Arsenic removal in groundwater by integrated ozonation and adsorption by activated carbon and zeolite

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Abstract. In this study, we investigated the effectiveness of arsenic removal from groundwater with a hybrid process integrating oxidation with ozone and adsorption with activated carbon and zeolite in a 2 L volume batch reactor. Artificial ground water was used in this study, using sodium arsenite (NaAsO₂) as an As (III) source. Artificial ground water is made to resemble natural groundwater conditions which contain 3 mg/ L arsenic. The experiment shows that the arsenic adsorption efficiency in integrated ozonation-adsorption process is higher than individual adsorption process. For individual adsorption process, either with GAC or zeolite, both reached maximum removal in 2 hours. For integrated ozonation-adsorption process, adsorption efficiency reached maximum removal in 45-90 minutes. Maximum removals for individual adsorption with adsorbent dose 12.5 g/L are 69% and 55% for GAC and zeolite respectively. Maximum removal for integrated ozonation-adsorption process with adsorbent dose 12.5 g/L and ozone dose 10.1 mg/minute is 99.97% for both cases of ozone-GAC and ozone-zeolite. Total arsenic concentration in solution reached <0.001 mg/L in 90 minutes for both cases of ozone-GAC and ozone-zeolite with adsorbent dose 10 g/L.

1. Introduction
Arsenic is a natural component of the earth's crust and is widely distributed throughout the water, air, and soil environment. This compound is very toxic, especially in the form of trivalent arsenic (As (III)) which dominates in anaerobic conditions and pentavalent arsenic (As (V)) which dominates in aerobic conditions. Long-term exposure to inorganic arsenic, especially through drinking water and food, can cause chronic arsenic poisoning [1]. There are several case studies reported regarding the problem of arsenic pollution in Indonesia. One example of the latest case study is the contamination of shallow groundwater in the Ciwidey Sub-watershed with arsenic in concentrations ranging from 0.001 mg/L to 3.25 mg/L exceeding the safe limit set by WHO and Indonesian drinking standard, 0.01 mg/L. Whereas 80.25% of the people in Ciwidey area use shallow ground water as a source of drinking water [2]. Therefore, it is necessary to remove arsenic compounds in groundwater prior consumption as an effort to prevent public health problems.

Groundwater tends to be anaerobic so As (III) dominates. Compared to As (V), As (III) is more difficult to be removed from solution. This causes the need for As (III) oxidation to As (V). The oxidation process alone has not removed arsenic compounds from the solution, so that additional
processes are needed [3]. In this study, we investigated the effectiveness of arsenic removal from groundwater with a hybrid process integrating oxidation with ozone and adsorption with activated carbon and zeolite.

2. Material and Methods

2.1. Materials
Artificial ground water was used in this study, using sodium arsenite (NaAsO$_2$) as an As (III) source. The pH value of the artificial groundwater was adjusted to the desired level using H$_2$SO$_4$ and NaOH. The granular activated carbon (GAC) used in this study was made from coconut shell. Zeolite used in this study was natural zeolite which is composed of cristobalite, albite, quartz, and clinoptilolite. Ozone was generated from a corona discharge type ozone generator with natural air used as the feed gas. H$_2$SO$_4$ 2N, Na$_2$S$_2$O$_3$ 0.005N, potassium iodide (KI), and starch indicator were used to determine ozone dose from ozone generator. Sulfuric acid (H$_2$SO$_4$) 18 N, chloroform (CHCl$_3$), and potassium iodate (KIO$_3$) were used to determine As (III) concentration in solution by colorimetric method using spectrophotometer UV-VIS.

2.2. Adsorbent preparation
The granular activated carbon (GAC) was crushed and sieved with 210µm in hole size of the sifter. It was then washed and dried in oven at 105°C overnight. Afterwards, it was cooled in a desiccator for 2 hours at room temperature before use [4]. The zeolite was crushed and sieved with 210µm in hole size of the sifter. It was then washed and dried in oven at 105°C overnight. Afterwards, it was submerged in 0.5 M HCl for 48 hours. The ratio of zeolite to HCl solution was 1 g in 5 mL. The mixture was filtered and washed with water, dried in oven at 105°C for 3 hours. The product of this is called active zeolite [5]. Iron (III)-modified zeolite was obtained by treatment with iron (III) chloride (FeCl$_3$) solution using the following procedure: an aqueous solution 125 cm$^3$ FeCl$_3$ was shaken with 100 g of zeolite at room temperature. The mixture was stirred for 15 min and then left for 24 hours. After filtration, the iron (III)-modified zeolite was rinsed with distilled water, and dried at 105°C [6].

2.3. Ozonation experiment
The experiments were carried out by batch process. Ozone was produced by a corona discharge type ozone generator with natural air used as the feed gas. The ozone was fed into the bottom of the reactor to produce bubbles. The excess ozone leaving the reactor was destroyed by sequential 20 % KI traps incorporated to the reactor set-up. The volume of the reactor is 2 L. O$_3$ is produced from ozone generator with O$_2$ output of 5.0; 7.4; and 10.1 mg/minute and flow rate of the gas stream of 1.0; 1.5; and 2.0 LPM. Determination of ozone dosage is measured by iodometry method [7]. As (III) initial concentration used in this study was 3 mg/L. During the experiments, a sample was taken from the sampling port every 5 minutes until all As (III) were oxidized into As (V). Determination of As(III) concentration in water is measured by colorimetric method [8].

2.4. Adsorption experiment
Adsorption isotherm for As (III) on the GAC and zeolite was obtained using the batch equilibration technique. In this experiment, artificial groundwater containing As (III) was treated with 2.5; 5.0; 7.5; 10.0; and 12.5 g/L adsorbent. The adsorbent was shaken at 100 rpm with 500 mL of As (III) with concentrations of 3 mg/L. The optimum pH values for the adsorption of As (III) onto GAC and zeolite are 12 and 11 respectively [9] [10]. The pH value of the solution was adjusted to the desired level using H$_2$SO$_4$ and NaOH. During the experiments, a sample was taken every 30 minutes until the As (III) concentration reached equilibrium. Determination of As(III) concentration in water is measured by colorimetric method [8].
2.5. Integrated ozonation and adsorption experiment
The experiments were carried out by batch process in a 2 L reactor. At the beginning of the experiment, the desired amount of adsorbent was added into the reactor; then 2 L of artificial groundwater was added, while ozone gas was immediately admitted; the experiment then started. In this experiment, artificial groundwater containing 3 mg/L As (III) was treated with 2.5; 5.0; 7.5; 10.0; and 12.5 g/L adsorbent and 10.1 mg/minute of ozone. As (III) in the solution was expected to be oxidized into As (V). The optimum pH values for the adsorption of As (V) onto GAC and zeolite is 3 [9] [10]. The pH value was adjusted to the desired level using H2SO4 and NaOH. During the experiments, a sample was taken periodically until the total arsenic concentration reached equilibrium. Determination of As (III) and As (V) concentration in water is measured by colorimetric method [8]. Determination of total arsenic concentration in water is measured by Manual Hydride Generation/Atomic Absorption Spectrometric Method [11].

3. Results and Discussion
This study will discuss about the effect of ozone dose to oxidize As (III) into As (V), the effect of adsorbent dose and contact time, and the effect of integrated ozonation and adsorption in removing arsenic from the water. Furthermore, this study will also discuss about the adsorption isotherm and kinetic.

3.1. Effect of ozone dose
The effect of As (III) oxidation to As (V) at fixed initial As (III) concentration 3 mg/L by various ozone doses is shown in Figure 1. Figure 1 shows that higher ozone dose results in faster oxidation process. With ozone input 10.1 mg/minute, all As (III) is oxidized into As (V) in 20 minutes.

![Figure 1. Effect of ozone dose in oxidizing As (III) to As (V)](image)

3.2. Effect of adsorbent dose
The effect of arsenic adsorption at fixed initial As (III) concentration 3 mg/L and fixed ozone dose 10 mg/L by various adsorbent doses is shown in Figure 2 and Figure 3. The figures show that the adsorption efficiency of total arsenic from the solution increases with the increase in adsorbent dose from 2.5-12.5 g/L. The increase in the removal efficiency of total arsenic may be attributed to the fact that with the increase in adsorbent dose, available surface for adsorption increases for the solute to be adsorbed [12]. The figures also show that the arsenic adsorption efficiency in integrated ozonation-adsorption process is higher than individual adsorption process. This may be attributed to the fact that the As (III) is oxidized into As (V) which is easier to be removed from the solution than As (III) [3].
3.3. Effect of contact time

The effect of contact time on arsenic adsorption at fixed initial As (III) concentration 3 mg/L and fixed ozone dose 10 mg/L is shown in Figure 4 and Figure 5. From the figures, it is clear that adsorption efficiency increases with the increase of contact time. For individual adsorption process, either with GAC or zeolite, both reached maximum removal in 2 hours, thereafter removal becomes nearly constant. For integrated ozonation-adsorption process, adsorption efficiency reached maximum removal in 45-90 minutes, thereafter removal becomes nearly constant for both the cases of ozone-GAC and ozone-zeolite. The reason may be due to the fact that, initially all adsorbent sites were empty and the arsenic concentration was high. Afterward, the arsenic adsorption capacity of the adsorbent was decreased significantly due to the decrease in available adsorption sites as well as arsenic concentration[12][13]. Maximum removals for individual adsorption with adsorbent dose 12.5 g/L are 69% and 55% for GAC and zeolite respectively. Maximum removal for integrated ozonation-adsorption process with adsorbent dose 12.5 g/L and ozone dose 10.1 mg/minute is 99.97% for both the cases of ozone-GAC and ozone-zeolite.

3.4. Effect of integrated ozonation and adsorption

The effect of integrated ozonation and adsorption on As (III) oxidation and arsenic removal at fixed initial As (III) concentration 3 mg/L, fixed ozone dose 10 mg/L, and fixed adsorbent dose 10g/L is shown in Figure 6 and Figure 7. The figures show that within the first 20 minutes, the main process that occurred is oxidation of As (III) into As(V) by ozone. Thereafter, the main process that occurred is adsorption of As (V). For both process, either ozone-GAC or ozone-zeolite, total arsenic concentration in solution reached <0.001 mg/L in 90 minutes.
Figure 5. Effect of contact time on the adsorption of arsenic onto zeolite

Figure 6. Plots of arsenic concentration versus time in arsenic removal with integrated oxidation and adsorption process with ozone and GAC

Figure 7. Plots of arsenic concentration versus time in arsenic removal with integrated oxidation and adsorption process with ozone and zeolite

3.5. Adsorption isotherm
The adsorption isotherm of arsenic onto GAC and zeolite was investigated by studying the Langmuir and Freundlich isotherm.
3.5.1. Langmuir isotherm. The Langmuir equation is applicable to homogeneous adsorption where the adsorption of each adsorbate molecule on to the surface has equal sorption activation energy [14]. The linear form of this isotherm is represented by the expression [15]:

\[
\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L \times C_e}
\]  

(1)

where \( q_e \) (mg/g) and \( C_e \) (mg/L) are the amount of adsorbed adsorbate per unit weight of adsorbent and unadsorbed adsorbate concentration in solution at equilibrium, respectively. The constant \( K_L \) (L/g) is the Langmuir equilibrium constant and \( q_m \) is the theoretical monolayer saturation capacity.

The essential feature of the Langmuir isotherm can be expressed in terms of a dimensionless constant called separation factor (\( R_L \), also called equilibrium parameter) which is defined by the following equation:

\[
R_L = \frac{1}{1 + K_L \times C_0}
\]  

(2)

where \( C_0 \) (mg/L) is the initial adsorbate concentration. The value of \( R_L \) indicates the shape of the isotherms to be either unfavourable (\( R_L > 1 \)), linear (\( R_L = 1 \)), favourable (\( 0 < R_L < 1 \)) or irreversible (\( R_L = 0 \)).

3.5.2. Freundlich isotherm. The most important multisite adsorption isotherm for heterogeneous surfaces is the Freundlich adsorption isotherm [14]. The linear form of this isotherm is represented by the expression [16]:

\[
log q_e = K_F + \frac{1}{n} \times log C_e
\]  

(3)

where \( K_F \) (L/g) is the Freundlich constant and \( n \) (g/L) is the Freundlich exponent. Therefore, a plot of log \( q_e \) versus log \( C_e \) enables the constant and exponent \( n \) to be determined.

**Table 1. Adsorption isotherm of arsenic onto GAC**

|                  | GAC                  | Ozone - GAC                |
|------------------|----------------------|----------------------------|
| Langmuir         |                      |                            |
| Linear Equation  | \( y = 5.0611x + 0.9046 \) | \( y = 0.0012x + 2.9944 \) |
| \( q_m \)        | 0.91                 | 0.79                       |
| \( K_L \)        | 0.11                 | 0.33                       |
| \( R_L \)        | 0.18                 | 2495.33                    |
| \( R^2 \)        | 0.91                 | 0.00013                    |
| Freundlich       |                      |                            |
| Linear Equation  | \( y = 0.8725x - 0.7832 \) | \( y = 0.0822x - 0.393 \) |
| \( K_F \)        | 0.91                 | 0.78                       |
| \( n \)          | 0.16                 | 0.40                       |
|                    | 1.15                 | 12.17                      |

**Table 2. Adsorption isotherm of arsenic onto zeolite**

|                  | Zeolite             | Ozone - Zeolite            |
|------------------|---------------------|----------------------------|
| Langmuir         |                      |                            |
| Linear Equation  | \( y = 9.9207x + 0.5808 \) | \( y = 0.0016x + 1.7016 \) |
| \( q_m \)        | 0.87                 | 0.65                       |
| \( K_L \)        | 1.72                 | 1.06                       |
| \( R_L \)        | 0.06                 | 0.85                       |
| \( R^2 \)        | 0.87                 | 0.00163                    |
| Freundlich       |                      |                            |
| Linear Equation  | \( y = 0.991x - 1.0367 \) | \( y = 0.1032x - 0.2066 \) |
| \( K_F \)        | 0.87                 | 0.72                       |
| \( n \)          | 0.09                 | 0.62                       |
|                    | 1.01                 | 9.69                       |

Table 1 and Table 2 show that \( 0 < R_L < 1 \) indicating that Langmuir isotherm is favourable for each process. The constant \( K_F \) is an approximate indicator of adsorption capacity, while \( 1/n \) is a function of the strength of adsorption in the adsorption process [17]. If \( n \) lies between one and ten, this indicates a favourable sorption process [18]. Table 1 and Table 2 show that \( 1 < n < 10 \) for GAC, zeolite, and ozone-zeolite processes which indicates that those processes have favourable sorption processes.
3.6. Adsorption kinetics
The adsorption isotherm of arsenic onto GAC and zeolite was investigated by studying the pseudo first order and pseudo second order.

3.6.1. Pseudo first order. Lagergren proposed a method for adsorption analysis namely pseudo first-order kinetic equation. The linear form of this equation is[19]:

\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]

(4)

where \(q_e\) (mg/g) and \(q_t\) (mg/g) are the amounts of adsorbed adsorbate at equilibrium and at time \(t\), respectively, and \(k_1\) (min\(^{-1}\)) is the rate constant of pseudo first-order adsorption.

3.6.2. Pseudo second order. The sorption kinetics can also be described by pseudosecond-order model. The linear form of pseudo second order equation is expressed as[20]:

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}t
\]

(5)

where \(k_2\) (g/mg min) is the equilibrium rate constant of pseudo second-order adsorption.

| Table 3. Adsorption kinetic of arsenic onto GAC |
|-----------------------------------------------|
| GAC                                           | Ozone - GAC |
| Pseudo first-order kinetic                    |             |
| Linear Equation                              | R\(^2\)  | k\(_1\)  |
| \(y = -0.0205x - 1.7072\)                     | 0.98     | 0.02     |
| Pseudo second-order kinetic                  |             |
| Linear Equation                              | R\(^2\)  | k\(_2\)  |
| \(y = 3.1474x + 388.84\)                     | 0.94     | 0.03     |
| Zeolite                                      |             |
| Pseudo first-order kinetic                    |             |
| Linear Equation                              | R\(^2\)  | k\(_1\)  |
| \(y = -0.0185x - 1.9187\)                    | 0.91     | 0.02     |
| Pseudo second-order kinetic                  |             |
| Linear Equation                              | R\(^2\)  | k\(_2\)  |
| \(y = 3.4444x + 562.33\)                     | 0.80     | 0.02     |

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