

## Iron Removal from Water by Precipitation in Bicarbonated Water: Influence of Crystallization Companions

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### Abstract

Natural waters, especially in the Tahoua region, which are very salty, have a very high concentration of iron. They are the site of a significant precipitation of  $\text{Fe}(\text{OH})_3$  in the water supply pipes. Ferrhydrite is formed in Dan Daji Illela's waters at  $30^\circ\text{C}$ . In order to understand the behavior of natural waters, we studied the influence of ions frequently encountered in them ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$ , and  $\text{SO}_4^{2-}$ ) on the precipitation of iron in a bicarbonate medium. This study will allow us to determine if the addition of a particular ion can modify the behavior of water. Thus we studied the influence of  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  ions at  $30^\circ\text{C}$  on the polymorphic transformations of  $\text{Fe}(\text{OH})_3$ . The experiments were performed in the bicarbonate medium with a concentration of 488 mg/L, in the presence of 5 mg/L of iron, at  $\text{pH}_i$  (initial pH at the beginning of the experiment) and at room temperature for a precipitation time of 60 min. The  $\text{Na}^+$  and  $\text{Cl}^-$  ions have no effect on the precipitation of  $\text{Fe}(\text{OH})_3$  and promote the formation of the three varieties : ferrihydrite, lepidocrocite and goethite.  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  ions inhibit the formation of  $\text{Fe}(\text{OH})_3$ . The  $\text{SO}_4^{2-}$  ions are directed towards the formation of the three varieties with the predominance of lepidocrocite.  $\text{Ca}^{2+}$  ions direct towards the formation of the three varieties with the predominance of goethite. The  $\text{Mg}^{2+}$  ions orient towards the formation of the three varieties with the predominance of ferrihydrite.

**Keywords:** Iron removal; Crystallization companions; Precipitation; Bicarbonate water

### Introduction

Iron is the second most abundant metal in the earth's crust and the fourth most abundant element in the earth's crust [1-5]. The presence of iron in natural waters is generally due to the decomposition of minerals, rocks and discharges from industrial sectors containing iron [6,7]. An overload of iron in the human body can lead to primary hemochromatosis (poor regulation of iron absorption by the intestine) and even liver cancer (risk of liver cancer), these disorders generally occur when the concentration of iron in water is greater than 10 mg/L [7,8]. At concentrations above 0.3 mg/L (WHO Standard), the presence of iron in water intended for human consumption causes many inconveniences, usually of anesthetic and organoleptic nature.

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The existence of iron in these waters at very high concentrations can lead to the degradation of water storage and transport structures [6,9-11]. The treatment of iron in water is the subject of numerous studies, including chemical oxidation by more or less strong oxidants (chlorine, potassium permanganate, oxygen and ozone) and biological processes involving microorganisms, catalytic processes based on adsorption and oxidation on the surface of a specific material and membrane processes [12-15]. These treatment methods are not without limits in their application, both in terms of the use of certain materials and the control of certain physio-chemical parameters and especially in terms of the accessibility of the necessary materials and chemical products. This is why we have also considered another alternative technique to remove iron by precipitation in the bicarbonate medium in the form of an oxyhydroxide. The choice of this method is based on the cost/ efficiency ratio and ease of handling. The use of natural groundwater allows tests to be carried out that is close to reality but does not make it possible to study the influence of certain elements that frequently coexist with iron in water, such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ . In order to bypass this limit and avoid the presence of other unfixed elements that may exist in groundwater, the use of water containing only bicarbonate was the solution considered, to properly control the study of the influence of these parameters.

## Materials and Methods

### Principle of iron precipitation by aeration

In our study for deferrization by precipitation, we used an assembly consisting of a 1 liter beaker and a mechanical agitator (FIG. 1).

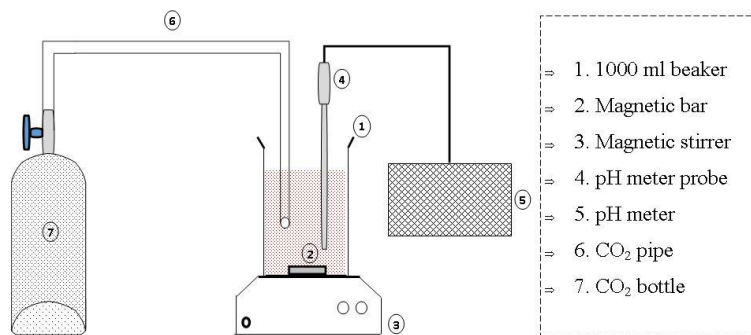
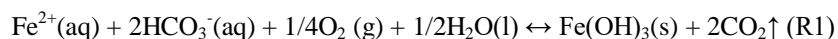


FIG. 1. Experimental set-up for  $\text{Fe}(\text{OH})_3$  precipitation test.

All manipulations were carried out in the beaker under magnetic stirring (500 rpm) at atmospheric pressure and  $30^\circ\text{C}$  in order to increase the contact between the oxygen in the air and the  $\text{Fe}^{2+}$  ions in the solution, which is the driving principle behind the evolution of the system leading to the oxidation of the  $\text{Fe}^{2+}$  ions and the precipitation of  $\text{Fe}(\text{OH})_3$ . Iron solutions were prepared by introducing variable amounts of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  iron sulfate heptahydrate into bicarbonated water. The bicarbonated water was prepared by dissolving varying amounts of  $\text{NaHCO}_3$  in distilled water. The amount of iron is introduced after setting a desired initial pH value by splashing  $\text{CO}_2$ . The stopwatch and the stirrer are triggered at the same time for a duration of 60 minutes, which corresponds to the time set for all the experiments. Agitation introduces atmospheric oxygen into the solution. Contact of the solution with atmospheric air causes the release of dissolved  $\text{CO}_2$ , which leads to alkalization of the medium, resulting in an increase in pH. This increase in pH favors the oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  and the precipitation of  $\text{Fe}(\text{OH})_3$  [12]. The overall precipitation response is as follows:



The iron hydroxide obtained according to the R1 reaction is very unstable, which explains its evolution towards another iron oxyhydroxide more thermodynamically stable; it is lepidocrocite in its non-hydrated form according to the following reaction:



Several series of tests were performed by adding variable amounts of these salts: NaCl, NaSO<sub>4</sub>.7H<sub>2</sub>O, MgCl<sub>2</sub>.6H<sub>2</sub>O, CaCl<sub>2</sub>.H<sub>2</sub>O in 1000 ml of bicarbonate solution with a concentration [HCO<sub>3</sub><sup>-</sup>]=488 mg/L; pH<sub>i</sub>=8; [Fe<sup>2+</sup>]<sub>0</sub>=5 mg/l and T=30°C. To determine the concentration of iron in solution during the precipitation experiment, 1 ml samples were taken using a 5 ml syringe with a 0.45 μm membrane filtration system. Samples of 1 mL were taken every 2 minutes, then every 10 minutes of precipitation. To the 1 mL sampled, we successively added 1 mL hydroxylamine, 2 ml ammonium acetate and 2 mL orthophenanthroline. After introducing these reagents, the mixture is completed to 50 mL with distilled water in a 50 mL vial. Iron levels were analyzed using a Zuzi Spectrophotometer Model 4101 spectrophotometer at a wavelength of 510 nm. The pH is measured using a pH meter marked VWR pHenomenal pH 1100 H. In order to determine crystallographic phases of obtained precipitates, Fourier Transform Infrared spectroscopy (FTIR) spectra were recorded with IRAfinity-1 FTIR spectrophotometer with KBr pellet technique at wave numbers of 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup>

## Results and Discussion

### 1. Determination of the precipitation rate

To understand the behavior of groundwater, we studied the influence of ions that are frequently encountered there such as Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>. This study determines whether the addition of a particular ion can influence iron precipitation. The influence of these parameters will be studied by comparing the deferrization rate or precipitation rate of iron hydroxide, τ<sub>p</sub> (Fe). The precipitation rate is calculated from the following equation (TABLE 1):

$$\tau_p(\text{Fe}) = \frac{[\text{Fe}]_0 - [\text{Fe}]_t}{[\text{Fe}]_0} \times 100$$

[Fe]<sub>0</sub>=The initial ionic iron concentration in mg/L

[Fe]<sub>t</sub>=The total iron concentration at a time t in mg/L

TABLE 1. Influence of ion concentrations accompanying iron precipitation.

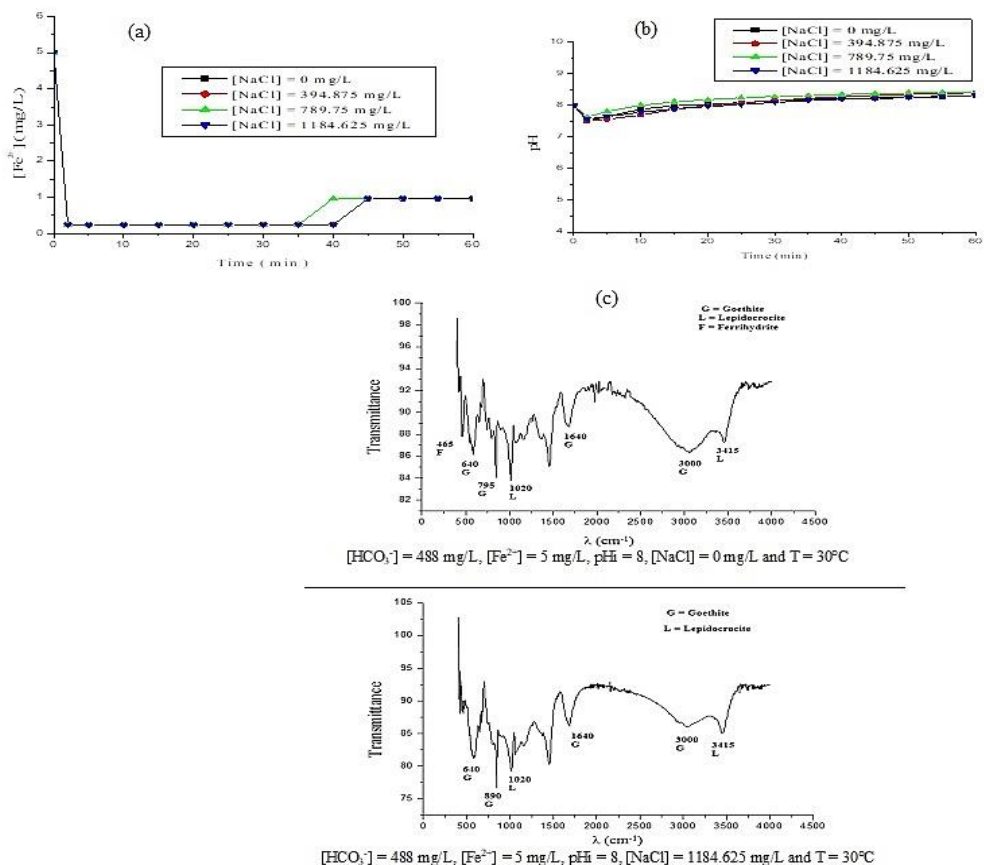
Concentration in mg/L	P <sub>t</sub> (min)	pH <sub>p</sub>	τ <sub>p</sub> (Fe) in %
[Ca <sup>2+</sup> ]=0	2	7.5	95.16
[Ca <sup>2+</sup> ]=100	2	6.96	75.72
[Ca <sup>2+</sup> ]=200	2	6.817	75.72
[Ca <sup>2+</sup> ]=400	2	6.777	75.72
[Mg <sup>2+</sup> ]=0	2	7.5	95.16
[Mg <sup>2+</sup> ]=24.3	2	7.581	75.72
[Mg <sup>2+</sup> ]=60.75	2	7.585	75.72
[Mg <sup>2+</sup> ]=121.5	2	6.52	70.8
[SO <sub>4</sub> <sup>2-</sup> ]=0	2	7.5	95.16
[SO <sub>4</sub> <sup>2-</sup> ]=300	2	7.59	85.4
[SO <sub>4</sub> <sup>2-</sup> ]=600	2	7.515	56.31
[SO <sub>4</sub> <sup>2-</sup> ]=900	2	7.581	56.31

$P_i$ : time of precipitation, the time at the beginning of the precipitation (min)

$pH_p$ : precipitation pH, the pH at the beginning of the precipitation

## 2. Influence of $Na^+$ and $Cl^-$

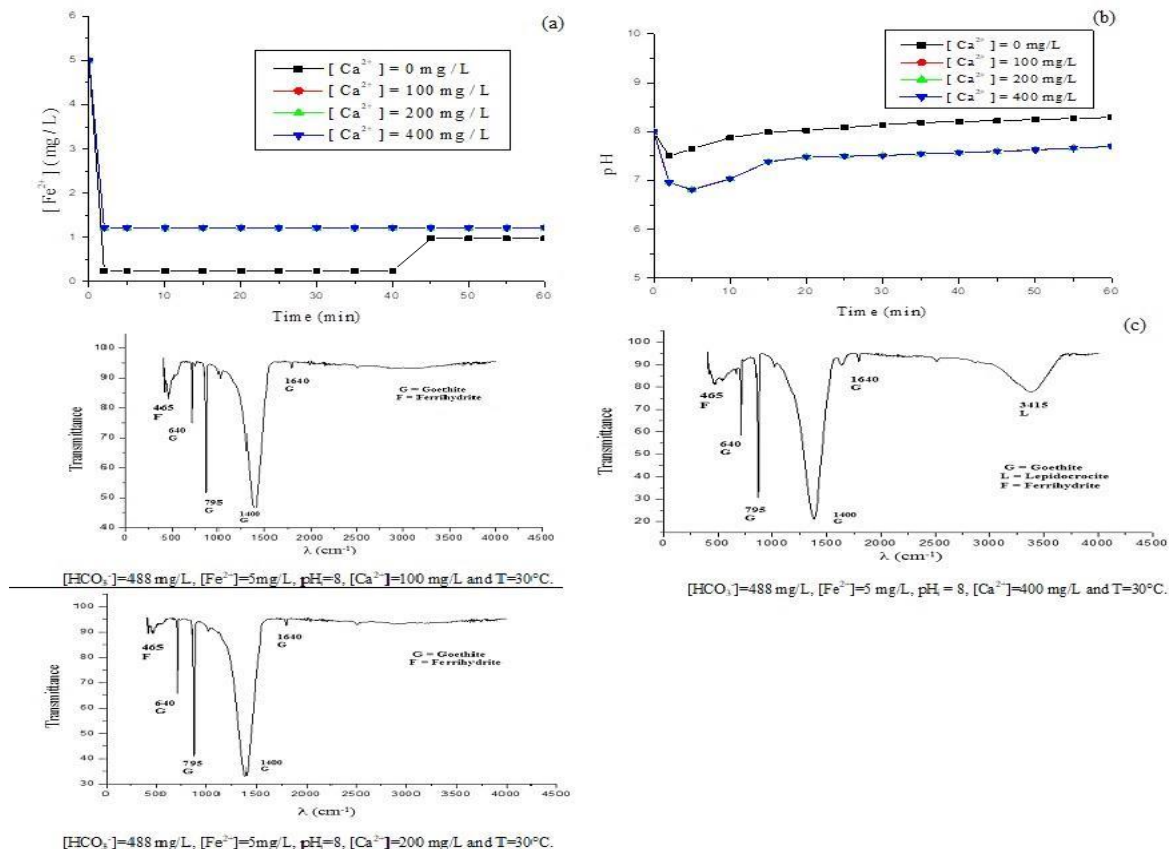
The  $Na^+$  and  $Cl^-$  ions increase ionic strength. For this purpose, we conducted four comparative tests from 0 mg/L to 1184.625 mg/L to verify if the precipitation curves were affected. The results are shown in **FIG. 1a and 1b**. **FIG. 1a** shows the evolution of iron (II) concentration over time. The curves are practically merged (**FIG. 1a**) despite an additional concentration of 1184.625 mg/L. Within the limits of the concentrations studied, the examination of these curves shows that the presence of  $Na^+$  and  $Cl^-$  ions have no effect on iron precipitation with the exception of concentration 789.75 mg/L, where at the 35<sup>th</sup> min the iron concentration increases until the 40<sup>th</sup> min and then stabilizes. These results are not in agreement with those obtained by Windsor Sung [16] where he found the presence of  $Na^+$  and  $Cl^-$  ions further increase the precipitation rate of iron(II) as their concentration increases. The pH evolution is identical for all NaCl concentrations studied. These results are similar to those obtained by Xuewu Liu et al. [17] through their studies on the stability of iron hydroxide in sodium chloride. Moreover, Ruiti et al. and Wided [7,18] showed that stirring in the open air causes a lot of pH increase. The infrared spectra obtained in **FIG. 1c** shows the existence of three varieties of crystallographic: the ferrihydrite the lepidocrocite and the goethite [5,19-22].



**FIG. 1. (a): Evolution of the dissolved iron content during precipitation for different NaCl concentrations;  $[Fe^{2+}]_0=5$  mg/L;  $[HCO_3^-]=488$  mg/L;  $pH_i=8$  and  $T=30^\circ C$ ; (b): pH evolution during iron precipitation for different NaCl concentrations;  $[Fe^{2+}]_0=5$  mg/L;  $[HCO_3^-]=488$  mg/L;  $pH_i=8$  and  $T=30^\circ C$ . (c) Infrared spectra of precipitated products.**

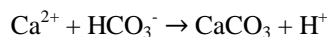
### 3. Ca<sup>2+</sup> influence

The Ca<sup>2+</sup> ions were introduced as CaCl<sub>2</sub>.H<sub>2</sub>O, since the Cl<sup>-</sup> ion was not active. For this purpose, we carried out 4 comparative tests from 0 mg/L to 400 mg/L to check if the precipitation curves were affected. The results are shown in **FIG. 2a and 2b**. The analysis of the curves presented in **FIG. 2a** shows a drop in Fe<sup>2+</sup> content with or without the addition of Ca<sup>2+</sup> after 2 minutes of precipitation.



**FIG. 2: (a): Evolution of the dissolved iron content during precipitation for different Ca<sup>2+</sup> concentrations; [Fe<sup>2+</sup>]<sub>0</sub>=5 mg/L; [HCO<sub>3</sub><sup>-</sup>]=488 mg/L; pH<sub>i</sub>=8 and T=30°C; (b): pH evolution during iron precipitation for different Ca<sup>2+</sup> concentrations; [Fe<sup>2+</sup>]<sub>0</sub>=5 mg/L; [HCO<sub>3</sub><sup>-</sup>]=488 mg/L; pH<sub>i</sub>=8 and T=30°C; (c): Infrared spectra of precipitated products.**

Beyond 2 minutes of precipitation, the curves were merged for concentrations 0 mg/L and 100 mg/L and concentrations 200 mg/L and 400 mg/L. For Ca<sup>2+</sup> 200 mg/L and 400 mg/L concentrations the drop was less significant than for 0 mg/L and 100 mg/L concentrations. For Ca<sup>2+</sup> 0 mg/L and 100 mg/L concentrations the content drops to 0.242 mg/L or a rate of 95.16% and for Ca<sup>2+</sup> 200 mg/L and 400 mg/L concentrations the content drops to 1.25 mg/L or a precipitation rate of 75.72%. This shows that the presence of Ca<sup>2+</sup> decreases the precipitation rate of Fe<sup>3+</sup> to Fe(OH)<sub>3</sub> and high concentrations of Ca<sup>2+</sup> inhibit the precipitation of Fe(OH)<sub>3</sub>. These results can be explained by the fact that in the bicarbonate medium the Ca<sup>2+</sup> ions react with HCO<sub>3</sub><sup>-</sup> and precipitate as CaCO<sub>3</sub> depending on the reaction:



This same phenomenon has been observed by Wided et al. [18] when working with high  $\text{Ca}^{2+}$  concentrations where iron (II) has a low inhibitory effect on  $\text{CaCO}_3$  precipitation. This explains the low pH for high  $\text{Ca}^{2+}$  concentrations (FIG. 2b) compared to pH for low concentrations. After the pH drop, we observed a progressive evolution of the pH indicating the competition between the production of  $\text{H}^+$  (R6) ions and the degassing of  $\text{CO}_2$  which overrides the production of  $\text{H}^+$  ions. Therefore, calcium ions decrease the  $\text{pH}_p$  precipitation pH from 7.50 in the absence of  $\text{Ca}^{2+}$  to 6.950; 6.817 and 6.777 respectively at calcium concentrations of 100 mg/L, 200 mg/L and 400 mg/L. In FIG. 2c the IR spectra show a predominance of goethite, a slight increase in lepidocrocite and residual ferrihydrite [5,19-23].

#### 4. $\text{Mg}^{2+}$ Influence

Magnesium was introduced as  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  since it was seen that  $\text{Cl}^-$  ions have no effect. The concentrations studied are: 0 mg/L, 24.3 mg/L, 60.75 mg/L, and 121.5 mg/L. The results are shown in FIG. 3a and 3b. According to these curves, the  $\text{Fe}^{2+}$  content falls with or without the addition of  $\text{Mg}^{2+}$  after 2 minutes of precipitation (FIG. 3a).

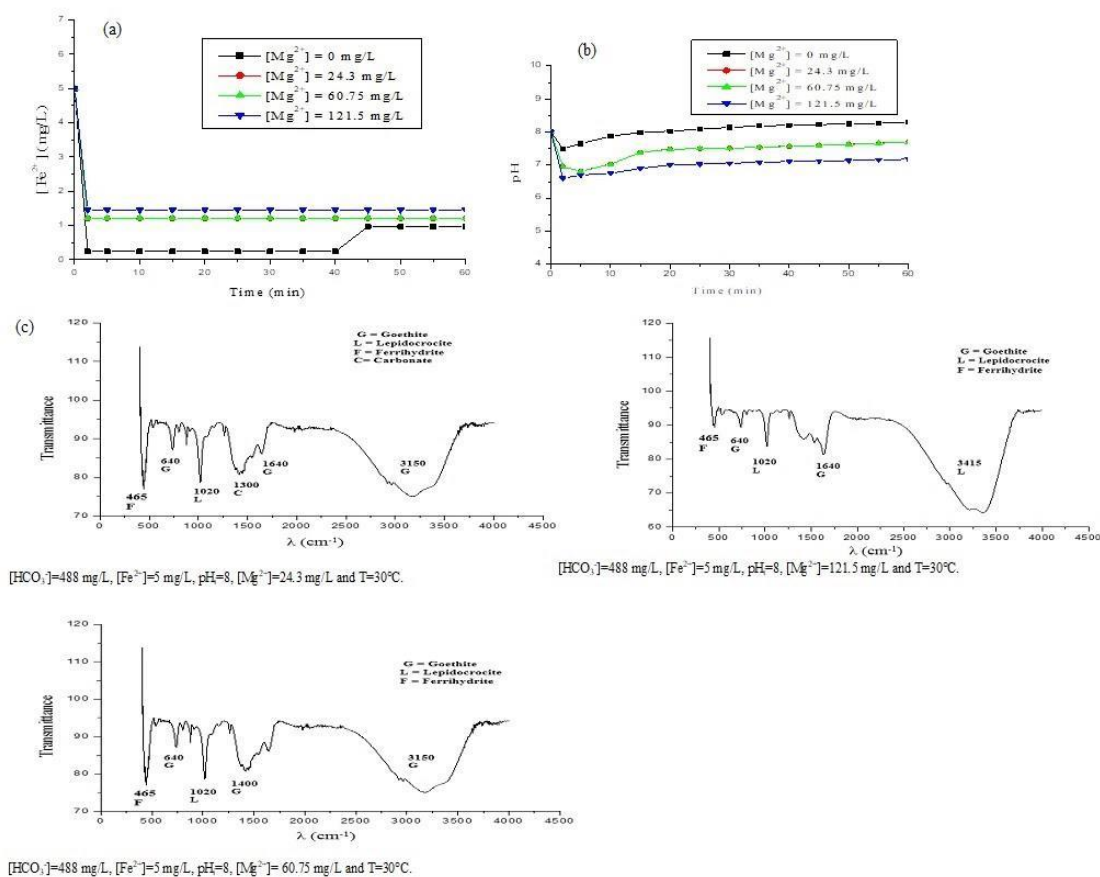
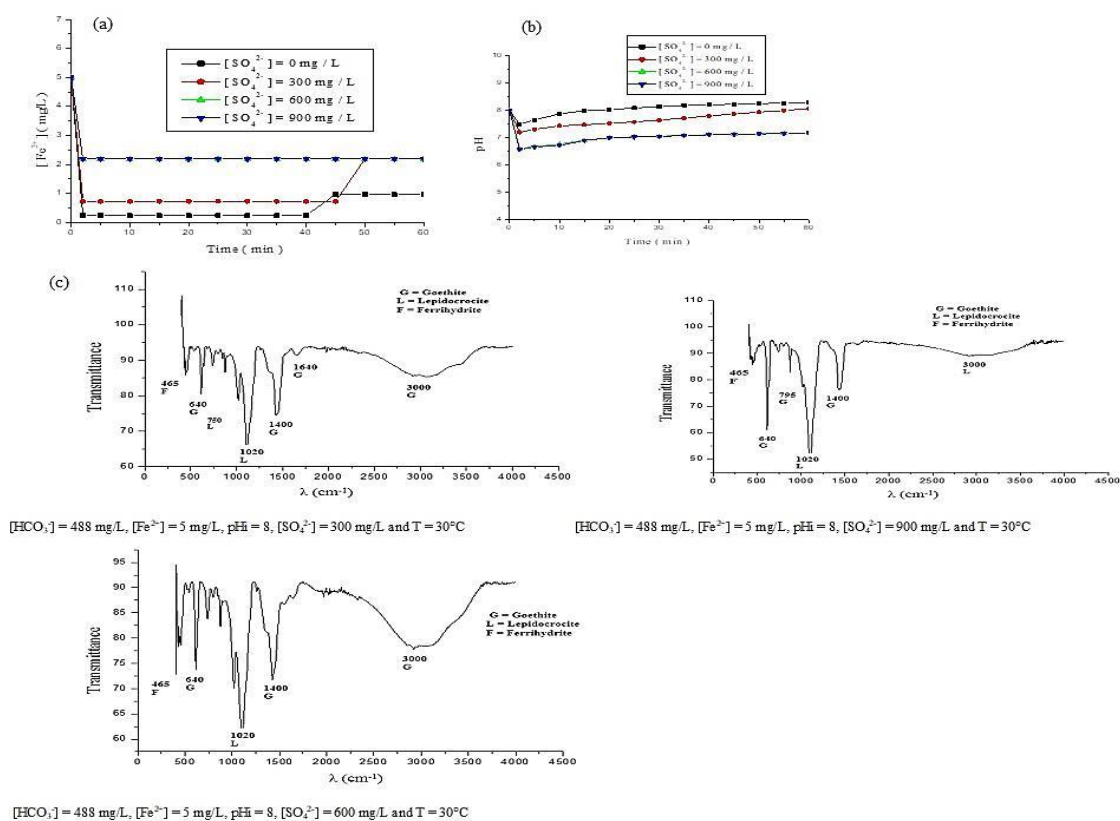


FIG. 3. (a): Evolution of the dissolved iron content during precipitation for different concentrations of  $\text{Mg}^{2+}$ ;  $[\text{Fe}^{2+}]_0=5$  mg/L;  $[\text{HCO}_3^-]=488$  mg/L;  $\text{pH}_i=8$  and  $T=30^\circ\text{C}$ ; (b): Evolution of pH during precipitation for different concentrations of  $\text{Mg}^{2+}$ ;  $[\text{Fe}^{2+}]_0=5$  mg/L;  $[\text{HCO}_3^-]=488$  mg/L;  $\text{pH}_i=8$  and  $T=30^\circ\text{C}$ ; (c): Infrared spectra of precipitated products.

Beyond 2 minutes of precipitation, the curves are merged for the concentrations of  $Mg^{2+}$  0 mg/L and 24.3 mg/L and stabilize at  $[Fe^{2+}] = 0.242$  mg/L, or a precipitation rate of 95.16%. For other  $Mg^{2+}$  concentrations, the higher the concentration increases, the higher the precipitation level becomes. Thus for  $[Mg^{2+}] = 60.75$  mg/L the level is reached at  $[Fe^{2+}] = 1.25$  mg/L and for  $[Mg^{2+}] = 121.5$  mg/L the level is reached at  $[Fe^{2+}] = 1.5$  mg/L or a precipitation rate of 75.72%. Thus the presence of the  $Mg^{2+}$  ion has a significant effect on growth retardation by decreasing the precipitation rate when the concentration of  $Mg^{2+}$  increases confirms the work of Santana-Casiano et al., [19]. In **FIG. 3c** the IR spectra show a predominance of ferrihydrite and a slight increase of lepidocrocite when the  $Mg^{2+}$  concentration decreases. We observed a residual goethite when the concentration of  $Mg^{2+}$  increases. This was confirmed by the presence of two humps with the disappearance of the goethite peak and the appearance of lepidocrocite peak [5,19-23].

## 5. Influence $SO_4^{2-}$

The  $SO_4^{2-}$  ions were introduced as  $Na_2SO_4 \cdot 7H_2O$  since the  $Na^+$  ion was not active. For this purpose, we carried out 4 comparative tests from 0 mg/L to 900 mg/L to check if the precipitation curves were affected. The results are shown in **FIG. 4a and 4b**. According to these curves, the  $Fe^{2+}$  content falls with or without the addition of  $SO_4^{2-}$  after 2 minutes of precipitation (**FIG. 4a**).



**FIG. 4. (a): Evolution of the dissolved iron content during iron precipitation for different concentrations of  $SO_4^{2-}$ ;  $[Fe^{2+}]_0 = 5$  mg/L;  $[HCO_3^-] = 488$  mg/L;  $pH_i = 8$  and  $T = 30^\circ C$ ; (b): pH evolution during iron precipitation for different concentrations of  $SO_4^{2-}$ ;  $[Fe^{2+}]_0 = 5$  mg/L;  $[HCO_3^-] = 488$  mg/L;  $pH_i = 8$  and  $T = 30^\circ C$ ; (c): Infrared spectra of precipitated products.**



Beyond 2 minutes of precipitation, we observe that the higher the concentration of  $\text{SO}_4^{2-}$  increases, the lower the precipitation rate decreases with higher and higher steps up to  $[\text{SO}_4^{2-}] = 600 \text{ mg/L}$ . Without sulphate the level is reached at  $[\text{Fe}^{2+}] = 0.242 \text{ mg/L}$  or a precipitation rate of 95.16%, for concentrations  $[\text{SO}_4^{2-}] = 300 \text{ mg/L}$  and  $600 \text{ mg/L}$  the levels reached are respectively  $[\text{Fe}^{2+}] = 1.25 \text{ mg/L}$ ,  $[\text{Fe}^{2+}] = 2.25 \text{ mg/L}$  and  $[\text{Fe}^{2+}] = 2.25 \text{ mg/L}$  are 85.40% and 56.31% precipitation rates. From  $[\text{SO}_4^{2-}] = 600 \text{ mg/L}$  the precipitation rate (56.31%) remains constant or the iron concentration stabilizes at 2.25 mg/L. Thus the presence of the  $\text{SO}_4^{2-}$  ion has a significant effect on growth retardation by decreasing the precipitation rate when the concentration of  $\text{SO}_4^{2-}$ . This decrease in precipitation rate in the presence of  $\text{SO}_4^{2-}$  ions can be explained by the adsorption of  $\text{SO}_4^{2-}$  ions on iron hydroxide  $\text{Fe}(\text{OH})_3$ . The adsorption of  $\text{SO}_4^{2-}$  by  $\text{Fe}(\text{OH})_3$  depends a lot on pH, in fact, the surface charge of hydrated oxides such as  $\text{Fe}(\text{OH})_3$  is strongly related to pH. In order to explain the evolution of adsorption as a function of pH, the zero charge point must be taken into account because the latter's values are very high due to the low polarization of the Fe-OH groups. According to several authors, the colloidal  $\text{Fe}(\text{OH})_3$  zero charge point is between 8.1 and 8.5 [25,26]. In this pH range, Fe-OH hydroxides are protonated to produce the  $\text{Fe-OH}_2^+$  group, which makes the charge on the surface of the ferric hydroxide positive, thus very favorable for the adsorption of sulphate ions using Coulomb attractions. This leads to the formation of the  $[\text{FeSO}_4]^+$  complex which hinders the formation of hydroxyl polymers in iron and therefore the formation of iron oxyhydroxide [27]. This explains the high pH for high  $\text{SO}_4^{2-}$  concentrations (**FIG. 4b**) compared to pH for low concentrations. In **FIG. 4c** infrared spectra show a predominance of lepidocrocite, a low increase of goethite and a residual ferrihydrite [5,19-23].

## Conclusion

From the present results, we can conclude as follows:

1. The presence of  $\text{Na}^+$  and  $\text{Cl}^-$  ions has no effect on iron precipitation
2. The presence of  $\text{Ca}^{2+}$  decreases the precipitation rate of  $\text{Fe}^{3+}$  to  $\text{Fe}(\text{OH})_3$  and high concentrations of  $\text{Ca}^{2+}$  inhibit the precipitation of  $\text{Fe}(\text{OH})_3$ . The  $\text{Ca}^{2+}$  ions promote the predominance of goethite, a slight increase in lepidocrocite and residual ferrihydrite
3. The presence of the  $\text{Mg}^{2+}$  ion has a significant effect on growth retardation by decreasing the precipitation rate when the concentration of  $\text{Mg}^{2+}$  increases. The  $\text{Mg}^{2+}$  ions promote the predominance of ferrihydrite, a slight increase in lepidocrocite and residual goethite
4. The presence of the  $\text{SO}_4^{2-}$  ions has also a significant effect on growth retardation by decreasing the precipitation rate when the concentration of  $\text{SO}_4^{2-}$  increases. The  $\text{SO}_4^{2-}$  ions promote the predominance of lepidocrocite, a low increase of goethite and a residual ferrihydrite

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## Conflicts of Interests

The authors declare that they have no conflict of interest.

## REFERENCES

1. Desjardins R, Water treatment. Edition of polytechnic School of Montreal. 1988.



2. Sergent AS. Biomineralization and reactivity of green rust carbonated by *Shewanella putrefaciens* in a firm heterogeneous system and in continuous flow. Doctoral thesis, University of Lorraine. 2012.
3. Dehou SC. Study of the properties of iron oxyhydroxides deposited on natural support: Application to the removal of iron in the water from drilling in the Central African Republic. Doctoral thesis, Lille University-Science and Technology. 2011.
4. Sara B. Thermal and photochemical reactivities of iron in aqueous solution with respect to organic molecules in homogeneous and heterogeneous phase. Master thesis in chemistry. Mentouri Constantine University Algeria. 2009.
5. Schwetmann U, Taylor RM. The transformation of lepidocrocite to goethite, *Clays and Clays Minerals*. 1972;20:151-58.
6. Vong L. Chemical speciation of iron in the ocean, iron-porphyrin complexes, detection method, and production mechanisms. Doctoral thesis, University of the Mediterranean-Aix-Marseille II. 2008.
7. Ruiti M, Bechir BT. Elimination of iron by processes of oxidation and by adsorption on the coal of pine. *Int J Innov Appl Stud*. 2015;10(2):694-700.
8. Fernand K, Lanciné GD, Touchard AJ. Removal of iron and manganese by aeration-filtration of fodder water in rural areas in developing countries: Case of the Tissalé region (south of the Ivory Coast). *European J Sci Res*. 2008;19(3):558-67.
9. Mouchet P. Removal of iron and manganese from groundwater: Classic problems, recent progress, water supply. 1985;3:137-49.
10. Benefield LD, Judkins JF, Weand BL. *Process chemistry for water and wastewater treatment*. 1982.
11. Ahmad BJ, Cheng WH, Low WM, et al. Study on the removal of iron and manganese in groundwater by granular activated carbon. *Desalination*. 2005;182:347-53.
12. Stumm W, Lee GF. Oxygenation of ferrous iron. *Industrial and Engineering chemistry*. 1961;53:143-46.
13. Ghosh MM, O'Connor JT, Elgelbrecht RS. Precipitation of iron in aerated groundwater. *J Sanitary Engineering Division*. 1966;92:199-213.
14. Azzaoui S, Hanbali EM, Leblanc M. Copper, lead, iron, and manganese in the Sebou watershed: Sources of intake and impact on the quality of surface water. *Water Qual Res J*. 2002;37(34):773-84.
15. Pacini VA, Ingallinella A, Sanguinetti G. Removal of iron and manganese using biological roughing up-flow filtration technology. *Water Res*. 2005;39:4463-75.
16. Windsor S. Catalytic effects of the  $\gamma$ -FeOOH (lepidocrocite) surface oxygenation removal kinetic of Fe(II) and Mn(II). Thesis Advisor. California Institute of Technology. 1980.
17. Xuewu L, Franck JM. The solubility of iron hydroxide in sodium chloride solutions. *Geochimica et Cosmochimica Acta*. 1999;63(19-20):3487-97.
18. Wided M. Contribution to the study of the removal of ionic iron from water and to the iron-calcium carbonate interaction. Doctoral thesis, University of Carthage Tunisia. 2017.
19. Carlson L, Schwertmann U. Natural ferrihydrites in surface deposits from Finland and their association with silica, *Geochimica et Cosmochimica Acta*. 1981;45(3):421-29
20. Schwertmann U. The effect of pedogenic environments on iron oxide minerals. *Advances in Soil Science*. 1985;1:171-200.

21. Cambier P. Infrared study of goethites of varying crystallinity and particle size: I. Interpretation of OH and lattice vibration frequencies. *Clay Minerals*. 1986;21(2):191-200.
22. Cambier P. Infrared study of goethites of varying crystallinity and particle size: II. crystallographic and morphological changes in series of synthetic goethites. *Clay Minerals*. 1986;21(2):201-10.
23. Laura T, Liisa C, Olli HT. Ferrihydrite in water wells and bacterial enrichment cultures. *Water Res.* 1992;26(9):1159-62.
24. Magdalena SCJ, Lez-Da´vila MG, Frank JM. The oxidation of Fe(II) in NaCl-HCO<sub>3</sub> and seawater solutions in the presence of phthalate and salicylate ions: A kinetic model, *Marine Chemistry*;2004;85:27-40.
25. Ajmal M, Afsarm S, Akhtar K. Surface entrapment of toxic metals from electroplating waste and their possible recovery, *Water Air and soil pollution*, 1993;68:485-492.
26. Parks GA. The isoelectric points of solid oxides, solid hydroxides, and aqueous hydroxo complex systems. *Chem Rev.* 1966;65:177-195.
27. Parida K , Das J. Studies on ferric oxide hydroxides II. Structural properties of goethite samples ( $\alpha$ -FeOOH) prepared by homogeneous precipitation from Fe(NO<sub>3</sub>)<sub>3</sub> solution in the presence of sulphate ions. *J Colloid Interface Sci.* 1993; 178:586-93.