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POTENTIAL USE OF OZONATION WITH LIMESTONE ADSORPTION IN GROUND TREATMENT: A CASE STUDY AT KELANTAN WATER TREATMENT PLANT

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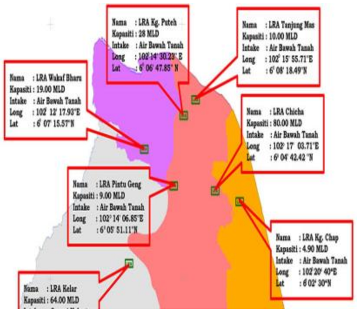
Graphical abstract



Abstract

Pollution of groundwater occurs due to rapid industrialization and agricultural activities. A desktop study was carried out to identify the actual groundwater problem occurs in Malaysia. The quality of groundwater was investigated to obtain the baseline groundwater data for an alternative integrated water treatment process that involved combination of ozonation and adsorption process. Preliminary data on groundwater pollution were collected from nine Mineral and Geoscience Department(JMG) groundwater monitoring wells, Air Kelantan Sdn Bhd (AKSB) water treatment plant and Natioal Hydraulics Research Institute of Malaysia (NAHRIM). The result shows that raw groundwater in Kelantan contains high concentration of Fe and thus an alternative treatment is necessary. However, based on the previous treated effluent data at one of the water treatment plants in Malaysia has indicated that the use of ozone alone may only remove Fe concentration up to 0.5- 0.8 mg/L. This exceeded the acceptable limit of 0.3 mg/L .1 Application of ozonation process for groundwater treatment has received more attention based on its capability to transform contaminants into non-harmful substance within a short period. Most previous literature found that limestone is very effective in removing more than 90% of heavy metal such as Cu, Zn, Cd, Ni, Cr, Fe and Mn in water. To improve the performance of ozonation process, an integrated treatment of ozonation and adsorption processes using limestone is proposed in the current study for groundwater treatment.

Keywords: Ozonation process, adsorption process, limestone, groundwater treatment

Abstrak

Pencemaran air bawah tanah berlaku disebabkan oleh perindustrian dan aktiviti pertanian yang pesat. Satu kajian desktop telah dijalankan untuk mengenal pasti masalah sbenar air bawah tanah yang berlaku di Malaysia. Kualiti air bawah tanah telah disiasat untuk mendapatkan data asas air bawah tanah sebagai alternative untuk proses rawatan air bersepadu yang melibatkan gabungan pengozonan dan penjerapan proses. Data awal mengenai pencemaran air bawah tanah telah dikumpulkan daripada Sembilan pemantauan air bawah tanah iaitu Jabatan Mineral dan Geosains (JMG), Air Kelantan Sdn Bhd (AKSB) loji rawatan air dan Natioal Hidraulik Institut Penyelidikan Malaysia (NAHRIM). Hasil kajian menunjukkan bahawa air bawah tanah mentah di Kelantan mengandungi kepekatan Fe yang tinggi dan dengan itu rawatan alternatif adalah perlu. Walau bagaimanapun, berdasarkan data efluen sebelum ini yng dirawat di salah satu loji rawatan air di Malaysia telah menunjukkan bahawa penggunaan ozon sahaja hanya boleh menyingkirkan kepekatan Fe sehingga 0.5- 0.8 mg/L. Ini adalah melebihi had yang boleh diterima iaitu 0.3 mg/L 0,1 Permohonan proses pengozonan untuk rawatan air bawah tanah telah menerima perhatian yang lebih berdasarkan kepada keupayaan untuk mengubah bahan cemar ke dalam bahan yang tidak berbahaya dalam masa yang singkat. Kebanyakan sastera sebelumnya mendapati bahawa batu kapur adalah sangat berkesan dalam membuang lebih daripada 90% daripada logam berat seperti Cu, Zn, Cd, Ni, Cr, Fe dan Mn dalam air. Untuk meningkatkan prestasi proses pengozonan, rawatan bersepadu pengozonan dan penjerapan proses menggunakan batu kapur telah dicadangkan dalam kajian semasa bagi rawatan air bawah tanah.

Kata kunci: Proses pengozonan, proses penjerapan, batu kapur, rawatan air bawah tanah

1.0 INTRODUCTION

Groundwater has been identified as a new water sources for the use of future generation. It is mainly used for drinking water supply in many countries in the world. Based on the report from National Groundwater Association (2005), about 75%,47%,32%,29% and 15% of the population in Europe, US, Asian- pacific region, Latin America and Australia respectively, depend on groundwater for their drinking water supply.2 Meanwhile, 26% of population in Canada used groundwater for their domestic needs.3 In Malaysia, there is almost 70% population use groundwater for public water supply.

Nowadays, pollution of groundwater occurs due to rapid industrialization and agricultural activities. Table 1 shows the initial concentration of groundwater polluted by Fe and Mn in previous literature. Basically, Malaysia Drinking Water Standard stated the maximum permissible limit of Fe and Mn concentrations are 0.3 mg/L and 0.1 mg/L respectively.

According to a desktop study that has been conducted in this study, groundwater in Kelantan contains high concentrations of iron which exceeding drinking water standard as 0.3 mg/L.1 The presence of iron in drinking water and water supplies can result in unpleasant tasting water, reddish color and odor, hereditary chronic iron overload (hemochromatosis) and plumbing fixtures.11-12 In groundwater, iron is normally present as diavalent (Fe2+) and contaminant because of organoleptic properties.

Besides, most of water treatment plant (WTP) in Kelantan utilized groundwater as drinking water. The groundwater quality is monitored by Department of Environment (DOE) and Ministry of Health (MOH) to comply Malaysia Drinking Water Standard. The initial concentration of Fe and Mn in groundwater normally exceeds the maximum permissible limit of drinking water standard. Therefore, an alternative of groundwater treatment is necessary. There are several groundwater treatment methods that have been applied in the WTP at Kelantan such as conventional and ozone systems. Both of the treatment methods can remove Fe and Mn depending on initial pollutant concentration in raw water flow. However, the treated effluent data at one of the water treatment plants in Malaysia has indicated that the use of ozone alone may only remove Fe concentration up to 0.5- 0.8 mg/L. This exceeded the acceptable limit of 0.3 mg/L. Thus, the aim of this study is to identify the actual groundwater problem that occurs in Malaysia and propose a new alternative in groundwater treatment. This information can be used as the baseline groundwater data for an alternative integrated water treatment process that involves combination of advanced oxidation process and adsorption process.

Table 1 Initial concentration of groundwater pollutant (Fe & Mn) in previous literature

Groundwater source	Fe (mg/L)	Mn(mg/L)	Author
Groundwater in northern Greece	0.165	0.235	[4]
Groundwater in Bangladesh			[5]
Groundwater in New Jersey	<0.020	<0.002	[6]
Groundwater in Genese County,Michigan	0.1-1.13	0.009-0.016	[7]
Groundwater in Kelantan	0.1-27	<0.1-19	[8]
Groundwater in Tioman Island, Pahang	0.6 – 1.0	<0.1	[9]
Groundwater in Jenderam Hilir ,Selangor	14 - 39	1.9 – 5.6	[10]

2.0 MATERIALS AND METHODS

Desktop Study: A desktop study was carried out to identify the actual groundwater pollution problem that occured in Malaysia. Preliminary data on groundwater quality was collected from National Hydraulics Research Institute of Malaysia (NAHRIM), Minerals and Geoscience Department (JMG) and Air Kelantan Sdn Bhd (AKSB).

2.1 Data Collection-NAHRIM

NAHRIM has done several studies on groundwater contamination in Malaysia such as groundwater contamination study in North Kelantan, Jenderam Hilir Selangor and Kampung Salang Tioman Island, Pahang. Preliminary data on groundwater pollutant was obtained from these study reports. Based on the reports, groundwater in Kelantan contains high concentration of Fe which originated from deposited sediment in Kelantan Delta.

2.2 Data Collection-JMG

There are 109 monitoring wells in North Kelantan belonging to JMG. In this study, only nine monitoring wells within the surrounding groundwater treatment plants were selected as shown in Table 2. The JMG groundwater monitoring data are categorized based on well screen depth. The historical data from 2003 until 2013 on Fe and Mn concentrations in each groundwater monitoring well are obtained from the existing compilation data from JMG Kelantan.

Table 2 Selected JMG groundwater monitoring well in this study[8]

JMG groundwater monitoring well location		Aquifer layer	Well screen depth
KB 30	Pintu Geng WTP	Shallow	0 - 20m
KB 43	S.K. Seribong	Shallow	0 - 20m
KB 51	S.K. Rambutan Rendang	Shallow	0 - 20m
KB 21	Perol Booster Pump	Intermediate	20 – 40m
KB 36	Pusat Kesihatan Peringat	Intermediate	20 – 40m
KB 9	Tanjung Mas WTP	Deep	>40 m
KB 28	Pintu Geng WTP	Deep	>40 m
KB 29	Pintu Geng WTP	Deep	>40 m
KB 32	Pusat Kesihatan Beris Kubur Besar	Deep	>40 m

2.3 Data Collection-AKSB

Six water treatment plants (WTP) that belong to AKSB were selected in treating the groundwater sources for drinking water purposes as shown in Figure 1. Five of AKSB WTP such as Kg Puteh WTP, Tanjung Mas WTP, Chicha WTP, Kg Chap WTP and Wakaf Baru WTP used conventional treatment method except for Pintu Geng WTP which used ozonation system. Pintu Geng WTP was selected as a study site according to ozonation system applied in this WTP since 2013. Sources of water are from groundwater borehole surrounding this WTP. Then, the water was pumped to the multiple tray aerator. Water was treated through integrated treatment by several processes such as aeration, ozonation, filtration and chlorination. In ozonation process, ozone was injected from the bottom to oxidation tank. Ozone dosage is depending on Fe concentration in raw groundwater. Increased in Fe concentration may increased in ozone dosage. Moreover, anthracite was used as filtration media in this WTP. Anthracite can remove odor, Fe, Mn and others. After filtration process, the water was through disinfection process using chlorine. Chlorination is a process to kill bacteria that are normally present in water such as total coliform and E-Coli. Finally, the treated water that complies with drinking water standard was supplied to comsumers around Kelantan.

For this study, the data on Fe concentration in raw water, after ozonation, after filtration and final treated water have been collected continuously since December of 2013 until now. Moreover,the ozone dosage data was also collected as a baseline data for an alternative water treatment process that will be proposed in the future.

3.0 RESULTS AND DISCUSSION

Table 3 shows the initial concentration of Fe and Mn data done by JMG monitoring well in North Kelantan from 2003 until 2013. Based on the historical data, the result shows that the concentration of Fe and Mn from JMG groundwater monitoring well exceeding the Drinking Water Quality Malaysia Standard of 0.3 mg/L and 0.1 mg/L respectively. Moreover, Fe and Mn concentration increases when the depth of aquifer layer increases. This is due to the Fe in the groundwater that originates from the deposited sediment in Kelantan Delta.

Table 4 shows the initial concentration of Fe in raw WTP abstracted from groundwater sources. The result shows that initial Fe concentration before treatment in most of WTP also exceeded the maximum permissible limit of 0.3 mg/L. Raw water that was treated using the conventional method or ozone system can remove Fe up to 65 -99%, depending on initial Fe concentration in raw water flow. Based on the previous ozone data at one of water treatment plants in Malaysia, the amount of ozone required for Fe oxidation increase up to 20-75 % (1-3 kg/hr) when dissolved Fe^{2+} concentration in raw water flow increased from 1.5 to 4.5 mg/L. Moreover, the treated effluent data at the same WTP has also indicated that the use of ozone alone may only remove Fe concentration up to 0.5- 0.8 mg/L. Figure 2 shows the analysis results of raw and treated effluent data collected from AKSB and it was proven that ozone alone may not remove Fe concentration to the standard of Drinking Water Malaysia. An integrated treatment is needed to improve the performance and efficiency of ozonation process. An integrated treatment of ozonation and filtration using anthracite done by AKSB hs proven to be better than ozone alone. This is because it can remove Fe concentration up to 0.1 mg/L and thus comply to the Malaysia Drinking Water Standard of 0.3 mg/L.

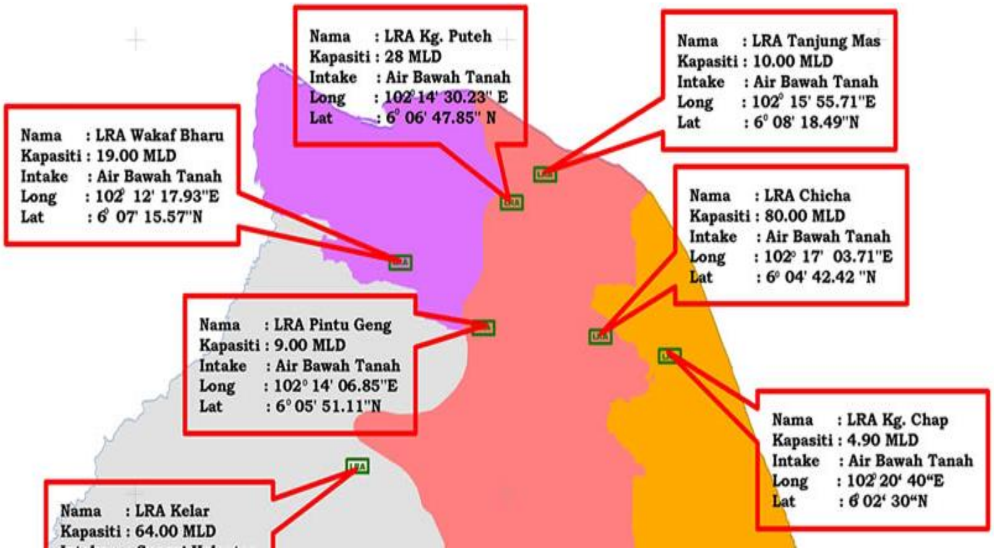


Figure 1 Location of WTP abstracted from groundwater sources in Kelantan

Table 3 Initial concentration of Fe and Mn from JMG monitoring well in North Kelantan (2003–2013)[31]

Monitoring well		Aquifer layer	Depth (m)	Fe (mg/L)			Mn (mg/L)		
				Min value	Max value	Average	Min value	Max value	Average
KB 9	Tanjung Mas WTP	Deep	56.5	8.6	13	10.75	<0.1	8.3	1.08
KB 28	Pintu Geng WTP		72.5	9.8	16	11.75	0.3	0.5	0.37
KB 29	Pintu Geng WTP		60.5	8.8	14	11.67	0.1	0.4	0.27
KB 32	Pusat Kesihatan Beris Kubur Besar		96	3.6	27	12.64	<0.1	19	1.48
KB 21	Perol Booster Pump	intermediate	25.5	2.4	16	8.92	0.2	4.6	2.4
KB 36	Pusat Kesihatan Peringat		36	0.4	13.3	10	<0.1	2.5	0.45
KB 30	Pintu Geng WTP	shallow	11.5	0.2	12	0.9	<0.	0.2	0.1
KB 43	S.K. Seribong		15.5	0.1	12	5.82	<0.1	0.9	0.28
KB 51	S.K. Rambutan Rendang		12.6	0.1	16	4.6	<0.1	1.5	0.56

Table 4 Initial concentration and efficiency of Fe removal in WTP[32]

location	Raw concentration of Fe (mg/L)			% removal			Treatment method
	Min value	Max value	Average	Min value	Max value	Average	
Kg Puteh WTP	5.0	5.5	5.43	97	99	97.8	Conventional
Tanjung Mas WTP	7.6	9.25	8.27	88	92	90.6	Conventional
Pintu Geng WTP	0.23	0.74	0.44	74	94	84.7	Ozone System
Chicha WTP	-	-	-	-	-	-	Conventional
Kg Chap WTP	7.16	7.43	7.3	96.5	98.5	97.5	Conventional
Wakaf Baru WTP	0.9	1.5	1.23	10	65	45.8	Conventional

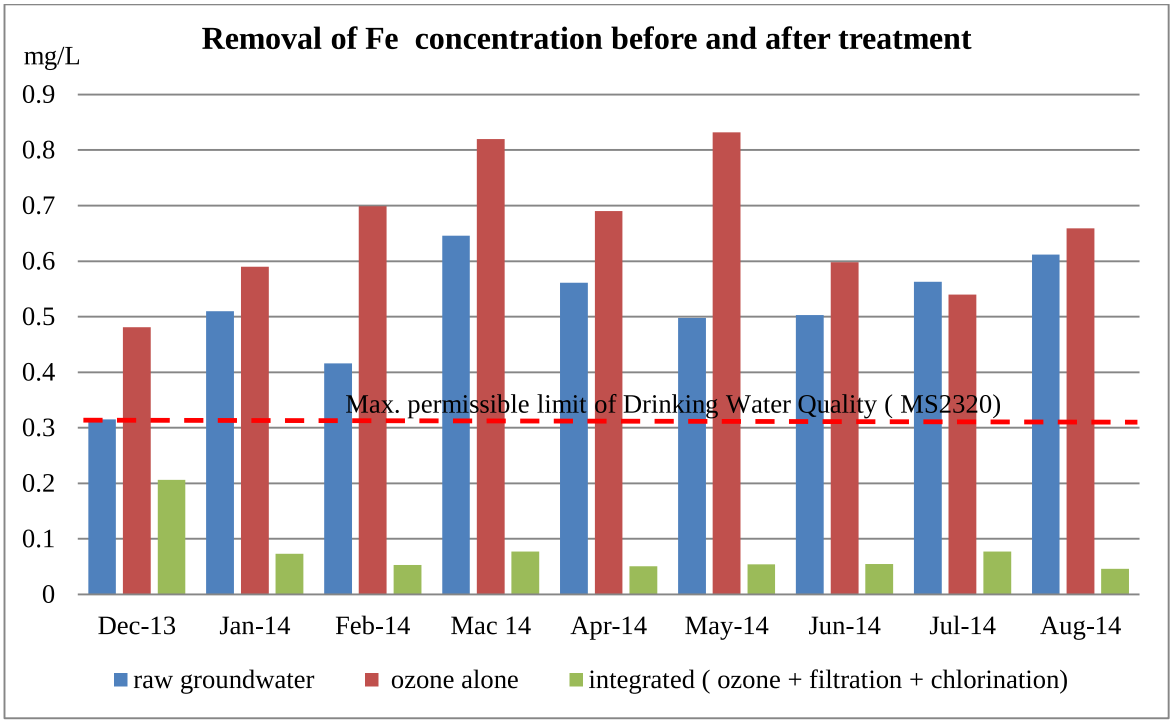


Figure 2 Average removal of Fe concentration before and after treatment[32]

4.0 PROPOSED NEW TREATMENT

Based on the previous information and results, an integrated process of ozonation and adsorption using limestone media is being proposed. Ozonation is a chemical treatment while adsorption using limestone is a physical treatment. Three different treatment processes will be conducted in this study. The treatment processes are the ozonation process alone, the limestone adsorption process alone and the combination of ozonation and adsorption process for optimization study. The schematic diagram of proposed an integrated treatment of ozonation and adsorption process is shown in Figure 3.

Limestone adsorption: In single process of adsorption, characterization study of limestone as adsorbent was done using X-Ray Fluorescence (XRF). The result shows that limestone that will be used in this study contained 97.9297% $CaCO_3$, 0.8682% MgO and 1.2% others. Most of the previous literature found that limestone is very effective in removing more than 90% of heavy metal such as Cu, Zn, Cd, Ni, Cr, Fe and Mn in water as shown in Table 4. Limestone can also be used as reactive materials for in-situ iron removal from groundwater. [13] found that 99.9% of Fe was removed by carbonate material. The removal of Fe increased when neutral pH increased in the range of pH 5 to 9.

Other than Fe, limestone can also be used in removing manganese (Mn).[16] The study revealed that limestone could remove Mn of 95% at final pH 8.5 and the presence of carbonate and rough solid media were useful in precipitation of Mn^{4+} from water. The oxidation of Mn^{2+} to Mn^{4+} by aeration alone become a faster process when pH is raised above neutral (pH>7). Mn removal was efficient when small particle size, a greater depth and a lower flowrate. Therefore, limestone could be used as low cost media in removing contaminant especially heavy metals from water and wastewater. [1]

In groundwater treatment, the adsorption process is the most common application being used especially for heavy metal removal. There are several factors influencing adsorption process such as pore size and surface area, the chemical nature of the carbon source, chemical composition and concentration of contaminant, temperature and pH of water and flowrate or time exposure of water to adsorbent. [22] In this research, batch and column study will be conducted to establish the kinetic of pollutants using limestone adsorbent. According to[18], batch study experiment will be run using optimum shaking speed of 350 rpm, shaking time of 60 minutes and settling time of 90 minutes for this study.

Ozonation process: Ozonation process is an advanced oxidation process (AOP) that has been found to be very effective in treating drinking and groundwater. This process is based on the use of ozone gas which is a strong oxidizing agent. It can also generate hydroxyl radicals as a strong oxidizing agent to eliminate a wide variety of organic, inorganic and microbiological, taste and odor problems. This treatment is efficient in removing metals such as Fe, Mn[23] and As.[7]

In groundwater treatment, Fe^{2+} is oxidized to Fe^{3+} while Mn^{2+} is oxidized to Mn^{4+} which is insoluble that can be filtered out using filtration process. Generally, both Fe^{2+} and Mn^{2+} are oxidized in the alkaline pH in range of pH6-9 and pH 8 respectively. Based on study done by[23] it was proven that the maximum removal of Fe^{2+} and Mn^{2+} in alkaline pH (pH 9-10). Therefore, pH is one of the important factors that influences the ozonation process.

Other than pH, ozone dosage is also a main factor influencing the performance of ozonation process. The high amount of ozone dosage required high operating cost of treatment. The ozone dosage can be reduced by optimizing the amount of ozone delivered at sufficient time. Meanwhile, optimum contact time may also improve the biodegradability of pollutants because the mineralization can be achieved biologically and thus reduce ozone dosage.[24] Thus, in this study, the initial pH of groundwater, initial concentration of pollutants, reaction time and ozone dosage varied to optimize the study. Design expert of Response Surface Method (RSM) will be used to determine the most effective treatment for this study. Therefore, application of ozonation process in this study is predicted to oxidize Fe and Mn and eliminate the microbiological problems such as E-Coli and total coliform in groundwater.

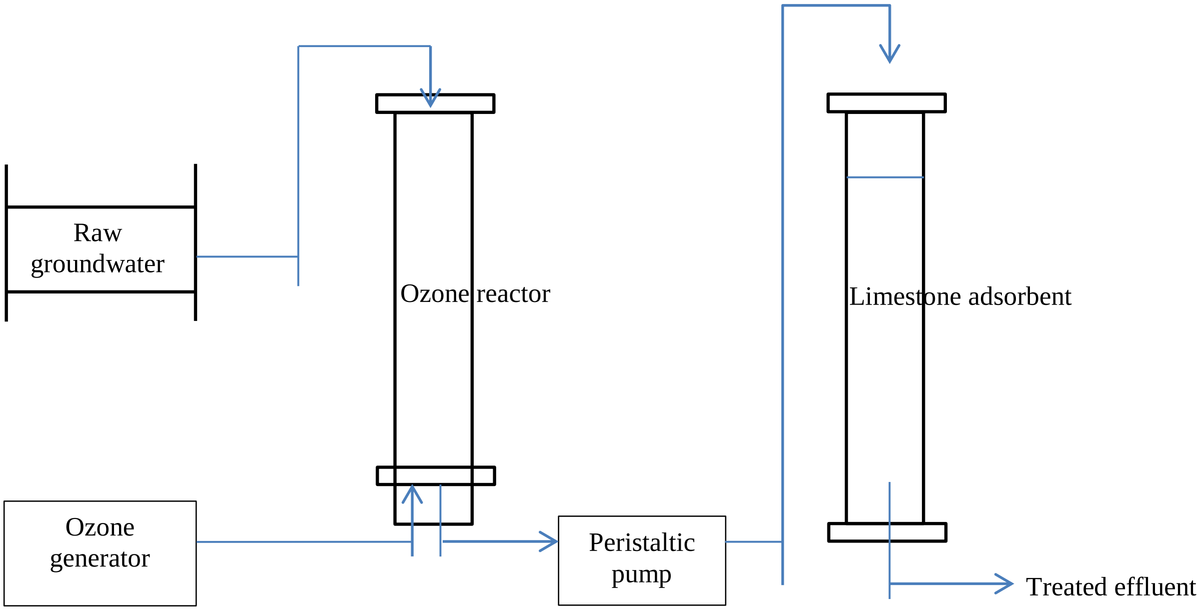


Figure 3 Proposed schematic diagram of ozonation and adsorption process

Table 5 Removal efficiency of metals in water using limestone adsorbent media

Target contaminant	Water matric	pH	Removal efficiency (%)	Author
Cd, Pb, Zn, Ni, Cu & Cr (III)	water	pH 8.5 (final)	>90%	[14]
Mn	water	pH 7(initial)	90%	[15]
Mn	water	pH 8.5 (final)	95%	[16]
Cu	water		>90%	[17]
Fe	Semi-aerobic landfill leachate		90%	[18]
Fe & Al Zn Cd	Acidic leachate		100% 88% 91%	[19]
Cu^{2+}	Aquoes solution	pH 6-9	100%	[20]
Pb^{2+} Cd^{2+} Cu^{2+} Zn^{2+}	Aqueous solution		>75% (low grade)	[21]
Fe^{2+}	groundwater	pH 9	99%	[13]

Integrated treatment of ozonation and limestone adsorption process: Most of the studies on ozonation process revealed that ozone alone is less efficient than a combined process between ozonation and other processes. This due to the low reaction rate with ozone. Table 6 shows the comparison between the efficiency of integrated processes and a single process of ozone alone in water and wastewater. Based on Table 6, it is proven that the integrated process of ozonation and adsorption is more efficient than ozonation alone in terms of percentage removal of contaminant, ozone dosage and ozone consumption for wastewater treatment. The high ozone dosage required high operational cost. Therefore, the reduction of ozone dosage using integrated process of ozonation and adsorption will minimize the cost of ozone consumption.

Table 6 The comparison of efficiency of integrated and single process

Method	Water matric	Target contaminant	Single process (ozone alone)	Integrated process (ozone + adsorption)	Author
Ozonation & Adsorption by GAC	Textile wastewater	Color TOC		TOC (37%)	[25]
Ozonation & Adsorption by AC	wastewater	*p*-Nitrophenol		COD (91%)	[26]
Ozonation & Adsorption by GAC	Stabilized landfill leachate	COD NH_3-N	Removal : COD (35%) NH_3-N (50%)	Removal : COD (86%) NH_3-N (92%)	[27]
Ozonation & biological AC filtration	Wastewater treatment plant effluent	DOC Trace organic chemica (TrOC)		Removal : DOC (50%) TrOC (>90%)	[28]
Ozonation & adsorption by GAC	wastewater	phenolic	The worst for phenol degradation	The best for phenol degradation	[29]
Ozonation & adsorption by GAC	Food processing secondary effluent	COD TOC	Ozone consumption : 19g O_3/g TOC	Ozone consumption : 8.2–10.7 g O_3/g TOC	[30]

In this study, an integrated process combined of ozonation and adsorption with limestone is predicted to more effective than ozone alone in removing metals from groundwater. Ozone has capability to transform contaminants within a short period while adsorption using limestone media may predict to accelerate the kinetic rate of the ozone decomposition through the formation of .OH radicals in the groundwater.

Most of literature on adsorption found that limestone has capability of removing more than 90% of metals in water. From an economic point of view, limestone is an effective low-cost adsorbent and may reduce the amount of ozone dosage used in groundwater treatment. The previous treated effluent data at one of the water treatment plants in Malaysia has indicated that the use of ozone alone may only remove Fe concentration up to 0.5- 0.8 mg/L. Thus, an integrated process of ozonation and adsorption with limestone is proposed in this study, which can improve final effluent Fe concentration in Malaysian Drinking Water Standard requirement of 0.3 mg/L. The enhancement of groundwater treatment using limestone adsorption is predicted to increase the efficiency of Fe and Mn removal due to the minerals calcium carbonate that is in the limestone media.

4.0 CONCLUSION

In conclusion, a desktop study provides more information that can be used as a baseline groundwater data for an alternative integrated water treatment process that involves combination of advanced oxidation process and adsorption process. The proposed integrated treatment of ozonation with limestone adsorption can be a good alternative of groundwater treatment. This is because it can improve the removal efficiency of the treatment, reduce the ozone consumption and it is also more economical method compared to the conventional ones.

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