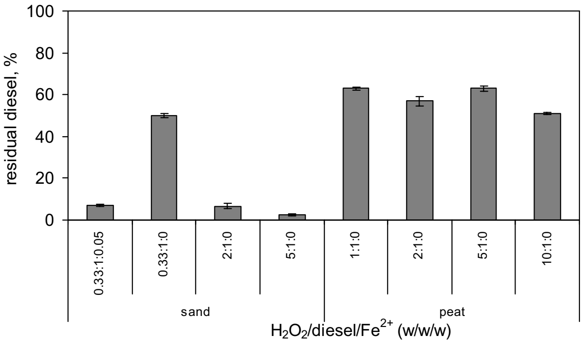

Fig. 3 Residual diesel in sand and peat after a 72-h hydrogen peroxide treatment at different w/w ratios of H_2O_2/diesel (pH 3.0). Error bars represented standard deviation of the mean

The addition of catalyst was favourable for diesel degradation (93%) in sand that allowed applying lower hydrogen peroxide dosage (w/w/w ratio of H_2O_2/diesel/Fe^{2+}=0.33:1:0.05).

In the experiments on diesel contaminated peat treatment, hydrogen peroxide only was added. The addition of H_2O_2 only aimed to increase iron availability leading to alternative pathways of Fe^{2+} production. The effect of hydrogen peroxide oxidation treatment obtained for diesel contaminated peat differs somewhat from this for sand (Fig. 3). The increasing of H_2O_2/diesel ratio did not enhance diesel degradation resulting in similar degree of diesel removal in peat, while the increasing of H_2O_2/diesel ratio definitely improved diesel degradation in sand.

D. Transformer Oil Removal

In the experiments on transformer oil contaminated sand and peat treatment, hydrogen peroxide only was added. Increasing the H_2O_2/transformer oil (w/w) ratio did not substantially influence the contaminant degradation in sand with the hydrogen peroxide treatment (Fig. 4). Even a hundred-fold increase of H_2O_2/transformer oil ratio (from 0.04:1 to 4:1) did not improve transformer oil degradation resulting in the same removal of the contaminant. Thus, the application of higher H_2O_2/transformer oil ratios may be not reasonable as the similar removal of transformer oil was achieved with a moderate addition of H_2O_2.

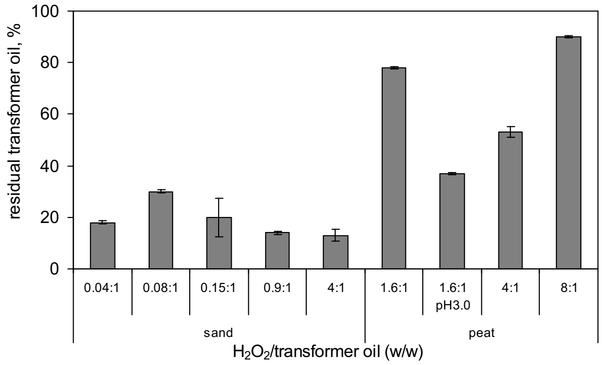

Fig. 4 Residual transformer oil in sand and peat after a 72-h hydrogen peroxide treatment with different w/w ratios of H_2O_2/transformer oil. Error bars represented standard deviation of the mean

Contrary to the result obtained on the treatment of sand raising the H_2O_2/transformer oil ratio increased the transformer oil removal in peat until it reached the optimum. The optimal ratio of H_2O_2/transformer oil obtained from the results of the present study on the transformer oil degradation in peat by a 72-h hydrogen peroxide oxidation treatment (with 1 addition of H_2O_2 per day) was 4:1.

It was hypothesized by Walling et al. [9] that at high concentrations, hydrogen peroxide could compete with organics for hydroxyl radicals reducing the efficacy of organic compounds oxidation with hydroxyl radicals. This is also in concordance with the data of Petigara et al. [10], who indicated that OH radicals are produced more efficiently at lower concentrations of H_2O_2 in soil. Thus, the competition between H_2O_2 and organics for the hydroxyl radicals suggests that there is an optimum H_2O_2/contaminant ratio for the effective oxidation of organics that will vary with the reactivity of organic molecules toward OH radicals.

The influence of pH on the effectiveness of transformer oil contaminated soil remediation was also investigated. The hydrogen peroxide oxidation treatment of contaminated soil under the constant H_2O_2/contaminant (w/w) ratio and pH 3.0 led to higher removal of transformer oil than at natural soil pH (Fig. 4).

E. General Notes

As a rule, the acidic pH conditions 2.0-4.0 favoured the oxidation of organic compounds, as it is known that the decomposition rate of hydrogen peroxide reaches the maximum in this pH range [11]. This phenomenon is attributed to the progressive hydrolysis of the ferric ion, which provides a relatively large catalytically active surface for contact with H_2O_2. The accelerator Fe^{2+} ion in H_2O_2 decomposition will yield more hydroxyl radicals.

In general, if the natural pH of the contaminated zone is not low enough for efficient hydroxyl radical generation, acids may be added to adjust the pH of a subsurface prior to the hydrogen peroxide oxidation treatment application. Decreasing pH will be very useful when the emergency response actions must be taken within few hours after pollution and for *ex situ* remediation of soil.

However, pH adjustment of soil during *in situ* treatment will be complicated by the technological restrictions in remediation of the deeper layers and the difficulty of mixing big portions of soil. This makes the treatment less cost-effective. Also, sudden variation in soil pH can have a harmful effect on the soil microbial community and thereby retard subsequent biodegradation of residual contaminants or their oxidation by-products.

The efficacy of the hydrogen peroxide treatment was dependent on the soil matrix. The hydrogen peroxide treatment of contaminants in peat - used as a model of organic-rich soil - resulted in lower contaminants removal and required higher addition of hydrogen peroxide than the treatment of contaminants in sand representing the mineral part of the soil. As can be seen in Figs. 2-4, under the same treatment conditions (treatment manner and time) and constant w/w ratios of H_2O_2/contaminant (PAH, diesel and transformer oil) contaminant removal in sand was higher than in peat.

Organic matter content can be one of the factors that control the rate of hydrogen peroxide decomposition and hydroxyl radical formation that are responsible for contaminant desorption and oxidation. Petigara et al. [10], who measured the OH radicals formation rate in four different soil suspensions, have also shown that OH radicals were a major product of H_2O_2 decomposition in soil with low organic matter but they were a minor product in soil containing high amount of organic matter. This can contribute to higher removal of contaminant in sand than in peat.

IV. CONCLUSION

The remediation of chlorophenols, PAH, diesel and transformer oil contaminated soil with the hydrogen peroxide treatment was found to be effective. Application of the hydrogen peroxide treatment for contaminated soil remediation made possible a rapid reduction of contaminants' concentration. Therefore, this treatment method is indispensable for fast reduction of contaminants in soil when it is necessary to avoid their penetration to deeper layers of soil or to aquifer. Moderate doses of hydrogen peroxide should be applied in order to support the following biodegradation of the residual contamination in soil by the indigenous microorganisms survived after the chemical oxidation treatment.

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