Remediation on underground water pollution using Fenton Oxidation Method

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Abstract. Fenton oxidation, one of the advanced oxidation processes (AOP), has high efficiency in the eradication of total petroleum hydrocarbon (TPH), including those persistent organic compounds, with minimal time. Fenton oxidation is employed for further study in the remediation of hydrocarbon-contaminated groundwater sample collected from site. In this study, the efficiency of Fenton Oxidation is investigated toward the degradation of hydrocarbon in groundwater samples. The percentage removal of hydrocarbon, in terms of chemical oxygen demand (COD) in different operating condition for Fenton oxidation of contaminated groundwater was determined. The treatment parameters were selected by carrying out Factorial Design in which pH 3 to 6, concentration of hydrogen peroxide 0.01 mg/L to 0.1 mg/L, concentration of ferrous ions 0.01 mg/L to 0.5 mg/L, and Reaction Time 30 minutes to 120 minutes were proven to be significant model terms.

1. Introduction
Scarcity of fresh surface water in North Kelantan has rendered the locals to exploit underground source for domestic use. Approximate 41% of water production in Kelantan originated from groundwater in 2011, even more in the present. It was stated in the “Review of the National Water Resources (2000 – 2050) and Formulation of National Water Resources Policy – Volume 10 Kelantan, Final Report, August 2011” that 95 percent of domestic water supply in Kota Bharu was groundwater.

Apart from that, groundwater in Kota Bharu is used to supply the agriculture scheme and glove-making factory at Pengkalan Chepa. This indicates that abandonment or discard of contaminated water or site is not an option due to the substantial demand of groundwater in Kota Bharu. As a result, strict monitoring and prevention for contamination of groundwater must be implemented in Kelantan. Groundwater contaminated by hydrocarbons was investigated in the vicinity of the town and the characteristics were tested as shown in Table 1.
Among the hydrocarbons that potentially originate from petroleum (also known as “oil”), monoaromatic and polycyclic aromatic compounds, benzene, toluene, ethyl benzene, xylene (BTEX) and dense non-aqueous phase liquid (DNAPL) are threatening and damaging to the environment [1-4]. They are highly toxic, carcinogenic and mutagenic, thus harmful to terrestrial and marine ecosystem. It hinders domestic consumption and causes secondary contamination at the underground soil and grains. Moreover, conventional coagulation, flocculation and filtration processes has low efficiency in treating hydrocarbons. Hence, this study aimed to investigate the effect of Fenton oxidation, advanced oxidation process (AOP) in remediating petrol-contaminated groundwater and evaluate the treatment operating condition of using AOP for groundwater remediation.

### Table 1. Characteristics of groundwater sample and Malaysia Drinking Water Quality Standard

| Characteristics                      | Malaysia Drinking Water Quality Standard |
|--------------------------------------|------------------------------------------|
| pH                                   | 6.00                                     | 6.50 - 9.00 |
| Dissolved Oxygen, DO (mg/L)          | 2.86                                     | N/A         |
| Nitrate (mg/L)                       | 1.1                                      | 10.0        |
| Chemical Oxygen Demand, COD (mg/L)  | 68                                       | -           |
| Total Organic Carbon, TOC (mg/L)     | 17.3                                     | -           |
| Total Oil and Grease, TOG (mg/L)     | 23.0                                     | N/A         |
| Iron (mg/L)                          | 0.5                                      | 0.3         |
| Phosphorus (mg/L)                    | 0.4                                      | N/A         |
| Copper (mg/L)                        | 0.0                                      | 1.0         |
| Salinity (mg/L)                      | 200                                      | N/A         |

## 2. Literature Review

### 2.1 Advanced Oxidation Process (AOP)

AOP or in situ chemical oxidation is well-known in its rapid treatment of organic-compounds-contaminated water bodies with respect to conventional treatments, especially those highly refractory substrates [2, 5]. The effect of integration of multiple AOP was prominent in the treatment of hydrocarbon 6, 7]. Studies of combinations of AOP such as UV light/Persulfate, UV/Hydrogen Peroxide (H2O2), Ultrasound/Persulfate (S2O82-), Ultrasound/H2O2, ozone (O3)/H2O2, UV/O3, Fenton reaction H2O2/Fe2+ or Fe3+ and photo Fenton reaction UV/H2O2/Fe2+ or Fe3+ are commonly seen in treating groundwater and soil contaminated with organic compounds [2, 6, 8]. Total petroleum hydrocarbon (TPH) treatment in any polluted water bodies through AOP depends on the pH, temperature, presence of humic acid, the production rate of free radicals and the extent and time of the radicals contacting contaminant molecules [2, 6, 9].

### 2.2 Fenton Oxidation

Hydrogen peroxide (H2O2) solution has been widely used as reactant to treat organic compounds rapidly. The addition of ferrous ions into the system catalyses the production of hydroxyl radicals as strong oxidants for the degradation of organic pollutants in water or wastewater. This process is known as Fenton Oxidation. It was first introduced in 1984 with H2O2 found to initiate enhanced oxidative potential under the influence of iron (Fe) as catalyst at acidic condition [1]. The reactions involved in Fenton Oxidation, also known as Fenton Reagent Treatment, are [2]:

1. \[ \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \cdot\text{OH} + \text{OH}^- \]
2. \[ \text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^- + \text{H}_2\text{O} \]
3. \[ \text{Fe}^{2+} + \cdot\text{OH} \rightarrow \text{Fe}^{3+} + \text{OH}^- \]
Through Equation (1), hydroxyl radical (·OH) and hydroxide ion (OH⁻) are produced. The difference between ·OH and OH⁻ is that the former possesses an unpaired electron, whereas the latter is an anion with all electrons paired. ·OH is the key to Fenton processes as its valent unpaired electron imposes high oxidative ability that reacts with most compounds that it came across. In the case of hydrocarbons treatment, the expected degraded product would be carbon dioxide, water, hydroxyl group, carboxyl group as displayed [11]. Although the production of mobile secondary products is inevitable as shown in Equation (6), the impact of the post-reaction should be included in remediation plan that proposes Fenton oxidation [7]. Goi and Trapido [12] suggested that ultraviolet (UV) light radiation helps improving the Fenton treatment in the rapid decomposition of organic contaminants. Despite that, Fenton reagent treatment is still preferred as it requires less complicated design (without UV source facility) resulting in lower operational cost. The residual concentration of H₂O₂ in the system is likewise much lower than in UV/ H₂O₂ process. As described in Equation (5), excessive ·OH is undesirable because they will reform into H₂O₂ in which H₂O₂ contamination will be induced.

3. Methodology
The experiments are performed using synthetic water by mixing 0.15 mL of RON 95 Petrol with 300 mL of distilled water to yield 0.05% of hydrocarbon contamination water to simulate the petroleum contamination. Early preparation may cause the petrol to evaporate and cause variation in the results, thus precaution step should be taken.

300 mL of the prepared sample was poured into a 500 mL beaker using a 250 mL measuring cylinder. The beaker was then placed on a stirring plate to ensure the sample was constantly stirred. 0.15 mL of RON95 was added into the beaker. 2 mL of the sample was pipetted into the COD vial to obtain initial COD value. The pH of the sample is adjusted by adding 2.0N sulphuric acid (R&M Chemicals) to decrease the pH and 1.54N sodium hydr...
Table 3 shows the analysis of variance for the model based on the inputs and responses in Table 2. The model F-value of 152.60 implies the model is significant. There is only a 0.08% chance than an F-value this large could occur due to noise (disturbance). Values of “Prob > F” less than 0.05 indicate model terms are significant. In this case $x_1$-pH, $x_2$-[H$_2$O$_2$], $x_3$-[Fe], $x_4$-time, $x_1x_4$, $x_2x_4$, $x_3x_4$, $x_1x_3x_4$, $x_2x_3x_4$ are significant model terms. Values greater than 0.1 indicate the model terms are not significant. If there are many insignificant model terms, model reduction (modification) is required.

The “Lack of Fit F-value” of 0.27 implies the Lack of Fit is not significant relative to the pure error. There is a 65.49% chance that a “Lack of Fit F-value” this large could occur due to noise (disturbance). Non-significant lack of fit is good as the model is deemed fit. As a result, optimisation can be performed on the model without any changes on the range of inputs. R-squared is a measure of the amount of variation around the mean explained by the model. In this case, the R-squared has a value of 0.9987, close to 1 which indicates minimal variation present in the model.

### Table 2. Factorial Design of Groundwater Fenton Remediation

| Run No | pH | [H$_2$O$_2$] (g/L) | [Fe] (g/L) | Time (min) | COD Removal (%) |
|--------|----|-------------------|-----------|------------|-----------------|
| 1      | 3  | 0.01              | 0.01      | 30         | 32.37           |
| 2      | 6  | 0.01              | 0.01      | 30         | 30.00           |
| 3      | 3  | 0.1               | 0.01      | 30         | 39.02           |
| 4      | 6  | 0.1               | 0.01      | 30         | 42.51           |
| 5      | 3  | 0.01              | 0.5       | 30         | 12.20           |
| 6      | 6  | 0.01              | 0.5       | 30         | 5.61            |
| 7      | 3  | 0.1               | 0.5       | 30         | 15.64           |
| 8      | 6  | 0.1               | 0.5       | 30         | 14.98           |
| 9      | 3  | 0.01              | 0.01      | 120        | 41.52           |
| 10     | 6  | 0.01              | 0.01      | 120        | 47.16           |
| 11     | 3  | 0.1               | 0.01      | 120        | 44.78           |
| 12     | 6  | 0.1               | 0.01      | 120        | 42.33           |
| 13     | 3  | 0.01              | 0.5       | 120        | 18.89           |
| 14     | 6  | 0.01              | 0.5       | 120        | 28.11           |
| 15     | 3  | 0.1               | 0.5       | 120        | 22.58           |
| 16     | 6  | 0.1               | 0.5       | 120        | 30.00           |
| 17     | 4.5| 0.055             | 0.255     | 75         | 28.63           |
| 18     | 4.5| 0.055             | 0.255     | 75         | 30.98           |
| 19     | 4.5| 0.055             | 0.255     | 75         | 29.27           |

### Table 3. Analysis of Variance Table for Factorial Design of Groundwater Fenton Remediation

| Source  | Sum of Squares | Mean Square | F Value | p-value | Remarks |
|---------|----------------|-------------|---------|---------|---------|
| Model   | 2557.34        | 170.49      | 152.60  | 0.0008  | significant |
| $x_1$-pH| 11.70          | 11.70       | 10.47   | 0.0480  | significant |
| $x_2$-[H$_2$O$_2$] | 80.95        | 80.95       | 72.46   | 0.0034  | significant |
| $x_3$-[Fe] | 1842.18     | 1842.18     | 1648.90 | < 0.0001 | significant |
| $x_4$-Time | 431.00       | 431.00      | 385.78  | 0.0003  | significant |
| $x_1x_2$ | 0.22          | 0.22        | 0.20    | 0.6844  |          |
| $x_1x_3$ | 1.62          | 1.62        | 1.45    | 0.3146  |          |
5. Conclusion
In this study, effect of Fenton Oxidation and its treatment operating conditions were investigated in remediating petrol-contaminated groundwater in terms of COD removal. The treatment parameters were selected by carrying out Factorial Design in which $x_1$-pH, $x_2$-[H2O2], $x_3$-[Fe], $x_4$-Reaction Time were proven to be significant model terms. The highest yield of COD removal rate can be as high as 47.16%. Despite the efficiency of Fenton Oxidation in remediation of petrol-contaminated water, the production of secondary products may cause other form of pollution.

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