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Development and *in situ* implementation of a chemical process for reductive dechlorination of chlorinated solvents in polluted aquifers

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Reductive dechlorination (RDC), using strong reducers, is one of the most important emerging remediation techniques for chlorinated hydrocarbons (CHC). RDC by Nanosized Zero Valent Iron (NZVI) is a powerful electrochemical redox system that has shown promising experimental results for the development of remediation technologies to treat contaminated sites [1, 2]. Although NZVI has excellent characteristics as environmental reactant, its application to the contaminated sites often meets technical challenges. *In situ* current treatment processes are systematically threatened to the problem of homogeneity of the treatment quality, which closely depends on: (i) the capacity of the porous media to convey reagents towards the polluted zone and (ii) the reactivity and stability of the NZVI as NZVI suffers from agglomeration and passivation [2]. Among other strong reducers, sodium dithionite ($S_2O_4^{2-}$; $2Na^{2+}$; DT) presents reducing characteristics close to those of NZVI ($E_0 = -1.12$ V/NHE at pH 7). DT has a weak S-S bond allowing the formation of two reactive radical species [3]. Literature reports [3-5] that the use of DT in aquifers or soils increases the Fe(II) content and the capacity to reduce CHC. DT is also used to compensate Fe⁰ passivation phenomena described beforehand [6]. The use of NZVI coupled with strong reducers for RDC appears thus as good alternative and promising technological to clean up polluted environments by CHC. The optimization of an industrial process, using DT and NZVI, for RDC of aquifers or unsaturated soils contaminated by CHC, appeared as a sustainable alternative for *in situ* RDC, more especially as development of processes where DT is involved do not exceed the stage of the laboratory.

This study is accomplished within the framework of DECHLORED. The objective of the work is to develop and prove the efficiency of a novel *in situ* RDC process in polluted aquifers by using strong reducers and illuminate, by an improved monitoring, the field under the RDC process. For this purpose, four key steps have been identified: i) define, at laboratory scale, the operating conditions, ii) determine the performances iii) draw up the list of the equipment and the technical conditions of implementation on site and iv) make a complete assessment of the processes application. The purpose of this communication is to present the work accomplished (i) to set up an enhanced procedure for the RDC of CHC at lab scale and (ii) to perform RDC experiments *in situ* as demonstration at a selected polluted site (Néry-Saintines, 60, Oise, France).

For lab experiments (performed by using batch and columns), perchloroethene (PCE) was chosen as the target compound as it is one of the most widespread chlorinated pollutants in groundwaters and its degradation produces many known molecules.

Batch experiments carried out in hermetically closed cells allowed the setting up of protocols making it possible to study the feasibility of RDC for PCE. Tests were carried out using DT and NZIV particles while varying operating parameters: nature and contents of reagents, temperature (from 12°C to 25°C), concentrations in pollutants, reagent/pollutant molar ratios, treatment duration, physical and chemical parameters.

Columns experiments were then conducted in designed Kynar® columns (Figure 1, height 50 cm; diameter 15 cm) that were fully equipped with sophisticated systems for non-destructive monitoring of time changing physical parameters and chemical compositions (Figure 2). The entire system (filled with reference sand from Fontainebleau and with Cuisian sand from the selected polluted site) was placed in air-conditioned cupboard under different operating conditions. The monitoring was complemented by probes (T, pH, redox, conductivity, oxygen, sulfide and chloride ions). Gas Chromatography (GC) led to monitor PCE (and its degradation products) migration and dispersion over the entire columns. Ion Chromatography (IC) was used for the quantitation of Cl^- at the column outputs to correlate RDC.



Figure 1.

Complete experimental device of percolation (feed bottles with reagents and pollutants, pumps, columns, flow-through-system carrying the monitoring probes), placed in air-conditioned cupboard



Figure 2.

Setup up and apparatuses for the monitoring of the physical and chemical parameters of the column output water and geophysical electrical measurements into the column (and over the length of the column)

Results showed the effective reduction of PCE by NZVI, firstly by direct electron transfer and secondly from native H_2 . The association NZVI+DT was demonstrated to be more powerful; probably due to a concerted mechanism. IC analyses confirmed the superiority of the combination DT+NZVI than DT alone. GC analyses suggested that the combination DT+NZVI led to minimize the formation of chlorinated intermediate species; which represents a significant advantage for *in situ* groundwater treatments. Experiments carried out in columns allowed us to:

- evaluate the applicability of the selected operating conditions close to those being able to be met on the aquifers or soils
- improve understanding of reactant efficacy, and also their transformation and persistence,
- model these flow-through systems (1D or 2D column set up) by numerical modeling softwares (PHREEQC® and MARTHE® reactive transport simulations).

Our results also recommended combining of geophysical measurements with electroanalytical measurements to monitor RDC process and will allow us to give an advantageous method for monitoring and checking *in situ* remediation.

Concerning the implementation *in situ*, the site was carefully selected because it presented a well-documented pollution (with a majority of CHC and their metabolites) provided by analyses since 1980. The processing of all historical data allowed highlighting the existence of a slow natural reductive bio-dechlorination process. It also allowed selecting the right emplacement for the implementation of the RDC process (40.5 m width, 25 m length x 25 m depth). Before any implementation of the process, geological and hydrogeological investigations allowed dimensioning the demonstration pilot. In order to define the initial conditions and later to appreciate the effectiveness of treatment, a network of 12 piezometers (PZ) were installed. They were disposed along a transect intercepting perpendicularly

the polluted water flow. Three of them, made in carbon steel, were injection wells, judiciously equipped for simultaneous injection over four different levels, from 0 to -25 m. The other nine PZ have been realized as control PZ. For this purpose they have been fully equipped with probes for physical and chemical monitoring.

It is worth noting that all the 12 PZ were firstly dedicated to monitor the groundwater quality. Data acquired before the treatment allowed us to obtain a 3D-representation of the geochemical parameters of the whole contaminated zone. The total CHC content at this location was about 30 mg/L.

The whole RDC process *in situ* is under operation (injection at four levels of reagent solutions according to ratios defined during the preliminary experiments and monitoring) since October 2014. During and after the treatment application, the 9 PZ were used for regular and judicious sampling at different depth. This lead to (i) comfort the physical and chemical data acquired by the probes, (ii) provide T, pH, redox, alkalinity, chloride, sulfate, Fe(II) and total Fe contents and (iii) monitor CHC and their metabolites (mechanisms of RDC) and estimate the RDC process efficiency. At that time (May 2015), tested RDC processes are efficient at minus 85%. At the end on the treatment (July 2015), the performances of the process will be thoroughly investigated. The processes will be economically assessed and compared to other treatments in terms of efficiency, limits, and costs.

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