Iron in Water: Study of Iron Removal Kinetics in Chemically Reconstituted Waters: Application to Groundwater of South Pout (PS2 Site)

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Abstract

The goal of this topic is a synthesis of the main characteristics of iron in groundwater and the oxidation process used to remove it. Indeed, the kinetics of chemical oxidation of iron (II) was examined with reconstituted water (distilled water + iron sulphate) and proceeded to the application in the groundwater samples taken from *South Pout* (Senegal) precisely in the drilling **PS2**. The sources of iron are natural or anthropogenic. In Senegalese waters, its content is variable and sometimes exceeds the standards of potability. Despite the diversification of iron removal process, chemical oxidation is the most used solution in drinking water treatment plants in Senegalese rural areas. Applied oxidation processes such as aeration and chlorination, however, are insufficient to produce drinking water with an iron concentration in accordance with standards of potability.

Keywords

Iron, Kinetics, Chemical Oxidation, Groundwater, Drilling

1. Introduction

In abundance, iron is the fourth element in the Earth's crust and the first among heavy metals [1]. It is found mainly in the form of Fe(II) or Fe(III). In reducing medium, as in some groundwater, some lakes or reservoirs, and in the absence of sulphide and carbonate, soluble Fe(II) can be found in high concentration [2]. The presence of iron in natural sources of water supply is attributable to the decomposition of rock and minerals, acidic mine drainage waters, sewage effluent

and releases from industrial sectors that process iron [3] [4].

In Senegal, the concentration of iron in groundwater is generally less than 10 mg·L^{-1}. Data obtained from Senegalese Water Company (SWC) between 2000 and 2014 indicate that the concentration varies between less than 0.02 mg·L^{-1} and 5.76 mg·L^{-1} in central, southern and eastern areas of Senegal [5].

Iron is an essential part of nutrition; it is included in the composition of cytochromes, porphyrins and metalloenzymes. Iron deficiency, however, may have some effects, including poor mental development and activity in children [6], elevated catecholamine levels, and a tendency for agitation in children [7], loss of work performance in adults and, in severe cases, anemia and compromised oxygenation [8].

It is possible to reduce the excessive amount of iron in groundwater by several conventional techniques including the chemical method. The fundamental principle of the chemical removal of iron is based on an oxidation-reduction reaction between Fe^{2+} iron and a more or less strong oxidant. The reaction is then the following [9]:

$$\text{Fe}^{2+} + \text{oxidant} \rightarrow \text{Fe(OH)}_{3(s)} + \text{reducer} \tag{1}$$
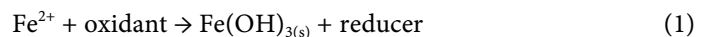
The oxidants used can be oxygen (aeration is then sufficient to remove iron), potassium permanganate, chlorine, chlorine dioxide or ozone. The precipitates formed during the oxidation are then removed by filtration on sand or bilayer medium. In the case of aeration, for example, and therefore of the oxidation of iron by dissolved oxygen, studies have made it possible to determine in kinetic oxidation. The equation is as follows [9]:

$\Rightarrow$ Iron [10]:

$$-\frac{d\left[\text{Fe}^{2+}\right]}{dt} = K \cdot \left[\text{Fe}^{2+}\right] \cdot \left[\text{O}_2\right] \cdot \left[\text{OH}^-\right]^2 \tag{2}$$

which can be simplified in:

$$-\frac{d\left[\text{Fe}^{2+}\right]}{dt} = K_1 \cdot \left[\text{Fe}^{2+}\right]; \text{ avec } K_1 = K \cdot \left[\text{O}_2\right] \cdot \left[\text{OH}^-\right]^2 \tag{3}$$

In the present study, the chemical oxidation of iron by various oxidants oxygen (O$_2$), potassium permanganate (KMnO$_4$), sodium hypochlorite (NaClO) was studied during the treatment of iron-doped water in beakers. The kinetics of chemical oxidation of iron has been examined with reconstituted waters and to determine the kinetics model that describes our experimental results well. The main objective of this paper is to study the iron removal capacity present in groundwater samples in contact with oxidants and even the oxidant with the best treatment rate.

2. Material and Methods

2.1. Methodologies and Material

Beaker tests are carried out in order to study the oxidation capacities of iron in

contact with different oxidants with variable pH. The oxidation kinetics of iron is carried out by oxygen, potassium permanganate and finally sodium hypochlorite. For this, a solution of water doped with 5 mg·L^{-1} Fe^{2+} is prepared from iron sulphate (FeSO$_4$). The amount of oxidant (O$_2$, KMnO$_4$, NaClO) added is evaluated on the basis of the stoichiometric proportion of the reactions; in this case, 0.73 mg O$_2$/L should be bubbled, add 3.61 mg KMnO$_4$/L and 2.4 mg NaClO/L theoretical masses respectively in each beaker. As a result of these tests, we have moved to the application phase to remove iron from groundwater. The sampling was done in South Pout (Dakar/Senegal) precisely in the drilling **PS2** (Figure 1).

The physic and chemical characterization study (Table 1) of the groundwater in South Pout (Senegal) is focused in situ measurements (pH, electrical conductivity, turbidity) and the laboratory determination of the major components and metallic trace elements (chloride Cl$^-$, sulphates SO$_4^{2-}$, nitrates NO$_3^-$, nitrites NO$_2^-$, calcium Ca^{2+}, magnesium Mg^{2+}, total iron (Fe^{2+} and Fe^{3+}), manganese Mg^{2+}, etc.).

2.2. Dosage Protocol

In order to be in the calibration range, [Fe^{2+}]$_0$ < 6 mg·L^{-1}, we prepared an initial solution of 4.10^{-5} mol·L^{-1} iron sulfate (FeSO$_4$) dissolved in distilled water. In 100 mL volumetric flasks numbered 1 to 7, put the reagent volumes indicated in the following table, and adjust to the mark with distilled water (Table 2) and (Figure 2).

After adjusting to volume, mix thoroughly and let sit for 5 to 10 minutes. Meanwhile, prepare the reference, and then measure the optical density at 510 nm relative to the reference solution. Prepare a volumetric flask of 100 mL of the
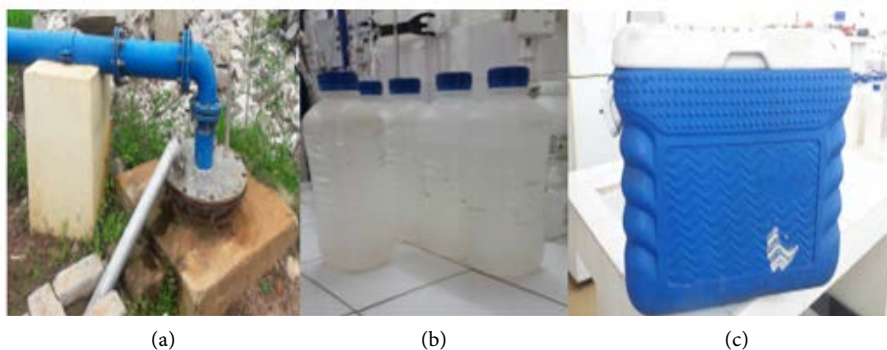

| (a) | (b) | (c) |

Figure 1. (a) South pout drilling (PS2); (b) Polyethylene bottles; (c) Cooler at 4˚C.

Table 1. Physic and chemical characterization of groundwater in South Pout (Senegal).

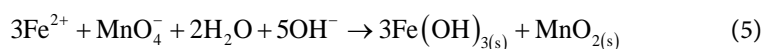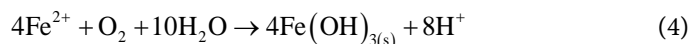|	South Pout (PS2 Site)										
	Tablecloth Captured: Maestrichtian										
Parameters	Cond µs·cm^{-1}	pH	Turb NTU	Cl$^-$ ˚F	SO$_4^{2-}$ mg·L^{-1}	Ca^{2+} ˚F	Mg^{2+} ˚F	NO$_3^-$ mg·L^{-1}	NO$_2^-$ mg·L^{-1}	**Fer total** mg·L^{-1}	Mn^{2+} mg·L^{-1}
Value	567	7.01	13.40	3.00	5.00	5.60	21.60	0.60	0.004	**5.76**	0.054

Table 2. Preparation of solutions for the calibration curve.

Initial solution (mL)	Hydroxylammonium chloride 10% (mL)	Sodium acetate 2M (mL)	Ortho-Phenanthroline 0.25% (mL)	Final concentration $[Fe^{2+}]$ (mole·L^{-1})
1	10	1	8	4×10^{-7}
2	10	2	8	8×10^{-7}
3	10	3	8	1.2×10^{-6}
4	10	4	8	1.6×10^{-6}
5	10	5	8	2×10^{-6}
6	10	6	8	2.4×10^{-6}
7	10	7	8	2.8×10^{-6}

(a)   (b)

Figure 2. (a) Preparation of the calibration range; (b) UV-Visible spectrophotometer.

reference solution by pouring 10 mL of methylene chloride of 10% hydroxy-lammonium, 5 mL of 2M sodium acetate, 8 mL of ortho-phenanthroline 0.25% and make up to gauge with distilled water (Figure 2).

2.3. Oxidation of Iron (II)

The principle is to dissolve the theoretical mass of the oxidant (O_2, $KMnO_4$, $NaClO$) in the already known concentration of the iron (II) solution, while checking the pH and temperature, allowing the oxidation reaction to proceed with thorough agitation of the reaction medium (Figure 3). At the end of each operation, the precipitates deposited at the bottom of the beaker before proceeding to the spectrometric determination of the mixture are filtered. The oxidation reactions are summarized as following:

$$4Fe^{2+} + O_2 + 10H_2O \rightarrow 4Fe(OH)_{3(s)} + 8H^+ \tag{4}$$

$$3Fe^{2+} + MnO_4^- + 2H_2O + 5OH^- \rightarrow 3Fe(OH)_{3(s)} + MnO_{2(s)} \tag{5}$$

$$2Fe^{2+} + HClO + 5H_2O \rightarrow 2Fe(OH)_{3(s)} + Cl^- + 5H^+ \tag{6}$$

3. Results and Discussion

3.1. Iron Calibration Curve

The calibration curve is then obtained from the measurement of the absorbance of each standard solution (Figure 4).
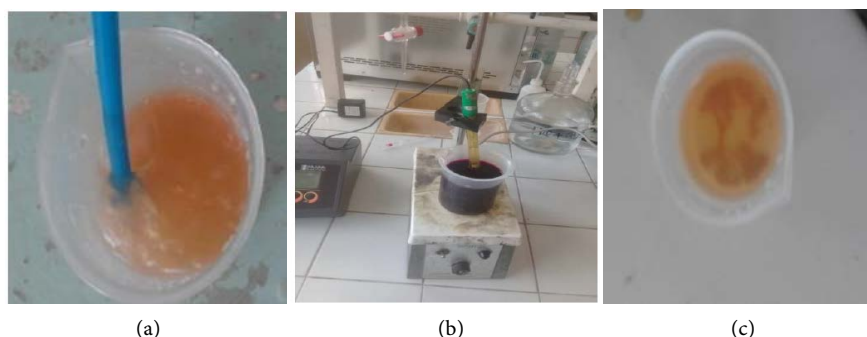
Figure 3. (a) Oxidation of iron by Oxygen (O_2); (b) Oxidation of iron by potassium permanganate ($KMnO_4$); (c) Oxidation of iron by sodium hypochlorite (NaClO); ([Fe^{2+}]$_0$ = 5 mg·L^{-1}, P_{atm} = 1.013 bar and T = 21°C ± 1°C).
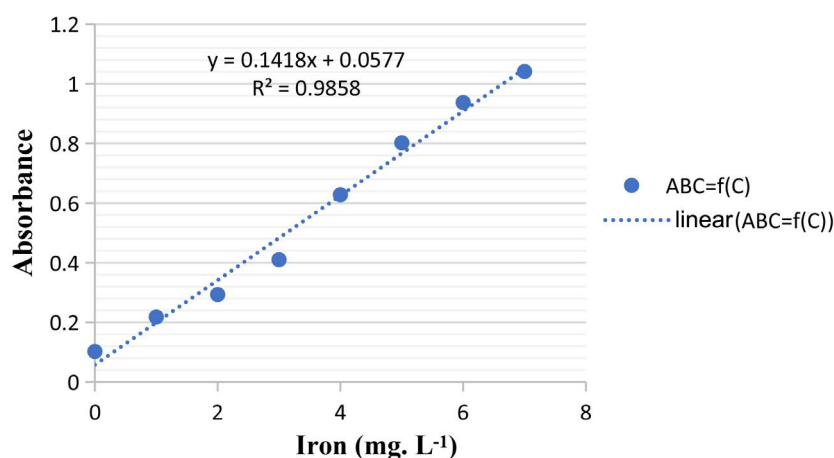

Figure 4. Calibration curve of the absorbance of the solution as function of concentration.

The concentration of the sample taken is calculated by multiplying by 10 the concentration obtained (to take into account the dilution factor). The corresponding iron concentration is calculated from the following relation:

$$\left[Fe^{2+}\right]_{total} = \frac{ABS - 0.0577}{0.1418} \qquad (7)$$

3.2. Oxidation Kinetics

A series of tests in beaker is carried out in order to verify the kinetics of oxidation of iron by different oxidants as a function of the pH. For this, the pH of the water is adjusted by concentrated hydrochloric acid (HCl) and sodium hydroxide (NaOH) solutions. The results obtained for each of the oxidants used are shown in **Figures 5-7**.

Fe^{2+} oxidation tests in beaker are carried out at three different pH ranges, pH = 3.4 - 3.6; pH = 7.3 - 7.5 and pH = 9.8 - 10. Indeed, for **Figure 5**, the results show that at pH = 9.8 in less than five minutes, 95% of ferrous iron (Fe^{2+}) is removed whereas at pH = 7.3, only 60% of ferrous iron has disappeared. In the other hand, at acid pH, there is no removal of iron, and then iron is not oxidized by
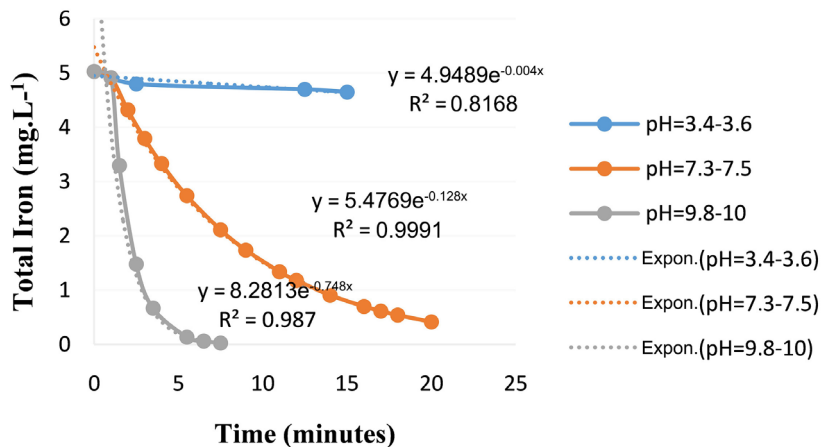
Figure 5. Kinetics oxidation of iron by oxygen (O_2) at different pH; ($[Fe^{2+}]_0 = 5$ mg·L^{-1}, $P_{atm} = 1.013$ bar, T = 21˚C ± 1˚C and redox potential = 300 mV).

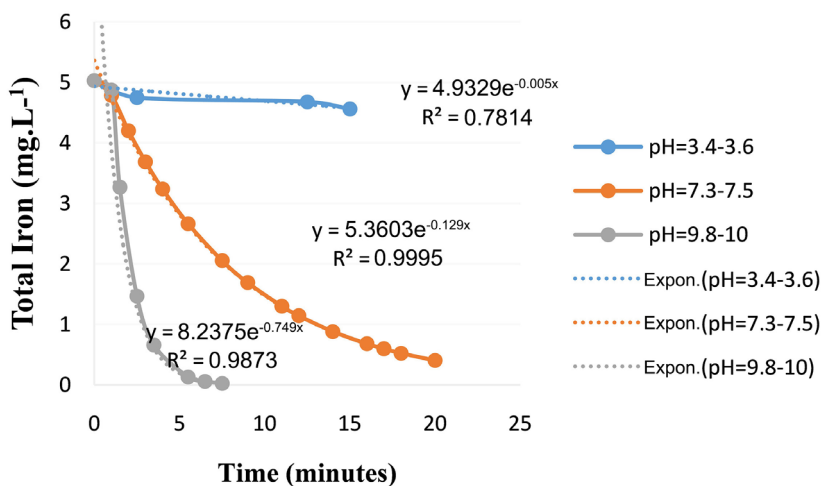**Figure 6.** Kinetics of iron oxidation by potassium permanganate ($KMnO_4$) at different pH; ($[Fe^{2+}]_0 = 5$ mg·L^{-1}, $P_{atm} = 1.013$ bar, T = 21˚C ± 1˚C and redox potential = 300 mV).

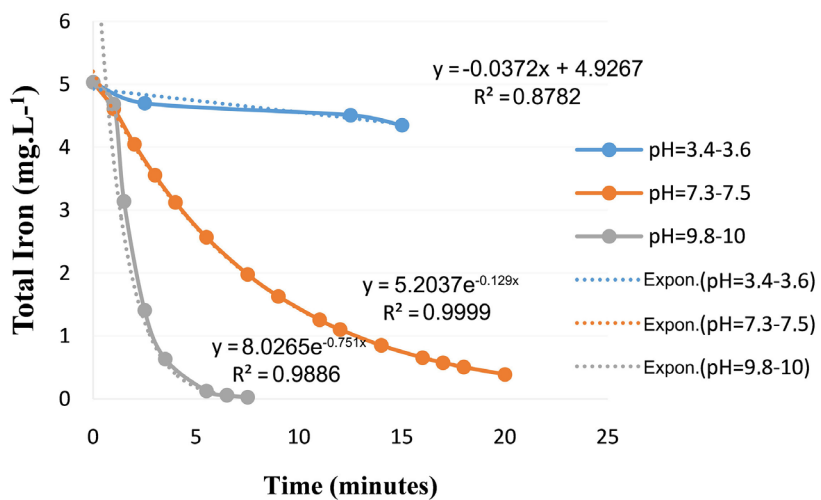**Figure 7.** Kinetics of iron oxidation by sodium hypochlorite (NaClO) at different pH; ($[Fe^{2+}]_0 = 5$ mg·L^{-1}, $P_{atm} = 1.013$ bar, T = 21˚C ± 1˚C and redox potential = 300 mV).

oxygen at acidic pH. Depending on the pH of the water, the kinetics will be more or less rapid. It is possible to find the order of the kinetics by applying a trend line to the curves determined experimentally (here the exponential type allows to find an order line). This kinetics can therefore be modeled as follows:

$$-\frac{d\left[Fe^{2+}\right]}{dt} = Kt \tag{8}$$

These results are consistent with the results obtained by [11] [12] which showed that, in the presence of iron, a significant fraction of the iron can be oxidized by O_2 and at a relatively basic pH (Figure 5).

Beaker tests were also carried out with potassium permanganate ($KMnO_4$) as oxidant at different pH. The kinetics of oxidation of dissolved iron is reported in the graph of Figure 6. The results show that at pH = 9.85 in less than five minutes, 96.85% of ferrous iron (Fe^{2+}) is removed while at pH = 7.5, only 63% of the ferrous iron is removed. In the same way, at acidic pH, the removal of iron is very weak or even non-existent. The kinetics of chemical oxidation of experimental values is written by the kinetic model of the equation above. These results are consistent with the work of some authors [11] [12] who showed that, in the presence of iron, a significant fraction of iron can be oxidized by $KMnO_4$ as well.

With regard to the removal of ferrous iron by sodium hypochlorite (NaClO) at different pH, the dissolved iron disappears after five minutes which is consistent with the work of KNOCKE *et al.*, (1990a) who showed that the oxidation kinetics of Fe^{2+} by NaClO was very fast. The results (Figure 7) show that at pH = 9.8 in less than five minutes, 98.25% ferrous iron (Fe^{2+}) is removed and has the most effective oxidant. The theoretical stoichiometric dose of NaClO is therefore too much to eliminate iron. Hence the possibility of the theoretical quantity being put in contact with the sample reduces by 1/3.

3.3. Removal of Iron in the Waters of South Pout (PS2 Site)

The oxidation capacity makes it possible to find the maximum amount of iron that the oxidant is capable of reducing Fe^{2+} ions to Fe^{3+}. To find the oxidation capacities, groundwater samples of 5.403 mg Fe^{2+}/L with an initial pH of 7.01 are regulated at pH = 9.8. In three 100 mL beakers, we put 30 mL of the sample plus the calculated theoretical oxidant mass. This suspension is placed in a rotary shaker for 5 minutes so that the maximum oxidation capacity of the iron is reached. The results of this experiment make it possible to calculate the percentage of iron eliminated by the various oxidants. They are presented in Table 3.

The results presented above make it possible to evaluate the treatment efficiency of the three oxidants used for the removal of iron (II) in groundwater of South Pout (PS2 site).

We recorded a percentage of iron removed of 93.74% for the use of oxygen as oxidant. Indeed, the iron is very unstable in the water in the presence of oxygen as seen on the diagram of Pourbaix of the iron [13], which is why the removal of

Table 3. Chemical oxidation of groundwater of South Pout (PS2 site).

V sample (mL)	Oxidizing mass (mg)	Contact time (minutes)	Measured initial concentration (mg·L⁻¹)	Final measured concentration (mg·L⁻¹)	% of Total Iron eliminated
Oxygen (O_2) at pH = 9.8					
30	0.73	5	5.403	0.321	93.74
Potassium permanganate ($KMnO_4$) at pH = 9.8					
30	3.61	5	5.403	0.285	94.43
Sodium hypochlorite ($NaClO$) at pH = 9.8					
30	2.4	5	5.403	0.205	96.01

this element in presence only of aerated water (9.5 mg O_2/L) is very fast unless the pH of the water is basic (pH = 9.8). A second oxidant is then tested, potassium permanganate, oxidizing stronger than oxygen. For this experiment, the stoichiometric dose is respected, *i.e.* a dose of 3.61 mg $KMnO_4$/L starting from a theoretical initial concentration of Fe^{2+} of 5 mg/L. Potassium permanganate is a very strong oxidizer that achieves the almost complete oxidation of soluble iron almost instantaneously. Indeed, the results show that after one minute of experience, 85% of the soluble iron in groundwater is removed at pH = 9.8. This oxidant seems to be the most suitable for the removal of Mn^{2+}, however, it should not be introduced in excess under penalty of a pink coloration of the samples. It is therefore necessary to dose it well so that it is present in order to only remove the soluble iron present in the water to be treated. The results show that the most efficient oxidant is sodium hypochlorite ($NaClO$), with a percentage of iron eliminated by 96% under the conditions of these tests. These results confirm the kinetics of iron oxidation by sodium hypochlorite ($NaClO$).

The advantage of these three systems is the need for a single filtration stage. By comparing them with each of the systems, it can be seen that the difference in the percentage of iron eliminated is relatively small. The difference is on average 1.58%, which could guide the choice of the type of oxidant to use. From the economic point of view, the use of oxygen as an oxidant would result in a lower investment cost compared to potassium permanganate ($KMnO_4$) or sodium hypochlorite ($NaClO$) because it is sufficient to air ventilate to reduce Fe^{2+}.

4. Conclusions

Three oxidants, two of which were marketed for their potential iron (II) removal, were tested in this topic: oxygen (O_2), potassium permanganate ($KMnO_4$), sodium hypochlorite ($NaClO$). The batch tests (solution of water doped with 5 mg Fe^{2+}/L prepared from iron sulphate ($FeSO_4$)) bring out the following results:

- iron removal efficiency increases with pH;
- the kinetics of chemical oxidation of the iron of our experimental results is of exponential type which allows to find a one (1) order;
- under the conditions of these tests, the results of sodium hypochlorite ($NaClO$)

show that at pH = 9.8 in less than five minutes, 98.25% of ferrous iron (Fe^{2+}) is removed and presents the most effective oxidant.

The tests carried out on the groundwater of South Pout (Dakar/Senegal) precisely on PS2 drilling to remove iron give the following main results:

- results similar to those obtained in batch iron solutions prepared in terms of percentage of removal. Batch tests on reconstituted water are therefore recommended to study the kinetics of oxidation;

- iron is rapidly oxidized by dissolved oxygen (O_2) when the pH is adjusted to 9.8, and therefore it is not necessary to use potassium permanganate ($KMnO_4$) or sodium hypochlorite (NaClO) to oxidize it. This is justified by high economic costs related to the chemical implementation of the process using $KMnO_4$ or NaClO as oxidant compared with O_2;

- the results show that the most efficient oxidant is sodium hypochlorite (NaClO), with a percentage of iron removed by 96% under the conditions of these tests on groundwater of PS2. These results confirm the kinetics of iron oxidation by sodium hypochlorite (NaClO).

In the economic approach, the use of oxygen as an oxidant would result in a lower investment and exploitation cost compared to potassium permanganate or sodium hypochlorite because a simple aeration is enough to reduce the dissolved iron.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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