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## Removal of Iron and Manganese from Groundwater by Adding Calcite



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### ABSTRACT

The removal of iron (II) and manganese (II) from groundwater intended for human consumption has been re-investigated through batch experiments by adding calcite. This technique, based on the accelerated oxidation-precipitation of iron (II) into ferric iron by dissolving calcite, offers complete elimination of ferrous iron contained in groundwater in high concentrations (35 mg / L). An average elimination is obtained for manganese (II) when it is in high content in water (2.5 mg / L). This technique offers a better advantage, on the one hand, its simplicity and on the other hand its very good performance.



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## 1. INTRODUCTION

Iron is one of the most abundant metals in the earth's crust. It occurs naturally in water in soluble forms like ferrous iron (divalent iron in dissolved form Fe (II) or Fe (OH)<sup>+</sup>) or in complexed form like ferric iron (trivalent iron: Fe (III) found in iron oxyhydroxydes precipitation or also in bacterial form The presence of iron and manganese in groundwater can also have an industrial [1] or geological [2] origin. When the concentration of iron (II) and manganese ( II) exceeds 0.3 mg / L and 0.1 mg / L respectively in contact with oxygen in the air, they oxidize and form insoluble oxyhydroxides which sediment in the form of a silt and give a color rust and an unpleasant taste in water [3]. At very high concentrations, iron (II) and manganese (II) cause corrosion, clogging of storage structures and the pipes which carry them water as illustrated on Figure 1 which shows a water pipe whose diameter is completely reduced by ferric deposition.

There are several techniques to eliminate iron and manganese in water intended for consumption such as, chemical oxidation by chemical oxidants (O<sub>3</sub>, ClO<sub>2</sub>, KMnO<sub>4</sub>,...) [4], ion exchange [5], by electrocoagulation [6] adsorption on activated carbon and other materials [7], membrane technologies [8-9], by supercritical fluid [10], ash treatment [11], treatment based on of limestone [12]. However, all these techniques cannot be applied in some developing countries for lack of sufficient resources such as energy, the cost of installation. This study aims to eliminate iron (II) and manganese (II) from groundwater by a very simple technique based on the addition of calcite, which is a low-cost mineral that is abundant in most countries in the world.



**Figure No. 1: Water pipe scaled by a ferric deposit**

## 2. MATERIALS AND METHODS

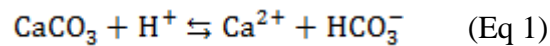
The experimental set-up consists of a two-liter beaker, a magnetic plate and bar. A volume of 1 L of groundwater was enriched with iron (II) salt and / or with manganese (II) salt, then the mineral was added, the solution-mineral mixture was kept under continuous stirring at using a magnetic bar at room temperature ( $\sim 20^\circ \text{C}$ ) and atmospheric pressure. At different stages of the experiment, samples were taken (10 mL) using a syringe equipped with a  $0.22 \mu\text{m}$  filter in specific tubes (ICP-AES tubes) to which a drop of a 3 mol / L nitric acid solution to prevent subsequent precipitation of  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  in the samples. Then simultaneously the pH and the redox potential were checked in a time interval.

## 3. RESULTS AND DISCUSSION

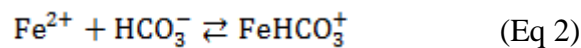
### 3.1 Fe (II) elimination test at 35 mg / L at the solution-calcite interface

Figure 2 gives us the evolution of the residual iron concentration, during the elimination of Fe (II) in natural waters enriched in iron (II) salts, in contact with 1 g of calcite. The Fe (II) elimination test by calcite in enriched natural water shows a gradual drop in the iron content as soon as the calcite is added to the reactor. After 10 minutes of solution-calcite interaction with continuous stirring, more than 90% of the iron has been removed. After 20 minutes of interaction all the iron is completely eliminated, by a calcite dissolution process, which very effectively catalyzes the oxidation-precipitation of iron (II) as supported by the following mechanism:

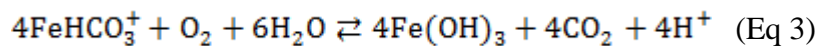
Dissolution of calcite

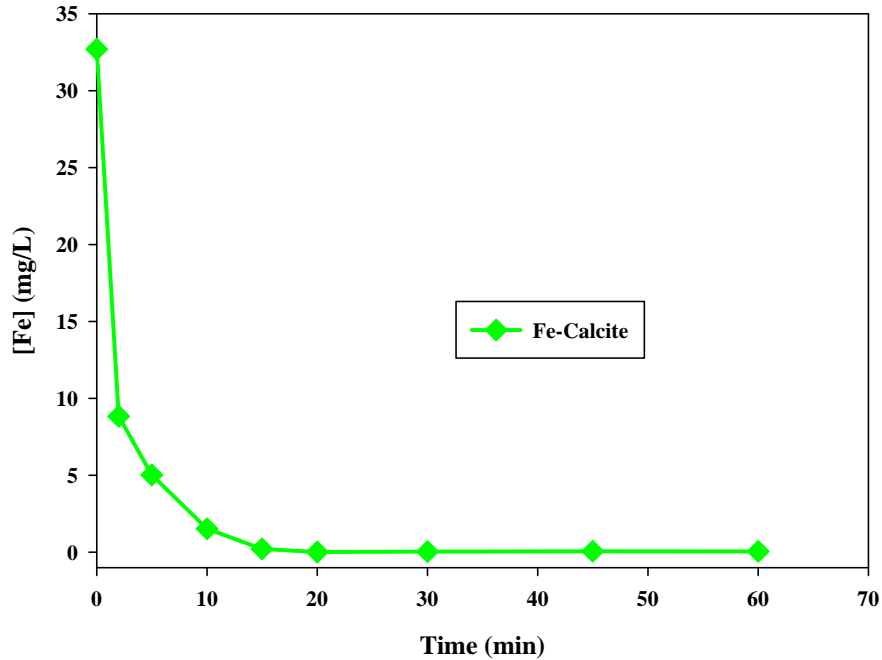


Iron complexation on the calcite surface:



The third is that of iron oxidation coupled with its precipitation:



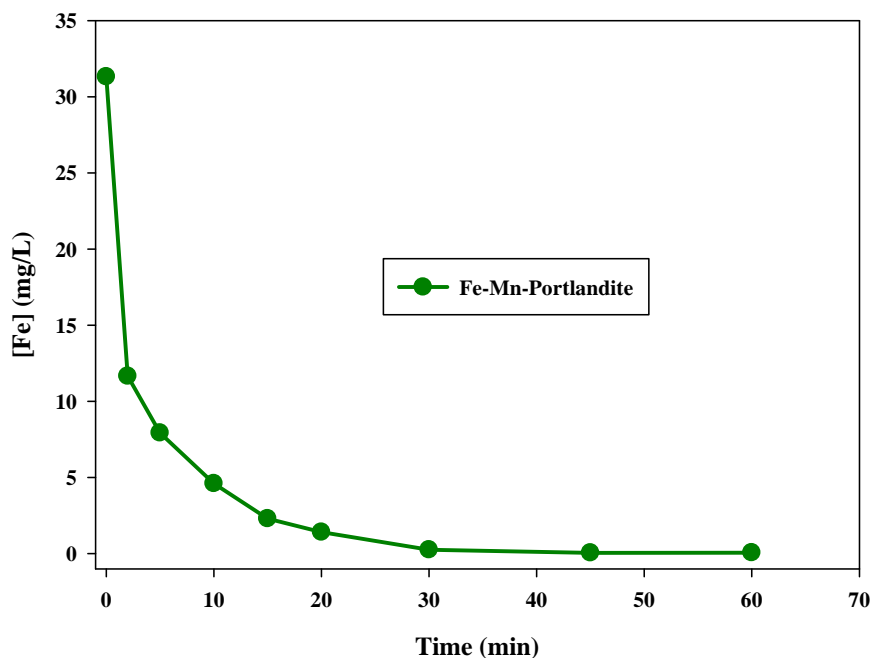


**Figure No. 2: Results of batch reactor experiments: Behavior of the Fe (II) elimination kinetics with calcite in a monoionic system ( $\text{Fe}^{2+}$ ). With an initial concentration of approximately 35 mg / L for Fe (II) and 1 g of calcite in real solution**

### **3.2.1 Removal test for Fe (II) and Mn (II) at the solution-calcite interface for 35 mg / L of Fe (II) and 2.5 mg / L of Mn (II)**

### **3.2.2 Evolution of Fe at the solution-calcite interface in a competitive system**

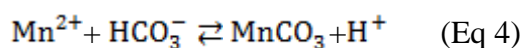
When iron (II) is associated with manganese in real water, by interacting with calcite in a batch reactor, the evolution of its residual content over time is different from that observed when iron is alone in a real solution. As soon as the calcite is added to the reaction medium, the iron concentration begins to drop, within 10 minutes of the process 85% of the iron is removed, compared to 90% when the iron (II) was alone in solution. Complete elimination is obtained within 30 minutes of solution-calcite interaction. It seems that the presence of manganese impacted the kinetics of the elimination of ferrous ions by calcite.

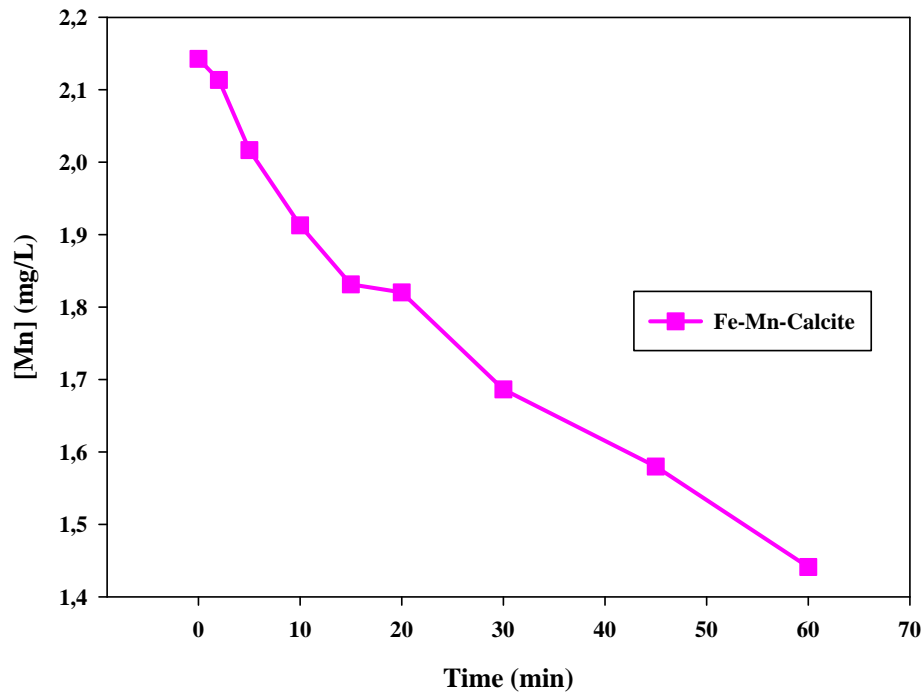


**Figure No. 3: Results of batch reactor experiments: Behavior of the Fe elimination kinetics with portlandite in a competitive system (Fe<sup>2+</sup> and Mn<sup>2+</sup>). With an initial concentration of approximately 35 mg / L for Fe (II) and 2.5 Mn (II) on 1 g of calcite in real solution**

### 3.2.3 Evolution of Mn at the solution-calcite interface in a competitive system

In a competitive system (Figure 4), monitoring the residual manganese content over time in a real solution shows that as soon as the mineral is introduced into the solution, a few minutes after stirring, the manganese concentration begins to decrease slightly. As agitation continues, the concentration of manganese also decreases. After 60 minutes of stirring, only about half of the manganese has been eliminated by the calcite, this shows that the elimination of manganese in high concentration by the calcite is not total and that the catalytic effect of calcite on the ions manganous is not effective as was observed with ferrous ions. This could be due to the low oxidation rate of manganese (II) in solution and/or the removal of manganese (II) in the presence of calcite is a more complex process. The mechanism envisaged is as follows:

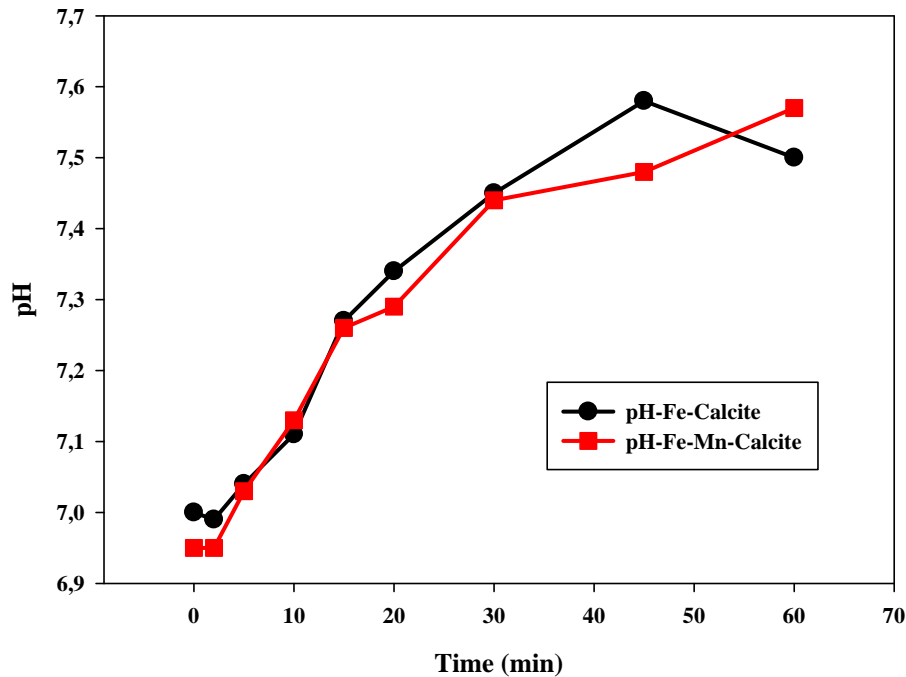




**Figure No. 4: Results of batch reactor experiments: Behavior of the Mn elimination kinetics with portlandite in a competitive system ( $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$ ). With an initial concentration of approximately 35 mg / L for Fe (II) and 2.5 Mn (II) on 1 g of calcite in real solution**

### **3.3 Evolution of the pH during the elimination of iron (II) and manganese (II) in natural waters by adding calcite**

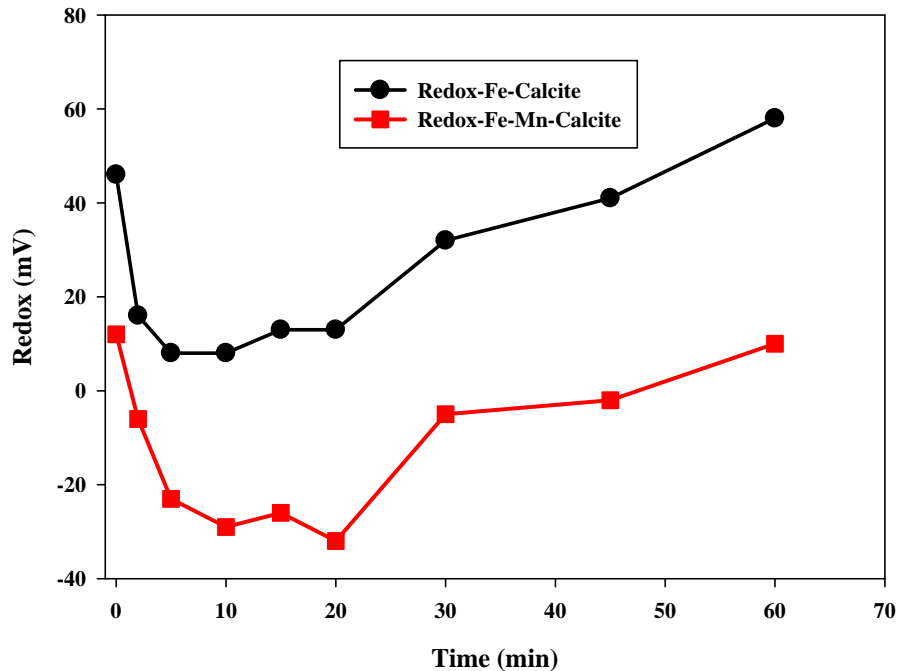
Figure 5 gives us the evolution of the pH of the reaction medium over time, as soon as the calcite is added to the medium, the pH slowly increases gradually. This slight increase in pH is directly linked to the production of bicarbonate ions which result from the dissolution of calcite, which accelerates the oxidation-precipitation of ferrous iron and manganous ions. At the end of the experiment, the pH of the mixture is within the range of values accepted by the WHO to ensure potability of the water.



**Figure No. 5: Change in pH as a function of time when using calcite for the removal of Fe (II) and/or Mn (II) in natural waters**

### **3.4 Evolution of the redox potential during the removal of iron (II) and / or manganese (II) in natural waters by adding calcite**

The evolution of the redox potential followed over time during the elimination of Fe (II) and / or Mn (II) in real solution is summarized in figure 6. Following the addition of calcite, the redox potential decreases very slowly towards negative values, this translates a consumption of dissolved oxygen which is directly involved in the oxidation-precipitation of Fe (II) in ferric iron as indicated in equation 3. Then the redox potential begins to increase slightly, thanks to the equilibrium established between the solution and the atmosphere, thus promoting an exchange of oxygen from the air in the solution.



**Figure No. 6: Evolution of the redox potential as a function of time during the elimination of iron (II) and / or Mn (II) in natural waters by addition of calcite**

## CONCLUSION

This study shows that calcite can also be used to remove iron and manganese from groundwater to a desired level without increasing the pH beyond the WHO tolerated limit. It offers a relatively short treatment time (<1 h) and less sludge production.

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