# 1Pa-50

## Arsenite Oxidation and Treatment by Ultrasonic/Iron in Aqueous Solutions

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#### 1. Introduction

Arsenic is present in natural waters and soils in two oxidation states, As(III) and As(V), which are characterized by different chemical behaviors, bioavailability, and toxicity. Available information on the rates of arsenic oxidation in groundwater and the specific rate constants are inconsistent.

Over the past ten years, many methods have been applied for the oxidation of As(III) to the less toxic As(V), including photocatalysis, zero-valent iron, Fenton's reaction, ozonation, etc. [1-2]

Sonochemistry has attracted attention among the different AOPs methods used in remediation processes because of its simple operational requirements and its ability to be used along with simple oxidants.

Also, with the petty removal technique several techniques are available for removing arsenic in groundwater, including precipitation/coagulation, ion exchange, adsorption onto activated alumina and other oxyhydroxides, lime softening, reverse osmosis, and electrodialysis [3-4].

Ultrasonic/Fe(II) oxidation of As(III) to As(V) mechanism:

$H_2O \rightarrow OH + H$ (1)	1)	)	
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$$^{\bullet}OH + ^{\bullet}H \rightarrow H_2O \tag{2}$$

$$OH+OH \rightarrow H_2O_2$$
 (3)

$$\dot{H} + H_2O \rightarrow \dot{O}H + H_2 \tag{4}$$

where ))))) refers to the application of ultrasound. In the presence of Fenton,

$$Fe( \coprod) + H_2O_2 \rightarrow Fe(\coprod) + OH^- + OH$$
 (5)

$$Fe(\coprod) + H_2O_2 \rightarrow Fe-O_2H^{2+}$$
 (6)

$$Fe-O_2H^{2+} \rightarrow Fe(II)(Isolated) + HO_2$$
 (7)

Fe( 
$$\coprod$$
 )(Isolated)+H<sub>2</sub>O<sub>2</sub> $\rightarrow$ Fe( $\coprod$ )+OH<sup>-</sup>+\*OH (8)

where ))))) refers to ultrasonic oxidation of

$$As(\coprod) + OH \rightarrow As(IV) + OH$$
 (9)

$$As(V) + OH \rightarrow As(V) + OH$$
 (10)

$$As(\coprod) + O_2 \longrightarrow As(\square) + H_2O_2$$
 (11)

$$As(V) + O_2 \rightarrow As(V) + O_2^{-1}$$
(12)

# Precipitated $Fe(OH)_3$ Removal of As(V) mechanism:

The co-precipitation reaction is

$$Fe^{2+} + AsO_4^{3-} \rightarrow FeAsO_4^{-}$$
 (13)

$$FeAsO4 + OH \rightarrow FeAsO4(s) + OH$$
 (14)

The adsorption/complexation reaction is

$$\equiv \text{Fe-OH+AsO}_4^{3-} + 3\text{H}^+ \rightarrow \equiv \text{Fe-H}_2 \text{AsO}_4 + \text{H}_2 \text{O}$$
 (15)

Edwards (1994)<sup>[4]</sup> showed that the precipitation of iron as Fe(OH)<sub>3</sub> controlled the efficiency of arsenic removal during oxidation. His adsorption capacities for arsenic were 2.4-9.5 mg/g Fe(OH)<sub>3</sub>, and he also found that As(V) removal by freshly precipitated iron hydroxide was much more efficient compared to the preformed solids. From data reported by Jekel (1986)<sup>[5]</sup>, we have been able to derive an adsorption capacity of 33.8 mg As/g Fe(OH)<sub>3</sub>, a value that is similar to the 29.7 mg As/g Fe(OH)<sub>3</sub> derived from the study of Clifford and Lin (1991). Our value thus falls within the ranges reported under a range of experimental conditions. This report presents the rates of oxidation of naturally occurring arsenic in groundwater samples in the presence of sonication and sono-Fenton. Coupling of arsenite oxidation to adsorption/complexation reactions by precipitated amorphous Fe(OH)3 was also studied. The results of this study should be useful in developing effective methods for removing low levels of arsenic from drinking water supplies.

#### 2. Materials and methods

#### 2.1. Materials

All chemicals used in this study were analytical grade and were used without further purification: Sodium (meta) arsenite (NaAsO<sub>2</sub>) had a purity of 94%, and Iron sulfate heptahydrate (FeSO<sub>4</sub> '7H<sub>2</sub>O) had a purity of >99%. All solutions were prepared with DI water. A stock solution containing 0.2 mg/L of As(III) was prepared and diluted to the required initial concentration of As(III) as needed. Fe(II) had an initial concentration of 0.4 to 8 mg/L.

### 2.2 Reactor set-up and analysis methods

The reactor was made up of a glass coupon type with 1 L capacity equipped with an ultrasonic transducer (MEGA-100 MIRAE ULTRASONIC, 35, to 1,000 kHz, maximum power 100 w), When using all solutions, the total is 500 mL.

At regular time intervals, approximately 2-3 mL samples were taken out from the reactor, and were filtered using a 0.25  $\mu m$  membrane filter with a disposable syringe filter unit. The filtrate was then collected using an anion-exchange cartridge (Supelclean LCSAX SPE 3 mL, 57017) that separated the As(III) and As(V). The As(III) and iron concentration was then measured using an ICP-AES instrument. The minimum arsenic detection limit of the ICP-AES instrument is 0.005 mg/L.

#### 3. Results and discussion

### 3.1 Effect of ultrasonic frequency

The effect of different ultrasonic frequencies on the OH radical was analyzed. The experimental conditions were as follows: KI solution concentration 10 g/L, ultrasonic power 80 w, pH: 7, Temp.  $20\pm2\,^{\circ}\mathrm{C}$ , reaction time: 30 min. The experimental resultant optimum ultrasonic frequency was 500 kHz. (See Fig. 1)

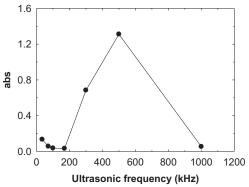


Fig. 1 Effect of different ultrasonic frequencies on the OH radical.

### 3.2Effect of Fe( $\Pi$ ) concentration

The effect of iron concentration on the sonolysis for the generation of OH radicals was demonstrated in the experiment. The result shows that the optimal concentration of Fe( II ) was 0.4 mg/L. OH radicals were not further generated after 0.4 mg/L of Fe( II ) concentration. In addition, the amount of OH radical was slightly decreased after 0.4 mg/L of Fe( II ) concentration. It seems that there is an optimal ratio between  $\rm H_2O_2$  and Fe( II ). An increased input of Fe( II ) does not increase the generation of OH radical without a certain ratio of  $\rm H_2O_2$  present, which was 1:1[ $\rm H_2O_2$ : Fe( II )] in the experiment (See Fig. 2).

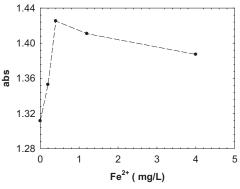


Fig. 2. Effect of iron concentration on the OH radical.

# 3.3 Effect of different initial $Fe(\coprod)$ concentrations of As (III) on the oxidation

The ultrasonic/Fe(II) oxidation of As(III) solutions (500 mL) over the initial concentration of 0.2 mg/L and iron initial concentration range of 0-20 mg/L was

carried out and the results are shown in Figure 3. It can be seen that a rapid, and in some instances complete oxidation of As(III) to As(V), was achieved within 10 min of reaction time and with an initial iron concentration of 0.4 mg/L. The oxidation efficiency was 99.1 %.

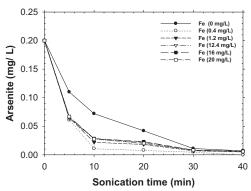


Fig. 3 Effect of different iron concentrations of arsenite on the oxidation

# 3.4 As(V) removal by precipitation with amorphous $Fe(OH)_3$

The results are shown in Figure 4. Several researchers have found that iron concentration is an important factor in As(III) and As(V) removal via adsorption onto ferric hydroxides. When the initial concentration of iron was 12.4 mg/L, the concentration of arsenic was 0.0018 mg/L with an adsorption capacity of 16.12 mg arsenic/g iron.

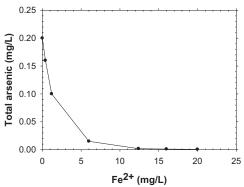


Fig.4 Effect of different iron concentrations of total arsenic on the concentration (reaction time 30 min)

### Acknowledgement

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