MECHANISM AND KINETICS OF REDUCTIVE DECHLORINATION OF HEXACHLORO-BUTADIENE AND HEXACHLOROETHANE BY BIMETALLIC Pd/Fe MICROPARTICLES USING AN INDIRECT AND CONTINUOUS MONITORING OF IRON CORROSION

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ABSTRACT

Background information

Chlorinated organic compounds (COCs) are common contaminants of soil and groundwater, especially in industrial areas. They are known to be toxic for human health and represent a major environmental concern. Among them, hexachlorobutadiene (HCBD) is a byproduct in the manufacture of carbon tetrachloride and tetrachloroethylene (PCE). HCBD has been added to Annexes A and C of the Stockholm Convention on persistent organic pollutants (POPs) in 2015. Hexachloroethane (HCA) is a solid, which exists in three different crystalline phases depending on temperature. It is produced by chlorination of ethane and aliphatic chlorinated ethanes. Their density greater than that of water (d_{HCBD} = 1.66 g·mL^{-1} and d_{HCA} = 2.091 g·mL^{-1}) and their strong hydrophobicity (Rodrigues *et al.,* 2017a), characterized by their high octanol-water partition coefficient K_{ow} (log K_{ow} > 4), cause their vertical migration and slow release in soils and groundwater, which is responsible for a long-term pollution by these dense nonaqueous phases (DNAPs). Remediation of DNAPs polluted groundwater is necessary and strongly recommended.

Main results

This study is dedicated to the comprehension of the mechanism of reductive dechlorination of HCBD, (C_4Cl_6) and HCA (C_2Cl_6) by bimetallic Pd/Fe microparticles in suspension in a mixture of polymers and oligomers of lactic acid (PLA). It is based on the use of an indirect continuous monitoring of the iron corrosion by measurement of the pH, the redox potential and the conductivity of the solution, in addition to chromatographic analyses allowing the quantification of the different chlorinated organic compounds. The tests were made out in closed reactor (thermo-regulated 1 L cylindrical Pyrex double-walled water-jacketed), following various experimental conditions aiming at determining the influence of the quantity of Pd/Fe microparticles, the initial concentration of pollutants, the quantity of PLA and the temperature. The results showed that the evolutions of pH, redox potential and conductivity are related to changes in the solution chemistry due to the iron corrosion and that the system is initially controlled catholically by the mass transport of H$^+$. Figure 1 shows an example of obtained results on the effect of the quantity of Pd/Fe particles for the dechlorination of 10 mg L^{-1} of HCA with 850 mg of PLA and at 25 °C.

The intercomparison of the results in the absence and in the presence of the pollutant made it possible to elucidate the dechlorination mechanism of the two pollutants (Rodrigues *et al.,* 2017b; 2019). The first stage is the diffusion and the sorption of the pollutant on the surface of the particles on the PLA level. Different experimental conditions have shown that hydrogen is the main reductant of the system. Indeed, the aqueous corrosion of iron involves the generation of atomic hydrogen on palladium, allowing the hydrodechlorination of the pollutants. Only PCE was quantified during the reduction of HCA; thus, no accumulation of toxic chlorinated by-products in solution such as TCE and vinyl chloride were observed. The continuous measurement of pH, redox potential and conductivity during each experiment made it possible to understand the effect of each investigated parameter on the corrosion of the particles and on the dechlorination reaction.

Conclusions

The results showed a good correlation between the evolution of the parameters, the kinetics of corrosion of the particles and the reductive dechlorination of HCBD and HCA under the different experimental conditions. Different kinetic laws were then used for modeling the disappearance of HCBD and HCA.

Finally, the results also confirmed the interest of this type of continuous monitoring for in situ remediation. Indeed, it can easily be implemented in situ and can provide deeper information on the evolution of groundwater geochemistry during the reductive dechlorination of recalcitrant chlorinated compounds.

$\blacklozenge$ (1) = 150 mg Pd-mZVI, $\blacksquare$ (2) = 375 mg Pd-mZVI, $\blacktriangle$ (3) = 600 mg Pd-mZVI, $\bullet$ = blank, $\times$ = H$^+$/H$_2$ redox couple
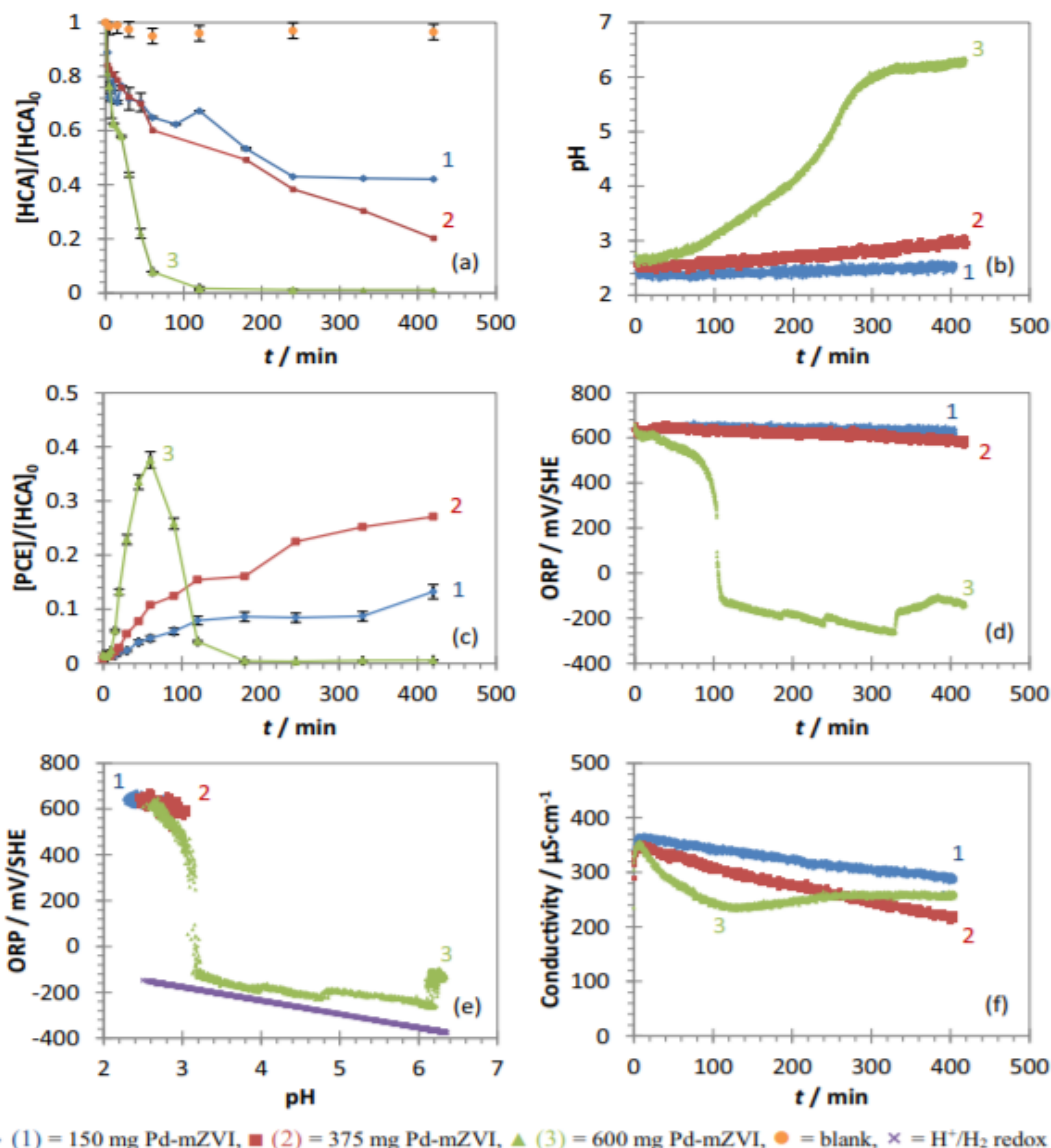
Figure 1. Effect of the quantity of Pd/Fe particles on the reducing dechlorination of HCA. (a) Evolution of the concentration in HCA, (b) Evolution of the pH, (c) Evolution of the concentration in PCE, (d) Evolution of the redox potential, (e) Evolution of the potential redox as a function of pH, (f) Evolution of conductivity.

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