

M.F.M. AKHIR¹, N.A. SAAD^{1*}, H. ZABIDI², M.R.R.M.A. ZAINOL¹**REMOVAL OF SULFUR CONTENT IN GROUNDWATER USING MARBLE FILTER IN A CASCADE DESIGN**

Alluvial aquifer are one of Malaysia's most abundant groundwater resources, highly demanded in East Coast area. However, the presence of sulfur in these aquifers causes the emission of hydrogen sulfide gas. This research aimed to provide an alternative study for removing sulfur using marble filter media in a cascade column design, where water flows from the highest to the lowest column. Two groups of marble sizes were involved in this filter: pebbles and sand-sized particles. The treatment used raw groundwater with the highest concentration of total sulfur being 537.1 ppm. Sand-sized marble had the highest efficiency of sulfur removal, reaching 98.3% at a flow rate of 0.011 l/s. As a result of the effective filtration, the true color reached 33-34 pt/Co, significantly reduced from the source value of 1000-1012 pt/Co. The application of marble for treating groundwater with the sulfur issue is still novel and promising for groundwater filtration, potentially benefiting consumers facing this problem.

Keyword: Alluvial Aquifer; Sulfur Contamination; Marble Filter; Sand-Sized Particles

Glossary

CaCO ₃	: Calcium carbonate
CaO	: Calcium oxide
DO	: Dissolved oxygen
FeS	: Iron sulfide
H ₂ S	: Hydrogen sulfide
ICP-OES	: Inductively coupled plasma optical emission spectroscopy
l/s	: litre per second
LOI	: Loss of ignition
Na ₂ S.9H ₂ O	: Sodium sulfide hydrate
NH ₃	: Nitric acid
ppm	: Part per million
Pt/Co	: Platinum-Cobalt
SEM-EDX	: Scanning electron microscopy-energy dispersive X-ray analysis
XRD	: X-Ray diffraction

morphic basement, marine sulfate-rich intrusions, marine aerosols produced by precipitation (rainwater), and anthropogenic activities are the main possible sources for sulfur presence in the groundwater system [1,2]. FeS appears as a brownish-black precipitate [2]. It is also well-known for its corrosion problem in the petroleum industry, referred to as rust sulfuration [3]. Due to its instability, FeS degrades and reacts with hydrogen gas to form H₂S [4-6]. Enzyme degradation mechanisms can also produce H₂S from sulfate-reducing bacteria [1]. H₂S is harmful due to its characteristics as a colorless, highly flammable, and toxic gas with a distinctive rotten egg odor. It is naturally produced in the environment by the decay of organic matter, sulfur origin alteration, and as a byproduct of many industrial processes.

In nature, H₂S can be found in hot springs, volcanic gases, natural gas, crude oil, and sulfur-base mineral ores. It is also produced by certain bacteria in the human body, where it plays a role in various physiological processes. This gas can cause shortness of breath, low blood pressure and loss of consciousness at higher exposure levels. Notably, H₂S is often present in high concentrations and partially dissolved in water. Ingestion and inhalation H₂S can be poisonous to humans, causing diarrhea, dehydration, nausea, and affecting skin and lung problems. It affects the central nervous system, particularly the medulla and pons, leading to unconsciousness and respiratory failure. From the respiratory system, H₂S dissolves in blood and

1. Introduction

Sulfur itself is a non-toxic element. However, its derivation leads to the formation of iron sulfide (FeS) and hydrogen sulfide (H₂S). The weathering of sulfide minerals in the meta-

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quickly oxidizes by molecular oxygen. Consequently, it reduces hemoglobin's oxygen-carrying capacity [7]. High concentration of H_2S significantly impacts to human health, notwithstanding low levels of H_2S can cause eye irritation, headache, and nausea. Thus, removing sulfur from water prevents the production of H_2S and the associated problems like "black water".

Several water purification techniques exist for removing sulfur, including aeration with pre-acidification ($pH < 5$), electrooxidation, chemical oxidation, coagulation, and oxidation by microorganisms [8]. Regarding physical filtration, researchers are exploring the potential of calcium carbonate ($CaCO_3$) rock due to its acid-neutralizing properties [9]. Optimizing the size of filter media plays a crucial role in targeting specific pollutants and improving the filtration performance. In 1984, gravel and sand (1mm-10mm) were used as filter media for protecting fine-grained silts and clays [10]. Wegelin further developed a roughing filter with gravel sizes ranging from 28 mm-3 mm in 1986 [11]. Since 2000, limestone has been used for ion exchange and pre-treatment with a size of 4 mm-8 mm [12]. Improving on this method, Aziz et al. [13] used smaller limestone (2-4 mm) to remove 90% of copper (up to 50 ppm). In 2008, Adlan et al. [14] further improved limestone application by arranging the sizes in descending order (16.28 mm, 4.6 mm, and 1.91 mm) in a roughing filter, achieving removals of 88% suspended solids, 67% biochemical oxygen demand, 81% turbidity, and 96% coliform organisms from wastewater.

Application of physical filtration using marble rock as filter media in a cascade design offer a novel approach in sulfur filtration studies. Therefore, this paper aims to assess the effectiveness of marble filters in cascade design with various sizes and inlet flowrate in removing sulfur. The finding of this research can benefit consumers by providing an alternative method for treating high sulfur levels in groundwater.

2. Study area

The study utilized groundwater from an alluvial marine region approximately 8 km from the coastline. During groundwater sampling from a borehole inside Universiti Sains Malaysia, Nibong Tebal, colorless gas with a rotten egg odor indicative of H_2S was detected. The borehole was 57 m in length and had openings at both ends of the tube. The tube well was non-porous, notably, ensured the sampled groundwater quality exclusively represented deep well condition (>30m depth), thereby minimizing the influence of contaminants from other depths.

3. Methodology

As shown in Fig. 1, characterization of the groundwater was conducted before and after filtration using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), X-Ray diffraction (XRD), Scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDX), and true color analysis.

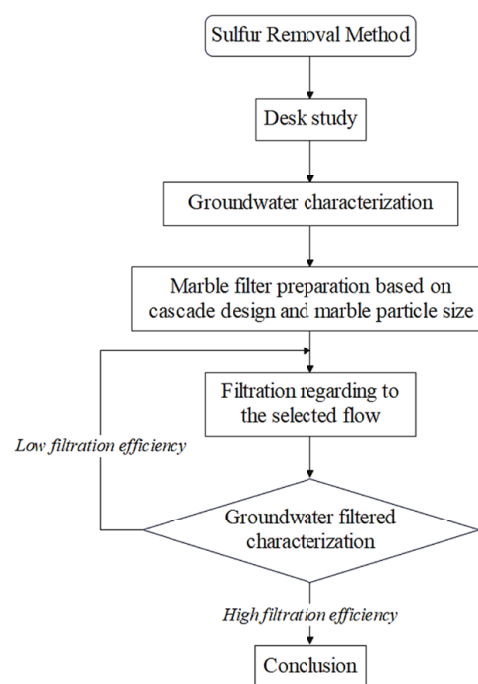


Fig. 1. Experimental work for sulfur removal method using marble filter

3.1. Groundwater characterization analysis

ICP-OES was used to analyze the concentration of sulfur in the groundwater sample. Prior to analysis, samples were filtered through 45 μm nylon syringe filters to remove the suspended solid. The standard calibration range was set at 1, 2, 3, 10, 25 and 50 ppm. In addition, the Relative Standard Error (RSE) was set at 5%.

XRD is commonly used to characterize crystalline phases or compounds in a solid-state sample. The sample is typically ground to a powder for analysis. The XRD machine was set to 45 kV and 10mA. The background pattern from the data analysis was modified and corrected to determine the background signal. Then sample label peaks were matched with the compound names in the pattern list in order to know accurately identify the compound of the sample.

SEM-EDX analysis is a useful tool for studying material composition information. In this case, it was used to identify the residue that trapped on the marble. The sample was sputter-coated with a conductive layer for 20 minutes to enhance image quality and prevent charging during imaging. True water color analysis is an effective way to indicate water pollution by true color measurement. DR3900 spectrophotometer was programmed to read the blank and sample within the 450 nm range. A 10 ml of distilled water was filtered through a 0.45 μm nylon membrane syringe filter for blank preparation.

3.2. Marble filter preparation

High-grade marble rocks sourced from Zantat Sdn Bhd, a quarry company in Simpang Pulau, Malaysia were used as filter

media. Initially, the provided marble rocks were cobble-sized. A jaw crusher was used for marble sample larger than 8 mm in diameter, while a cone crusher was used for smaller than 8 mm to produce pebble and sand size. After crushing, the crushed marble was sieved using a Gilson sieve to separate the different sizes according to Wentworth's scale [15].

Several samples from the marble that had been prepared for filter media were collected to determine the CaCO_3 content. XRF was used to measure the mass percent of calcium oxide (CaO). Before conducting the XRF analysis, the loss on ignition (LOI) test was carried out on the marble sample by heating it to 1000°C in a muffle furnace with a temperature increment of 5°C per minute. The LOI test was purposely to find out the carbon dioxide (CO_2) content of the marble sample, so that the result of XRF analysis which was CaO could be used to calculate the CaCO_3 content of the marble by adding it up with the LOI.

Four column filters were used for each size (pebble and sand-sized marble), as shown in Fig. 2. These filters were sorted as a cascade design and divided into two rows containing two filters each. The first row was pebble-sized marble, while the second row contained sand-sized marble. Each row featured columns filled with media of a different size, reducing in size progressively as the column height decreased. Coarser grains were placed at the top of each column, followed by progressively finer grains towards the bottom. The pebble-sized media comprised medium (10 mm-14 mm), medium-fine (6 mm-10 mm), fine (4 mm-6 mm) and very fine grain (2 mm-4 mm). The sand sized media consisted of very coarse (1 mm-2 mm), coarse (0.6 mm-1 mm), coarse-medium (0.4 mm-0.6 mm) and medium grain (0.3 mm-0.4 mm). Marble particles smaller than 0.3 mm tends to bind and form cementation after reacting with water.



Fig. 2. Two rows of marble filtration system consist of pebble and sand-sized particles

3.3. Filtration process and sampling

The groundwater was purged for at least three time the volume of a single tube well to eliminate stagnant water before collecting raw samples. The raw samples were then pumped into a 300-litre potable tank and transported to the laboratory for filtration. The filtration began immediately after the groundwater sample was transferred into the top tank. All column filters and the top tank have valves for controlling the flowrate during filtration. The volume media was set constant at 10 litres in each column filter.

The flowrate was set to collect a 1-litre sample in 30 seconds (0.033 l/s), 60 seconds (0.017 l/s), 90 seconds (0.011 l/s), 120 seconds (0.008 l/s), and 150 seconds (0.007 l/s). Samples were initially taken from the top tank and the outlet of the last column filter to calculate the total removal and removal efficiency of total sulfur. Prior to preservation sample, the collected samples were put into a 50ml centrifuge tube and added with 3% nitric acid (NH_3) to reach a pH below 2. If the pH of the sample is below 2, NH_3 is not needed. Then, the sample were kept in a refrigerator at $4-6^\circ\text{C}$ to minimize chemical changes.

3.4. Normality test and regression analysis method

Normality test and regression analysis were performed using SPSS software version 27. Accessing data normality is important for selecting appropriate central tendency measures and determining the next steps in statistical analysis, specifically choosing between parametric or non-parametric methods. There are various approaches to evaluate data normality, this testing likely used skewness and kurtosis value. Typically, a range of $-2 \leq \text{skewness} \leq 2$ and $-4 \leq \text{kurtosis} \leq 4$ value indicates acceptable normality [16]. It is important to note that when the sample size is greater than 100, normality becomes less critical. In such cases, the Central Limit Theorem suggests that the sampling distribution will tend towards normality regardless of the underlying population distribution.

Regression analysis is applied when the error term of the model is normally distributed, especially with sample sizes below 30. It is used to determine whether the independent variable has statistically significant linear relationship with the dependent variables and estimate the strength and direction of that relationship. Typically, a P-value should be less than 0.05 for a 95% confidence level to be considered statistically significant. The predictor (independent variable) in this model was the concentration of DO, while the dependent variables were removal percentage.

4. Results and discussion

4.1. Purity of calcium carbonate

The presence of magnesium, aluminium, and silica in marble can reduce CaCO_3 content and alter the white coloration.

Effective comminution and sieving helped to separate these impurities. Based on the XRF analysis result, the marble was composed of an average of 98.02% CaCO_3 , with magnesium oxide (MgO), aluminium oxide (Al_2O_3), Silica (SiO_2) being the major impurities. Other trace oxides like phosphorus pentoxide (P_2O_5), potassium oxide (K_2O), iron oxide (Fe_2O_3), nickel Oxide (NiO), copper Oxide (CuO), manganese oxide (MnO) and strontium oxide (SrO) were present in very small amounts.

4.2. Characterization of the raw groundwater

The presence of H_2S gas and FeS was possibly formed from the oxidation of the high sulfur ion content. The concentration of sulfur content in the groundwater exceeded 200 ppm, reaching a maximum of 500 ppm. The observed reaction resembles FeS production described by Y. Liu et al. [17], O'Day et al. [18], Walker [19], and Tostevin et al. [1], based on its visual and olfactory features, as shown in Fig. 3, where the color changed from yellow to black in 14 seconds. As noted by Roelands et al. [20], the yellow color originates from the unstable sodium sulfide hydrate ($\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$). The emission of H_2S gas stems from the decomposition result of the unstable Na_2S in aqueous state. $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ changed into a more porous and spongy structure after being exposed to heat above 60°C . In this research, the crystal structure of the dried groundwater sample presented in Fig. 4 aligned with these finding.



Fig. 3. The reaction of iron and sulfur turned the yellowish groundwater into black in 14 seconds

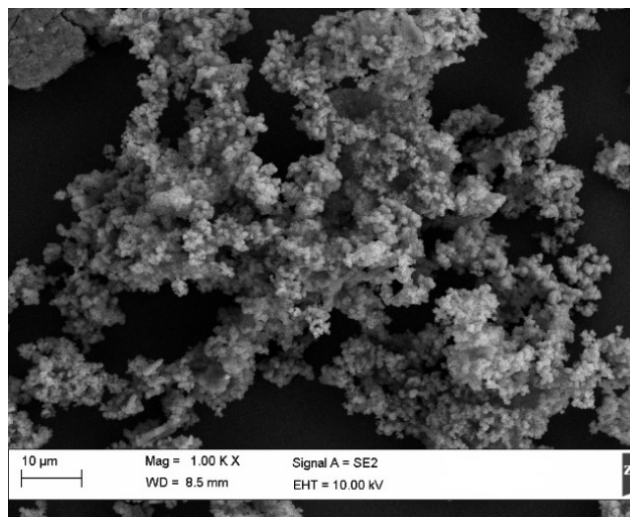


Fig. 4. $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ image crystal structure with more porous and spongy

XRD analysis of the dried groundwater sample in Fig. 5 revealed the presence of two sulfur-based compounds: troilite (FeS) and pyrrhotite (less sulfur in FeS , $\text{FeS}(1-x)$). The exposure of temperature at 115°C during drying the sample likely induce the transformation of amorphous FeS and mackinawite into troilite and pyrrhotite, respectively. Additionally, SEM-EDX analysis was carried out on the black residue that trapped on the marble during the filtration. The result showed the residue containing only Iron (Fe) (with percentage weight 3.6%) and Sulfur (S) (2.25%) while the oxygen (O) (53.03%) and Calcium (Ca) (41.12%) originated from the marble itself.

4.3. Filtration efficiency

Fig. 6 and Fig. 7 showed that sand-sized marble was more effective at removing sulfur than pebble-sized marble, although both sizes were capable in removing sulfur. Their efficiency varied depending on the flowrate. The removal efficiency of sand-sized marble was above 90% for all flowrates. In addition, filtration using sand-sized marble at flowrate 0.011 l/s achieved the highest sulfur removal efficiency of 98.32%, as shown in Fig. 7.

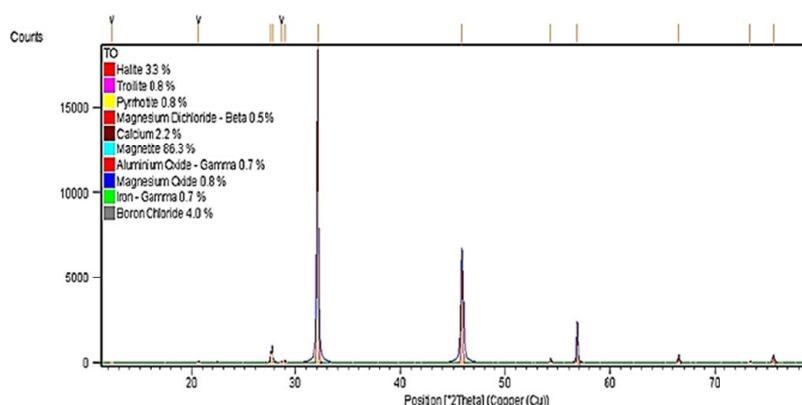


Fig. 5. Illustration of XRD analysis from a raw groundwater sample

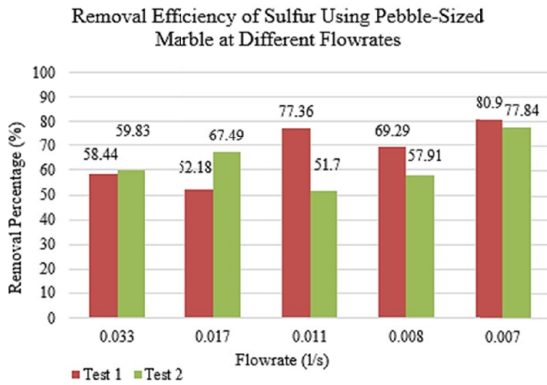


Fig. 6. Two tests of sulfur removal based on filtration flowrate using pebble-sized marble

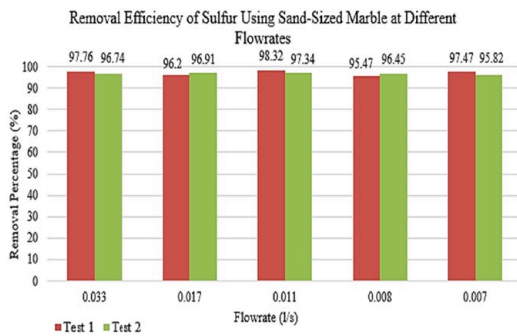


Fig. 7. Two tests of sulfur removal based on filtration flowrate using sand-sized marble

As a result of sulfur filtration using the marble filter, the groundwater sample turned to reduce black precipitate and became more transparent, as shown in Fig. 8 and Fig. 9. Sand-sized marble showed clearer color compared to pebble-sized marble. Based on true water color analysis, the initial value before filtration ranged of 1000-1012 Pt/Co. Sand-sized marble achieved a true color value of 33-34 Pt/Co, while pebble-sized marble was significantly higher 172-175 Pt/Co.

4.4. Contribution of dissolved oxygen for marble filter efficiency

Generally, groundwater is commonly found in anaerobic conditions with very low of DO concentration. The groundwater in this study had a low DO concentration of 0.9 ± 0.1 ppm. Exposing the yellow-colored groundwater to oxygen caused a reaction that resulted in black precipitation. Application of aeration using a cascade design improved the DO concentration in the groundwater to 7.0 ± 0.7 ppm. This increased the suspension reaction of H_2S to a suspended form and concomitantly removed the dissolved gas of H_2S . The increase in the suspended sulfur contributed to the marble filter's efficiency in trapping and adsorbing the sulfur compounds.

Based on of the normality test using skewness and kurtosis method showed a normal distribution (skewness = -0.453 , -1.735 ; kurtosis = -0.317 , 1.495) with a sample size of 20. The

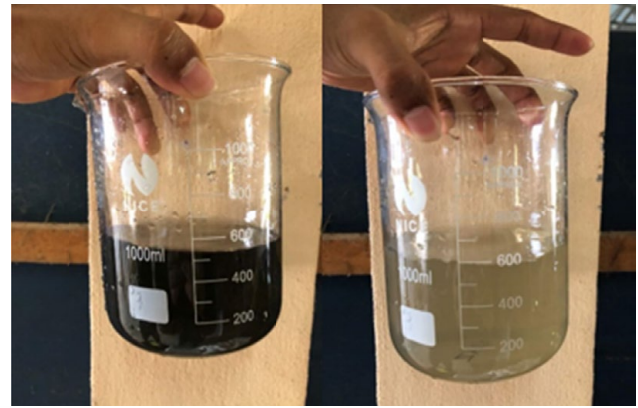


Fig. 8. Filtration result of pebble-sized marble



Fig. 9. Filtration result of sand-sized marble

regression model of DO and removal percentage was highly significant with a P-value below than 0.001. The R-squared (R^2) value and the best-fit line in Fig. 10 displayed that DO had strong influence on the changes in marble filter efficiency, with a R^2 value of 0.663. In addition, the Pearson correlation coefficient (R -value) indicated a strong positive correlation between DO and removal percentage with a value of 0.814. This positive value means that increasing the DO concentration led to an increase in the filtration efficiency.

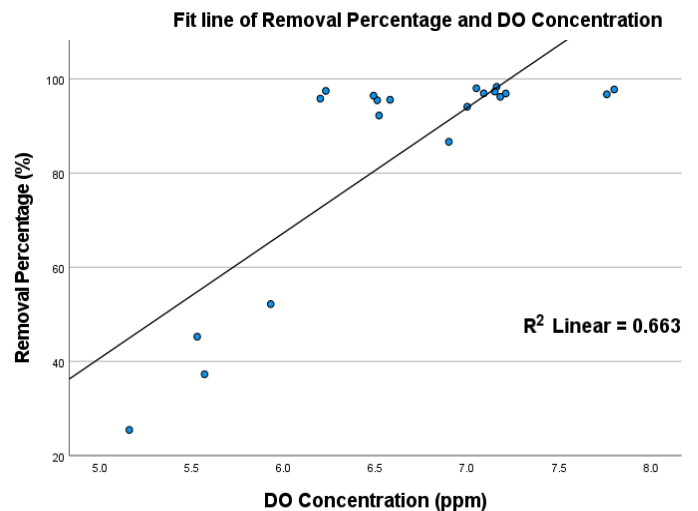


Fig. 10. Best fit line of removal percentage and DO concentration

5. Conclusion

Groundwater with high levels of sulfur can be filtered effectively using physical filtration, specifically with marble in both pebble and sand-sized. Interestingly, sand-sized marble was more effective at removing sulfur than pebble-sized marble. Both sizes showed different removal efficiencies depending on the flow rate. Notably, the removal efficiency of sand-sized marble remained above 90% for all tested flow rates, with the highest efficiency (98.3%) achieved at a flow rate of 0.011 l/s. As a result of the filtration, the true color of the treated water reached 33-34 Pt/Co, nearly meeting the drinking water standard of 20 Pt/Co. The cascading design of the filter significantly increased the dissolved oxygen (DO) in the groundwater, which played a crucial role in enhancing the filtration efficiency of the marble filter.

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