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In-Situ Chemical Oxidation of Sodium Persulfate in the Remediation of Chlorobenzene Contaminated Groundwater

Haoyang Mao[1,a,*], Shenggang Yin[1,b], Xin Shu[2,c]

[1]School of Geography, Earth and Environmental Sciences, University of Birmingham, Birmingham, West Midlands, United Kingdom
[2]Hunan Huaneng Yangtze River Environmental Protection Technology Co., Ltd., Changsha, Hunan Province, China
[a]hxm120@alumni.bham.ac.uk, [b]sxy074@alumni.bham.ac.uk, [c]shuxin320@126.com
[*]Corresponding author

Abstract: *Sodium persulfate has been widely used as an oxidant for the remediation of organic-contaminated soil and groundwater. SO_4^- and OH^- with strong oxidative properties could be produced by sodium persulfate after activation by sodium hydroxide, which could degrade chlorobenzene and other organic substances. In this study, sodium persulfate was chosen as the oxidant, and in-situ chemical oxidation (ISCO) remediation of chlorobenzene contamination in the groundwater of pesticide factories was conducted under the activation of sodium hydroxide, and the removal rate could achieve 95% maximum. Analysed by the results of the Pearson correlation coefficient, the environmentally friendly oxidation product sulphate was negatively correlated with the concentration of chlorobenzene during the ISCO remediation process. However, the remediation effect was also affected by the concentration of pollutants, the nature of the geological horizons, and other factors.*

Keywords: *Groundwater Remediation, Soil Remediation, Chlorobenzene Contamination, In-Situ Chemical Oxidation*

1. Introduction

Chlorinated hydrocarbons (HCFCs) are important raw materials in the production of pesticides, and the groundwater contamination could be generated due to the spilling of HCFCs during production, relocation, and dismantling through downward migration through the soil into the groundwater[1]. Since chlorinated hydrocarbons are volatile organic compounds, unacceptable risks to human health and serious damage to the ecosystem would be caused because of their volatility and persistence after entering the soil and groundwater system[2].

In recent years, multi-phase extraction (MPE) combined with in-situ chemical oxidation (ISCO) is an important technical approach for in-situ treatment of groundwater contamination[3][4], but due to the differences in the lithology of the soil layers in the treatment area and the destruction of the stratigraphic structure of the land parcels would be caused by MPE[5], the big difference in the effectiveness of the treatment by carrying out ISCO (i.e. in-situ chemical injection) after MPE. Meanwhile, different organic contaminations could be degraded by various of oxidantal chemicals such as permanganate[6][7][8], hydrogen peroxide[9], Sodium percarbonate[10][11], and persulfate combined with activators. Persulfate can produce strongly oxidising sulfate radicals ($\cdot SO_4^-$) with a significant potential of 2.6 V in the subsurface environment with the presence of chelating agents when activated by conditions such as heat, light, and transition metal catalysis[12]. Besides, persulfate can be transported in the soil system for a long distance due to its slow activation kinetics and stable characteristics[13]. Therefore, the persulfate oxidation system can be widely used to degrade organic pollutants in soil and groundwater[14][15][16].

Up to now, the research was mostly a single ISCO study and remained at the laboratory bench test and pilot stage. Remediation of groundwater contaminated with chlorinated hydrocarbons has rarely been published due to the influence of hydrogeological and climatic factors. On the other hand, numerous uncertainties brought about by the effects of MPE on the geological horizons for ISCO need to be studied and analysed with construction cases. Therefore, in this study, for the chlorobenzene contaminated groundwater of a pesticide factory in the Yangtze River Delta, People's Republic of China, sodium persulfate was chosen as the oxidant and produced highly active sulfate radicals to remove chlorobenzene from the groundwater under the activation condition of NaOH after carrying out groundwater pumping and treatment for 6 months. Correlation analysis between the concentration of OH^- in groundwater and degraded chlorobenzene concentration was performed. Technical support for groundwater management and contamination remediation was provided via this study.

2. Materials and Methodology

2.1 Research Area

The study area is located to the south of the tank farm area of the synthesis workshop of a pesticide factory in the Yangtze River Delta, People's Republic of China, which has been engaged in the production of pesticides since its establishment and has been planned as an industrial site at a later stage. The study area is mainly contaminated with chlorobenzene to varying degrees, with monitoring well GW-4 undergoing a 6-month groundwater dual-phase extraction (DPE) treatment with water and gas prior to this ISCO remediation.

Impacted groundwater area extent 415 m^2 with higher contamination concentration and approximately 2 m impacted zone thickness (8.0 ~ 10.0 m bgs or 9.0 ~ 11.0 m bgs) with groundwater table at ~3 m bgs.

2.2 Geology and Hydrogeology

In the study area, it can be roughly divided into 2 layers within the depth of the study: fill material was present to a maximum depth of 7.5 m and mainly consists of grey to grey-yellow, moist to wet, loose, sandy silt with a small amount of gravel and broken bricks; grey-brown to dark grey, wet to saturated, soft plastic to low plastic, silty sand was encountered below the fill layer, extended to the maximum drilling depth of 13.5m (undiscovered), the sandy content became bigger with the increase of depth. The geotechnical laboratory results indicated the soil porosity ratio (eo) ranged from 0.778 ~ 0.965, total porosity (qT) ranged from 0.43 ~ 0.49 (average 0.45). The static water level range was from 2.34 to 3.00 metres below ground surface (m bgs), and the overall direction of groundwater flow was from southwest to northeast which was influenced by seasons and rainfall.

2.3 In-Situ Chemical Oxidative Remediation

2.3.1 Chemicals

Sodium persulfate was chosen as the oxidant, and sodium hydroxide was used as the activator and pH adjusted chemicals. The weight ratio of sodium persulfate and sodium hydroxide was 1:1, and the solution was prepared with water by the ratio of 1:5. Strong oxidative sulfate radicals ($\cdot SO_4^-$) and hydroxyl radicals ($\cdot OH^-$) can be generated by alkaline activation of sodium persulfate, and can have a significant oxidative effect on the chlorobenzene in the groundwater, and the oxidation products will not cause secondary pollution to the groundwater.

2.3.2 Injection Points

The injection points in this study were developed in equilateral triangles, which ensured that there was no blind zone of influence within the injection area. Based on available information including the hydrogeological setting (sandy silt and 1.1×10^{-3} cm/s at soil aquifer, i.e., silty sand), an effective radius of influence (ROI) of 2.25 metres was estimated. A total of 20 injection points were deployed for the first-round chemical injection. The second-round injection points were shifted 1.5 metres to the centre point of the original triangles from the locations of first-round injection points, so that the newly injection points developed remained in a positive triangular distribution. At the same time, further injection points were developed around the tank farm area (injection points were spaced at half the original intervals) to ensure that the source of contamination could be treated with more chemicals. The location of injection points was shifted to avoid encountering underground utilities to ensure the constructors' health. Schematic layout of injection points and the locations of the 2 rounds of injection points are shown in Figure 1 below.

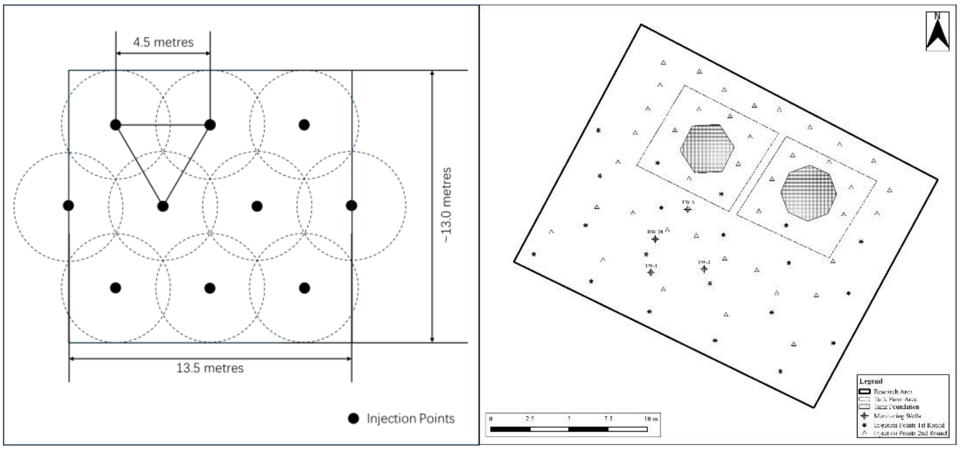

Figure 1: Schematic Layout of Injection Points (Left) and Layout Map with Injection Points (Right)

2.3.3 Injection Method

The Geoprobe in-situ injection system was selected for this study to inject the configured chemicals into the groundwater aquifer to be remediated and conducted in a bottom-up way through GeoProbe direct push probe, which allowed the contaminants to remain within the range of action of the chemicals as they diffuse and migrate outwarde, ensuring effective remediation of the contaminated area and preventing it from expanding further.

This allowed the contaminants to remain within the range of action of the chemicals as they diffused and migrated outwards, ensuring effective remediation of the contaminated area and preventing it from expanding further. The vertical injection spacing depth was 0.5 metres, and the injection volume was 300 liters, which could achieve adequate distribution. The next injection would be started after pulling the probe upward by 0.5 metres when one injection was completed, and the procedure was repeated until all injections were completed.

The equipment system consisted of the Geoprobe drilling rig, injection line instrumentation and valves, injection pumps, and chemical dispensing system. The in-situ chemical oxidation process is shown as bellow in Figure 2.

Two batches of chemical injections were designed for this study with an injection interval of 40 days.

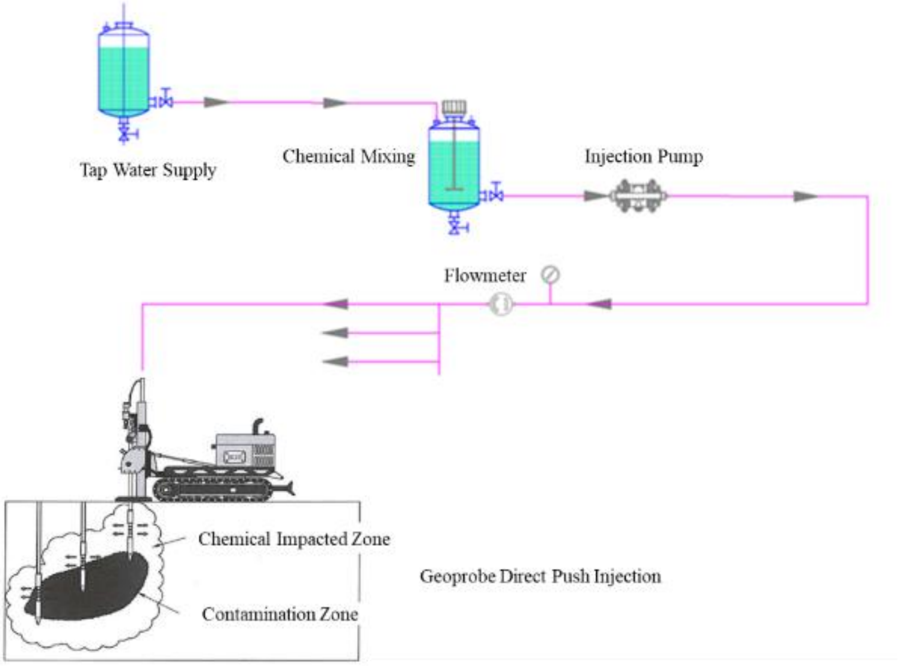

Figure 2: In-situ Chemical Oxidation Process Schematic

2.4 Analysis of Chlorobenzene Concentrations in Groundwater

All groundwater samples collected were shipped to SGS Laboratories for concentration of Chlorobenzene according to USEPA method 8270D (US Environmental Protection Agency, 1996b). All groundwater samples were extracted and filtered through silica gel and anhydrous sodium sulfate, the samples were analysed by gas chromatography according to USEPA Standard Method 8260C (US Environmental Protection Agency, 1996a). Samples with high concentrations of chlorobenzene were analyzed prior to dilution.

2.5 Correlation Analysis of Sulphate, OH^- ion Concentration and Chlorobenzene Concentration

The Pearson correlation coefficient, also known as the Pearson product-moment correlation coefficient (Pearson correlation), is a measure of the strength and direction of the linear relationship between two parameters, defined as the product of the sample covariance of a variable divided by its sample standard deviation. In this study, Pearson correlation coefficient-based analysis was used to measure the strength of the relationship between sulphate concentration and degraded chlorobenzene concentration in each groundwater monitoring well. The Pearson correlation coefficient was calculated as shown below:

$$r=\frac{\mathrm{Cov}(x,y)}{\sigma_x\sigma_y}$$

Cov: the covariance

σ: the standard deviation of the measured data (sulphate concentration or OH^- concentration) and the degraded chlorobenzene concentration.

In the calculations, the correlation coefficient r was calculated for each measurement data, and then the significance level (T-test) was calculated.

3. Results and Discussions

3.1 Analysis of Groundwater Parameters

The groundwater parameters were measured regularly after the start of injection, and most of the redox potentials in the experimental site were positive and high, with a peak value up to 590 mV, indicating that the groundwater in this region was in a good oxidative environment after the injection of the agent, and the pH was mostly between 9.0 to 12.0, which could provide an alkaline environment for the oxidative reaction of sodium persulphate, and was conducive to the degradation of the pollutants.

3.2 Analysis of the Effect of Sodium Persulfate on the In-situ Oxidation of Chlorobenzene in the Study Area

Four monitoring wells were installed in the experimental area to detect the concentration of chlorobenzene in groundwater. As shown in Figure 3 below, sodium persulfate has a good effect on removing chlorobenzene in most wells of the test area, with a removal rate of more than 95%, of which the monitoring wells GW-1 and GW-2 have been decreased to below the standard limit of Class IV (GB 14848 Chinese Standard for Groundwater Quality). However, the concentration of chlorobenzene in the GW-4 area increased compared with the pre-injection area, which was presumed to be the source of pollution.

As a product of the oxidation reaction, the concentration of sulphate was increasing with the decrease of pollutants.

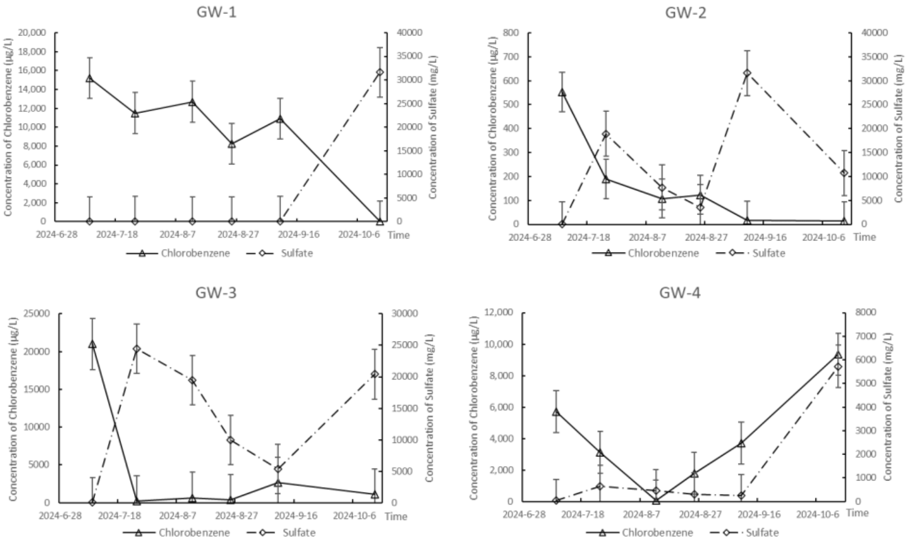

Figure 3: Effect of sodium persulfate on the oxidation of chlorobenzene in groundwater in the experimental area.

3.3 Relationship between OH^- ions and Chlorobenzene Concentration

The oxidation of chlorobenzene by sodium persulfate is affected by the acidity and alkalinity of the environmental setting in which it is found. The Pearson's correlation coefficients and t-test results of the correlation analyses between OH^- ions concentration and chlorobenzene concentration at different stages of the monitoring wells are shown as follow Table 1. From the results, it could be seen that the concentrations of chlorobenzene in GW-1, GW-2, and GW-3 were negatively correlated with OH- ions concentration, among which GW-1 had the strongest negative correlation and the correlation coefficients were significant at the 95% confidence level. Since the OH^- ion concentration (pH) could be affected by many factors, such as temperature, salinity, geology, etc., the chlorobenzene concentration degraded and the OH^- ion concentrations were the result of the multifactorial effects under complex environmental conditions. On the other hand, the data samples used for correlation analysis were less, and the correlation coefficients were easily affected by extreme values. In addition, the in-situ test used in this experiment could not be performed as a one-way control experiment, and the role of OH^- ions concentration in the degradation process of chlorobenzene still need to be further verified.

Table 1: Summary of Pearson Correlation Coefficient

Monitoring Well No.	Pearson Correlation Coefficient	P Value
GW-1	-0.903	0.014
GW-2	-0.570	0.237
GW-3	-0.725	0.103
GW-4	0.778	0.069

3.4 Analysis of Factors Influencing the Effectiveness of Remediation

3.4.1 Geology and Hydrogeology

The geological horizons in the study area were mainly sandy chalk (with increasing sand content with depth), which made it easier to form priority channels due to water flushing during the mechanical injection process. Monitoring well GW-4 had been treated with DPE, which might have increased the development of priority channels. The remediation effect would be affected due to the rapid discharge of the chemicals through priority channels and the uneven chemical spatial distribution after injection into the target aquifer.

3.4.2 Influence of Organic Substance Attached to Soil Particles on Groundwater

The data results suggested that the concentration of chlorobenzene at point GW4 showed an increasing trend after an initial decrease, and the concentration of chlorobenzene at the rest of the monitoring wells also showed a staged increase during the injection process. This might be caused that the pollutants were attached to the soil particles in the air envelope, the groundwater level was rising with the injection of large quantities of chemical solution, which redissolved the pollutants in the air envelope into the groundwater, and resulted in the concentration increasing again.

3.4.3 Impact of Pollutant Concentration

The source of pollution in the study area was not yet clear, and the amount of chemicals added was not enough to oxidize and decompose all the pollutants in the heavily polluted area, and high concentrations of chlorobenzene might not be degraded in the groundwater due to limitations in the oxidative properties of sodium persulfate with the activator sodium hydroxide.

4. Conclusion

The ISCO of chlorobenzene in the groundwater of the pesticide factory by sodium persulfate under the activation of hydroxide was effective, and the removal efficiency achieved 95% maximum. Analysed by the results of the Pearson correlation coefficient, the environmentally friendly oxidation product sulphate was negatively correlated with the concentration of chlorobenzene during the ISCO remediation process. In this study, the Geoprobe rig system was used for chemical solution injection with minimal exposure to contaminants, which reduced the health risk to the field workers. Meanwhile, the on-site field work of this study took only 40 days for two rounds of injections, which was a great reference for in-situ remediation projects with a short work schedule and had a huge market promotion and application value.

However, the chlorobenzene concentration at the beginning of the ISCO remediation showed an increasing trend after an initial decrease, and the chlorobenzene concentration in a few monitoring wells even exceeded the initial concentration. We concluded that the reasons for this situation mainly include:

Reduced oxidation efficiency led by the chemical solution loss through priority channels due to the disruption of the geological horizons by DPE treatment; The organic pollutants adhering to the soil particles were redissolved into the groundwater by the rise of the water table after the injection of the chemical solution; and the oxidative property of sodium persulphate activated by sodium hydroxide was not sufficient to completely remediate the chlorobenzene contamination in the groundwater, etc.

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