

The removal efficiency of iron and manganese from pre-ozonated groundwater using limestone filter

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ABSTRACT

This paper investigates the suitability of limestone to attenuate Fe and Mn from pre-ozonated groundwater samples using batch study and fixed column bed. The effects of limestone dosage, shaking speed, contact time, and pH on the removal efficiency of Fe and Mn are discussed. Pre-ozonated groundwater samples were prepared to present actual samples from Pintu Geng water treatment plant. A general characterization for groundwater as well as for limestone was conducted. In addition, the breakthrough and exhaustion points for limestone were determined. Results showed that limestone has good potential to remove more than 90% of Fe and Mn at optimum dosage of 40 g. The removal percentage for both metals was also affected by changing the contact time, where the maximum removal of Fe and Mn was observed at 90 and 120 minutes, respectively, at pH 8 and shaking speed of 350 rpm. The breakthrough time and exhaustion time of Fe were 40 hours and 210 hours, respectively. However, faster breakthrough time (30 minutes) and exhaustion time (16 hours) were observed for Mn sorption. The findings showed that an integrated ozone-limestone adsorption process significantly enhanced the removal of Fe and Mn up to 99.5% and 92%, respectively.

Key words | adsorption, filtration, groundwater, iron, limestone, ozone

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INTRODUCTION

Groundwater is the main source of drinking water in many countries around the world. It is an essential source of water for domestic, industrial and agricultural activities. Over the last few decades and due to rapid industrialization and agricultural activities, numerous cases of groundwater pollution have been reported (Alfarrah & Walraevens 2018). These pollutants affect the quality of groundwater and make it unsuitable for human and irrigation uses (Dippenaar *et al.* 2005). One of the major problems related to groundwater is its reddish and blackish properties due to the high content of iron (Fe) and manganese (Mn) (Du *et al.* 2017; Dou *et al.* 2018). Fe and Mn often exist together in groundwater, but the occurrence of Mn is much lower than Fe. Both Fe and Mn readily exist in drinking water supplies (El Araby *et al.* 2009). Several factors influence the concentration of heavy metals in groundwater, which

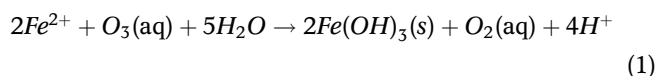
include soil condition or environmental reaction such as oxidation and reduction, alkalinity or acidity, and ion exchange or sorption (Hashim *et al.* 2011). The main source of Fe and Mn in groundwater originates from the weathering process of natural minerals in the soil, sediment and bedrock. In addition, excessive Fe and Mn in groundwater can occur due to rain filtration through soil, sediment and rocks. The presence of Fe in drinking water may also occur due to the corrosion of Fe pipes in water distribution systems (Chaturvedi & Dave 2012; Hu *et al.* 2018). When the concentration of both metals is high and exceeds the permissible limits, it will result in aesthetic problems such as metallic taste, discoloration, turbidity and staining of laundry (Chaturvedi & Dave 2012).

Numerous techniques used for heavy metal removal have been reported by many researchers such as adsorption,

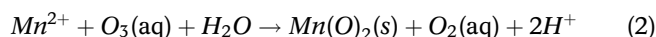
precipitation, oxidation/filtration, electro-chemical and ion exchange process (Chaturvedi & Dave 2012; Patil *et al.* 2016). Among these methods, adsorption is favourable and has gained more attention for the removal of heavy metals due to the effectiveness and simple process of the treatment (Meena *et al.* 2008; Ngah & Hanafiah 2008; Crini *et al.* 2018). In recent years, low-cost adsorbent has been regarded as a promising sustainable, cost-effective and eco-friendly technology for the removal of organic and inorganic compounds in water and wastewater (He & Chen 2014). Attention has been focused on low-cost adsorbent, which is capable of binding metals and removes heavy metals from water and wastewater (Rahman & Sathasivam 2015). Different studies have been conducted, especially on the use of a low-cost adsorbent for removal of heavy metals, which includes natural materials such as limestone, clay, laterite, zeolite and chitosan (Babel 2003; Uddin 2017). Some mineral deposits such as Fe-oxide and Fe-Mn oxide have demonstrated good adsorption capacities. Maji *et al.* (2013) found that Fe-oxide coated natural rock showed an excellent removal of heavy metal (98.5% removal) at 13 g/L dose and 6 hours' contact time and which exhibited the adsorptive capacity of 1.647 mg/L. Ghosh *et al.* (2014) suggested the usage of Mn-incorporated Fe(III) oxide, which can remove high heavy metal contaminated groundwater through the packed fixed-bed column. Agricultural waste by-products such as sugar cane bagasse (Homagai *et al.* 2010), rice husk (Ligate & Mdoe 2015), coconut husk (Okafor *et al.* 2012) and palm oil have also been used for heavy metal removal. Among these adsorbents, limestone proved its capability in removing more than 90% of heavy metals (Aziz *et al.* 2004). High purity limestone can offer a high performance of adsorption due to the high carbonate content in the limestone media. In addition, the surface charge of adsorbent also contributes to heavy metal removal (Aziz *et al.* 2004). Aziz *et al.* (2001) reported that more than 90% of copper (Cu) with a concentration of up to 50 mg/L could be removed from solution with a limestone volume above 20 mL (equivalent to 56 g). Limestone also can be used for Mn removal (Aziz & Smith 1992; Mojiri *et al.* 2016). Limestone can remove 95% of Mn at pH 8.5, and the presence of carbonate and rough solid media were useful in the precipitation of Mn from water (Dashti *et al.* 2019).

Recently, the advanced oxidation process using ozone has gained more attention from researchers due to the

powerful oxidizing agent for heavy metal removals (Jiang & Lloyd 2002; Deng & Zhao 2015; Bethi *et al.* 2016). Ozone has the multi-function of oxidizing heavy metals (El Araby *et al.* 2009), disinfection bacteria (Verma *et al.* 2016), color removal (Mustapha 2015) and oxidizing organic matter (Linlin *et al.* 2011). Unlike other chemical purifying processes (Aziz *et al.* 2001), ozone is an environmentally friendly chemical with no environmentally harmful residues. Removal of Fe and Mn consists of transforming the soluble form to insoluble that can be filtered out of the water; the ferrous iron is, therefore, easy to oxidize by ozone according to the following reaction:



Similarly, the oxidation of Mn goes through the same processes, but the conversion of Mn^{2+} into MnO_2 needs more oxidizing power than the conversion of Fe^{2+} into $\text{Fe}(\text{OH})_3$ because it needs higher energy (El Araby *et al.* 2009). The oxidation reaction of Mn by ozone takes the following form:



The treatment process of using ozone alone is less effective than using a combined process between ozonation and other processes for heavy metal removal. An alternative process of combined ozone oxidation with adsorption may enhance the treatment process. Konsowa *et al.* (2010) used a combination of ozonation with activated carbon adsorption for decolorization of industrial wastewater. They found that the integrated treatment resulted in higher removal of color and total organic carbon (TOC). This result was in agreement with the findings of Reungoat *et al.* (2012) for dissolved organic carbon (DOC) and traced organic chemicals (TrOCs) from wastewater treatment plant effluents. The integrated process of ozonation and adsorption could increase the exhaustion time of adsorbent and thus improve the performance of a column filtration system, as proven by Lei *et al.* (2007).

The main objective of this paper is to study the effectiveness of limestone to attenuate Fe and Mn from pre-ozonated groundwater samples using a fixed-bed column. Specifically,

synthetic pre-ozonated samples were prepared. The pH of the synthetic pre-ozonated samples was 8, and the Fe and Mn concentrations ranged from 0.3 to 0.5 mg/L for both parameters. Sodium hydroxide (NaOH), hydrochloric acid (HCl), Fe and Mn standard solutions were added accordingly to adjust the samples following the selected optimum conditions. The effects of limestone dosage, shaking speed, contact time and pH on the percentage removal of Fe and Mn have also been investigated.

MATERIALS AND METHODS

Groundwater sampling

Groundwater samples were collected from two different locations. The first location was Pintu Geng water treatment plant (WTP) (6° 05' 50.3" N, 102° 14' 6.2" E) at Kota Bharu, Malaysia while the second location was a USM tube well which is located at the Universiti Sains Malaysia Engineering Campus, Nibong Tebal, Penang (5° 08' 50.5" N, 100° 29' 34.7" E). The samples were collected once every three months from September 2014 until December 2016, from Pintu Geng WTP horizontal well at four different locations (location 1: raw groundwater effluent; location 2: effluent after ozonation; location 3: effluent after filtration; and location 4: final effluent). Therefore, the total number of samples was 24 samples. The samples were collected every 2 weeks from February 2015 until January 2016 from the USM tube well, where the total number of samples was 24 samples, similar to Pintu Geng WTP. An electrical clean water submersible pump with 100 kW of power and 240 V of voltage was used in the pumping process. The groundwater samples from the USM tube well were used for characterization analysis, batch adsorption and column study. To use these samples for the experimental work, the samples were simulated. This step is required to ensure that the sample characteristics are similar to the characteristics of the actual water samples at Pintu Geng WTP. The initial concentration of Fe and Mn in the USM tube well samples was recorded.

In situ characteristics of groundwater were conducted using a multi-parameter instrument YSI multi-parameter probe, which was pre-calibrated before every sampling.

The major tested parameters were temperature, total dissolved solids (TDS), pH, dissolved oxygen (DO), conductivity and salinity groundwater characteristics. The samples were stored in 20-L high-density polyethylene (HDPE) bottles and kept at 4 °C in a cold room after transfer to the laboratory. The preserved samples were allowed to condition at room temperature (25 °C) before starting any experiment. The major tested parameters in the laboratory were color, turbidity, total hardness, heavy metals (Fe and Mn) natural organic matter (NOM) and coliform bacteria. All procedures and analyses were in accordance with the *Standard Methods for the Examination of Water and Wastewater* (APHA 2012).

Synthetic pre-ozonated samples were prepared using USM groundwater based on the levels found after ozonation at Pintu Geng WTP. The pH of the synthetic pre-ozonated samples was 8, and the Fe and Mn concentrations ranged from 0.3 to 0.5 mg/L for both parameters. Sodium hydroxide (NaOH), hydrochloric acid (HCl), iron and manganese standard solutions were added accordingly to adjust the samples following the selected optimum conditions.

Batch adsorption study

Batch adsorption experiments were conducted to determine the adsorption capacity and removal efficiency of limestone particles in removing Fe, Mn, UV₂₅₄ and color. The effect of various dosages, pH, contact time and shaking was speed investigated. 200 mL of a simulated groundwater sample was placed into each conical flask (250 mL) and a fixed amount of limestone was added into each conical flask. The flasks were sealed with laboratory film (Parafilm M, USA) to ensure there was no adsorbent loss during the shaking process. Then, the samples were agitated using CERTOMAT SII orbital shaker. The effect of limestone dosage, shaking speed, pH and contact time was investigated using several experiments to determine the optimum values. In the first experiment, the dosage of limestone was varied from 5 g to 50 g. The experiment was conducted at operating conditions of 60 minutes' contact time, 350 rpm and pH of 7 (Aziz et al. 2001). The samples were allowed to settle for 90 minutes, after which, approximately 30 mL of samples were drawn using a syringe (Aziz et al. 2001). After that, the sample was filtered using 0.045 µm Millipore

cellulose-acetate filters before analysis. The second experiment was conducted to determine the optimum shaking speed required for the removal of Fe, Mn, UV_{254} and color. In this experiment, the shaking speed was varied from 50 to 400 rpm at an interval of 50 rpm. Each flask was added with an optimum dosage of limestone obtained from the previous experiment, and the pH was fixed at 7. Then, the sample was shaken for 60 minutes. After the shaking process, the samples were allowed to settle for 90 minutes. The final concentration of Fe, Mn, UV_{254} and color was measured, and thus the optimum shaking speed could be determined by plotting the percentage removal against the varied shaking speed. The third experiment was conducted to determine the optimum pH with adjusting the pH from pH 4 to pH 11 using 0.1 M NaOH and 0.1 M HCl and the operating conditions obtained from the previous experiments were used. Then, the samples were agitated for 60 minutes and allowed to settle for 90 minutes. After the settling process, 30 mL of the sample was drawn from the supernatant for analysis. The optimum pH was determined from the graph of pollutant removal against pH. The last experiment was conducted to determine the optimum contact time by using the optimum limestone dosage from the first experiment with the optimum operating conditions. The experiment was run at different shaking times (15, 30, 45, 60, 75, 90, 105, 120 and 135 minutes). Each conical flask was shaken at different times and continued with the settling process of 90 minutes. Then, the samples were analyzed to determine the final concentration of Fe, Mn, UV_{254} and color. The optimum contact time was obtained from the relationship between the removal efficiency and the contact time. All of the experiments were carried out in triplicate. The final sample was analyzed to determine the Fe, Mn, UV_{254} and color concentrations using the atomic absorption spectrophotometer (AAS), Genesys 100S UV-VIS spectrophotometer and Hach DR6000 spectrophotometer.

Fixed bed column study

Column setup

A rectangular column made of Perspex material with an inner diameter of 1.6 cm and a height of 55 cm was employed

for this study. A wire mesh was placed at the bottom (inlet) while cotton wool was placed on the top (outlet) of the column filter, as shown in Figure 1. The column was cleaned with dilute nitric acid and rinsed with distilled water before the experiments. Limestone was air-dried at room temperature ($25 \pm 2^\circ\text{C}$) for 24 h before filling the column. After that, limestone with a size of 1.18–2 mm was compacted until it reached 50 cm of the height of the column. After that, the limestone in the column was cleaned with distilled water for 24 hours in an up-flow mode to remove any trapped air and unwanted impurities from the bed. A 20 L plastic container was used to deliver the synthetic pre-ozonated groundwater to the column where the flow rate (1 mL/min) was controlled using a plastic valve. The retention time was set for 2 hours and the effluent was collected every hour for the first 8 hours, and subsequently every 2 hours for the next 14 hours. The column effluent was collected in a 60 mL plastic bottle and filtered using 90 mm Whatmann filter paper. Then, all samples were acidified with 1%–2% of HNO_3 before storing in a cool room for preservation.

Breakthrough time

The performance of column adsorption can be explained in terms of the breakthrough curve. The breakthrough curve can be expressed as C_t/C_o against time where C_t and C_o represent the initial and final concentration of pollutant. The curve represents the breakthrough point, and the breakthrough time (t_b). Breakthrough point is the point where the effluent concentration, C_t , reaches 5–10% of the initial concentration (C_o). The exhaustion point is determined when the final effluent reaches 95% of the initial effluent concentration when the column is considered ineffective.

RESULTS AND DISCUSSION

Groundwater characteristics

Table 1 summarizes the major water quality parameters in the USM tube well, while the water quality parameters at Pintu Geng WTP for all locations are shown in Table 2. As shown in Tables 1 and 2, the turbidity at Pintu Geng horizontal well was recorded between 0.85 and 9.95 NTU and

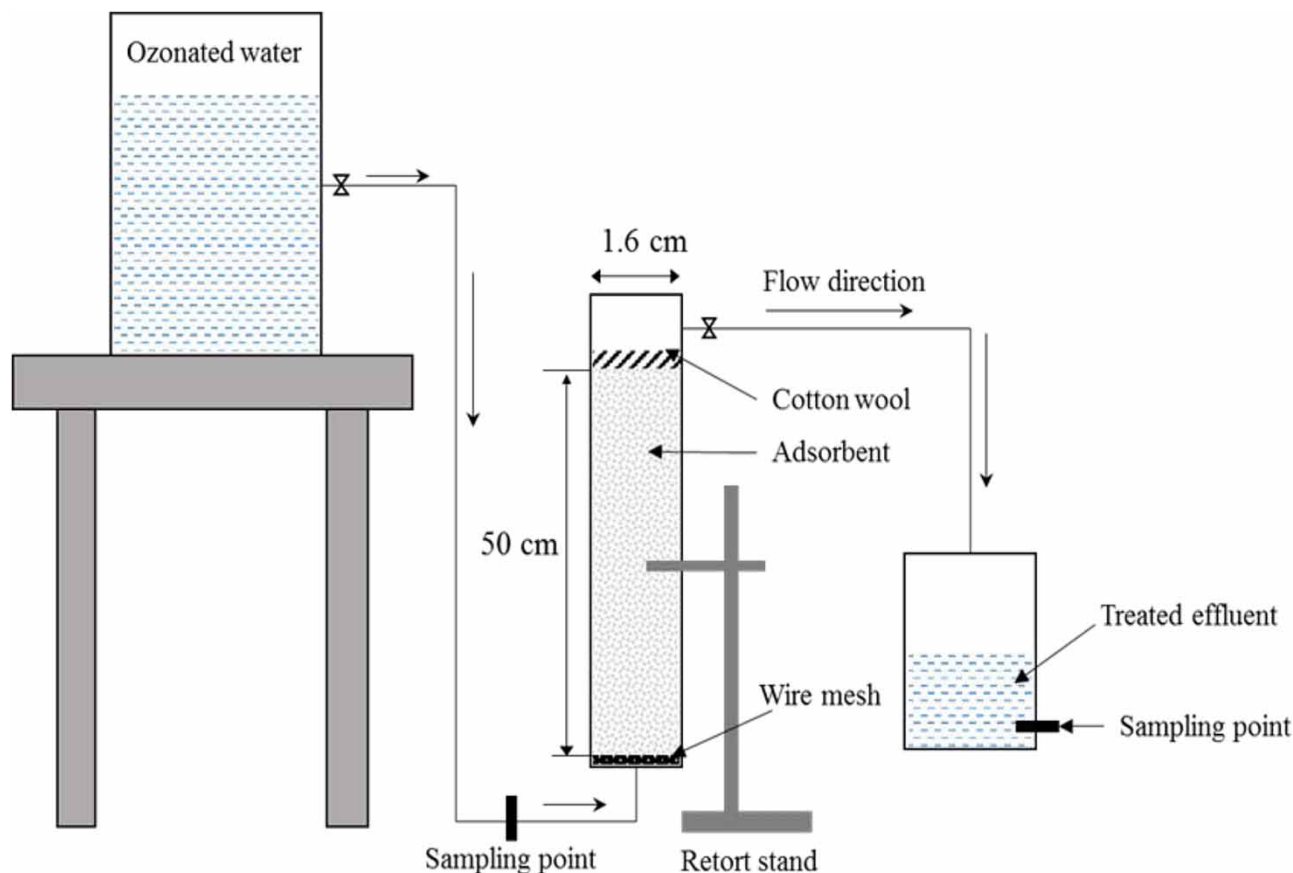


Figure 1 | Schematic diagram of column experiment.

Table 1 | Groundwater characteristics for USM tube well

Parameters	Unit	USM tube well (<i>n</i> = 12)				Drinking Water Standard by MOH
		Sample 1	Sample 2	Sample 3	Average	
Turbidity	NTU	24.90	24.57	27.58	25.68	5
pH	–	6.79	6.77	6.81	6.79	6.5–9.0
TDS	mg/L	5,620	5,833	6,326	5,926	1,000
Total hardness		1,260	1,374	1,512	1,382.0	500
Fe	mg/L	2.465	2.442	2.454	2.454	0.3
Mn	mg/L	0.387	0.389	0.388	0.388	0.1

the average turbidity was 3.87 NTU. According to the Malaysian Standard of Drinking Water Quality (MS2320 2010), the recommended raw and drinking water standard for turbidity are 1,000 NTU and 5 NTU, respectively. Results showed that the raw groundwater at Pintu Geng horizontal well complied with the standard. On the contrary, the value

of turbidity determined at the USM tube well was in the range of 1.123–40.5 NTU with the average value of 17.098 NTU, and exceeded the standard level for drinking. The concentration of color at Pintu Geng horizontal well shows low level with the minimum value of 0.33 PtCo and the maximum value of 5 PtCo which fall within the permissible

Table 2 | Water samples characteristics at Pintu Geng WTP

Parameters	Unit	Raw groundwater				Effluent after ozone (settled water)				Effluent after filter				Final treated effluent			
		Min.	Max	Ave.		Min.	Max	Ave.		Min.	Max	Ave.		Min.	Max	Ave.	Drinking water std
Turbidity	NTU	0.853	9.947	3.869		1.043	15.267	5.833		0.307	3.140	0.844		0.197	0.663	0.366	5
True color	PtCo	0.333	5.000	2.444		0.333	3.667	1.833		0.000	4.333	2.389		0.333	5.000	1.944	15
TDS	mg/L	83.633	134.500	101.928		65.000	130.233	102.692		82.533	131.300	98.278		87.800	136.500	109.522	1000
pH	-	5.323	6.723	5.972		5.927	7.143	6.332		6.117	7.303	6.741		6.213	7.257	6.826	6.5-9
Conductivity	$\mu\text{S}/\text{cm}$	135.867	218.967	165.706		102.567	210.900	154.706		127.600	213.000	158.522		144.767	219.700	175.411	NA
Total hardness	mg/L	39.667	60.000	44.444		37.333	60.667	44.667		37.333	59.667	43.111		37.000	58.000	42.389	500
Fe	mg/L	0.004	0.240	0.152		0.050	0.404	0.106		0.000	0.210	0.070		0.000	0.120	0.053	0.3
Mn	mg/L	0.018	0.119	0.057		0.000	0.086	0.053		0.000	0.047	0.008		0.000	0.046	0.015	0.1
DOC	mg/L	0.000	1.000	0.650		0.000	1.200	0.550		0.200	2.900	0.867		0.200	1.100	0.611	NA
UV254	cm^{-1}	0.002	0.018	0.009		0.006	0.023	0.013		0.003	0.015	0.010		0.005	0.012	0.009	NA
<i>E. coli</i>	MPN	0.000	8.950	2.075		0.000	24.600	2.483		0.000	4.150	1.192		0.000	0.000	0.000	Absent/100 mL sample
Total coliform	MPN	1.000	98.700	31.442		29.900	429.300	158.613		13.500	557.150	223.383		0.000	0	0	Absent/100 mL sample

limit for drinking water (<15 PtCo) (MS2320 2010). On the other hand, high color concentration was observed in the USM tube well, ranging from 76 PtCo to 286.5 PtCo. This is possibly due to algae growth, which increased the organic activity in the groundwater. Moreover, the presence of soluble minerals such as Ca^{2+} , Mg^{2+} , Fe^{2+} and Mn^{2+} may also attribute to high color concentration in the USM tube well. These mineral ions are dissolved from sediment, soil particles and rock, which travel along the mineral surface in the aquifer (Harter 2003). pH was monitored on site using the multi-parameter probe, and recorded an average of pH 5.97 and pH 6.39 for both Pintu Geng horizontal well and USM tube well. According to MS2320 (2010), the recommended ranges for pH are pH 5.5 to pH 9 and pH 6.5 to pH 9 for raw and drinking water, respectively. For TDS values, it was observed that the TDS level at the USM tube well was much higher than Pintu Geng horizontal well. TDS for USM tube well samples was in the range of 5,620 mg/L–8,021 mg/L with a mean value of 6,325.67 mg/L. However, for Pintu Geng horizontal well, it was very small as compared with the TDS concentration at the USM tube well due to deep groundwater which had been in contact with the bedrock for a long time. The high concentration of TDS at the USM tube well was due to percolation of agricultural activity such as palm plantation in the surrounding area of USM Nibong Tebal (Shirazi *et al.* 2015). Therefore, groundwater from the USM tube well is unfit for drinking or irrigation purposes because it exceeds the permissible limit of raw water (TDS <1,500 mg/L) and drinking water (TDS <1,000 mg/L).

For total hardness, it was found that the mean concentration of hardness at the USM tube well was 1,512 mg/L as CaCO_3 which indicates that the water is classified as very hard water that contains a high concentration of total hardness. The high concentration of total hardness or hard water is not harmful to human health, but it can break down in boilers, cooling towers and instruments that handle water (Ramya *et al.* 2015). At Pintu Geng WTP, the source of groundwater abstracted from the horizontal well was classified as soft water with minimum and maximum values of 40 and 60 mg/L as CaCO_3 .

For heavy metals, the concentration of Fe at Pintu Geng horizontal well was in the range of 0.004 mg/L to 0.24 mg/L, and the mean Fe concentration was

0.152 mg/L. However, Fe concentration at the USM tube well was much greater than Pintu Geng horizontal well. Fe content was at maximum up to 10.65 mg/L, which is not recommended as drinking water. On the other hand, the concentration of Mn from the USM tube well was higher than Pintu Geng horizontal well, which has a similar pattern to Fe concentration.

The performance of Pintu Geng WTP shows that the average level of turbidity follows the sequence of effluent after ozone (5.85 NTU) > raw groundwater (3.87 NTU) > effluent after the filter (0.84 NTU) > final treated effluent (0.37 NTU). Ozone gas supplied in the oxidation chamber leads to the cloudiness of groundwater. Pre-ozonation is very effective to reduce turbidity after being integrated with the filtration process. Ozone gas could enhance the particles to coagulate and filter out particulate through the filtration process. The ozonation process is also effective for color removal (Reungoat *et al.* 2012). Moreover, pH of the samples was increased from 5.97 to 6.33 after the ozonation process which affected the rate of decomposition ozone, the formation of hydroxyl radical and thus, enhances the mineralization at higher pH (Konsowa *et al.* 2010). Meanwhile, total hardness did not show a significant difference between raw and after the treatment process with the range of hardness between 42 and 44 mg/L as CaCO_3 .

Excessive Fe and Mn in groundwater were due to rain filtering process through the soil as well as minerals and rocks (Chaturvedi & Dave 2012). As stated in Table 2, the average Fe concentration decreased after the groundwater passed through ozonation, filtration and final treatment. The reduction of Fe concentration followed the sequence raw groundwater (Fe mean = 0.156 mg/L) > ozonation (Fe mean = 0.106 mg/L) > filtration (Fe mean = 0.07 mg/L) > final effluent (Fe mean = 0.053 mg/L). In the ozone oxidation process, dissolved Fe (Fe^{2+}) oxidized into ferric iron (Fe^{3+}) and slowly hydrolysed to form $\text{Fe}(\text{OH})_3$ (El Araby *et al.* 2009). Also, raw water containing Mn ion dropped drastically to <0.1 mg/L and was acceptable for drinking water standard after applying ozone oxidation and filtration process in groundwater treatment. Mn^{2+} was oxidized to Mn^{+4} and converted into MnO_2 , which requires more energy in the oxidation process (El Araby *et al.* 2009). The removal of particulate compounds of MnO_2 was very effective by continuous integration with the filtration

process. Therefore, low concentrations of dissolved Fe (0–0.12 mg/L) and Mn (0–0.0046 mg/L) were obtained for the final treated effluent at Pintu Geng WTP.

Limestone characteristics

Sieve analysis showed that the mean particle size of limestone was 1,620 μm which is classified as poorly graded coarse sand. XRD demonstrated that the limestone is composed of 95.5% CaCO_3 , 3% MgCO_3 and 1.5% impurities. This is also confirmed with the XRF results. The density of limestone was 2,598 kg/m^3 , and the surface area as measured by single-point BET was 11.12 m^2/g , where the pore volume and diameter were 0.002 cm^3/g and 7.5 nm, respectively. The surface morphology of limestone was investigated using FESEM, as shown in Figure 2.

Batch adsorption study

Effect of limestone dosage

Figure 3 shows the effect of limestone dosage on the removal of Fe, Mn, UV_{254} and color. It was observed that the removal efficiency was increased with increasing the limestone dosage. The removal of Mn increased significantly compared to Fe when the dosage of the limestone was increased from 5 g to 40 g. This can be explained due to the availability of the number of binding sites increasing proportionally with limestone dosage and the adsorbents conglomerated (Aziz *et al.* 2001). The maximum removal of Fe and Mn were 99% and 72%, respectively, at 40 g of limestone dosage. The equilibrium was achieved when the rate of sorption was equal to the rate of desorption. According to Aziz *et al.* (2001), more than 90% of Cu was removed using 56 g of limestone. Limestone has lower performance to remove color and UV_{254} in groundwater samples. The removal of color and UV_{254} were only 33% and 10%, respectively, when the dosage of limestone was above 35 g. Therefore, it can be concluded that the limestone has a good efficiency to remove Fe and Mn rather than organic pollutants such as color and UV_{254} . The values of the adsorption capacity of Fe and Mn adsorbed onto limestone were 0.024 mg/g and 0.007 mg/g, respectively.

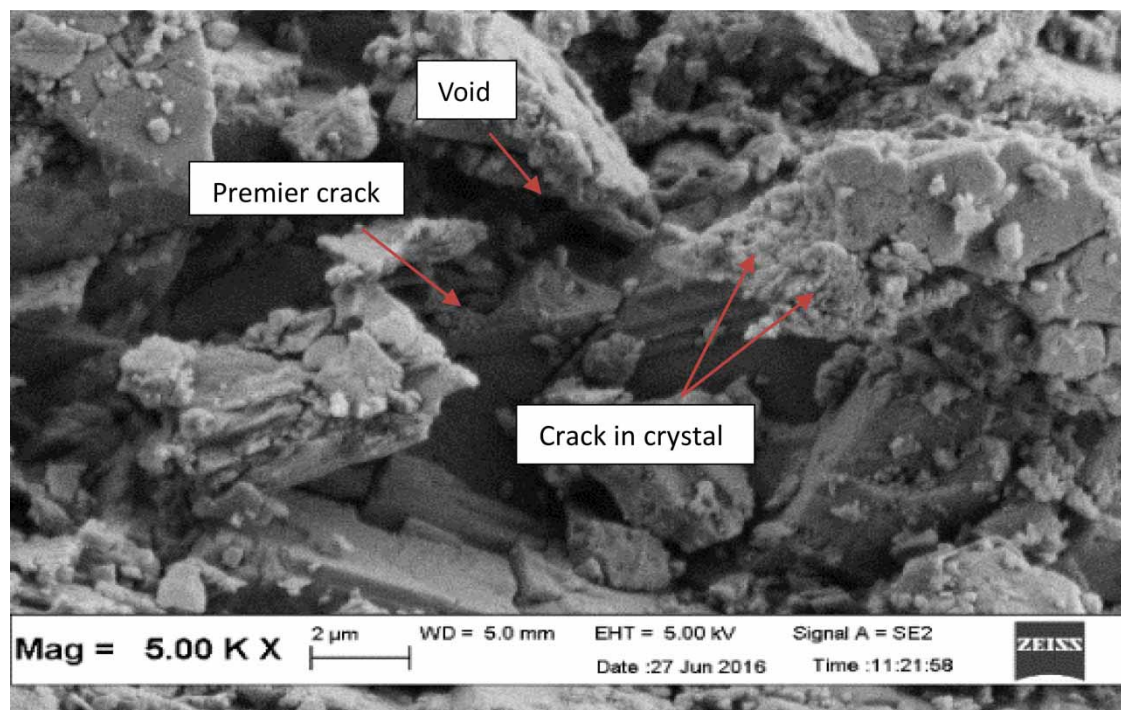


Figure 2 | Surface morphology analysis of raw limestone using FESEM.

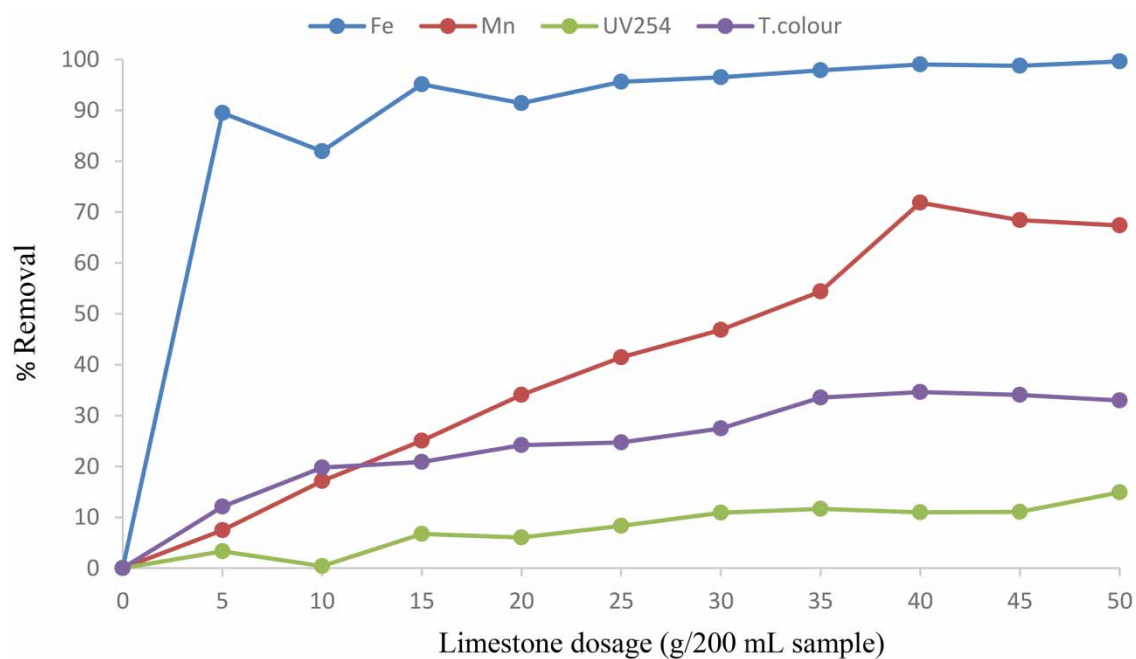


Figure 3 | The effect of limestone dosage on pollutant removal (pH = 7, shaking speed = 300 rpm, contact time = 60 minutes).

Effect of shaking speed

Eight different shaking speeds were applied during the batch experiments, as mentioned earlier. The effect of shaking speed is illustrated in Figure 4. Results show that the capacity uptake by limestone increases with the increase of shaking speed. It can be observed that at 350 rpm, the removal efficiencies of Fe, Mn, UV₂₅₄ and color were more than 90%, 85%, 10% and 30%, respectively. After 350 rpm, the removal efficiency of all pollutants reached the saturated condition. As shown in Figure 4, the removal of Fe and Mn sharply increased by 60% when the shaking speeds are in the range of 200–350 rpm, which means that the higher shaking speed the better removal of both metals. This result is because the rigorous mixing had better interaction between limestone and groundwater samples (Foul *et al.* 2009). At 400 rpm, the removal efficiency of Fe, Mn and UV₂₅₄ slightly decreased due to desorption process. This process could happen when adsorbed particles were released from limestone media.

Effect of pH

Figure 5 shows the effect of pH on the removal of Fe, Mn, UV₂₅₄ and color by limestone media. The results

demonstrate that the removal efficiency of Fe and Mn was influenced by limestone media at the acidic condition. However, the sorption of Fe and Mn was found to be affected by pH in strong alkaline condition. As shown in Figure 5, the removal efficiency of Fe and Mn increased with an increase of pH. The removal of Fe increased more than 85% from pH 4 to pH 6 and achieved the highest removal of 90% at pH 6. However, it was significantly decreased after pH 6 to pH 8 and suddenly decreased at pH 9 (<10%). This observation is most likely because Fe was precipitate in the form of ferric hydroxide Fe(OH)₃ after pH 6 (Meena *et al.* 2008; Biswas & Mishra 2015). The capacity uptake of Mn by limestone increased with the increase in pH. On the other hand, the removal of Mn was low (30%) at pH 4. There is more H⁺ at low pH, which forms a positive charge to the active site of limestone adsorbent. In this condition, Mn ions were competing with H⁺ to attach to the active site of limestone, which gives minimum binding between Mn ions and the active site of limestone. However, in the alkaline condition, the limestone becomes less positive due to the decreasing concentration of H⁺ in the groundwater solution. As a result, it increases the removal of Mn in the groundwater solution. In this study, the removal of Mn was increased drastically from 30% at pH

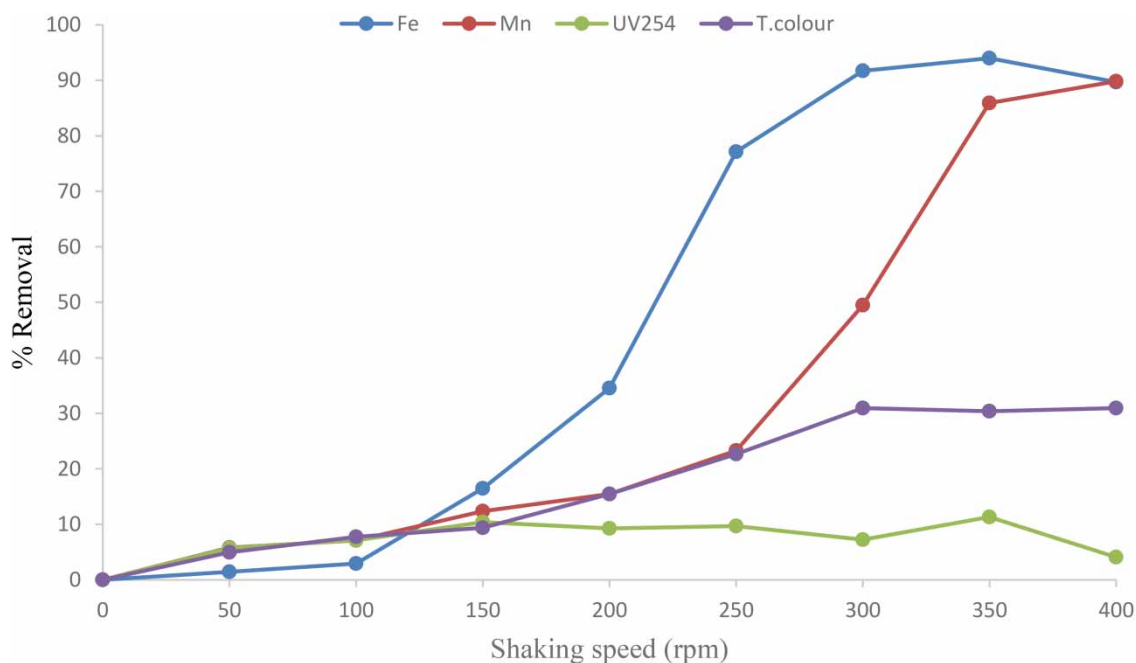


Figure 4 | The effect of shaking speed on pollutant removal (pH = 7, contact time = 60 minutes).

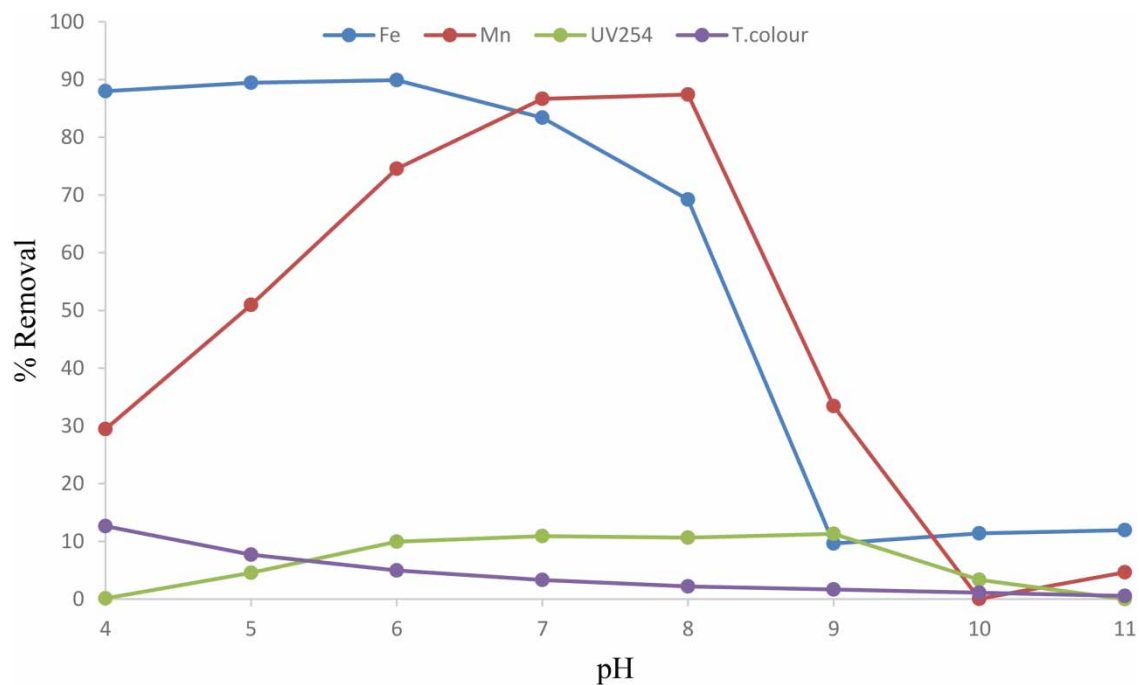


Figure 5 | The effect of pH on pollutant removal (experimental conditions: contact time = 60 minutes).

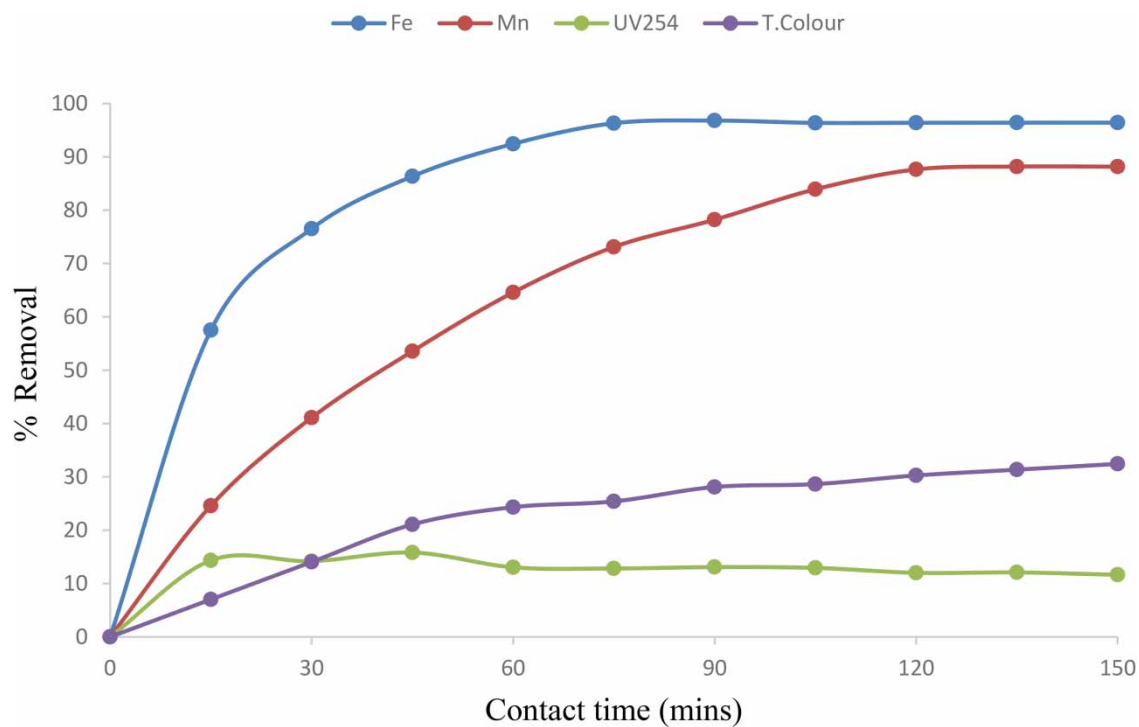


Figure 6 | Effect of contact time on pollutant removal using limestone.

4 up to 86% at pH 7. After neutral pH, the increasing rate becomes slow and achieved the maximum removal of 87% at pH 8. In strong alkaline condition, the removal of Mn decreased to the minimum value. Based on the theory of solubility, Mn will form a complex with OH^- (for example, $\text{Mn}(\text{OH})^+$, $\text{Mn}(\text{OH})^2$, $\text{Mn}(\text{OH})^{-3}$ and $\text{Mn}(\text{OH})^{-4}$) at higher pH and thus Mn hydroxyl precipitates through adsorption and precipitation onto limestone surface (Doula 2006). Therefore, it can be concluded that pH is an important controlling parameter for the removal of Fe and Mn using limestone adsorbent. However, there is no significant effect of pH for the removal of UV_{254} and color in the groundwater samples. Regarding the limestone characteristic, it contained high carbonate content in the limestone sample creating an alkaline condition for the water sample (Aziz et al. 2001). The finding was proved by results of XRF analysis as discussed earlier. The increase in pH may increase the removal of Fe and Mn in the samples (Aziz et al. 2004). Moreover, limestone, which has a rough surface, provides solid contact to the low concentration of metal ions via chemisorption process and thus improves flocculation of Mn precipitate (Aziz & Smith 1992). The presence of dissolved CaCO_3 will form manganese carbonate (MnCO_3) which increases the performance removal of Mn in the groundwater samples. Although the pH in water samples was varied, the addition of limestone media may change water pH to an alkaline condition. As shown in Figure 5, the removal of Fe and Mn on limestone was greater than 80% at pH 7. The removal rate declined sharply beyond pH 7 and pH 8 for Fe and Mn, respectively. Thus, pH 7 was designated the optimum value for the adsorption process by limestone.

Effect of contact time

The effect of contact time on the removal efficiency of the different pollutants is presented in Figure 6. For this experiment, the optimum parameters measured from the previous experiments were applied. It was observed that the removal of Fe had increased sharply up to 57% in the first 15 minutes of continuous shaking. This shows that a large quantity of Fe was adsorbed in the initial stage of the adsorption process. A rapid increment of Fe removal in the first 15 minutes occurred due to the increase of driving

force in the solution that might increase the number of available active sites on the surface of limestone media. Figure 6 shows that Fe adsorption was higher than 90% when the contact time achieved 60 minutes, and thus reached equilibrium at 90 minutes. Therefore, the best contact time for Fe removal was 90 minutes with the maximum removal of 96.8%, while for Mn, the percentage removal was gradually increased until the optimum contact time of 120 minutes. At the best contact time, 88% of Mn was removed using limestone adsorbent media. After 120 minutes, the removal was slightly increased. The results of the batch adsorption experiment are summarized in Table 3.

Performance of fixed-bed column

Pre-ozonated water was simulated by spiking dedicated levels of Fe and Mn into the USM groundwater samples when necessary. Fe and Mn concentrations were 0.43 and 0.50 mg/L, respectively. Column performance was

Table 3 | Optimum values for the batch adsorption experiments

Pollutant	Limestone	
	Removal (%)	Optimum dosage
Fe	99.04	40
Mn	71.87	40
UV_{254}	14.89	50
Color	33.52	35
Pollutant	Removal (%)	Optimum shaking speed
	Removal (%)	Optimum pH
Fe	93.94	350
Mn	85.91	350
UV_{254}	11.31	350
Color	30.94	300
Pollutant	Removal (%)	Optimum pH
	Removal (%)	Optimum contact time
Fe	89.90	6
Mn	87.41	8
UV_{254}	11.30	9
Color	12.64	4
Pollutant	Removal (%)	Optimum pH
	Removal (%)	Optimum contact time
Fe	96.7	90
Mn	87.63	120
UV_{254}	15.81	45
Color	32.43	150

expressed in terms of the breakthrough curve which plotted the ratio of initial effluent to the final effluent concentration as a function of time. The amount of pollutant present in the water samples was removed by limestone through a column filtration system. The plotted breakthrough curve measures several parameters such as breakthrough time, t_b , and exhaustion time, t_e . The breakthrough point, t_b , and exhaustion point, t_e , are obtained usually when concentration ratio (C_t/C_o) reaches 10% and 95%, respectively (Biswas & Mishra 2015). Figures 7 and 8 show the analysis of the breakthrough curve for Fe and Mn adsorption, respectively. According to Aziz *et al.* (2004), divalent metals (Fe^{2+} and Mn^{2+}) will be attracted with a negative charge of limestone at a pH higher than 8. In a column experiment, the ozonated sample is in an alkaline condition (final pH \sim pH 8), and passes through the column in contact with the limestone media and generates pH higher than 8 for the final effluent. Thus, both metals precipitated in the form of carbonated metals. Besides that, when the ozonated sample passed through the limestone column, the time required to reach breakthrough and exhaustion point for Fe sorption is longer than Mn sorption. The breakthrough time, t_b , and exhaustion time, t_e , of Fe were 40 hours and 210 hours, respectively. However, faster breakthrough time ($t_b = 30$ minutes) and

exhaustion time ($t_e = 16$ hours) occurred for Mn sorption. It can be observed that the bed height of 50 cm was not sufficient for continuous column sorption of Mn. Thus, it was suggested that increased bed height might improve the column performance of Mn removal. This observation was consistent with that of Kamarudzaman *et al.* (2015), who studied the biosorption of Mn using *Pleurotus spent mushroom compost* in a fixed-bed column. The more adsorbent packed in the column, the greater sorption site of adsorbate due to the longer residence time of adsorbate in the column. In addition, increase in the mass of adsorbent in the column provides a larger surface area of adsorbent, which resulted in higher removal efficiency of heavy metals in the column (Hana *et al.* 2009).

Performance of integrated process

The integrated treatment of ozonation followed by limestone adsorption was implemented at Pintu Geng WTP and proven as an effective treatment method for groundwater. Figure 9 shows that the Fe and Mn concentration of 1.56 mg/L and 1.207 mg/L, respectively, at the raw Pintu Geng WTP, exceeds the maximum permissible limit of the drinking water by MS2320 (2010). The data of ozonation process were collected from Akbar *et al.* (2015).

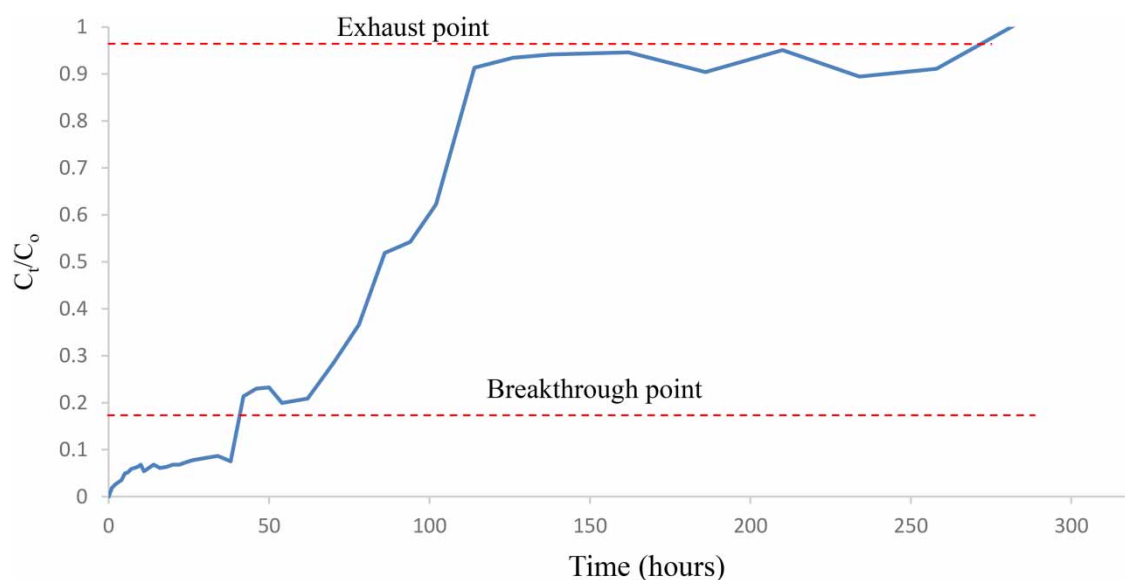


Figure 7 | Breakthrough curve for Fe adsorption on limestone.

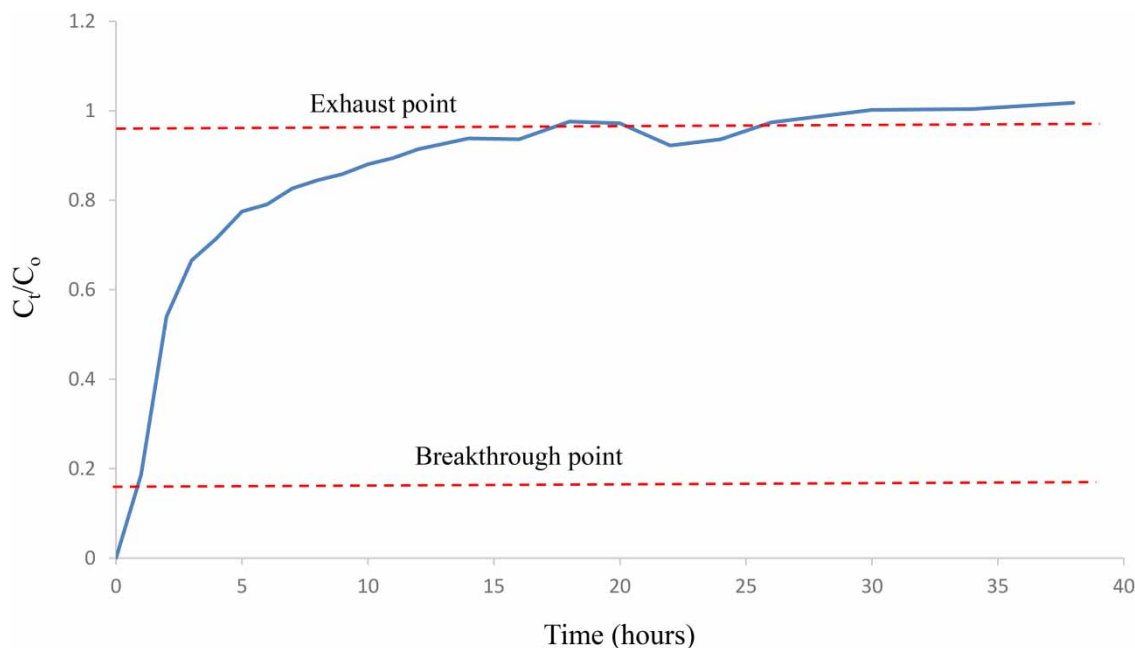


Figure 8 | Breakthrough curve for Mn adsorption on limestone.

In a previous study, Akbar *et al.* (2015) observed that ozone alone could remove only 72% of Fe and 58% of Mn. Also, they observed that ozone was very effective to remove color up to 98%. Moreover, ozone removed 75% of UV_{254} and reduced concentration of UV_{254} from 1.135 cm^{-1} to 0.239 cm^{-1} . On the other hand, the treatment using single ozonation is less effective for Fe and Mn removal. This finding is consistent with that of Kurniawan *et al.* (2006), Lei *et al.* (2007) and Reungoat *et al.* (2012). The performance of Fe and Mn removal was improved significantly when ozonation was combined with the filtration process. Pratarn *et al.* (2011) obtained the same result by using a combination of ozone and granular activated carbon (GAC), that provides the best result for complete degradation of phenolic wastewater treatment compared to single ozone treatment.

The integrated treatment using limestone media was highly effective to remove both Fe and Mn up to 99.5% and 92%, respectively. This treatment reduced the Fe and Mn concentrations to 0.008 mg/L and 0.094 mg/L, respectively. The presence of hydroxyl (-OH), carboxyl (-COOH) and carbonyl (-C=O) groups attached on the limestone surface improved the adsorption capability of metals in solution (Atieh *et al.* 2010). In addition, a new manganese

oxide (MnO_x) group appeared at a lower wavelength (585 cm^{-1}) through Mn stretching proves that the Mn adsorption process has occurred (Parikh & Chorover 2005). The formation of MnO_x was due to precipitation and adsorption reaction (Tebo *et al.* 2004). It also has a high adsorption capacity and can absorb metal ions. Moreover, Fe-O stretching vibration mode also detected at 585 cm^{-1} , which related to the adsorption of Fe in the limestone sample. The presence of hydroxyl (-OH), carboxyl (-COOH) and carbonyl (-C=O) can attack both positive ions from pollutants (Fe^{2+} and Mn^{2+}) which resulted in better removal of both Fe and Mn through the adsorption process.

The surface morphology of limestone was observed after the treatment process, as shown in Figure 10. It was found that more crystal grains completely packed and covered the surface of limestone media. Large particles of the ferrihydrite attached to the limestone surface. As mentioned earlier, the pH of treated water was in an alkaline condition ($pH > 8$). Formation of hematite ($\alpha\text{-Fe}_2\text{O}_3$) or goethite ($\alpha\text{-FeOOH}$) occurred through the crystallization process of ferrihydrite in alkaline condition (Tebo *et al.* 2004). There are no pores or cracks presented on the limestone surface, which indicates that the interaction between

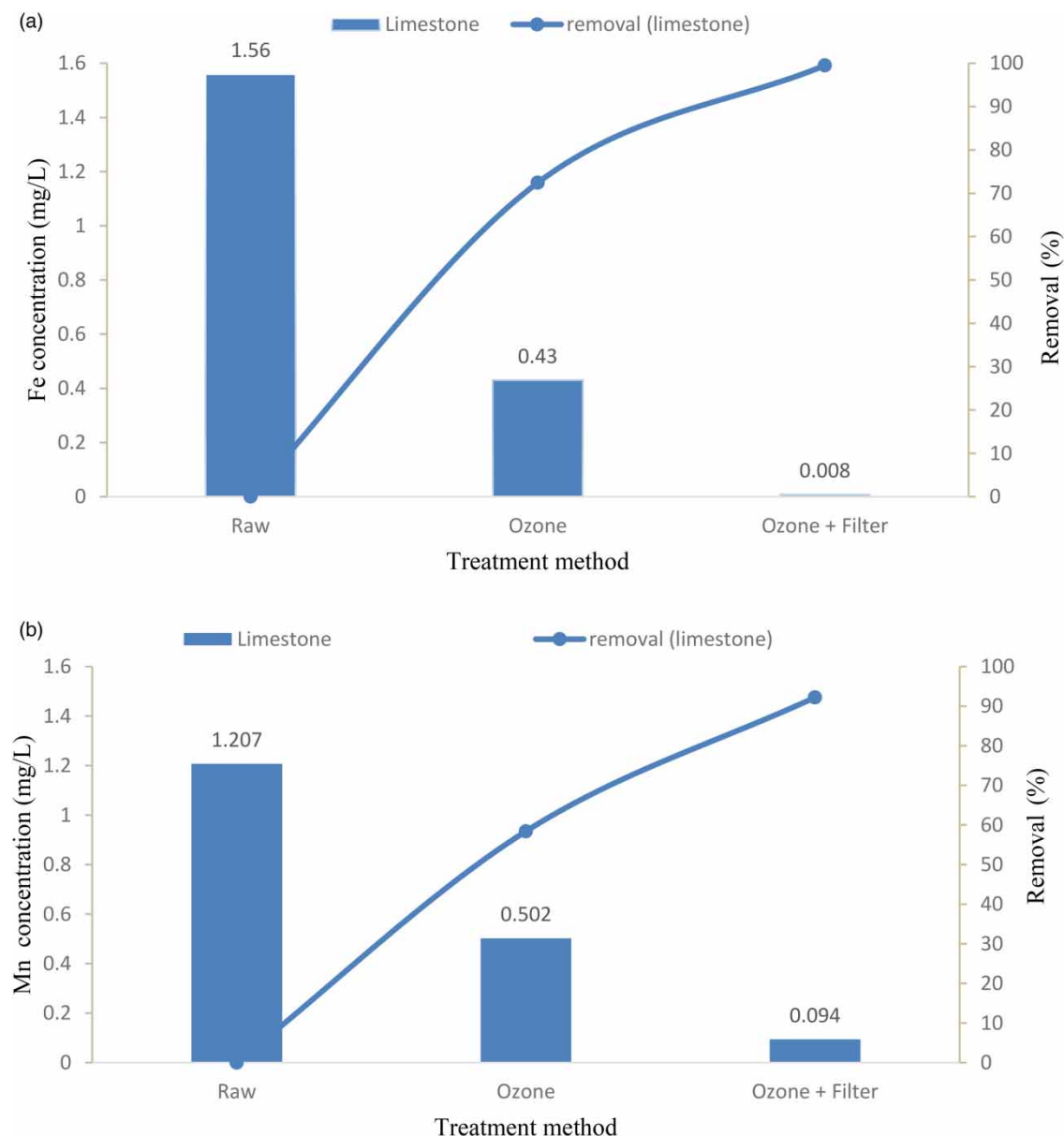


Figure 9 | Performance of limestone in removing (a) Fe and (b) Mn.

adsorbate and adsorbent occurred through the chemisorption process.

It can be summarized that the use of ozone alone is not sufficient to reduce the concentration of Fe and Mn at the final effluent according to the prescribed water quality standard by MS2320 (2010). The integrated treatment of ozonation followed by limestone filtration proved an excellent treatment method focused on Fe and Mn removal for groundwater as compared to the existing treatment

method at Pintu Geng WTP. The proposed treatment complied with drinking water standard by MS2320 (2010).

CONCLUSION

A fixed-bed column study was conducted using limestone as adsorbate media to investigate its viability to remove iron (Fe) and manganese (Mn). Results demonstrated that

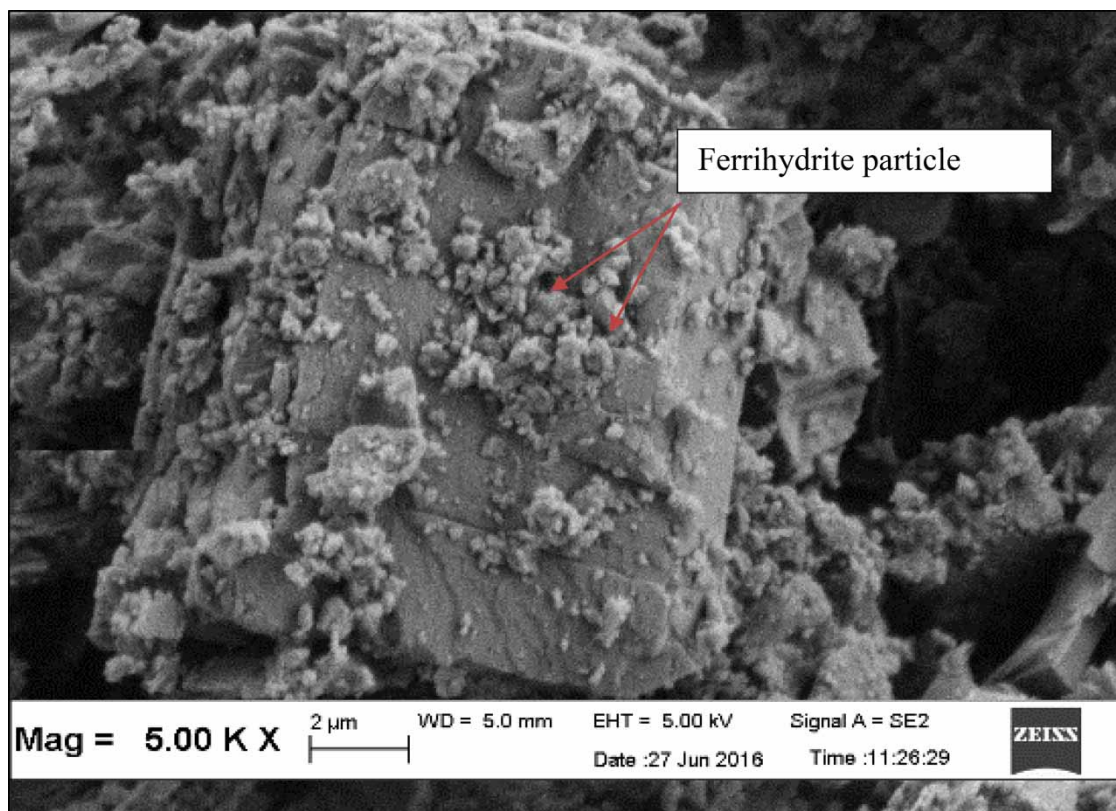


Figure 10 | Surface morphology of limestone after treatment.

limestone was capable of removing more than 90% of Fe and Mn from pre-ozonated groundwater at the optimum dosage of 40 g. The removal percentage for both metals was also affected by changing the contact time, where the maximum removal of Fe and Mn was observed at 90 and 120 minutes, respectively, at pH 8 and shaking speed of 350 rpm. The presence of hydroxyl (-OH), carboxyl (-COOH) and carbonyl (-C=O) groups attached on the limestone surface improved the adsorption capability of metals in the solution. The breakthrough time and exhaustion time of Fe were 40 hours and 210 hours, respectively. However, faster breakthrough time (30 minutes) and exhaustion time (16 hours) occurred for Mn sorption. This was because the bed height of 50 cm was not sufficient for continuous column sorption of Mn. Thus, it was suggested to increase the bed height to improve the column performance of Mn removal. Overall, the findings show that an integrated ozone-limestone adsorption process improved the removal of Fe and Mn up to 99.5%

and 92%, respectively, which comply with the drinking water standards.

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