Iron in Groundwater : Their removal by electrochemical process using aluminium electrodes

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Abstract— Neither iron nor manganese in water present a health hazard. However, their presence in water may cause taste, staining, and accumulation problems. Because iron and manganese are chemically similar, they cause similar problems. Iron will cause reddish-brown staining of laundry, porcelain, dishes, utensils, and even glassware. Manganese acts in a similar way but causes a brownish-black stain. Soaps and detergents do not remove these stains, and the use of chlorine bleach and alkaline builders (such as sodium carbonate) can actually intensify the stains. Iron and manganese are concentrated in water by contact with rocks and minerals, and occasionally man-made materials like iron and steel pipes. It is usually groundwater supplies that may require treatment for high levels of iron and manganese. Generally speaking, few surface water supplies have high enough levels of either to cause problems. Occasionally discharge of acid industrial wastes or mine drainage may increase iron or manganese to problem levels in surface water. The main objective of this study is to find an optimum condition to remove iron concentration to below 0.3 mg/L as allowed by World Health Organization (WHO)[1].

1.0 INTRODUCTION

1.1 Background of Study

Iron is a common constituent in soils and groundwater. It readily participates in subsurface redox reactions and under some conditions can cause problems with groundwater remediation systems. Not only iron is common, but it is also reactive and readily reflects changes in surrounding. In groundwater systems iron occurs in one of two oxidation states: reduced soluble divalent ferrous iron (Fe^{2+}) or oxidized insoluble trivalent ferric iron (Fe^{3+}). The modern atmosphere has 21% oxygen, causing most of the iron in shallow subsurface soils to be in oxidized ferric state[2]. Iron is usually encountered as soluble forms in groundwater or deep reservoirs. When this water is exposed to oxygen, it picks up oxygen which slowly oxidizes the iron. This oxidation causes the iron and manganese to become insoluble precipitates. This also causes a color change in the water[3]. Toxicity of iron may cause conjunctivitis, choroiditis, and retinitis if it contacts and remains in the tissues. Chronic inhalation of excessive concentrations of iron oxide fumes or dusts may result in development of a benign pneumoconiosis, called siderosis, which is observable as an x-ray change. No physical impairment of lung function has been associated with siderosis. Inhalation of excessive concentrations of iron oxide may enhance the risk of lung cancer development in workers exposed to pulmonary carcinogens. A more common problem for humans is iron deficiency, which leads to anemia. A man needs an average daily intake pf 7 mg of iron and a woman 11 mg; a normal diet will generally provided all that is needed[1].

1.2 Problem Statement

Dangerous iron concentrations have been reported mainly from USA especially in iron-producing areas such as Midwestern US and parts of California, Arizona and others as well. Industrial iron contamination may also occur anywhere[4]. Currently, there are several methods for removal of iron (Fe^{2+} and Fe^{3+}) from water. The most common method is oxidation. The other methods are including filtration, sequestration, iron exchange and precipitation of iron. Similarly, surface water treatment using coagulation, flocculation, sedimentation and filtration also will remove iron and manganese as long as they make certain iron and manganese get oxidized[5]. However, the problems occur that there are not many optimum existing techniques for removal of iron in terms of efficiency, reliability and maintenance, residual and cost. Due to all the problems mentioned above, simple yet efficient of optimum removal method for iron is needed in order to reduce or remove the existence of iron in water to prevent contamination or iron poisoning among world population.

1.3 Objective and Scope of Study

The objectives of this study:

- To study the optimum voltage for the electrode
- To study the optimum spacing required for the electrode
- To study the optimum surface area of the electrode
- To study the optimum time for the reaction
- To study the operational range of concentration of iron

The scope of study :

- Preparation of experiment
- Characterization of aluminium electrode by size
- Characterization of iron concentration
- Parameters that affect the removal process
- Comparisons between the parameters for optimum result

1.4 Relevancy of the Project

This study is relevant to human, health and environment implementation. The recognition of the high scale of iron concentration in groundwater especially for household used from water supply is a concern. The allowable limit according to WHO for iron is < 0.3 mg/l need to be reach. Most of the water treatment systems are struggling to meet the requirement. This study will allow the removal of excess iron in water supply at home for a safer daily usage. By producing an optimum result from electrochemical method, the effective yet economical technique will be able to be use for household purposes. This will minimize the probability of iron poisoning for a safer health and environment.

1.5 Iron Forms

Iron is one of the most abundant metals of the Earth's crust. It occurs naturally in water in soluble form as the ferrous iron (bivalent iron in dissolved form Fe(II) or $Fe(OH)^+$) or complexes form like the ferric iron (trivalent iron: Fe(III) met in the precipity $Fe(OH)_3$) or bacterial form, too. The occurrence of iron in water can also have an industrial origin; mining, iron and steel industry, metals corrosion, etc. There are many industrial situations where iron or impurities must be removed from solutions. This is usually induced by the precipitation of iron oxide/oxyhydroxides and often involves the co-removal of inorganic and organic impurities because of the strong adsorptive capacity of iron oxyhydroxides. Such processes are commercially significant. Iron precipitates are notoriously gelatinous, metastable, and difficult to settle and filter. World Health Organization (WHO) has set a guideline value of 0.3 mg/L, of iron in drinking water[6].

1.6 Iron in Groundwater

As water percolates through the soil, the dissolved oxygen in it is consumed by the decomposing organic matter and microbes in the soil; and the decomposition also results in a reduction of the pH due to the microbial action. The iron and manganese atoms are "reduced" to the Fe+2 and Mn+2 state as the soil is a reducing environment that is created by the lower pH values and the absence of oxygen. When we pump the groundwater up to the surface, the oxygen in the air comes into contact with the water and enters the solution which starts the oxidation process; and the release of hydrogen sulfide (H2S) and carbon dioxide (CO2) from the groundwater into the atmosphere, raises the pH of the water. This allows for the soluble Fe+2 and Mn+2 states to change into the insoluble Fe+3 and Mn+3 states. As in the groundwater source, when the water comes to the surface, the oxygen in the air comes into contact with the water and enters the solution which starts the oxidation process; the release of hydrogen sulfide (H2S) and carbon dioxide (CO2) from the water into the atmosphere, raises the pH of the water. Once again, this allows for the soluble Fe+2 and Mn+2 states to change into the insoluble Fe+3 and Mn+3 states. In many deep reservoirs, high concentrations of iron and manganese may be found in the deep sections due to this phenomenon[3].

1.7 Aluminium Behaviour as Electrode in Electrochemical

Electrochemical behavior of aluminium was investigated via electrolyses and potentiodynamic polarisation tests using sodium sulphate as background electrolyte. Electrolyses were performed in a thermostated electrolytic cell with (i) two opposing aluminum plates served as parallel–vertical electrodes and (ii) an aluminium anode and a platinized titanium mesh cathode. Electrolyses in a compartmentalized reactor with two aluminium plates were also carried out. The anolyte and catholyte were separated by cation exchange membrane (IONAC MC 3470) in Na^+ form. Aluminium plates were cut from a commercial grade aluminium sheet (99% purity). The electrode surface was first mechanically polished underwater with 400 grade abrasive paper in order to ensure surface reproducibility, rinsed with distilled water and dried prior to immersion in the electrolyte. The effective area of each electrode used for electrolysis was 30 cm^2. The electrodes were connected to a digital dc power supply with potentiostatic or galvanostatic operational options (CONVERGIE – CLES 60-3) providing current and voltage in the range of 0–3 A and 0–60 V. The current was kept constant for each run. The anode/cathode gap was kept constant at 4 cm except indication. The cell voltage was recorded using a data logger (LINSEIS L 6512). A gentle magnetic stirring rate of about 200 rpm was applied to the electrolyte in all tests. Electrolyte volume used was 500 mL. The total time duration of electrolysis was 30 min for most test runs unless noted otherwise[7].

It is well known that in EC process the main reactions occurring at the aluminium electrodes during electrolysis are:

$$Al \rightarrow Al^{3+} + 3e^- \text{ (anode)} \qquad \text{Eq. (1)}$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \text{ (cathode)} \qquad \text{Eq. (2)}$$

Aluminium ions (Al^{3+}) produced by electrolytic dissolution of the anode (Eq. (1)) immediately undergo spontaneous hydrolysis reactions which generate various monomeric species according to the following sequence (omitting co-ordinated water molecules for convenience):

$Al^{3+} + H_2O \rightarrow Al(OH)^{2+} + H^+$

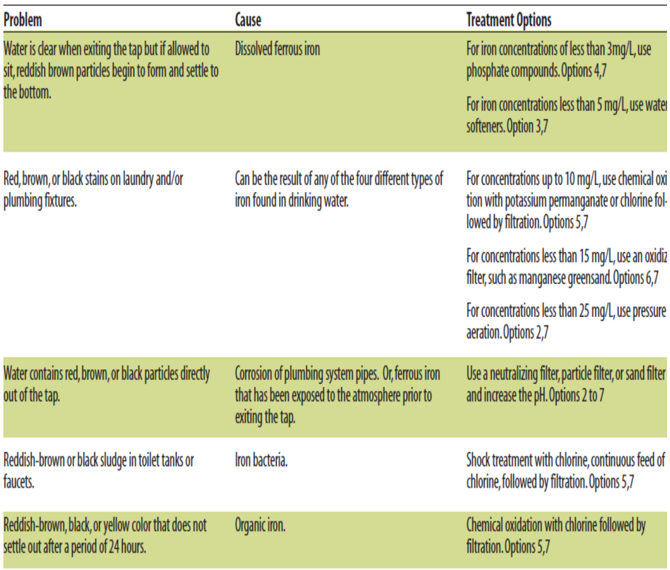
$Al(OH)^{2+} + H_2O \rightarrow Al(OH)_2^+ + H^+$

$Al(OH)_2^+ + H_2O \rightarrow Al(OH)_3 + H^+$

Actually, this is only an oversimplified scheme, since dimeric, trimeric and polynuclear hydrolysis products of Al can also form: $Al_2(OH)_2^{4+}$, $Al_3(OH)_4^{5+}$, $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}O_4(OH)_{24}^{7+}$, $Al_{13}(OH)_{34}^{5+}$[7].

1.8 Removal of Iron in Groundwater

When faced with an iron contamination problem, there are several ways can be conducted to resolve the problem. These methods can be adopted for laboratory and household purposes. For household purposes, several methods can be installed for treating the designated water supply from iron contamination. The actual costs are varied with the types of iron contamination, size of filter unit and system[8].



Problem	Cause	Treatment Options
Water is clear when exiting the tap but if allowed to sit, reddish brown particles begin to form and settle to the bottom.	Dissolved ferrous iron	For iron concentrations of less than 3mg/L, use phosphate compounds. Options 4,7 For iron concentrations less than 5 mg/L, use wate softeners. Option 3,7
Red, brown, or black stains on laundry and/or plumbing fixtures.	Can be the result of any of the four different types of iron found in drinking water.	For concentrations up to 10 mg/L, use chemical oxi tion with potassium permanganate or chlorine fol- lowed by filtration. Options 5,7 For concentrations less than 15 mg/L, use an oxidiz filter, such as manganese greensand. Options 6,7 For concentrations less than 25 mg/L, use pressure aeration. Options 2,7
Water contains red, brown, or black particles directly out of the tap.	Corrosion of plumbing system pipes. Or, ferrous iron that has been exposed to the atmosphere prior to exiting the tap.	Use a neutralizing filter, particle filter, or sand filter and increase the pH. Options 2 to 7
Reddish-brown or black sludge in toilet tanks or faucets.	Iron bacteria.	Shock treatment with chlorine, continuous feed of chlorine, followed by filtration. Options 5,7
Reddish-brown, black, or yellow color that does not settle out after a period of 24 hours.	Organic iron.	Chemical oxidation with chlorine followed by filtration. Options 5,7

Table 1: Identify iron-in-water problem before seeking the best solution[8].

2.0 METHODOLOGY

2.1 Optimum Voltage Test

This experiment will be conducted to achieve the optimum voltage required for the aluminium as electrodes to complete the reaction for iron removal. The voltage will be acting as a varied variable to conduct the experiments which range from 2 ~ 24V. The experiment will be conducted in room temperature. The size and spacing between electrodes will be set constant at 5 cm and 20 cm^2.

2.2 Optimum Electrodes Spacing Test

For this experiment, the varied variables will be the spacing of the aluminium electrodes. For optimum result, the aluminium electrodes spacing will be varied in a range of 1 cm ~ 5 cm. The experiment will be using the optimum voltage obtain in the first experiment. This will be conducted in room temperature.

2.3 Optimum Surface Area of Electrodes Test

A series of aluminium size will be used in these experiments. The aluminium will be varied in terms of their surface area of electrodes which are 20 cm^2, 40 cm^2, 60 cm^2, and 80 cm^2. The result will defined the optimum surface area of the aluminium electrodes which reacts the most with the aqueous iron solution. The experiments will be conducted in a room temperature.

2.4 Optimum Reaction Time Test

For these experiments, the objective is to determine the optimum reaction time for the aluminium electrode to remove the iron from the solution. The reaction time will be varied from 10 minutes ~ 2 hour. The most removed iron from the varied time will determined the optimum reaction time of the process.

2.5 Optimum Concentration Test

In order to achieve the result required for these experiments, the concentration of iron aqueous solution will be varied. The process will be done for several times using different concentration of iron solution. The experiment will be conducted in room temperature.

3.0 RESULT AND DISCUSSION

3.1 Determination of Optimum Voltage and Time Test

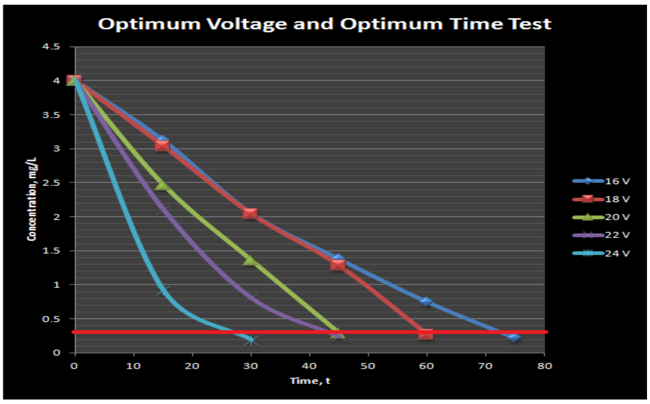


Figure 1: Optimum Voltage and Time Test

From the graph, the removal of iron from groundwater is higher and faster reaction can be observed as higher voltage is used. This proves that a higher voltage enhancing the time of reaction for iron particles to coagulate with each other using aluminium electrodes as anode and cathode. The highest and fastest removal of iron is when using 24 V, which removing the iron from the sample to desired value; below 0.3 mg/L of concentration in just 30 minutes.

3.2 Determination of Optimum Electrodes Spacing Test

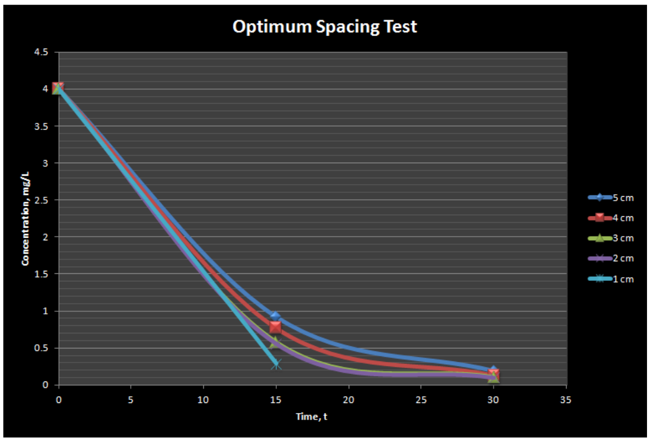


Figure 2: Optimum Electrodes Spacing Test

In theory, the lesser distance between both of electrodes will be resulted in a higher removal of iron. This can be proved by the graph above, where the optimum spacing is 1 cm. The lesser distance means higher current, enhancing the reaction rate of iron removal. From this finding, the optimum spacing between electrodes is 1cm. in this condition, the concentration of iron can be reduced to an allowable value which is below 0.3 mg/L in 15 minutes. This experiment is conducted by using 24V from the previous test as an optimum voltage.

3.3 Determination of Optimum Surface Area of Electrodes Test

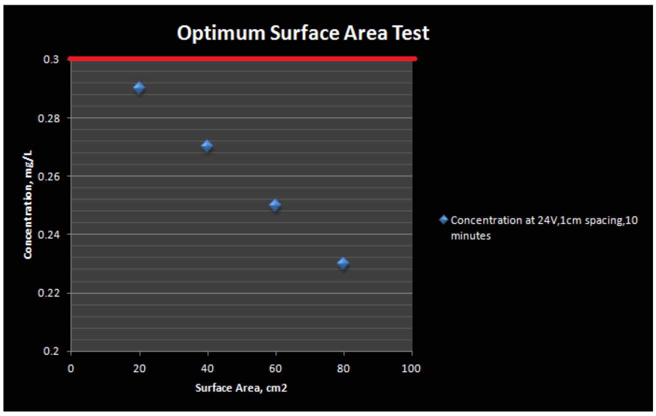


Figure 3 : Optimum Surface Area of Electrode

This graph shows that with a bigger surface area of electrode, a faster reaction can be created to reduce the iron concentration in the groundwater. The contacted surface area help the iron coagulating in terms of space.The result shows that with 80 cm^2 of surface area can remove the iron to 0.23 mg/L in 10 minutes. This value is meeting the requirement of the allowable iron concentration.

3.4 Determination of Operational Range of Concentration

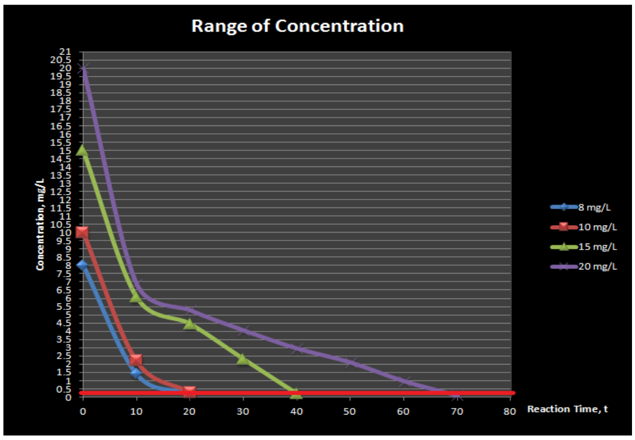


Figure 4 : Optimum Surface Area of Electrode

From this graph, the observation can be made that a higher voltage enhances the reaction process of removing iron from the groundwater. The higher voltage increases the flow of the current in the electrochemical process thus allowing the reaction to increase the rate of coagulation of iron molecules. The fastest reaction is by using 24V which can remove iron to below 0.3 mg/L in just 30 minutes. This can be stated as the optimum result from this experiment. This value will be use during the next experiment.

3.5 pH Observation

From all the experiment conducted, the pH of the groundwater solution is found decreasing from its initial value as the process of removing iron take place. The initial solution is identified as acidic. The final pH is recorded at the end of every experiment as the reading are slightly increase to a more neutral solution in a range from 6 to 8. This confirms that the iron concentration with an acidic character, has been successfully reduced within the process thus allowing the solution to become more neutral.

4.0 CONCLUSIONS AND RECOMMENDATIONS

4.1 Conclusions

Depending on the area, the water quality might not be of the quality we desire for bathing, laundering, cooking, cleaning or drinking. It might taste or smell bad, stain the plumbing fixtures, or be so hard that it leaves mineral deposits. No matter where are the locations, the water will probably need to be treated in some way to be of the highest quality for all uses. It is simple and economical to improve the quality of your water at the point of entry to your home. This project is justifiably relevant to the safer life application in which we can minimize the hazard of iron and manganese in water supply by finding the optimum condition for removing excess iron from home.

4.2 Recommendations

For further research, it is recommended to study more parameters and a better electrode to optimize this method in reducing the concentration of iron. In recommendation for an expansion of this experiment, more research is needed to produce efficient equipment in order to remove the excess iron using the findings from the experiments from home.

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