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TRICHLOROETHYLENE OXIDATION BY SODIUM PERSULFATE IN AQUEOUS SYSTEMS APPLYING DIFFERENT CHEMICAL ACTIVATORS

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Abstract: A wide range of technologies for remediation of contaminated soils and groundwater is available. In this context, the in situ chemical oxidation is one of them and the sodium persulfate oxidation ($Na_2S_2O_8$), an emerging approach for *in situ* remediation process. The interest in this attractive compound is related with its capability to generated sulfate radicals ($SO_4^{\bullet-}$), a strongest oxidizing species which can be applied to destruction of several organic contaminants in environmental aqueous and solid matrices. Given this, an important step for occurrence and propagation of $SO_4^{\bullet-}$ radicals is related to the presence of some type of activator, which can involve the temperature, initiation by UV radiation and chemical processes. In this study, two different processes for activation of sulfate radicals species, from $Na_2S_2O_8$ dissociation in aqueous systems, were evaluated: alkaline pH and dual oxidant system, and together, for comparison data, only sodium persulfate. Trichloroethylene, a DNAPL, commonly related with the studies case of contaminated land was employed for the bench scale tests, applying sodium persulfate oxidation technique. The results already observed until the current part of this study are showed.

Key words: activated sodium persulfate, sulfate radicals, remediation.

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1. INTRODUCTION

A wide range of physical, chemical, biological and also combined techniques (classic and emerging technologies) applied for the soils and groundwater remediation is available and, the persulfate chemical oxidation it is one of them. Known as the most powerful oxidant of the peroxygen family (peroxydisulfate) and also one of the strongest oxidation used and researched actually in remediation processes for contaminated sites, the interest of persulfate, principally sodium persulfate for environmental applications ($Na_2S_2O_8$), has recently grown (last decade), when considering their ability to degrade or effectively mineralize a broad range of organic contaminants, [1]. The dissociation of sodium persulfate in water is related to the presence of persulfate anion ($S_2O_8^{2-}$), which has a strong standard redox potential (E^0 = 2.01 V), greater than that of typical oxidizing redox potentials applied to the in situ chemical oxidation, like the hydrogen peroxide (H_2O_2, E^0 = 1.8 V) and the permanganate ion (MnO_4^-, E^0 = 1.7 V), [2, 3]. Although the persulfate is a strong oxidizing agent, higher reaction activation energy is need. This means that a lower kinetic of contaminant degradation is expected and thus, a thermodynamic stability increase is verified, [4]. Nevertheless, this emerging remediation technology have a particularly property for enable successfully on the $Na_2S_2O_8$ application, that is related to the activated persulfate (Eq.3), which involves free sulfate radicals ($SO_4^{\bullet -}$) generation, classified side by side with the hydroxyl radicals ($HO^{\bullet}$) as one of the strongest oxidizing species, with redox potential quite similar: 2.6 V and 2.8 V, respectively for $SO_4^{\bullet -}$ and $HO^{\bullet}$, [3, 5]. For occurrence of $SO_4^{\bullet -}$ radicals species, the presence of some *initiator* for their generation must be applied. The paths to this step may involve: heat, transition metals catalysts as Fe(II) or Fe(III), chelated metals (Fe-EDTA, Fe-Citrate), UV radiation, alkaline persulfate and also a dual oxidant systems (e.g., $Na_2S_2O_8$ / H_2O_2), [2].

In this study (in progress), the main objective is to evaluate the potential capability of sodium persulfate to degraded a DNAPL in aqueous systems, exploring the dual oxidation and alkaline pH as activators, for mediate the $SO_4^{\bullet -}$ radicals generation. The trichloroethylene (TCE) was chosen as target compound.

2. MATERIAL AND METHODS

Four procedures for sodium persulfate (NaP) oxidation of TCE were evaluated (Table 1). An initial concentration of 24.4 $mg.L^{-1}$ (0.19 mM) of TCE with an initial NaPer/TCE molar ratio of 41:1, were adopted in all tests. All experiments were performed applying 12 ml cylindrical glass vials and maintained stored during the experimental time inside of the polystyrene support (light protection and temperature control). The volumes of TCE, NaP,

NaP activator, and destilated water were calculated to ensure zero headspace and be agreeing with the established conditions for the tests. A total of 13 aliquots for each experiment were prepared to assess the kinetics of TCE degradation by NaP. Controls tests (i.e., only destilated water spiked with TCE) were performed to evaluate the losses influenced by others processes such as temperature and volatilization.

Table 1. Experiment description for sodium persulfate (NaP) oxidation of TCE.

Experiment	**Description – TCE degradation**	**NaP/Activator (molar ratio)**	**Initial pH**	**Initial conductivity (ms.cm^{-1})**
1	Only NaP (without activation)	-	5.3	14.8
2	NaP activated by H_2O_2 (dual oxidant system)	2:1	5.4	16.1
3	NaP activated by NaOH (alkaline system)	1:1	11.8	23.4
4	NaP activated by KOH (alkaline system)	1:1	12.1	23.6

Note: aliquots when removed were placed in ice bath (4ºC, 10 min) after ethanol addition (100 μL), both steps to quench the reaction.

At times 3.25 at 7.25 h (*n=5*, Δt=1h) and 101 at 311 h (*n=8*, Δt=24h), for each experiment, an aliquot was taken for pH (Qualxtron pH meter, QX 1500plus), conductivity (WTW conductivity, Cond 315i) and temperature (by pH meter) analysis. Another aliquot (3 ml) was used for TCE quantification by direct liquid chromatography with photo diode array detector (UFLC-PDA, Shimadzu). Before injection, samples were pH adjusted (6.5 and 7.5). The chromatography conditions were: ACN/ultrapure water (7:3 v.v^{-1}) as mobile phase, flow rate of 1 ml.min^{-1}, detection at wavelength 195 nm. The sample volume injected was 20 μL. External TCE calibration (0.1 – 10 mg.L^{-1}) was used (R^2: 0.996 – 0.999). Good reproducibility for standards and samples was obtained (RSD lower than 12%). Persulfate anion was determined by spectrophotometric method, [6].

3. RESULTS AND DISCUSSION

Figure 1 shows the TCE degradation mediated by persulfate (NaP) and activated persulfate (NaP/H_2O_2; NaP/NaOH/ NaP/KOH). It can be noted that when NaP was activated by alkaline pH using a molar ratio NaP/base (NaOH or KOH) equal a 1:1, the TCE concentration quickly go down within only 3 hours of reaction, remaining lees than 0.5% of TCE present in aqueous system. After 290 and 311 hours, the residual TCE quantified was 7.63 and 6.63 μg.L^{-1}, respectively for NaOH and KOH and pH kept alkaline value throughout the experimental time (NaOH: 11.6±0.1; KOH: 11.5±0.1) with low variation. Also, a small portion of initial $S_2O_8^{2-}$ ion concentration was reduced (Figure 2), most probably related to the $SO_4^{\bullet}$ radicals activation and also the generation of $HO^{\bullet}$ radicals [1, 2]. For NaP (not activated) and NaP/H_2O_2 tests, the interesting results for the oxidation of TCE was also verified, however, after 3 hours the TCE concentration in this time was relatively higher (17.0% and 15.6%, respectively), when compared with alkaline persulfate activation. The pH value for both experiments significantly dropped (after 311 hours: 3.3 for NaP and 2.6 for NaP/H_2O_2), compared to initial measure (Table 1). Along with this, a reduction more pronounced for $S_2O_8^{2-}$ anion in these systems was evaluated, indicating different kinetics involved in the sodium persulfate activation (alkaline and dual oxidant) and non activation system (only NaP) for the TCE oxidation. Therefore, some initial results were here presented, considered the evolution of this study.

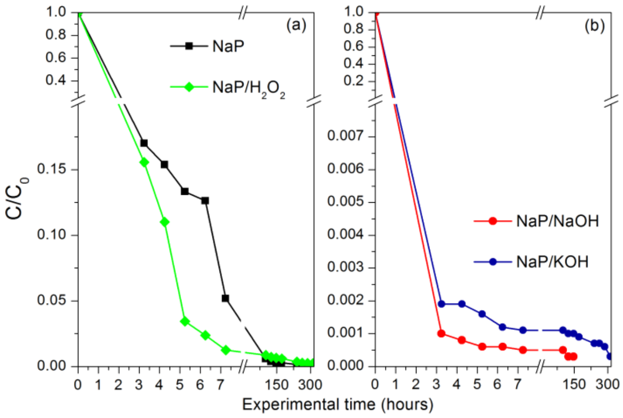

Figure 1. NaP and activated NaP applied for TCE oxidation in aqueous systems.

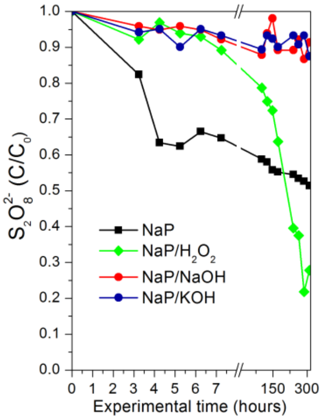

Figure 2. Concentration of $S_2O_8^{2-}$ anion during the experimental time of persulfate oxidation of TCE.

4. REFERENCES

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