AN INVESTIGATION ON THE REMOVAL OF ARSENIC FROM SIMULATED GROUNDWATER BY ADSORPTION USING IRON AND IRON OXIDE[III]

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This work aims to investigate the removal of arsenic from the simulated groundwater by batch adsorption using Iron (ZVI) and Iron[III] Oxide (IO). The effect of initial arsenic concentration, adsorbent dose and pH were investigated. Adsorption equilibrium and its kinetics were also studied. The results showed that both ZVI and IO have a high efficiency for adsorption of arsenic from groundwater. Langmuir isotherm described well the adsorption equilibrium and the pseudo-second order kinetic model gave the best fit with the experimental kinetic data for both ZVI and IO.

Key Words : *Adsorption, Arsenic, Iron Oxide, Iron, Simulated groundwater, Zero-Valent Iron*

1. INTRODUCTION

Arsenic is well-known as the "king of poison". Long-term exposure to which can cause cancer of the skin, lungs and many others. Therefore, the World Health Organization recommended that arsenic content in drinking water should not be higher than 0.01 mg/L. Recently, arsenic (As) contamination of groundwater - one of the most important sources for drinking water - has become a major concern on a global scale, especially in Bangladesh, India and South East Asia.

In groundwater, arsenic usually exists as oxy-anions compounds namely arsenite (tri-valent arsenic, As[III]) and arsenate (penta-valent arsenic, As[V]) where As[III] is known as the predominant specie in groundwater, more toxic and more difficult to remove than As[V] [1].

There are several techniques to remove arsenic from groundwater including physico-chemical, biological, membrane and other methods. However, almost all of these techniques have a difficulty for applying in the rural areas, especially of developing and poor countries. One of the promising methods for arsenic removal that can be considered as efficient and low cost method for wide scale application in rural areas is adsorption technique where appropriate adsorbents are used. There are many adsorbents which could adsorb arsenic from water such as activated carbon, alumina, iron, titanium, metal oxides, clay minerals, synthetic anion exchange resins, chitin chitosan, bone char, cellulose materials and many others. These adsorbents have the different properties, performaces and costs.

Iron and its compounds is one the most effective adsorbents for the removal of arsenic contamination from drinking water. Use of iron (Zero-Valent Iron, ZVI) to remove arsenic has been actively

investigated by many researchers [2), 3), 4), 5)]. Arsenic removal was dramatically affected by oxygen content, pH and surface area in both the adsorption kinetics and adsorption capacity. The maximum As adsorption capacity was 3.5 mg-As[III]/g-ZVI [5)]. Also, previous studies [6), 7), 8)] showed that iron oxides (IO), including oxy-hydroxides and hydroxides, such as amorphous hydrous ferric oxide (FeOOH), goethite (α-FeOOH) and hematite (α-Fe$_2$O$_3$), are promising effective adsorptive materials for the removal of both As[III] and As[V] from groundwater.

Many researchers have focused on ZVI and IO for arsenic removal from groundwater, however, two of these adsorbents have been evaluated at different pH, temperatures, As[III]/As[V] ratios, adsorbent doses and initial arsenic concentration ranges. They have been used for the removal of arsenic from different types of water, such as groundwater, surface water, or wastewater. Some specific information on the major factors affecting to the arsenic removal is still incomplete and the results are not yet very conclusive.

On the other hand, most studies have used either distilled or de-ionized water (pure water) which does not contain any other ions rather than arsenic ions, instead of actual contaminated groundwater, especially for the study on the adsorption equilibrium and its kinetics. The results, therefore, may not be reflective of the true behavior in the actual treatment system.

In addition, many researchers have used linear regression method to estimate the isotherm coefficients which may cause errors due to the transformation of the non-linear isotherm equation (Langmuir, Freundlich isotherms) into a linear expression of the isotherm equation [9)]. Thus, the non-linear regression method could be a better way to obtain the equilibrium isotherm coefficients [10)].

This work aims to investigate the removal of both As[III] and As[V] (use of mixture of 70% As[III] and 30% As[V]) from simulated groundwater by batch adsorption using Iron (ZVI) and Iron[III] Oxide (IO). The effect of initial arsenic concentration, pH, and adsorbent dose were investigated. Three most commonly used adsorption isotherms: Langmuir, Freundlich, and Langmuir-Freundlich were examined. Both linear and non-linear regression methods were used for estimation and comparison of the isotherm coefficients. Adsorption kinetics was also studied.

In this study, the use of the simulated typical contaminated groundwater which represented the actual typical arsenic-contaminated groundwater. This contains both As[III] and As[V] as well as several other typical ions of actual groundwater (Ca^{2+}, Na$^+$, Mg^{2+}, Cl$^-$, HCO$_3^-$, etc).

The intended application of this study is to remove arsenic from groundwater or natural surface waters for household drinking water using a multiple-stages filter where the removal of arsenic by ZVI or IO is one of the most important stages, other toxic elements or compounds will be removed by another adsorbents such us AC activated carbon (AC) or/and silicate sand (SiO$_2$). The resulting water effluent will be safe for drinking, free from arsenic and other contaminants. Therefore, the use of simulated groundwater instead of pure water is more practical to represent the actual condition of arsenic treatment system.

2. EXPERIMENT

(1) Simulated groundwater

A typical groundwater with average concentration of the major components was simulated and used in this study. The major components of the simulated groundwater are shown in **Table 1** as referred from previous work [4)].

Table 1 Compositions of simulated water

Compositions	Concentration, mg/L
CaCl$_2$·2H$_2$O[*]	230
Na$_2$SO$_4$[*]	1200
NaHCO$_3$[*]	370
MgCl$_2$·6H$_2$O[*]	135

(* *These chemicals are from Wako Pure Chemicals Ltd, Japan*)

(2) Arsenic stock solution

The stock solutions of arsenite (As[III]) were prepared from As[III] standard solution of 1003 mg/L (Wako Pure Chemicals Ltd., Japan) by dilution with distilled water. The stock solutions of arsenate (As[V]), containing 4.1646 mg of Na$_2$HAsO$_4$.7H$_2$O (Wako Pure Chemicals Ltd, Japan), were mixed thoroughly with distilled water to make a total volume of 1000 mL. The stock solution has an arsenic concentration of 1000 mg/L.

(3) Preparation of Adsorbents

ZVI and *IO* (95% pure) obtained from Wako Pure Chemicals Ltd, Japan with particle size of 150μm were dried at 105°C in the oven for 24 hours to release the humidity and organic matter, if any.

(4) Experimental procedure

In this study, the first-batch experiment was

designed to investigate the effects of pH within the range of 5 - 9, initial arsenic concentration within the range of 0.11 - 0.97 mg/L and adsorbent dose within the range of 2.0 - 10.0 g/L.

The second-batch of experiments for the study on adsorption equilibrium and adsorption kinetics were conducted at different initial concentrations of arsenic from 0.11 - 2.13 mg/L for ZVI and 0.11 - 1.43 mg/L for IO at fixed adsorbent dose of 5 g/L with a pH of 8.18 (pH of simulated groundwater).

Both batch experiments were performed in a series of 50 mL flasks, each flask contained 50mL of simulated groundwater and adsorbents with initial arsenic concentration at given pH and open to the air (aerobic condition) and were carried out in a temperature-controlled shaking bath for 24 h under room temperature (25 °C) and atmospheric condition. The sample flasks were stirred well (fast shaking). The time span and sampling interval for all runs were the same. A mixture of 70% As[III] and 30% As[V] were used for all of experiments and the total arsenic content was analyzed by ICP-MS (Seiko SII).

3. RESULTS AND DISCUSSION

(1) Effect of pH

pH is an important factor in the removal of arsenic by adsorption, especially by using alumina or iron-based adsorbents. Iron and its compounds are known as the most effective adsorbents, but strongly dependent on pH for arsenic adsorption.

Previous studies used zero-valent iron (ZVI) for arsenic remediation and indicated that arsenic removal is dramatically affected by pH. More than 99.8% of the As[V] was removed whereas only 82.6% of the As[III] was removed at pH 6 after mixing for 9h under atmospheric condition [5]. Indeed, this study found out that most of the arsenic was removed quickly at pH of 5 (**Fig.1a**). After 9h, the percentage removals of total arsenic were 97.99, 97.24 and 94.63% for pH of 5, 7 and 9 respectively. After 24 h, 99.70, 99.44 and 96.69% of total arsenic was removed for pH of 5, 7 and 9 respectively. The mechanism of arsenic adsorption using ZVI could be attributed mainly by both affinity adsorption and chemical reaction. Affinity adsorption includes molecule-surface interaction, electrostatic interaction (i.e., ion exchange, coulombic attraction); while chemical reaction includes ligand exchange, surface complexation, covalent bonding, and Van der Waals forces [11], [12], [13], [14], [15]. These mechanisms may occur depending on the nature of the adsorbent and the existing forms of the arsenic species. The affinity adsorption and chemical reaction may occur simultaneously.
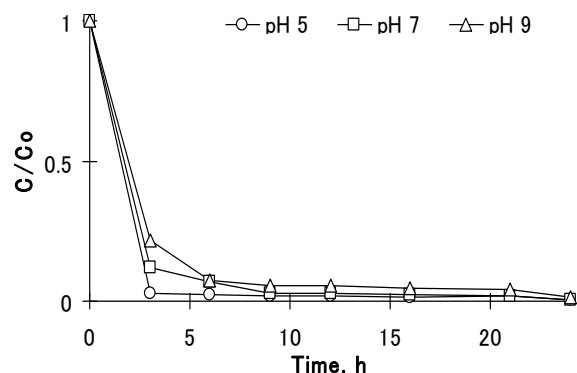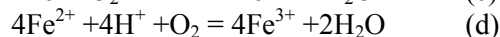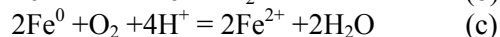

Fig.1a Effect of pH for ZVI (Fe powder 95%, particle size 0.15mm, Co 0.49mg/L, dose 5g/L)

At the considered range of pH in this study (pH 5-9), tri-valent arsenic (As[III]) is stable at pH 0–9 as neutral H_3AsO_3; whereas penta-valent arsenic (As[V]) exists as the oxy-anions $H_2AsO_4^-$ and $HAsO_4^{2-}$ [16]. Since As[V] exists in the solution as negative ions, the adsorption of As[V] may be a result of electrostatic attraction between anionic As[V] and the positively-charged iron on the surface of the adsorbent. The negatively-charged arsenic ions and positively-charged adsorbent surface favor the arsenic adsorption by electrostatic attraction. These have been explained in detail by Ronald, Prasenjit and co-workers [17], [18]. On the other hand, although As[III] exists in the solution as a neutral compound (H_3AsO_3), it may be rapidly removed by chemical reaction as follows:

$$Fe(OH)_3 + H_3AsO_3 \rightarrow FeAsO_3 . 2H_2O + H_2O \quad (a)$$

Ferric hydroxide has been known to have a high arsenic adsorption capacity which was formed from *ZVI* by the presence of oxygen in an open air condition (aerobic condition) as shown in the following equations [19]:

$$Fe^0 + 2H^+ = Fe^{2+} + H_2 \qquad (b)$$
$$2Fe^0 + O_2 + 4H^+ = 2Fe^{2+} + 2H_2O \qquad (c)$$
$$4Fe^{2+} + 4H^+ + O_2 = 4Fe^{3+} + 2H_2O \qquad (d)$$
$$Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+ \qquad (e)$$

Therefore, both forms of arsenic (As[III] and As[V]) may be removed by ZVI in the pH range of this study (pH 5-9). However, the formation of $Fe(OH)_3$ is more favorable at low pH. This explains why adsorption of arsenic using ZVI is better at pH 5. In addition, a possible formation of amorphous hydrous ferric oxide FeOOH may have the highest adsorption capability for arsenic since it has the highest surface area [20], [21].

With IO, Ranjan and co-workers [22] used the synthesized hydrous ferric oxide for arsenic sorption

and showed that the As[V] sorption strongly depended on pH, while As[III] sorption was pH insensitive. In **Fig.1b**, the arsenic adsorption by *IO* at pH of 5, 7 and 9 are not very different and most of the arsenic was removed after 24 h. However, similarly with *ZVI*, the low pH is favorable for arsenic removal because after 24 h, the percentage removals of total arsenic were 97.21, 94.94, and 92.44% at pH 5, 7, and 9 respectively. The same results were obtained from earlier study of Gupta and co-workers [23] using iron oxide-coated sand for the removal of As[III] and As[V].
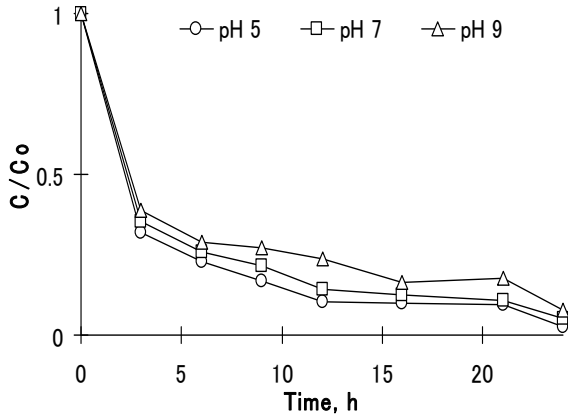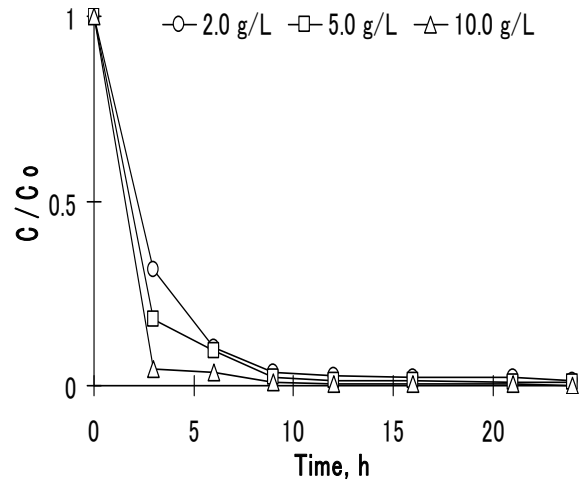

Fig.1b Effect of pH for IO (Fe$_2$O$_3$ powder 95%, particle size 0.15 mm, Co 0.49mg/L, dose 5g/L)

The mechanism of arsenic adsorption using IO may be due mainly to the affinity adsorption only (no chemical reaction) since IO is insoluble in water at pH range of the study (pH 5-9). At this pH range, As[V] with negative charge (H$_2$AsO$_4^-$ and HAsO$_4^{2-}$) could be attached onto IO surface by electrostatic interaction whereas As[III] with neutral charge (H$_3$AsO$_3$) may be adsorbed onto the pores of crystal lattice of IO particles. Both forms of arsenic can be removed by physical adsorption only using IO. This could be a possible reason why arsenic adsorption using IO was less effective than ZVI. However, IO is usually an industrial waste or a by-product in several production processes and therefore it may be considered as a cheap adsorbent.
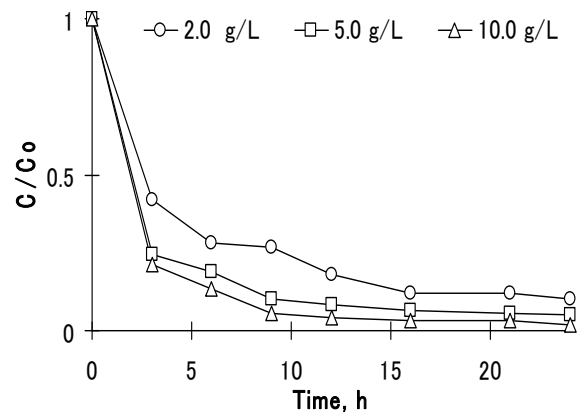
(2) Effect of adsorbent dose

The effect of adsorbent dose is depicted in **Fig.2a** for *ZVI* and **Fig.2b** for *IO*, which show that the adsorption efficiency increases very rapidly with an increase in adsorbent dose from 2 to 10g/L. After 9h, 96.45, 97.78 and 99.02% of total arsenic were removed with *ZVI* and 77.30, 89.83 and 94.53% of total arsenic with *IO* were removed for doses of 2, 5 and 10g/L, respectively. At 10g/L, almost all of total arsenic (both As[III] and As[V]) were removed after 9 and 21 hours for ZVI and IO, respectively. A high

amount of adsorbent has more available adsorption sites for the arsenic to be adsorbed. The same observation was reported by Gupta and co-workers [23]. However, with *ZVI*, the use of lower dose (2 g/L) could still remove arsenic completely after 12 h. This may be due to the amorphous FeOOH or iron hydroxide that is formed after some hours of adsorption and led to an increase of the surface area and more active sites for arsenic adsorption.

Fig.2a Effect of adsorbent dose for *ZVI* (Fe powder 95%, particle size 0.15mm, Co 0.49mg/L, pH of simulated groundwater, pH8.18

**Fig 2b** Effect of adsorbent dose for *IO* (Fe$_2$O$_3$ powder 95%, particle size 0.15mm, Co 0.49mg/L, pH of simulated groundwater, pH8.18)
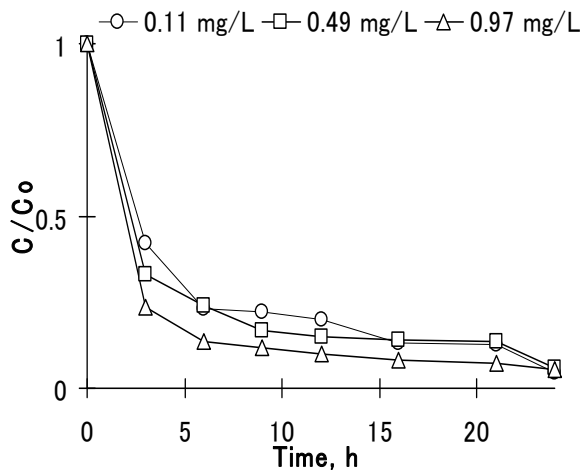
(3) Effect of initial arsenic concentration

The effect of initial arsenic concentration (from 0.11 to 0.97 mg/L) on uptake of arsenic by *ZVI* and *IO* is shown in **Fig.3a** and **Fig.3b**, respectively. The results show that the efficiency in removal of arsenic is higher with a lower initial concentration (0.11 mg/L) and a gradual decrease at higher initial concentration of arsenic was observed. However, although with highest initial concentration of arsenic (0.97 mg/L), the percentage removal of total arsenic was still high as 95.65% compared to the 95.95 and

96.11% for initial concentration of 0.11 and 0.49 mg/L, respectively. This shows that *ZVI* is a very effective adsorbent in the removal of arsenic at high initial concentration of arsenic. This may be due to the formation of amorphous hydroxide iron which is known as the most effective adsorbent for arsenic adsorption [20], [21].
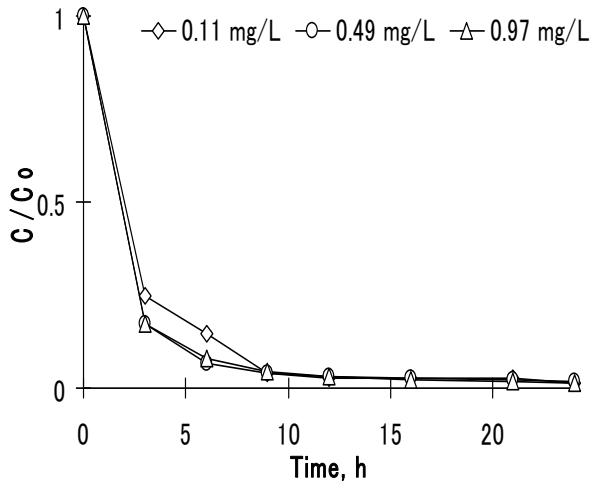
Fig.3a Effect of arsenic initial concentration for ZVI (Fe powder 95%, particle size 0.15 mm, dose 5 g/L, pH of simulated groundwater, pH 8.18)

Fig.3b Effect of arsenic initial concentration for IO (Fe_2O_3 powder 95%, particle size 0.15mm, dose 5g/L, pH of simulated groundwater, pH 8.18)

(4) Adsorption isotherm

The distribution of arsenic between the liquid phase and the solid phase at the equilibrium in the adsorption process can be described by adsorption isotherm. Several adsorption isotherms based-on different assumptions have been suggested and used by some authors. Among them, Langmuir and Freundlich isotherms, and the combination of these two isotherms known as Langmuir-Freundlich isotherm are commonly used [24]. To calculate the isotherm coefficients, linear and nonlinear regression methods are used for both Langmuir and Freundlich

isotherms. However, for Langmuir–Freundlich isotherm, nonlinear regression method must be employed. Several computer softwares can be used for solving the nonlinear regression problem; Microsoft Excel (solver add-in) was used in this study.

a) Freundlich isotherm

The Freundlich isotherm presented an empirical adsorption isotherm for non-ideal sorption on heterogeneous surfaces and multilayer sorption (one active site of adsorbent can adsorb more than one molecule). This isotherm is expressed by the equation as follows:

$$q_e = K_F C_e^{1/n} \qquad (1a)$$

A linear form of this expression is:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (1b)$$

where q_e is the adsorbed amount of arsenic per gram of adsorbent at equilibrium (*mg-As/g-adsorbent, mg/g*), C_e is the equilibrium arsenic concentration in solution (*mg/L*). $K_F(L/g)$ and n is the Freundlich constant and represents the significance of the adsorption capacity and intensity of adsorption, respectively. K_F and n were calculated from the intercept and slope of the plot $log q_e$ and $log C_e$ (linear regression method) and Microsoft Excel (non-linear regression method). The values of Freundlich isotherm constants as calculated from both linear and non-linear regression methods are summarized in the **Tables 2a** and **2b**.

b) Langmuir isotherm

Langmuir isotherm presented a theoretical adsorption isotherm for ideal sorption on the homogeneous surface of solid adsorbent with mono layer sorption (one site of adsorbent can adsorb only one molecule). This isotherm is expressed by the equation as follows:

$$q_e = \frac{Q_0 K_{LF} C_e}{1 + K_{LF} C_e} \qquad (2a)$$

One of the linear forms of this expression is:

$$\frac{1}{q_e} = \frac{1}{Q_0 K_L} \frac{1}{C_e} + \frac{1}{Q_0} \qquad (2b)$$

where q_e is the adsorbed amount of arsenic per gram of adsorbent at equilibrium (*mg-As/g-adsorbent, mg/g*), C_e is equilibrium arsenic concentration in

solution (*mg/L*). K_F is the Langmuir constant (*L/mgs*) and Q_0 represents the adsorption capacity of the adsorbent, (*mg/g*). K_L and Q_0 were calculated from the intercept and slope of the plot $1/q_e$ and $1/C_e$. The values of Langmuir isotherm constants as calculated from both methods are also summarized in **Tables 2a** and **2b.**

c) Langmuir –Freundlich isotherm

Combination of Langmuir and Freundlich isotherm is well known as Langmuir –Freundlich isotherm:

$$q_e = \frac{Q_0 K_{LF} C_e^{1/n}}{1 + K_{LF} C_e^{1/n}} \qquad (3)$$

where q_e is the adsorbed amount of arsenic per gram of adsorbent at equilibrium (*mg-As/g-adsorbent, mg/g*), C_e is the equilibrium arsenic concentration in solution (*mg/L*). K_{LF}, *n* are Langmuir-Freundlich constants and Q_0 represents the adsorption capacity of adsorbent, (*mg/g*). K_{LF} and Q_0 were calculated by nonlinear regression method. The graph and summary of the results are shown in **Fig. 4a; 4b** and **Tables 2a; 2b.**
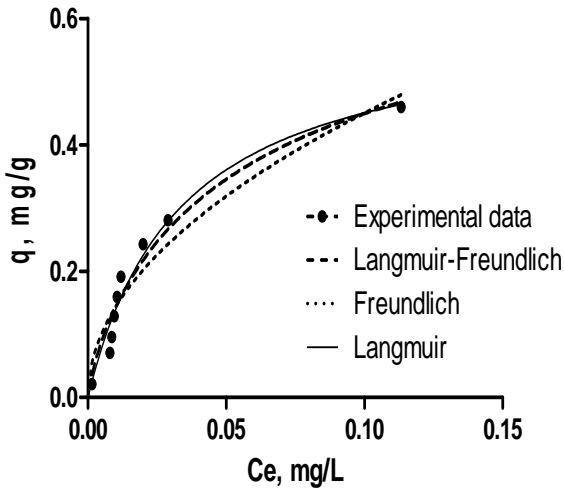
Fig.4a Non-linear plot of adsorption isotherms for ZVI (Fe powder 95%, particle size 0.15mm, Co 0.11-2.13mg/L, dose 5g/L, pH of simulated groundwater, pH 8.18)

d) Comparison of adsorption isotherms

In this study, both linear and nonlinear regression methods were used for the estimation of the isotherm coefficients. The results are shown in **Tables 2a** and **2b**. It can be seen from these tables that the estimated
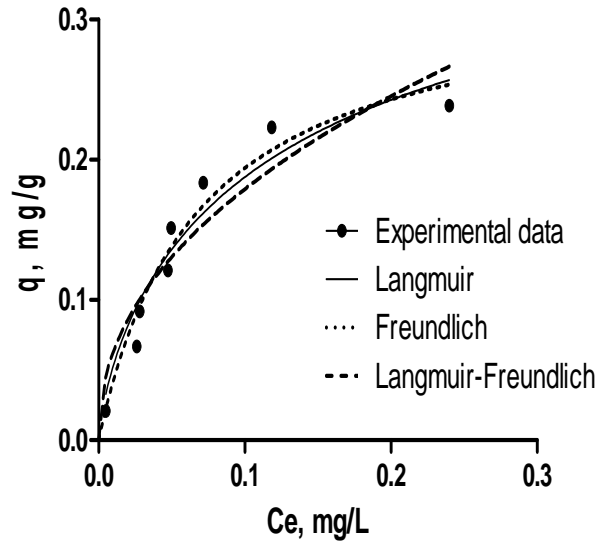
Fig.4b Non-linear plot of adsorption isotherms for IO (Fe$_2$0$_3$ powder 95%, particle size 0.15mm, Co 0.11-1.43mg/L, dose 5g/L, pH of simulated groundwater, pH 8.18)

values of the isotherm coefficients calculated by the two regression methods: linear and nonlinear are quite different but not far away from each other. This may be because of the linearized transformation problem. Indeed, Kumar and Sivanesan [10], Longhinotti and co-worker [9] showed that there are different forms of linear expression, especially Langmuir isotherm, which may give different results. In other words, the estimated values of Langmuir isotherm coefficients depend on the form of Langmuir linear expression when linear regression method is applied. Therefore, non-linear regression may be a more appropriate method to obtain the equilibrium isotherm coefficients from the experimental data.

Table 2a Comparison of adsorption isotherm coefficients for ZVI

Isotherm	Parameters			
	Q_0	K	1/n	r^2
Freundlich	-	(3.40)	(0.73)	(0.899)
		1.42	0.50	0.913
Langmuir	(0.67)	(22.32)	-	(0.943)
	0.60	**29.98**		**0.968**
Langmuir-Freunlich	0.76	9.81	0.81	0.916

Table 2b Comparison of adsorption isotherm coefficients for IO

Isotherm	Parameters			
	Q_0	K	1/n	r^2
Freundlich	-	(0.90)	(0.67)	(0.906)
		0.51	0.46	0.887
Langmuir	(0.32)	(14.03)	-	(0.949)
	0.33	**14.79**		**0.959**
Langmuir-Freunlich	0.43	4.22	0.74	0.914

Note: The values in the bracket ( ) are from linear regression method, others are from non-linear regression.

Tables **2a** and **2b** showed that both Langmuir, Langmuir-Freundlich isotherms seem to fit with the equilibrium experimental data for *ZVI* and *IO*, as shown in the nonlinear regression coefficients r^2 (r^2 is greater than 0.9). However, Langmuir isotherm give a better fit with equilibrium experimental data than the Langmuir-Freundlich isotherm. Hence, it is reasonable to conclude that the adsorption equilibrium of arsenic removal process from simulated groundwater by using *ZVI* and *IO* may follow Langmuir isotherm model. The adsorption capacity are 0.60 mg/g for *ZVI* and 0.33 mg/g for *IO* as shown in the Q_0 values of Langmuir isotherm - the best fit isotherm- in **Tables 2a** and **2b**.

(5) Adsorption kinetics

The understanding of batch adsorption kinetics is needed for design and operation of adsorption columns in a real scale up system of arsenic treatment. The nature of the arsenic adsorption kinetic process depends on physical or chemical characteristics of the adsorbent and also on the operating conditions. Two most popular adsorption kinetic models; pseudo-first order and pseudo-second order have been used by some previous studies to describe the process kinetics of arsenic adsorption. In this study, the applicability of the pseudo-first order (Lagergren model) and pseudo-second order kinetics (Ho model) were examined for the arsenic adsorption process by using *ZVI* and *IO*. The fitted evaluation was based on the regression correlation coefficient, r^2 values.

a) Pseudo-first order kinetics

Pseudo-first order kinetics model was derived by Lagergren in 1898 as follows [25]:

$$\frac{dq}{dt} = k_1(q_e - q) \tag{4a}$$

where q is the amount of arsenic adsorbed (mg/g) at time t, q_e is the amount of arsenic adsorbed (mg/g) at equilibrium, and k_1 is the observed adsorption rate coefficients (s^{-1}). By integrating the above equation

with respect to its boundary conditions $q = 0$ at $t = 0$ and $q = q_e$ at $t = t$, the linear form is:

$$\log\left(\frac{q_e}{q_e - q}\right) = -\frac{k_1}{2.303}t \tag{4b}$$

Thus, the rate constant k_1 (s^{-1}) can be calculated from the plot of $log(q_e/q_e-q)$ versus time t (**Fig.5a** and **5b**). The values of pseudo-first order kinetics coefficients as calculated from the plots are shown in **Table 3**.

Table 3 Value of observed rate coefficients for pseudo-first order kinetics

Adsorbents	Initial As concentration	k_1, (s^{-1})	r^2
ZVI	0.11 mg/L	0.27	0.731
	0.49 mg/L	0.31	0.720
	0.97 mg/L	0.30	0.840
IO	0.11 mg/L	0.22	0.660
	0.49 mg/L	0.16	0.487
	0.97 mg/L	0.14	0.690
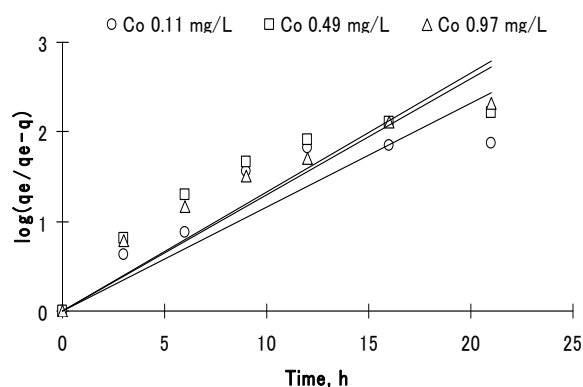
Fig.5a Plot of pseudo-first order kinetics for *ZVI* (Fe powder 95%, particle size 0.15mm, Co 0.11-0.97mg/L, dose 5g/L, pH of simulated groundwater, pH8.18)
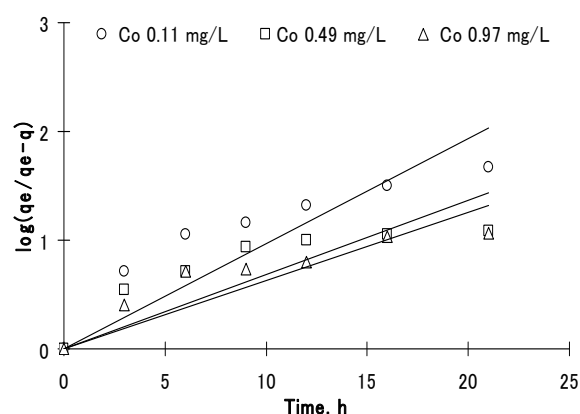
Fig.5b Plot of pseudo-first order kinetics for *IO* (Fe$_2$O$_3$ powder 95%, particle size 0.15mm, Co 0.11-0.97 mg/L, dose 5g/L, pH of simulated groundwater, pH8.18)

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b) Pseudo-second order kinetics

It can be seen from linear regression correlation coefficient, r^2 values that the first-order kinetics is not high enough to fit with the experimental data for *ZVI* and *IO*. Therefore, adsorption kinetics of the process should be further analyzed. Assuming that the rate of arsenic adsorption process using *ZVI* and *IO* is followed by pseudo-second-order kinetics which was first used by Ho and co-workers [25] as shown below:

$$\frac{dq}{dt} = k_2 \left(q_e - q \right)^2 \qquad (5a)$$

where q is amount of arsenic adsorbed (*mg/g*) at time t, q_e is the amount of arsenic adsorbed (*mg/g*) at equilibrium, and k_2 represents the observed adsorption rate coefficients (*g/mgs*). By integrating, using the boundary conditions $t = 0$ to $t = t$ and $q = 0$ and $q = q_e$, the linear form is given as:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (5c)$$

A plot between t/q versus t gives the value of the constants k_2 (*g/mg s*) and also q_e (*mg/g*) can be calculated (**Fig.6a** and **6b**).
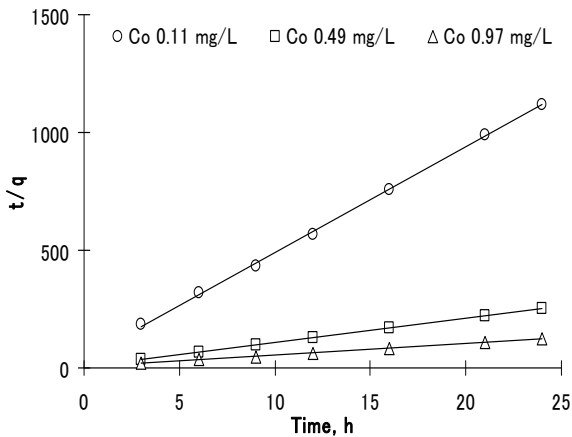
Fig.6a Plot of pseudo-second order kinetics for *ZVI* (Fe powder 95%, particle size 0.15mm, Co 0.11-0.97mg/L, dose 5g/L, pH of simulated groundwater, pH8.18)

Table 4 Value of rate coefficients for pseudo-2nd order kinetics

Adsorbents	Initial As concentration	q_e, (mg/g)	k_2, (g/mg.s)	r^2
ZVI	0.11 mg/L	0.02	47.68	0.999
	0.49 mg/L	0.10	21.13	0.999
	0.97 mg/L	0.20	8.49	0.999
IO	0.11 mg/L	0.02	18.66	0.992
	0.49 mg/L	0.09	6.77	0.995
	0.97 mg/L	0.19	6.10	0.999
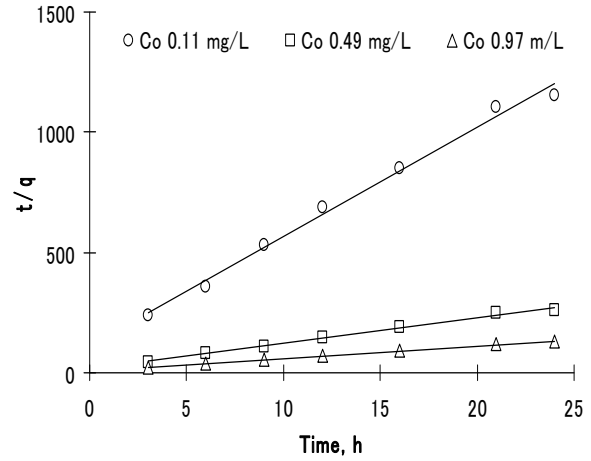
Fig.6b Plot of pseudo-second order kinetics for *IO* (Fe$_2$O$_3$ powder 95%, particle size 0.15mm, Co 0.11-0.97mg/L, dose 5g/L, pH of simulated groundwater, pH8.18)

The values of second-order kinetic coefficients as calculated from the plots are shown in **Table 4**.

c) Comparison of pseudo-first and second order kinetics

The values of the observed rate coefficients k_1, k_2, q_e of pseudo-first and second order kinetics were calculated and the corresponding linear regression correlation coefficients r^2 are shown in **Tables 3** and **4**. It can be seen that the values of r^2 for pseudo-first order are from 0.487 to 0.840, whereas the values of r^2 are almost one for pseudo-second order. In other words, the pseudo-second order kinetics has a much better fit with experimental kinetic data for both *ZVI* and *IO*. This shows the applicability of the pseudo-second order kinetic model in predicting the rate of arsenic adsorption from simulated ground water onto *ZVI* and *IO*. Indeed, Saeid [26] showed that the sorption process obeys pseudo first-order kinetics at high initial concentration of solute and pseudo-second order kinetic model at lower initial concentration of solute. In this study, the pseudo-second order kinetic expression was tested for predicting the amount of arsenic adsorbed for the overall adsorption time. The q_e was predicted by applying the calculated kinetic coefficients in their corresponding kinetic expressions. These predicted values of q_e from model and q_e from experimental data are not far from each other (**Table 5**). However, Saeid [26] reported that the observed rate coefficients from first and second order kinetic models, k_1 and k_2, are not the intrinsic rate coefficients. They represent not only the combinations of adsorption and de-sorption rate constants, but also the complex functions of initial concentration of the solute.

Table 5 Comparison of qe from pseudo-second order model and experiment

Adsorbents	Initial As concentration	q_e, (mg/g) from model	q_e, (mg/g) from experiment
ZVI	0.11 mg/L	0.022	0.022
	0.49 mg/L	0.098	0.096
	0.97 mg/L	0.196	0.191
IO	0.11 mg/L	0.022	0.021
	0.49 mg/L	0.094	0.092
	0.97 mg/L	0.188	0.184

4. CONCLUSION

In this study, iron (Zero-Valent Iron, *ZVI*) and iron[III] oxide (*IO*) were found out to be effective adsorbents for the removal of arsenic from groundwater. The results showed that both *ZVI* and *IO* have a high efficiency for adsorption of arsenic from groundwater. The arsenic adsorption was dependent on pH and varies with initial arsenic concentration, and adsorbent dose. The arsenic adsorption was better at low pH. The adsorption efficiency increases very rapidly with an increase in adsorbent dose for both *ZVI* and *IO*. *ZVI* is an effective adsorbent that can remove arsenic efficiently at high initial concentration of arsenic, low dose of adsorbent and at around neutral pH (pH from 6 to 8). This may be because of the ferric hydroxide precipitates that were formed rapidly from *ZVI* or the formation of amorphous FeOOH which has the highest adsorption capability. IO was less effective than ZVI for arsenic adsorption, however IO may be considered as a cheap adsorbent.

By using non-linear regression method, the experimental data for equilibrium study fitted well with Langmuir isotherm model for both *ZVI* and *IO*. Therefore, Langmuir adsorption isotherm may describe the adsorption process of arsenic from simulated groundwater by using *ZVI* and *IO*. The Langmuir adsorption capacities are 0.60mg/g for *ZIV* and 0.33mg/g for *IO*. The adsorption process followed the pseudo-second order kinetics for both *ZVI* and *IO*.

The results of this study could be used for design of a multiple-stages filter or column where the removal of arsenic by using ZVI or IO is a very important step in production of drinking water from ground or natural surface water for households.

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