Removal of Iron from Groundwater by Sulfide Precipitation

H. Jusoh, N. Sapari and R.Z. Raja Azie

Abstract—Iron in groundwater is one of the problems that render the water unsuitable for drinking. The concentration above 0.3 mg/L is common in groundwater. The conventional method of removal is by precipitation under oxic condition. In this study, iron removal under anaerobic conditions was examined by batch experiment as a main purpose. The process involved by purging of groundwater samples with H_2S to form iron sulfide. Removal up to 83% for 1 mg/L iron solution was achieved. The removal efficiency dropped to 82% and 75% for the higher initial iron concentrations 3.55 and 5.01 mg/L, respectively. The average residual sulfide concentration in water after the process was 25µg/L. The Eh level during the process was -272 mV. The removal process was found to follow the first order reaction with average rate constant of 4.52 x 10^{-3}. The half-life for the concentrations to reduce from initial values was 157 minutes.

Keywords—Anaerobic, chemical kinetics, hydrogen sulfide, iron, rate constant

I. INTRODUCTION

GROUNDWATER in Malaysia is the potential source of portable water for the future to meet the demand from increasing population and industries [1]. It constitutes the underground part of the 'water cycle' and represents 40% of the usage of fresh water in the world [2]. The utilization of groundwater can help to solve the water shortage in areas where surface water is limited [3]. Groundwater is generally less affected by pollution because it is protected by the soil that acts as a filter. However, groundwater usually contains dissolved mineral ions including iron that can affect the usefulness of the water [4]. Iron may present in the water higher than the limits for drinking of 0.3 mg/L. Thus, it is necessary to remove the iron prior to it consumption.

The quality groundwater is influenced by its parent materials particularly the contents of iron, sulphide, fluoride, hardness, total dissolved solids and pH [5]. An AWWA task group suggested a limit of 0.05 mg/L iron for public use [6]. The World Health Organization, WHO, recommends the iron concentration in drinking water should be less than 0.3 mg/L [7]. In Netherlands, the level of iron in drinking water is ≤0.05 mg/L and several water supply companies are aiming at a level of ≤0.03 mg/L in order to minimize maintenance costs of distribution system [8].

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Iron which is usually present in groundwater as divalent ions (Fe^{2+}) is considered as contaminants because of their organoleptic properties [9]. The presence of iron in groundwater is attributed to the dissolution of iron bearing rocks and minerals under anaerobic conditions in the presence of reducing agents like organic matter [10]. This contamination can cause problems including side effect to human's health [11]. Iron bearing rocks and minerals which include oxides (hematite, magnetite, and limonite), sulphides (pyrite), carbonates (siderite) and silicates (pyroxene, amphiboles, biotites and olivines) are the sources of iron [12]-[13]. Iron may present in groundwater in various forms including dissolved iron (II), inorganic complexes, organic complexes, colloidal and suspended iron. Water containing ferrous iron is clear and colorless because the iron is completely dissolved [14]. Some of the dissolved minerals are essential for good health but others if abundant can cause problem such odor and stain. Therefore treatment is necessary to remove or reduce the excess minerals before the water can be used for its intended purposes.

Oxidation and filtration is the common method of iron removal. It has been applied since 1874 in German to treat the groundwater [12]. However, theoretically iron also can be removed by anaerobic process. This method involves a process without the presence of oxygen, a treatment which permanently removes the interference in groundwater. Dissolved oxygen (DO) level less than 1.0 mg/l is considered anaerobic [15]. Anaerobic process is classified as either anaerobic fermentation or anaerobic respiration depending on the type of electron acceptors [16]. In anaerobic groundwater, iron can be found in high concentrations [17]. It can be reduced by precipitation as sulfide under anaerobic condition [18]. In this process, normally high purity nitrogen was purged to lower the oxygen content [19].
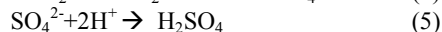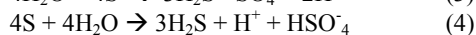
Iron can be removed by precipitation with H_2S and filtration [20]. Removal by introduction of sulfides, typically in the form of hydrogen sulfide (H_2S), at pH 8.5, was found to remove the metal by combining with aqueous bi-sulfide ion to form precipitate as solid sulfide [21]. Sufficient sulfide ion can precipitate heavy metals to a safe level of concentration [22]. In acid solution, precipitation is not possible, because the sulfide ion concentration (S^{2-}) is insufficient to exceed solubility products of iron sulfide. The sulfide ion concentration can be made available by the addition of sodium acetate solution, to allow precipitation of black iron sulfide to occur [23]. In anaerobic condition, sulfide reacts with metals in solution to form precipitate that is highly insoluble which can then be disposed of [24]-[25]. The chemical composition

of the iron-sulfides is equivalent to pyrrhotite (FeS). When the iron reacts with sulfide, a black FeS will form and precipitate [21],[24,[26]. The chemical reactions of the process are described as follow:

$$H_2S + Fe^{2+} \rightarrow 4FeS_{(S)} + 2H^+ \qquad (1)$$
$$Fe^{2+} + HS^- \rightarrow FeS_{(S)} + H^+ \qquad (2)$$
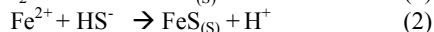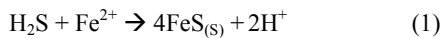
The reactions produce hydrogen ions that lead to the drop in pH. Thus buffering is necessary. Sodium acetate is one of the buffers that were applied for FeS precipitation [23].

Hydrogen sulfide are formed by the combination of hydrogen and sulfur. Hydrogen sulfide can also be produced by boiling sulfur at temperature $200^\circ C$ [27]. This reaction is called self-oxidation and reduction reaction (shortly self-redox reaction). In self-redox reaction, reactant is reduced and oxidized by itself simultaneously. In case of sulfur–water interaction, elemental sulfur is reduced to hydrogen sulfide (H_2S), which dissociates to HS^- and S^- in alkaline solution, and elemental sulfur is also oxidized to sulfuric acid [28]-[30]. These chemical reactions are described as follow:

$$4H_2O + 4S^0 \rightarrow 3H_2S + SO_4^{2-} + 2H^+ \qquad (3)$$
$$4S + 4H_2O \rightarrow 3H_2S + H^+ + HSO_4^- \qquad (4)$$
$$SO_4^{2-} + 2H^+ \rightarrow H_2SO_4 \qquad (5)$$

Consequently, the amount of dissolved metals and sulfate concentration are reduced under anaerobic condition [31]. Willow and Cohen 2003 [32], studied the removal of high amounts of iron and manganese in the presence, or absence, of dissolved organic matter. They found that anaerobic bioreactor can remove nearly 100% of the metals. Grindstaff and Office 1998 [33], found anaerobic process in the tubewells reduced 69% of the metals. Jong and Parry 2003 [34], found removal of Fe around 82% from laboratory experiment using water containing 1.95 mg/L iron with 14 days contact time. Increasing redox potentials (Eh) improve the removal efficiently to 99% over almost the same [20],[35],[36].

The iron removal process takes place at redox potential of around 0 mV to -100 mV under anaerobic condition [37]. The anaerobic process should be maintained constantly at pH 7 with Eh value -218 mV for iron to be removed [38]. The growth of the anaerobes requires Eh level from −200 to −350 mV at pH 7 [39-40] as shown in Fig. 1. Redox potentials as low as −400 mV, ensure constant reducing environment can be provided for metal removal process [16].

Therefore, the objectives of this study are to remove iron under anaerobic condition and to measure the efficiency of reducing process using this method. This study also is trying to introduce native sulfur and water as production of hydrogen sulfide gas. The contamination of samples especially the sulfide concentration will be analyzed after the experiment in order to meet the WHO standard.
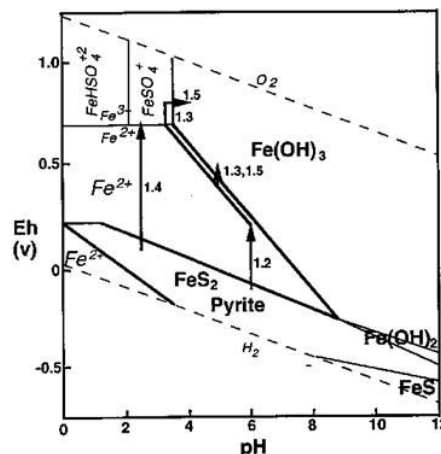

Fig. 1 Effect Eh-pH on stability of iron minerals

II. MATERIAL AND METHOD

A. Material Preparation

The materials were prepared for two phases: preliminary studies and actual experiment using groundwater. In preliminary study, prepared iron solution and H_2S were used. Actual groundwater was used in the second phase of the study instead of iron solution.

B. Preliminary Experiment

These experiments were conducted in order to determine the optimum contact time and pH of iron removal under anoxic condition.

1. pH Optimization

This experiment was conducted by varying the pH from pH 2 to pH 9. The pH was adjusted using hydrochloric acid (HCl) and sodium hydroxide (NaOH) to a specified pH level. Experiment was conducted using jar test. Iron solution was prepared according to standard method [41]. The water was purged with nitrogen to remove oxygen for 30 minutes as shown in Fig. 2 followed by hydrogen sulfide. Hydrogen sulfide (H_2S) was prepared by boiling the native sulfur in the water at temperature $200^\circ C$ according to Tsuchiya et al., 2008. Total iron was analyzed every hour to determine the reducing process of iron by using phenanthroline method. The experiment was repeated eight times for pH 2 to pH 9 of the iron solution.
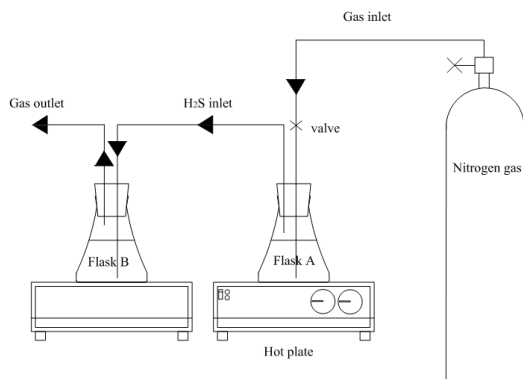
Fig. 2 Preliminary experiment using iron solution at 1mg/L

2. Experiments on Iron Removal From Groundwater

Experiment on iron removal under anaerobic condition by using actual groundwater was conducted at room temperature of 25°C. Three of groundwater samples were collected from monitoring wells in the campus of Universiti Teknologi PETRONAS. The iron concentrations in the samples were 1.5, 3.55 and 5.01 mg/L. Spectrophotometer was used to determine the total iron by using phenanthroline method (APHA 1980).

The experiment was conducted using a stainless steel reactor of 3 L capacity. The reactor was equipped with pH and Eh probes for the monitoring hydrogen ion activity and redox potential as shown in Fig. 3. Three liters of groundwater samples were placed in the reactor. Thirty gram of sodium acetate was added to the samples and stirred by using magnetic stirrer. The water was purged with Nitrogen gas was for 30 minutes to remove the oxygen from the reactor. Subsequently the water was purged with H_2S for 6 hours. Water samples were collected every 30 minutes for analysis of iron level over the 6 hours period. Simultaneously, total sulfide was determined out by using methylene blue method.
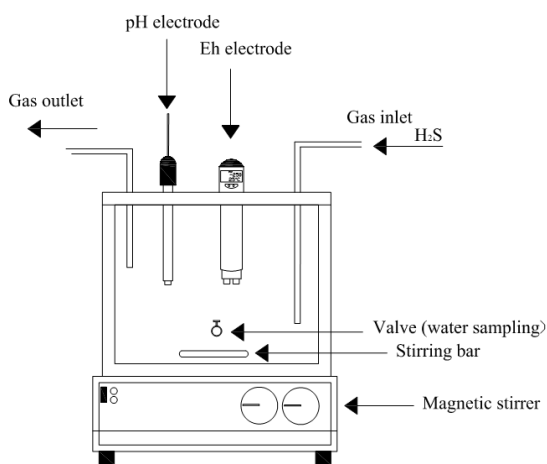

Fig. 3 Experiment using actual groundwater

C. Chemical Kinetics Studies

The results of the experiment using actual groundwater were used to analyze the kinetics and the order of the reactions. From the slopes and intercepts of the plotted data, the rate constant of the process was determined. By using the rate constant (K), the time required for the concentration of reactant to complete to half of its initial value also was calculated according to [42]-[43]. The calculations were based on the equations as follow [44]-[45]:

First order reaction:

$$Rate = k\,[A] \qquad (6)$$

k = rate / [reactant], from here it can be derived in logarithm equation as:

$$\ln [A]_t \text{ (certain time) } - \ln [A]_0 \text{ (at initial) } = -kt \qquad (7)$$

Where units of k are in $time^{-1}$

Half life equation for first order reaction:

$$T_{1/2} = \ln [2] / k \qquad (8)$$

Second order reaction:

$$Rate = k\,[A]^2 \qquad (9)$$

k = rate / $[A]^2$, in calculus equation, this rate law it can be derived as :

$$-1 / [A]_t + 1 / [A]_0 = -kt \qquad (10)$$

Where units of k are in $mol^{-1}time^{-1}$

Half life equation for second order reaction:

$$t_{1/2} = 1 / k[A]_0 \qquad (11)$$

Zero order reaction:

Rate = k

Where units of k are in mol/time, while linear equation can be derived as:

$$[A]_t \text{ (certain time) } - [A]_0 \text{ (at initial) } = -kt \qquad (12)$$

Half life equation for zero order reaction:

$$t_{1/2} = [A]_0 / 2k \qquad (13)$$

III. RESULTS AND DISCUSSION

A. Results on Preliminary Experiments

Results from the preliminary experiment on the effect of pH levels on iron removal are shown in Fig. 4. Iron concentrations in every hour during the process from pH 2 to pH 9 indicated the lowest was at pH 7.
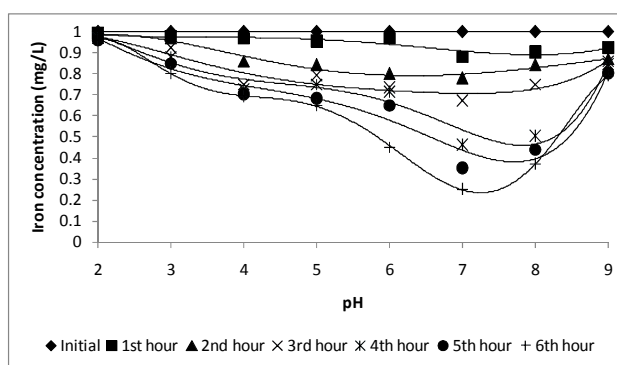

Fig. 4 Effect of initial pH on removal process of iron with initial concentration 1 mg/L; temp; 25°C

At optimum pH 7, the lowest iron level was 0.25 mg/L. This corresponds to a removal of 75%. These results were in-line with earlier findings where iron can precipitate between pH 7 and pH 8 in sulfide forms [46]-[47]. At pH 2, 3 and 4, the iron concentration was reduced to 0.96, 0.8 and 0.69, respectively. The removal at these pH levels were very poor and does not even remove half of the initial concentrations. At pH 9, the removal efficiency was again poor. It removed only 21% with of the iron, leaving the final concentration at 0.79 mg/L. At pH 5 and 6, the iron concentration was reduced to 0.65 and 0.45 mg/L, respectively. The reduction was only 35% and 55% from the initial concentration of 1mg/L.

The reduction of iron concentration level from prepared solution of 1 mg/L under anaerobic condition is shown in Fig. 5.
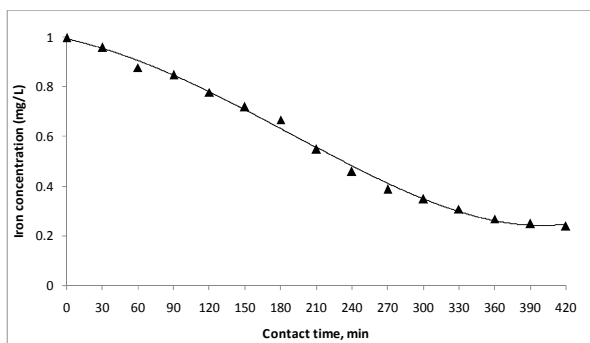

Fig. 5 Effect of contact time on removal process of iron with initial concentration 1 mg/L at pH 7

The results indicated after seven hours the iron concentration was reduced from 1 mg/L to 0.24 mg/L. The removal was 76 %. The iron level was below the allowable standards at 360 minutes of the process with the concentration of iron 0.27 mg/L with 73% of removal efficiency. The iron level was below the allowable standard of 0.3 mg/L after additional of one hour contact time of the process. Thus, the equilibrium of removal process was set in 360 minutes. However, the efficient of removal process might be changed with different concentration of iron.

B. Results on Experiment Using Actual Groundwater

Results on iron removal using actual groundwater from UTP wells under anaerobic condition are shown Fig. 6. The figure indicated the reduction of initial iron concentration varies from 1.5, 3.55 and 5.01 mg/L over 6 hours of contact time.
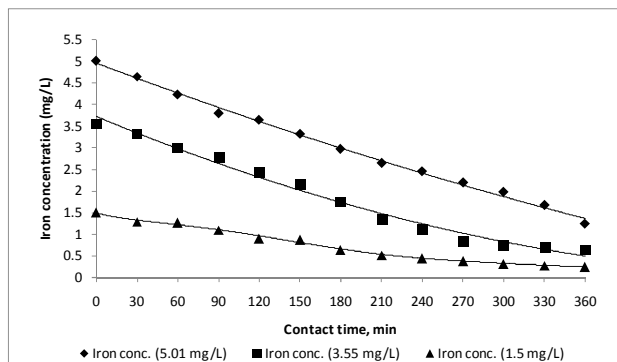

Fig. 6 Effect on initial concentration of iron at pH 7

The removal was 83%, 82% and 75% for each initial concentration of 1.5, 3.55 and 5.01 mg/L, respectively. Iron concentration of 5.01 mg/L and 3.55 mg/L was reduced to 0.65 mg/L and 1.24 mg/L, respectively. These levels are higher than WHO standard for drinking where the contact time should be increased more than previous experiment.

The residual on sulfide concentration in the water is shown in Fig. 7. The sulfide levels were determined in the treated water to meet the drinking water standard. However, since the sample is groundwater, it is possible to see the sulfide content where there value was 4.3μg/L in an average. This probably happens due to the decomposition of organic matter underground, such as decaying plant material or by chemical reduction of sulphate [48].
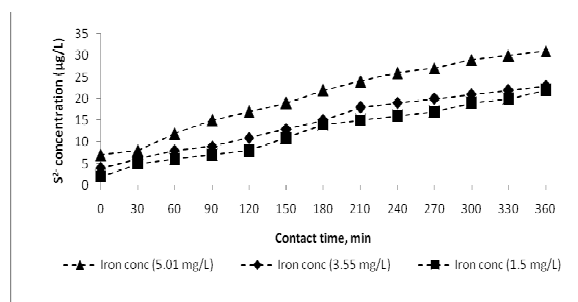

Fig. 7 Effect on initial concentration of sulfide at pH 7

At initial iron concentration of 5.01 mg/L, the sulfide levels increased 77% from 7μg/L to 31μg/L over 6 hours of contact time. While at 3.55 mg/L of iron concentration, the sulfide levels increased 82% from 4μg/L to 23μg/L. For the lower concentration, 1.5 mg/L, 91% increment of sulfide levels from 2μg/L to 22μg/L was observed. Overall these levels are is still below the standard of WHO where the allowable limit was 50μg/L [7].

The effect of redox potential (Eh) with different initial iron concentration is shown in Fig. 8.
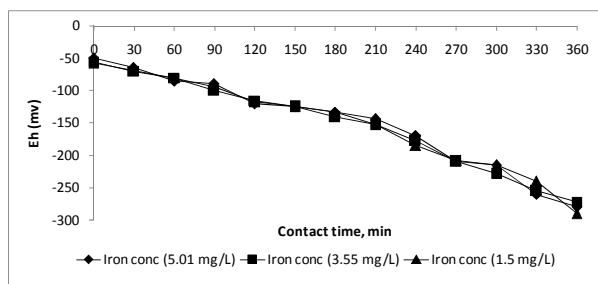
Fig. 8 Effect redox potential on initial concentration of iron at pH 7

From the figure, it shows that, the Eh was gradually decreased to -300 mV after six hours of contact time. Initially, the redox potential (Eh) value of the samples was -54 mV in an average. It is shows that the groundwater samples were already in anoxic condition [37]. In the first 30 minutes, of purging with nitrogen gas, the Eh value decreased to an average of -80 mV. The Eh values during the experiment using groundwater with iron concentration of 1.5, 3.55 and 5.01 mg/L were -290, -280 and -272 mV for 1.5, 3.55 and 5.01 mg/L, respectively. This result related with previous statement where anaerobic process should be maintained constantly at Eh value -218 mV for iron to be removed [38].

C. Kinetics Analysis

Table I shows the result of analyzed parameters for first order of kinetics reaction with different concentration. The average rate constant and time for the concentration to decrease to half from the initial concentration were 4.52×10^{-3} per time and 150 minutes, respectively.

TABLE I
PARAMETERS OF CHEMICAL KINETIC STUDIES ON FIRST ORDER

Parameters	Chemical kinetics of first order		
Iron conc. (mg/L)	1.5	3.55	5.01
slope, K (time^{-1})	4.97×10^{-3}	4.71×10^{-3}	3.87×10^{-3}
Half life, $t_{1/2}$	140	150	180
R^2	0.987	0.974	0.969

Fig. 9 shows the plots of applying the kinetics reaction after 6 hours of contact time. The plotted data in figure below indicate the correlation between the reductions of concentration over time. The value of correlation coefficient, R^2 was 0.976 in average where the highest R^2 was 0.987 at concentration 1.5 mg/L.
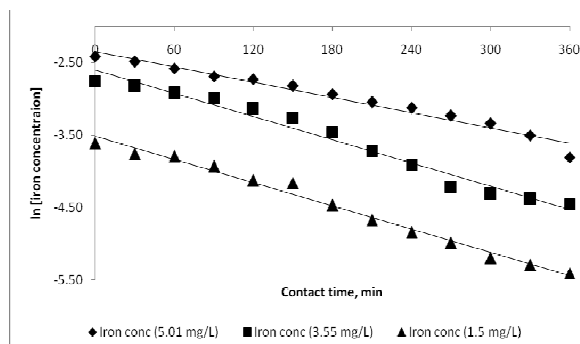

Fig. 9 The first order of chemical kinetic on initial concentration of iron at pH 7

Table II shows the result of analyzed parameters for second order of kinetics reaction with three different concentrations. The average half life was 92 minutes for the concentration to reduce into half from the initial value. The data shows that, the half-life was very high at 5.01 mg/L of iron concentration.

TABLE II
PARAMETERS OF CHEMICAL KINETIC STUDIES ON SECOND ORDER

Parameters	Chemical kinetics of second order		
Iron conc. (mg/L)	1.5	3.55	5.01
slope, K (mol^{-1}time^{-1})	0.52	0.19	0.09
Half life, $t_{1/2}$	71	82	123
R^2	0.858	0.92	0.932

Fig. 10 shows the plots the kinetics reaction after 6 hours for second order. The plotted data in figure below indicated the average of correlation and rate constant values were 0.90 and 0.26 per mol per time, respectively.
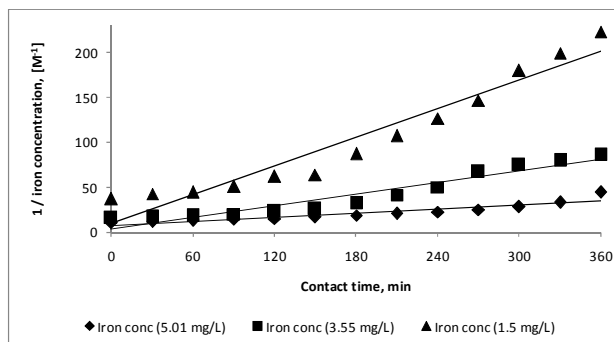

Fig. 10 The second order of chemical kinetic on initial concentration of iron at pH 7

Table III shows the result of analyzed parameters for zero order of kinetics reaction with different concentrations. The average half life was 225 minutes while the average rate constant was 3.17mol per time.

TABLE III
PARAMETERS OF CHEMICAL KINETIC STUDIES ON ZERO ORDER

Parameters	Chemical kinetics of zero order		
Iron conc. (mg/L)	1.5	3.55	5.01
slope, K (mol/time)	6.22×10^{-4}	1.44×10^{-4}	1.9×10^{-4}
Half life, $t_{1/2}$	216	220	239
R^2	0.961	0.97	0.993

Fig. 11 shows the plots of concentration over time for six hours period. The average correlation coefficient was 0.974.
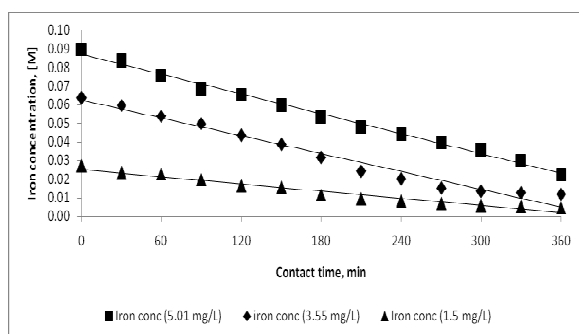

Fig. 11 The zero order of chemical kinetic on initial concentration of iron at pH 7

From the tables that have been discussed, Table I indicated that the chemical kinetics of the reaction fit with first order. This is because the correlations between the plotted data from three different concentrations were in linear line as suggested by Robson 2005 [49]. This has been confirmed by [50]-[52] who did the same correlation but with chromium. It is also shows that, the reduction process is depends on the kinetics studies [53].

IV. CONCLUSION

Iron in groundwater can be removed up to 83% of the initial concentration of 1.5 mg/L. The treated water meet the WHO standard for drinking of 0.3 mg/L. Optimum iron removal was at pH between 7 and 8. However at higher initial concentrations of 3.55 mg/L and 5.01 mg/L the efficiency drop to 82% and 75%, respectively. Sulfide levels in the water were below the allowable limits with an average 25μg/L after the process. The Eh level of the process was up to -290. The removal process was found to follow the first order reaction with average rate constant of 4.52×10^{-3} per time while the half-life was about 157 minutes.

ACKNOWLEDGMENT

REFERENCES

[1] A. F. Mohamed, W. Z. Wan Yaacob, M. R. Taha, and A. R. Samsudin, "Groundwater and soil vulnerability in the Langat basin Malaysia", *European Journal of Scientific Research*, vol. 27, no. 4, 2009, pp. 628-635.
[2] P. Sampat, "Groundwater shock", *World Watch*, vol. 13, 2000, pp. 16-24.
[3] T. Mohammed, and A. Ghazali, "Evaluation of yield and groundwater quality for selected wells in Malaysia", *Pertanika Journal of Sciences and Technology,* vol. 17, no.1, 2007: p. 33 - 42.
[4] A. Jusoh, W. M., Low, A. Nora'aini, and M. J. M. M, Noor, "Study on the removal of iron and manganese in groundwater by granular activated carbon", *Desalination*, vol. 182, 2005, pp. 347–353.
[5] V. K. Murukesan, S. Timothy, and F. Christina, "Qualitative examination of groundwater from yap and some of its neighboring island", *Technical Report : Water and Environmental Research Institute of the Western Pasific University of Guam*, no. 115, May 2006, pp. 10 - 12.
[6] E.L. Bean, "Progress report on water quality criteria", *Journal AWWA*, vol. 54, no. 11, 1962, pp. 1313-1331.
[7] WHO, "Guidelines for drinking-water quality", *Health criteria and other supporting information*. World Health Organization, Geneva, 1996, vol. 2.
[8] VEWIN, "VEWIN Recommendations",*In Dutch: VEWIN Aanbevelingen (a. de hoedanigheid van het water waterkwalitiet), VEWIN, The Netherlands,* 1993.
[9] D. Ellis, C. Bouchard, and G. Lantagne, "Removal of iron and manganese from groundwater by oxidation and microfiltration", *Desalination*, 2000. vol. 130**,** no.3, 2000, pp. 255-264.
[10] S. Sharma, " Adsorptive iron removal from groundwater", *CRC*, 2001, pp. 3 - 32.
[11] L. Fewtrell, and J. Bartram, "Water quality: guidelines, standards, and health: assessment of risk and risk management for water-related infectious disease", *IWA Publishing* , 2001.
[12] J. T. O'Connor, "Iron and manganese. In: Water quality and Treatment – A handbook of public water supplies", *New York: McGraw Hill Book Company*, 1971.
[13] Hem, J. D., *Study and interpretation of the chemical characteristics of natural water. Third Edition, United States Geological Survey Water-Supply Paper 2254.* 1989.
[14] S.D. Faust, and O.M. Aly, "Chemistry of Water Treatment", Second Edition, *Ann Arbor Press Inc.,* USA. 1998.
[15] R. J, Castle II, and J.N. Harn, "Case studies: aerobic vs anaerobic pretreatment of groundwater", *Groundwater,* Avsapof, 2002.
[16] S.K. Khanal, "Overview of Anaerobic Biotechnology: Anaerobic Biotechnology for Bioenergy Production", *Wiley-Blackwell*, 2009, pp. 1-27.
[17] A. Wolthoorn, E. Temminghoff, and W. van Riemsdijk, "Effect of synthetic iron colloids on the microbiological NH4+ removal process during groundwater purification.",*Water research*, vol. 38, no.7, 2004, pp. 1884-1892.
[18] U. Rott, "Protection of groundwater quality by biochemical treatment in the aquifer", *IAHS Publ,*vol. 173, 1990.
[19] D. John, "*Chemical equilibrium diagrams for ground-water system",* 2003.
[20] D. Alkalay, L. Guerrero, J. M. Lema, R. Mendez, and R. Chamy, "Review: Anaerobic treatment of municipal sanitary landfill leachates: the problem of refractory and toxic components"*, World Journal of Microbiology and Biotechnology*, vol. 14, no. 3, 1998, pp. 309-320.
[21] Cohen, R.R.H., *Use of microbes for cost reduction of metal removal from metals and mining industry waste streams.* Journal of Cleaner Production, 2006. **14**(12-13): p. 1146-1157.
[22] R. D. Cameron, F. A. Koch, "Trace Metals and anaerobic digestion of leachate", *Journal of the Water Pollution Control Federation* , vol. 52, 1980, pp. 282-292.
[23] Vogel, "VOGEL'S : Textbook of Macro and semimicro qualitative inorganic analysis revised by G. Shevla ", 5ed, Longman Inc., 1979.
[24] M. M. M. Gonçalves, A. C. A. Da Costa, S. G. F. Leite, G. L. Sant'Anna, "Heavy metal removal from synthetic wastewaters in an anaerobic bioreactor using stillage from ethanol distilleries as a carbon sourc", *Chemosphere*, vol. 69, no. 11, 2007, pp. 1815-1820.
[25] A. H. Nielsen, P. Lens, Jes, Vollertsen, and T. H. Jacobsen, "Sulfide-iron interactions in domestic wastewater from a gravity sewer"*, Water research*, vol. 39, no.12, 2005, pp. 2747-2755.

[26] S.D. Kim, J. J. Kibane II, and K.C. Daniel, "Prevention of Acid Mine Drainage by Sulfate Reducing Bacteria: Organic Substrate Addition to Mine Waste Piles", *Environmental Engineering Science.*, 1999. vol. 16, no. 2,1999, pp. 139-145.

[27] S. Oana, and H. Ishikawa, "Sulfur isotopic fractionation between sulfur and sulfuric acid in the hydrothermal solution of sulfur dioxide", *Geochemical Journal*, vol.1, 1966, pp. 45 - 50.

[28] H. Lin, Z.Li, K. Tohji, N. Tsuchiya, and N. Yamasaki, "Reaction of Sulfur with Water under Hydrothermal Conditions", *Proc.14th Int. Conference on the Properties of Water and Stream*, 2005, pp. 365-368.

[29] N. Tsuchiya, y. Suto, T. Kabuta, S. Morikawa, and S. Yokoyama, "Sustainable hydrogen production system with sulfur–water–organic materials by hydrothermal reaction", *Journal of Materials Science*, vol. 43, no. 7, 2008, pp. 2115-2122.

[30] M. E. Böttcher, B. Thamdrup, and T.W. Vennemann, "Oxygen and sulfur isotope fractionation during anaerobic bacterial disproportionation of elemental sulfur", *Geochimica et Cosmochimica Acta*, vol. 65, no.10, 2001, pp. 1601-1609.

[31] B. Thamdrup, K. Finster, J.W. Hansen, and F. Bak, "Bacterial disproportionation of elemental sulfur coupled to chemical reduction of iron or manganese", *Applied and environmental microbiology*, vol. 59, no. 1,1993, pp. 101.

[32] M. Willow and R. Cohen, "Technical reports-Bioremediation And Biodegradation-Ph, Dissolved Oxygen, And Adsorption Effects On Metal Removal In Anaerobic Bioreactors", *Journal of Environmental Quality*,. vol. 32, no.4, 2003, pp. 1212-1221.

[33] M. Grindstaff, "Bioremediation of chlorinated solvent contaminated groundwater", *Citeseer*, United States Environmental Protection Agency. Technology Innovation Office, 1998

[34] T. Jong, and D.L. Parry, "Removal of sulfate and heavy metals by sulfate reducing bacteria in short-term bench scale upflow anaerobic packed bed reactor runs", *Water research*, vol. 37, no.14, 2003, pp. 3379-3389.

[35] J.A. Saunders, M. K. Lee, M. Shamsudduha, P. Dhakal, A. Uddin, M. T. Chowdury,and K. M. Ahmed, "Geochemistry and mineralogy of arsenic in (natural) anaerobic groundwaters", *Applied Geochemistry*, vol. 23, no. 11, 2008, pp. 3205-3214.

[36] G. Peters, W. Maher, J. Barford, and V. Gomes, "Selenium associations in estuarine sediments: Redox effects", *Water, Air, & Soil Pollution*, vol. 99, no.1,1997, pp. 275-282.

[37] H. Peterson., R. Pratt, R. Neapetung, and O. Sortehaug, "Integrated Biological Filtration and Reverse Osmosis treatment of cold poor quality groundwater on the North American prairies", *Safe Drinking Water Foundation*,IWA Publishing, vol. 5, 2006, pp. 424–432.

[38] L. Wang, Q. Zhou, and F.T. Li, " Avoiding propionic acid accumulation in the anaerobic process for biohydrogen production", *Biomass and Bioenergy*, vol. 30 no.2, 2006, pp. 177-182.

[39] R.W. Morris,and J.G. O'Brien, "Oxygen and the Growth and Metabolism of Clostridium acetobutylicum.", *Microbiology*, vol. 68, no. 3,1971, pp. 307-318.

[40] J. G. Morris, "The physiology of obligate anaerobiosis", *Adv. Microb. Physiol.*, vol. 12, 1975, pp. 169–246.

[41] A.D. Eaton, L.S. Clesceri, A. E. Greenberg, and M. A. H. Franson, "Standard methods for the examination of water & wastewater", *American Water Works Association*, 19th ed, Water Environment Federation, 1995.

[42] S.R. Logan, "Fundamentals of Chemical Kinetics", Addison Wesley Longman Limited, Edinburgh Gate, Harlow, England., 1996, pp. 9-11.

[43] Brown, Lemay and Bursten, *"Chemistry: The Central Science", Eigth Edition.* Prentice-Hall, Inc. Upper Saddle River, NJ 07458, 2000, chap. 14, pp. 509 - 558.

[44] E. Denisov, O.Sarkisov, and G. I. Likhtenshtein, "Chemical Kinetics: Fundamentals and Recent Developments", *Elsevier B.V .*, 2003.

[45] M. R. Wright, "An Introduction to Chemical Kinetics", John Wiley & Sons, Ltd., 2005.

[46] D. Rickard, S. Grimes, I. Butler, A. Oldroyd, and K. L. Daives, "Botanical constraints on pyrite formation", *Chemical Geology*, vol. 236, no. 4, 2007, pp. 228-246.

[47] R.A. Berner, "Iron Sulfides Formed from Aqueous Solution at Low Temperatures and Atmospheric Pressure", *The Journal of Geology*, vol. 72 ,no. 3, 1964, pp. 293-306

[48] C. O'Sullivan, W. Clarke, and D. Lockington, "Sources of Hydrogen Sulfide in Groundwater on Reclaimed Land.", *Journal of Environmental Engineering* vol. 131, no. 3, 2005, pp. 471 - 477.

[49] W.M. Robson, "An Introduction to Chemical Kinetics", John Wiley & Sons, Ltd., 2005.

[50] M. Chrysochoou, and A. Ting, "A kinetic study of Cr(VI) reduction by calcium polysulfide", *Science of The Total Environment*, vol. 409, no. 19, 2011 p. 4072-4077.

[51] Lan, Y., et al., *Catalysis of Elemental Sulfur Nanoparticles on Chromium(VI) Reduction by Sulfide under Anaerobic Conditions.* Environmental Science & Technology, 2005. **39**(7): p. 2087-2094.

[52] Kim, C., et al., *Chromium(VI) Reduction by Hydrogen Sulfide in Aqueous Media: Stoichiometry and Kinetics.* Environmental Science & Technology, 2001. **35**(11): p. 2219-2225.

[53] I. J. Buerge, and S. J. Hug, "Kinetics and pH Dependence of Chromium (VI) Reduction by Iron (II)", *Environmental Science & Technology,* vol. 31, no.5, 1997, pp. 1426-1432.