Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Kinetics of Peroxyacetic Acid Formation and Decomposition in Soil-Slurry Systems

Giacomo Cleriti[a]; Daniela Zingaretti[a]; Renato Baciocchi[a]
[a] Department of Civil Engineering, University of Rome "Tor Vergata", Via del Politecnico, Rome, Italy

To cite this Article Cleriti, Giacomo , Zingaretti, Daniela and Baciocchi, Renato(2010) 'Kinetics of Peroxyacetic Acid Formation and Decomposition in Soil-Slurry Systems', Separation Science and Technology, 45: 11, 1610 — 1616
To link to this Article: DOI: 10.1080/01496395.2010.487716
URL: http://dx.doi.org/10.1080/01496395.2010.487716

Separation Science and Technology, 45: 1610–1616, 2010

ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496395.2010.487716

Kinetics of Peroxyacetic Acid Formation and Decomposition in Soil-Slurry Systems

Giacomo Cleriti, Daniela Zingaretti, and Renato Baciocchi
Department of Civil Engineering, University of Rome "Tor Vergata",
Via del Politecnico, Rome, Italy

In this work, a comprehensive study on the kinetics of formation and decomposition of peroxyacetic acid in soil-slurry systems is presented. A model of peroxyacetic acid formation and decomposition was developed. It includes the kinetics of formation from hydrogen peroxide and acetic acid, peroxyacetic acid decomposition by hydrolysis and hydrogen peroxide and peroxyacetic acid decomposition due to interactions with soil components. The experimental results were properly described by the proposed model, where all kinetic constants were obtained through independent experiments or by fitting of the experimental data. Three application strategies of the process were compared, showing that the highest peroxyacetic concentration in the system is obtained when the soil is added after equilibrium with acetic acid and hydrogen peroxide is achieved.

Keywords advanced oxidation processes; contaminated soil; kinetics; peroxyacetic acid

INTRODUCTION

Advanced Oxidation Processes (AOPs) are an effective class of technologies for the remediation of soil and groundwater contaminated by a wide range of organic contaminants. Different oxidant formulations have been proposed so far, including hydrogen peroxide (1–4), permanganate (5), persulfate (6–9), peroxymonosulfates (10), and ozone (11–13). More recently even peroxyacids and other organic peroxy compounds have been proposed although still in lab-scale. Peroxy organic compounds are well known selective oxidants, previously applied in different fields, such as in the pulping industry for the delignification of wood pulp in order to avoid the degradation of cellulose and hemicellulose fibers. Peroxyacids are formed by the reaction between organic acids (e.g., acetic, propionic etc.) and hydrogen peroxide. They are relatively selective oxidizing agents, so they can target the electron dense structures, typically met in aromatic rings, double and triple bonds, and ether bonds with no further competing reactions with other organic compounds (like carbohydrates) (14,15). During a peroxyacid treatment, the formation of the oxidizing agent can be seen as a cyclical process during which hydrogen peroxide reacts with an organic acid (e.g., acetic acid) in solution to form peroxyacid. The peroxyacid may react either directly with the target compound, or with water, by regenerating the organic acid and by forming an hydroxyl cation; hydroxyl radical may also be released during the process.

The application of peroxyacetic acid for the treatment of contaminated sediments was first investigated by Levitt et al. (14), that achieved a 70–100% removal efficiency of α-metylnaphtalene in 24 hours. The process was then extended to other PAHs and soil or sediment types (15–18). In all these works, experimental treatment tests were performed by adding acetic acid and hydrogen peroxide to soil slurry systems, in order to generate peroxyacetic acid directly in the reaction system. N'Guessan et al. (16) compared these experimental conditions with the use of commercial peroxyacetic acid, observing in the latter case a faster oxidation reaction. The authors motivated this result, suggesting that the reaction with commercial peroxyacetic acid followed a different pathway. This explanation does not look convincing, since the chemical compounds involved are the same. On the contrary, it seems possible that such a difference can be due to a higher concentration of commercial peroxyacetic acid with respect to the one achieved when it is formed from acetic acid and hydrogen peroxide. Besides, although different papers have dealt with the kinetics of peroxyacetic acid formation in aqueous systems (19,20), no papers dealing with soil slurry systems were found.

The goal of this work is to investigate the kinetics of formation and reaction of peroxyacetic acid in soil slurry systems. To this aim, a kinetic model of peroxyacetic acid formation and decomposition was developed. It includes the kinetics of formation from hydrogen peroxide and acetic acid, peroxyacetic acid decomposition by hydrolysis, and hydrogen peroxide and peroxtacetic acid decomposition by disproportion due to interactions with

---

Received 5 December 2009; accepted 12 February 2010.

Address correspondence to Renato Baciocchi, Department of Civil Engineering, University of Rome "Tor Vergata", Via del Politecnico 1, Rome, Italy. E-mail: baciocchi@ing.uniroma2.it

soil components. The model results were compared with experimental data in aqueous and soil slurry systems, allowing to validate the model assumptions.

MODELLING

Synthesis of peroxyacetic acid in aqueous media is usually performed starting from hydrogen peroxide and acetic acid, through the following reaction:

$$CH_3COOH + H_2O_2 \Leftrightarrow CH_3COOOH + H_2O \qquad (1)$$

This is a reversible process, characterized by similar values of the kinetic constants of the forward and backward reactions. Therefore, an equilibrium condition is achieved, where usually both products and reagents co-exist.

The chemical kinetics of the reversible reaction (1) in aqueous phase has been described by Zhao et al. (19), assuming first-order kinetics with respect to acetic acid (A) and hydrogen peroxide (B) for the forward reaction and with respect to peroxyacetic acid (C) and water (D) for the backward one. Thus, the mass balance for hydrogen peroxide (B) and peroxyacetic acid (C) in a batch system can be written as follows:

$$\frac{dC_B}{dt} = k_{2obs}C_C C_D - k_{1obs}C_A C_B \qquad (2)$$

$$\frac{dC_C}{dt} = k_{1obs}C_A C_B - k_{2obs}C_C C_D \qquad (3)$$

where C_A, C_B, C_C, C_D are the concentrations of acetic acid, hydrogen peroxide, peroxyacetic acid, and water at a given time t, respectively, whereas k_{1obs} and k_{2obs} are the observed rate constant for the forward and backward reactions, respectively.

According to mass conservation, the concentration of acetic acid (C_A) and water (C_D) at a given time t can be calculated from their initial concentrations and from peroxyacetic acid concentration at the same time t, as follows:

$$C_A = C_{A0} - C_C \qquad (4)$$

$$C_D = C_{D0} - C_C \qquad (5)$$

Replacing Eqs. (4) and (5) in Eqs. (2) and (3), the following expressions are obtained: :

$$\frac{dC_B}{dt} = k_{2obs}C_C(C_{D0} + C_C) - k_{1obs}(C_{A0} - C_C)C_B \qquad (6)$$

$$\frac{dC_C}{dt} = k_{1obs}C_B(C_{A0} - C_C) - k_{2obs}C_C(C_{D0} + C_C) \qquad (7)$$

The values of both observed rate constant k_{1obs} and k_{2obs} were found to depend from H^+ concentration, according to the following equations (19):

$$k_{1obs} = k_1[H^+]^{\alpha};\ k_{2obs} = k_2[H^+]^{\beta} \qquad (8)$$

where k_1 and k_2 are the intrinsic rate constants for the forward and reverse reaction, respectively whereas α and β are the corresponding reaction orders.

The intrinsic rate constant at different temperatures can be calculated from the following expression (19):

$$k_1 = 6.83 \times 10^8 \exp\left(-\frac{57846.15}{RT}\right) \qquad (9)$$

$$k_2 = 6.73 \times 10^8 \exp\left(-\frac{60407.78}{RT}\right) \qquad (10)$$

The H^+ ions concentration is clearly a function of the concentration of the different acidic compounds in solution. In this case, they obviously include acetic acid and peroxyacetic acid, but also sulphuric acid, that is commonly added as catalyst for accelerating the achievement of equilibrium conditions (19):

$$[H^+] = \frac{2C_{so_4^{2-}} + \sqrt{(2C_{so_4^{2-}})^2 + 4(C_{A0} - C_c)K_{C,AA}}}{2} \qquad (11)$$

where $K_{C,AA}$ is the dissociation constant of acetic acid, given by:

$$K_{C,AA} \approx \frac{1.75 \times 10^{-5}}{\exp\Bigg\{ -2.342\Bigg[\sqrt{(C_{A0} - C_C)\alpha + 3C_{SO_4^{2-}}} \Big/ \left(1 + \sqrt{(C_{A0} - C_C)\alpha + 3C_{SO_4^{2-}}}\right) - 0.30[(C_{A0} - C_C)\alpha + 3C_{SO_4^{2-}}]\Bigg]\Bigg\}} \qquad (12)$$

The model outlined above does not take into account the decomposition of hydrogen peroxide and peroxyacetic acid. As reported by Zhao et al. (20), peroxyacetic decomposition in aqueous phase can take place by disproportion to acetic acid and oxygen, but it was found to be negligible at operating temperatures up to 50°C. As far as hydrogen peroxide is concerned, it is well known that this oxidant is rather stable in a pure aqueous system.

The situation becomes completely different if the same reactions discussed above take place in soil slurry systems. In this case, decomposition of both hydrogen peroxide and peroxyacetic acid through disproportion reactions may get accelerated by heterogeneous catalysis induced by the soil particles.

For this reason, both kinetics of decomposition were accounted for and added to the model developed above (Eqs. (6) and (7)), thus providing:

$$\frac{dC_B}{dt} = k_{2obs}C_C(C_{D0} + C_C) - k_{1obs}(C_{A0} - C_C)C_B - k_B C_B \qquad (13)$$

$$\frac{dC_C}{dt} = k_{1obs}C_B(C_{A0} - C_C) - k_{2obs}C_C(C_{D0} + C_C) - k_C C_C \qquad (14)$$

TABLE 1
Results of soil characterization

Parameter	Value
Moisture (%)	23.4
pH	9.2
Fixed solids (%)	97.5
Volatile solids (%)	2.5
TOC (%)	3.5
TOD (mg/kg) (*)	20.9
Iron (mg/kg)	320
Manganese (mg/kg)	10

(*) Total oxidant demand, measured using potassium permanganate.

where k_B and k_C are the decomposition kinetic constants of hydrogen peroxide and peroxyacetic acid, respectively, where first-order decomposition with respect to each peroxy compound was considered.

MATERIAL AND METHODS

Materials

Acetic acid glacial, hydrogen peroxide 30% wt/wt solution, sulphuric acid 96%, potassium iodide, sodium thiosulfate, cerium (IV) sulphate 0.1 mol/l volumetric solution, starch paste solution 1% in water, sodium sulphate anhydrous, ferroin solution, dichloromethane, were purchased by Sigma-Aldrich (HPLC-grade or ACS-grade). Distilled water was provided by a GFL 2008 generator. The soil used for the slurry phase experiments was collected from an Italian refinery site and homogeneized. It was a sandy soil characterized by a TOC of 1.2 g/kg and a slight contamination (below 200 mg/kg) mainly from heavy hydrocarbons (Diesel Range Oil). The results of the soil characterization are reported in Table 1.

Kinetics of Peroxyacetic Acid Formation and Reaction

The kinetics of peroxyacetic acid formation in aqueous phase from hydrogen peroxide and acetic acid were performed in 50 ml stirred water solution at 25°C and with 4 M H_2O_2. Acetic acid concentration (8.2 M) and sulphuric acid concentration (0.3 M added as catalyst) were set using the same operating conditions used by Zhao et al. (19). The reaction kinetics was monitored by collecting 0.1 ml samples at regular intervals within 24 hours, which were then analyzed for hydrogen peroxide and peroxyacetic acid concentration, as reported in the following. This test allowed to evaluate the time required to achieve the maximum (equilibrium) peroxy-acetic acid concentration. Kinetics of hydrogen peroxide decomposition in soil slurry systems were performed with a 1 to 5 soil/liquid ratio, using again a 4 M hydrogen peroxide concentration and 0.3 M sulphuric acid. Kinetics of peracetic acid formation and decomposition in soil slurry systems were also evaluated using the same initial acetic acid (8.2 M), hydrogen peroxide (4 M), and sulphuric acid (0.3 M) concentrations adopted in the aqueous phase experiments, with a 1 to 5 soil/liquid weight ratio. Three tests were performed at these operating conditions, although with a different operating strategy, which consisted of changing the time of soil addition to the reaction system. Namely, the soil was added after 3 h and 18 h from the beginning of the experiment and at the beginning of the experiment (t = 0 h), together with the addition of acetic acid, hydrogen peroxide, and sulphuric acid as catalyst.

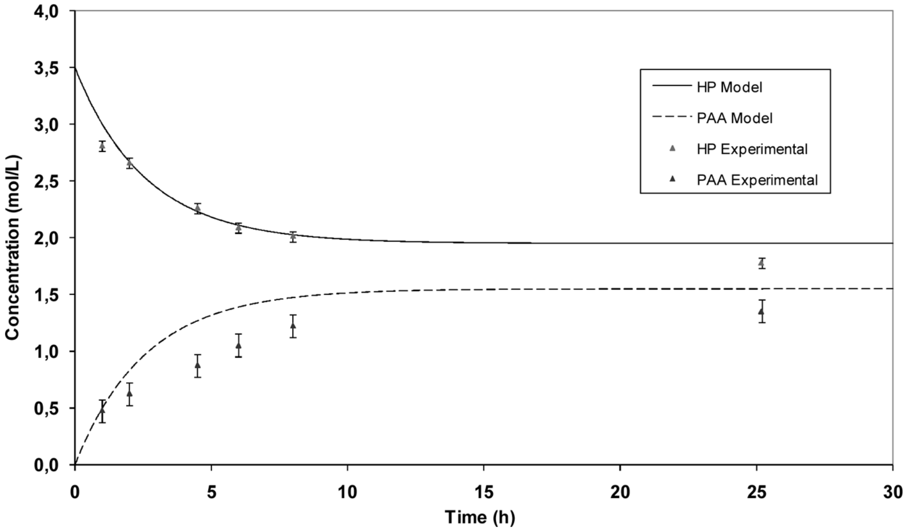


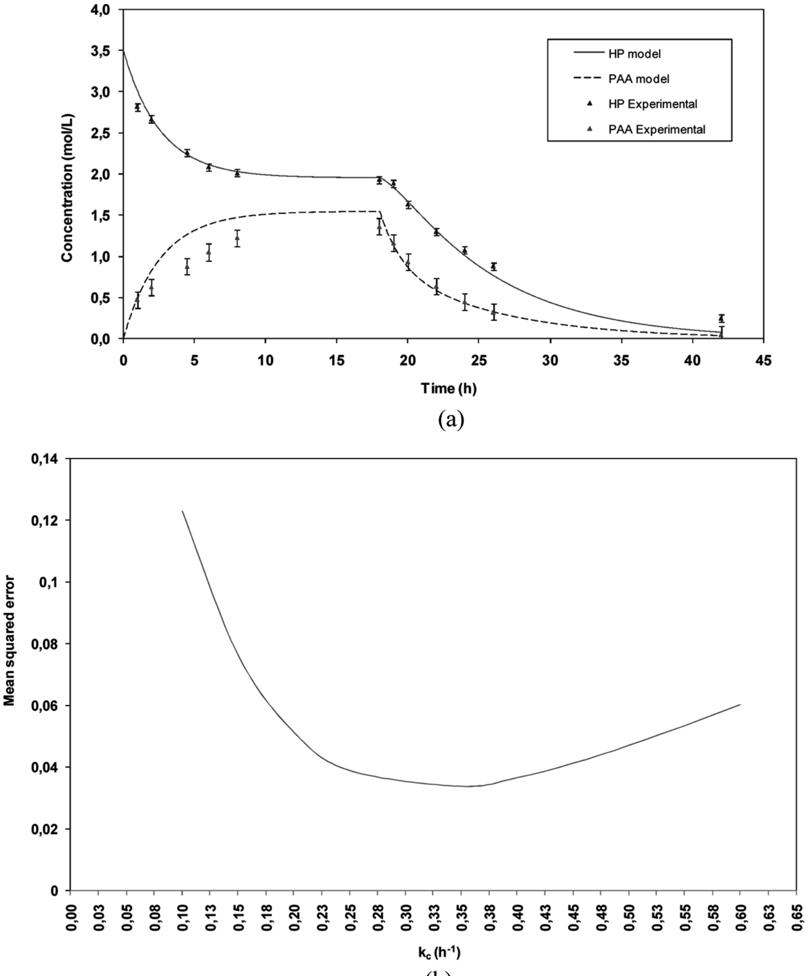
FIG. 1. Kinetics of peroxyacetic acid formation in aqueous phase. Experimental data (symbols) and model predictions (dashed/continuous) of peroxyacetic acid (PAA) and hydrogen peroxide (HP) concentration.

A sequential analytical method based on ceric sulphate for hydrogen peroxide, followed by iodometric titration of peroxyacetic acid was applied for evaluating the concentration of the peroxy compounds (21).

RESULTS AND DISCUSSION

The kinetics of peroxyacetic acid formation in aqueous phase from hydrogen peroxide and acetic acid are reported in Fig.1. The experimental data clearly show the decrease of hydrogen peroxide that, reacting with acetic acid, leads to the formation of peracetic acid, until chemical equilibrium is established. The kinetic model, given by Eqs. (6) and (7), assuming negligible dissociation of acetic acid in Eq. (12) and the kinetic constant values given by Eqs. (8–10) was observed to predict reasonably well the experimental data, suggesting that equilibrium was achieved after around 12 hours. Under these conditions, the maximum experimental (equilibrium) peroxyacetic concentration was 1.3 M, against 1.5 M predicted by the model.

Figure 2a reports the results of the soil-slurry experiment performed by adding the soil at the end of the aqueous phase experiment (i.e., after 18 h), when equilibrium concentrations of hydrogen peroxide and peroxyacetic acid had been largely achieved. The experimental data show a decrease of the concentration of both peroxy compounds with time after soil has been added (i.e., after 18 h), due to their disproportion induced by the heterogeneous catalytic effect of the soil particles. These data were fitted with the kinetic model given by Eqs. (13) and (14). In this model, the kinetic constant of peroxyacetic acid formation and decomposition, k_{1obs} and k_{2obs}, were evaluated using Eqs. (8–10); the rate constant of hydrogen peroxide decomposition, k_B, was evaluated by fitting the data collected through independent hydrogen peroxide



(a)

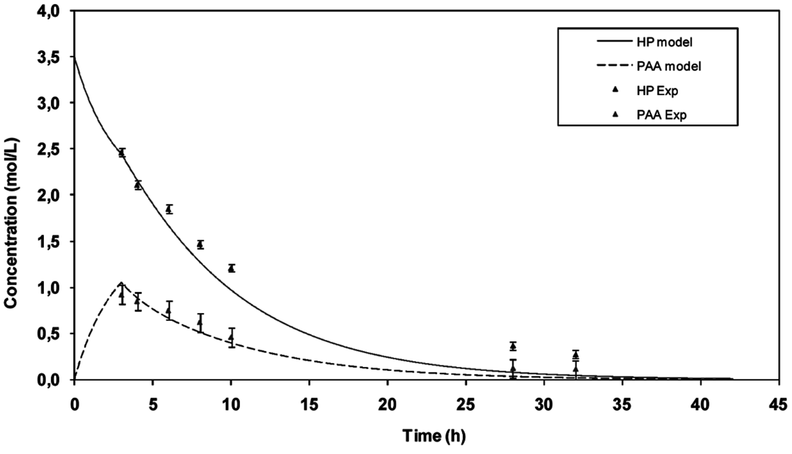
(b)

FIG. 2. Kinetics of peroxyacetic acid formation and reaction in soil slurry systems with soil addition at t = 18 h; (a) experimental data (symbols) and model predictions (dashed/continuous lines) of peroxyacetic acid (PAA) and hydrogen peroxide (HP) concentration. (b) mean squared error between experimental PAA concentration and model results.

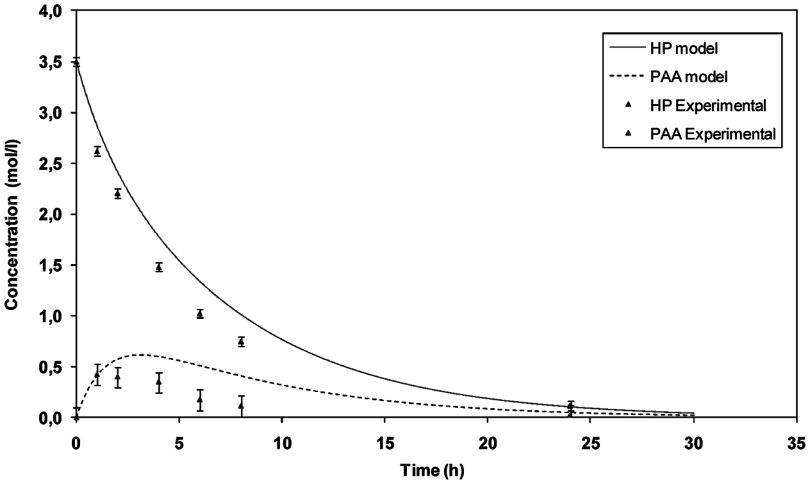
decomposition experiments (results not shown), which provided a value $k_B = 0.043\,h^{-1}$. As far as the decomposition of peroxyacetic acid is concerned, it was not possible to perform independent decomposition experiments, since also the commercial peroxy-acetic contains hydrogen peroxide and acetic acid in an unknown proportion. Thus, the rate constant of peroxyacetic acid decomposition, k_C, was evaluated by fitting the experimental peroxyacetic acid concentration data, measured after soil addition at t = 18 h, reported in Fig. 2a. As shown in Fig. 2b, the best fitting, corresponding to the minimum mean squared error between experimental data and model results, was obtained for $k_C = 0.358\,h^{-1}$. The difference between the values of the rate constant of hydrogen peroxide and peroxyacetic acid decomposition suggests that hydrogen peroxide is far more stable than peroxyacetic acid in the presence of soils.

The values of the kinetic constant calculated as above were then implemented in the full kinetic model given by Eqs. (13) and (14), providing the results shown in Fig. 2a, which shows a quite good agreement between model and experimental data.

Finally, the kinetic model has been applied in order to predict the peroxyacetic acid and hydrogen peroxide concentration in soil slurry systems for two different application strategies: in the first one (Fig. 3a), the soil was supposed to be added only 3 hours after the beginning of the experiment; in the second experiment (Fig. 3b), the soil was supposed to be added at the beginning of the experiment, together with hydrogen peroxide and acetic acid. The same initial concentration of all reagents was assumed. The results reported in Fig. 3 clearly show that the application route strongly affects the concentration of peroxyacetic acid in the reaction system. Namely, if the soil and the reagents (i.e., hydrogen peroxide and acetic acid)) are added at the same time (Fig. 3b), the maximum peroxyacetic acid concentration is only 0.7 M and it readily



(a)



(b)

FIG. 3. Kinetics of peroxyacetic acid formation and reaction in soil slurry systems: (a) soil addition at t = 3 h, (b) soil addition at t = 0 h. Experimental data (symbols) and model predictions (dashed/continuous lines) of peroxyacetic acid (PAA) and hydrogen peroxide (HP) concentration.

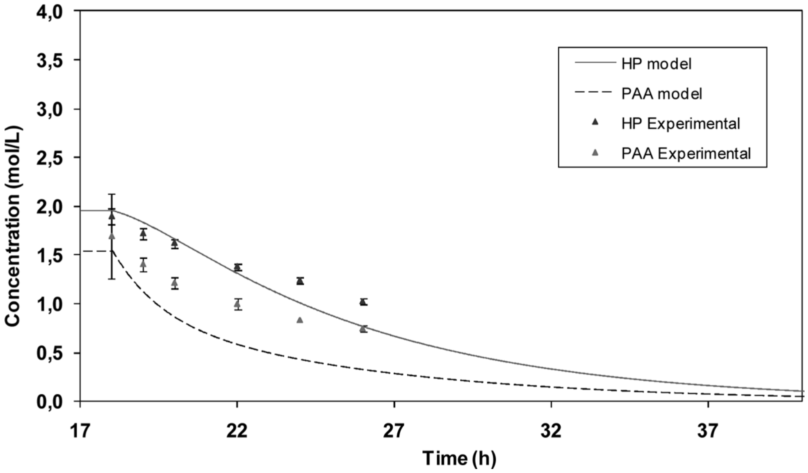


FIG. 4. Kinetics of peroxyacetic acid formation and reaction in soil slurry systems using an uncontaminated soil sample: soil addition at t = 18 h. Experimental data (symbols) and model predictions (dashed/continuous lines) of peroxyacetic acid (PAA) and hydrogen peroxide (HP) concentration.

disappears from the reaction system after a few hours. The situation slightly improves when the soil is added after 3 hours, with a 1 M maximum peroxy-acid concentration. The best application strategy is surely the one reported in Fig. 2a, with soil added only after the achievement of the equilibrium conditions between acetic acid, hydrogen peroxide, and peroxy-acetic acid, which allowed to achieve a 1.5 M maximum concentration of the latter compound. This result suggests that the latter application strategy (Fig. 2a), should provide the best potential for the treatment of contaminated soils.

All the results discussed above were obtained on a HC-contaminated soil. In order to assess the influence of the contamination on the behavior of peroxy-acetic acid, a further test was performed using an uncontaminated soil sample collected in the same site of the contaminated one used for the other experiments. Figure 4 reports the results of the soil-slurry experiment performed by adding this soil when equilibrium concentrations of hydrogen peroxide and peroxyacetic acid had been achieved. The model results shown in this figure are the same calculated with the model parameters discussed above and evaluated by fitting the data obtained on the contaminated soils. The results, compared with the ones obtained on the contaminated soil, reported in Fig. 2a, clearly show that the pattern of hydrogen peroxide and peroxyacetic acid concentration after the soil addition are quite similar in both cases, although peroxyacetic acid and hydrogen peroxide looks slightly more stable in the uncontaminated soils.

CONCLUSIONS

The formation of peroxyacetic acid from acetic acid and hydrogen peroxide and its behavior in soil slurry systems was described by a kinetic model, which was developed by upgrading the model already available for aqueous systems with the terms accounting for the decomposition of hydrogen peroxide and peroxyacetic acid catalyzed by the soil particles. The model is mostly predictive, since it relies on the rate constant of the forward and backward reaction of peroxyacetic acid formation from acetic acid and hydrogen peroxide, that are available from the literature, and on the rate constant of hydrogen peroxide decomposition, that can be evaluated through an independent and simple soil slurry test. The only parameter that needs to be evaluated through fitting of the peroxyacetic concentration data is the rate constant of peroxyacetic decomposition taking place in the presence of soils.

The experimental results obtained using a real soil were properly described by the proposed model, where all kinetic constants were obtained through independent experiments, except for the rate constant of peroxyacetic acid decomposition, that were evaluated by fitting of the experimental peracetic acid concentration data. Three application strategies of the process were compared, showing that the highest peroxyacetic concentration in the system can be obtained by adding the soil after equilibrium with acetic acid and hydrogen peroxide is achieved. Using this application strategy, the same concentration of commercial peroxyacetic acid should be obtained. This could allow to achieve the same treatment efficiency for the remediation of contaminated soils, but avoiding the safety issues connected to transport and storage of peroxyacetic acid, and reducing the treatment costs. Such an application strategy should also allow to achieve the best treatment efficiency when applying peroxyacetic acid to a contaminated soil.

REFERENCES

1. Watts, R.J.; Teel, A. (2005) Chemistry of modified Fenton's reagent (catalyzed H2O2 propagations-CHP) for in situ soil and groundwater remediation. *J. Envital. Eng-ASCE*, 131: 612–622.
2. Watts, R.J.; Stanton, P.C. (2002) Mineralization of a sorbed polycyclic aromatic hydrocarbon in two soils using catalyzed hydrogen peroxide. *Water Res.*, 36: 4283–4292.
3. Watts, R.J.; Stanton, P.C. (1999) Mineralization of sorbed and NAPL-phase hexadecane by catalyzed hydrogen peroxide. *Water Res.*, 33: 1405–1414.
4. Kong, S.H.; Watts, R.J. (1998) Treatment of petroleum-contaminated soils using iron mineral catalyzed hydrogen peroxide. *Chemosphere*, 37: 1473–1482.
5. De Souza e Silva, P.T.; da Silva, V. (2009) Potassium permanganate oxidation of phenantrene and pyrene in contaminated soils. *J. Hazard. Mater.*, 168: 1269–1273.
6. Liang, C.; Lee, I. (2008) Persulfate oxidation of trichloroethylene with and without iron activation in porous media. *Chemosphere*, 70: 426–435.
7. Kislenko, V.N.; Berlin, A.A. (1996) Kinetic of the oxidation of organic substances by persulfate in the presence of variable-valence metal ions. *Kinet. Catal.+.*, 37: 767–774.
8. Liang, C.; Huang, C.F. (2008) Potential for activated persulfate degradation of BTEX contamination. *Water Res.*, 42: 4091–4100.
9. Liang, C.; Lee, I. (2008) In situ iron activated persulfate oxidative fluid sparging treatment of TCE contamination a proof of concept study. *J. Contam. Hydrol.*, 100: 91–100.
10. Rastogi, A.; Al-Abed, S.R. (2009) Sulfate radical-based ferrous-peroxymonosulfate oxidative system for PCBs degradation in aqueous and sediment systems. *Appl. Catal. B-Environ.*, 85: 171–179.
11. O'Mahony, M.M.; Dobson, A.D.W. (2006) The use of ozone in the remediation of polycyclic aromatic hydrocarbon contaminated soil. *Chemosphere*, 63: 307–314.
12. Rivas, J.; Gimeno, O. (2009) Ozone treatment of PAH contaminated soils: Operating variables effect. *J. Hazard. Mater.*, 169: 509–515.
13. Yu, D.Y.; Kang, N. (2007) Characteristics in oxidative degradation by ozone for saturated hydrocarbons in soil contaminated with diesel fuel. *Chemospheres*, 66: 799–807.
14. Levitt, S.J.; N'Guessan, A.L.; Rapp, K.L.; Nyman, M.C. (2003) Remediation of a-methylnaphtalene contaminated sediments using peroxy acid. *Water Research*, 37: 3016–3022.
15. N'Guessan, A.L.; Levitt, S.J.; Nyman, N.C. (2004) Remediation of benzo(a)pyrene in contaminated sediments using peroxy-acid. *Chemosphere*, 55: 1413–1420.
16. N'Guessan, A.L.; Carignan, T.; Nyman, M.C. (2004) Optimization of the peroxy acid treatment of a-methylnaphtalene and benzo(a)pyrene in sandy and silty clay sediments. *Environmental Science and Technology*, 38: 1554–1560.
17. N'Guessan, A.L.; Alderman, N.S.; O'Connor, K.; Abdul Rahim, A.Z.; Nyman, M.C. (2006) Peroxy-acid treatment of selected PAHs. *International Journal of Environment and Waste Management*, 1: 61–74.
18. Alderman, N.S.; N'Guessan, A.L.; Nyman, N.C. (2007) Effective treatment of PAH-contaminated Superfund site soil with the peroxy-acid process. *Journal of Hazardous Materials*, 146: 652–660.
19. Zhao, X.; Zhang, T.; Zhou, Y.; Liu, D. (2007) Preparation of peracetic acid from hydrogen peroxide Part I: Kinetics for peracetic acid synthesis and hydrolysis. *Journal of Molecular Catalysis A: Chemicals*, 271: 246–252.
20. Zhao, X.; Cheng, K.; Hao, J.; Liu, D. (2008) Preparation of peracetic acid from hydrogen peroxide Part II: Kinetics for spontaneous decomposition of peracetic acid in the liquid phases. *Journal of Molecular Catalysis A: Chemical*, 284: 58–68.
21. Greenspan, F.P.; MacKellar, D.G. (1948) Analysis of aliphatic per acids. *Anal. Chem.*, 20: 1061–1063.