PERFORMANCE EVALUATION OF METAKAOLIN AS LOW COST ADSORBENT FOR MANGANESE REMOVAL IN ANOXIC GROUNDWATER

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A b s t r a c t

The recent climate condition and pollution problem related to surface water have led to water scarcity in Malaysia. Huge amount of groundwater has been identified as viable source for drinking water. This paper was aimed to investigate groundwater's quality at specific location and metakaolin's potential in the groundwater treatment in the removal of manganese. Groundwater purging was determined to be sufficient at 120 minutes where all three parameters (pH, dissolved oxygen and conductivity) were stabilized. The groundwater studied is classified as both anoxic and reductive due the low dissolved oxygen value. It also can be categorized as brackish due to high value of conductivity and total dissolved solid. Manganese content in groundwater was determined as higher than of that permissible limit for raw water and drinking water which makes it unsuitable for them not suitable for consumption and cleaning purpose. Average manganese concentration in samples was 444.0 ppb where the concentrations of manganese ranged

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from 229.4 ppb to 760.3 ppb. Manganese developed is not that a strong positive correlation against iron concentration, total dissolved solids and conductivity; whereas has a moderate negative correlation against dissolved oxygen. The capability adsorption of manganese by metakaolin was assessed via batch method which indicated optimum dosage and contact time was 14g that removed average 30.2% and contact time optimum at 120 minutes which removed 33.2% manganese from the sample.

Keywords: groundwater treatment, manganese removal, metakaolin

1. INTRODUCTION

As water scarcity will affects world population including Malaysia [1], [2], more water source need to be explored and utilized such as groundwater, [3], [4] and rainwater storage [5], [6]. Groundwater has become a very important water source globally due to water scarcity that resulted from surface water contaminations and climates effects. Depletion of surface water during dry season and current rapid urbanization and industrialization, the demand of clean water supply becomes more critical [7], [8]. In Malaysia, groundwater is treated as a secondary source where less than 2% of water consumed sourced from groundwater mostly at State of Kelantan and Perlis leaving groundwater storage untouched [9]–[11]. It is estimated there are 5000 billion cubic meters of groundwater in Malaysia with a recharge rate of 64-120 billion cubic meters annually [12] by recharge sources such as river and reservoir [13].

Unlike surface water, groundwater needs different sampling approach. Purging duration determination is important so that the quality of groundwater is similar with and within the aquifer. Generally, water in a well can be divided into three sections, which are which are casing water (stagnant water at the top surface to the screen) , screen water (mixture between top surface water and aquifer water) and aquifer water which is the actual ground water [14]. Purging duration determination is important to ensure representativeness of sample compared to the aquifer water. Parameters stabilization was established as a valid technique to determine the purging adequacy and represent the actual water quality in the aquifer [14]–[16].

The utilization of purging duration on groundwater sample is totally depends on water quality characteristics. There are abundance of studies on groundwater quality to determine physical [17], [18], chemical [17]–[20] and microbial properties [18], [19], [21], [22]. One of the chemical properties that are substantial to determine the suitability for human consumption is heavy metals concentration. Concentration of heavy metals in water bodies are varies depends on natural hydro-geochemical reaction [23] and anthropogenic activity [24]. Certain heavy

metals exist naturally in the forms of minerals from rocks and soils, which also can be leaching into the water via dissolution and soil weathering process [25]. Manganese as example, is the twelfth most abundant element in Earth [26] and a common element in groundwater as a result of manganese solubilization from nature and numerous biological, chemical, and physical processes including redox transformation, sorption, mineral precipitation/dissolution, and transport [23], [25]. Manganese has been recognized as one of the aesthetic value (colour and odour) reducing substances. The World Health Organization in Guideline for drinking water quality stated the manganese concentration higher than 0.1 mg/L will give distinctive taste to the drinking water and affects laundry by leaving stains [27]. The presence of manganese will develop layer of deposits in distribution system as well. There are numerous studies have proved that high consumption of manganese can develop Mn-induced Parkinsonism or manganism [26], reduce IQ level in kids [28] and increases infant mortality rate [29].

There are variety methods ranging from physical, chemical and biological treatment to remove manganese from water. Most extensively used method to remove manganese is by oxidation of manganese from Mn(II) to Mn(IV) followed by physical filtration as Mn(IV) is insoluble in water. However the kinetic of oxidation by oxygen (O_2) is quite slow compared to hydraulic retention times typically encountered in drinking water treatment systems when pH is less than 9 [30] thus stronger oxidation are required which normally produced toxic byproduct [23]. Membrane filtration also possesses good performance on manganese removal. However membrane filtration requires relatively high pH which accelerates fouling of the membrane which is not economical [23].

Contrarily, adsorption in general is a reliable choice due to its efficiency and economic properties[31]. Adsorbents such as granular iron oxide [32], limestone [33], modified sand [34], clays [35], green waste [36] and zeolite [37] were extensively studied where clays has been selected to be a treatment option for many heavy metal removal cases due its high porosity, high surface area and ion exchange capacity. Clay group such as kaolinite has been broadly used in study as in natural or modified forms [38]. In this study, the perfomace of thermally modified (calcination) kaolin namely metakaolin to remove manganese is evaluated.

The objectives of this study are is (i) to determine the purging duration for tubewell located in Universiti Sains Malaysia Engineering Campus (USM), (ii) characterization of groundwater with correlations of water quality parameters and (iii) investigate the ability of metakaolin to remove manganese in groundwater using dosage and contact time as factors.

2. MATERIALS AND METHODS

The groundwater samples were obtained from a tubewell located in USM (5°08'50.5"N, 100° 29' 34.7"E). The tubewell is 37 m deep, 28.5 cm in diameter and the water table is 1.9 m deep. Submersible pump was used for sampling purpose. Stagnant water was first removed by pumping out the water until respective parameters are stabilized [39], [40]. Data for purging determination duration were monitored using YSI Pro Plus Multi-parameter (Professional Plus, USA).

YSI Pro Plus Multi-parameter (Professional Plus, USA) were used for in-situ parameters (pH, conductivity, dissolved oxygen, total dissolved solids), heavy metals concentrations were measured by ICP-OES (Varian 715-ES) and UV_{254} was measured by UV spectrophotometer (Genesys UV-Vis 10s). HACH DR2800 spectrophotometer was used to obtain the parameter of total suspended solid and colour while HACH turbiditymeter were used to measure turbidity. Prior to heavy metal concentrations and UV_{254} measurement, samples were filtered through a 0.45 μm membrane filter (Pall GN-6 Metricel 47mm) to ensure only dissolved portion of contaminant is present. Correlation of Mn concentration with other water quality parameter was performed using Minitab 17.1.0.

Metakaolin is an anhydrous form of kaolin after heat treatment process known as calcination. Metakaolin used in this study was purchased from Kaolin (Malaysia) Sdn. Bhd with code (KM5CL) and was calcined at 1025°C in Tapah Perak, until the loss of ignition value is less than 0.03%. Metakaolin was stored in airtight container to minimize moisture absorption. Physical properties and chemical composition are stated, are shown in Table 1 and Table 2.

Table 1. Chemical composition of metakaolin

Content	Value (%)
Aluminium (Al_2O_3)	43.0 – 49.0
Silica (SiO_2)	49.0 – 55.0
Iron (Fe_2O_3)	<0.6

Table 2. Physical properties of metakaolin

Parameters	Value
Moisture Content (%)	< 1.0
325 Mesh Residue (%)	< 0.05
Average Particle Size (μm)	0.5 – 2.0

The determination of purging duration was conducted in triplicate at different date. Submersible pump was used to pump the water out from the tubewell. All measurements during purging were performed using YSI Pro Plus Multi-parameter (Professional Plus, USA). Three parameters were selected to determine

the purging adequacy which are pH, conductivity and dissolved oxygen (DO) based on previous study [40], [41]. Turbidity was not included in thre purging adequacy determination due to its unstable nature and can be easily affected by the precipitation of metal oxides. Temperature also not included due to heat effect from the submersible pump [14], [40].

Batch studies were performed with 2 parameters variations which are dosage and contact time. All apparatus used in each batch study were previously soaked with 5% HNO_3 and rinsed 3 times using ultrapure water. Eleven (11) batches with dosage variations from 0.0 g to 20 g with 2 g interval were executed and eighteen (18) variations of contact time were studied from 4 minutes to 12 hours. Samples were filtered using 0.45µm membrane (Pall GN-6 Metricel 47mm) with a vacuum filtration system and acidified prior to ICP-OES measurement. All the tests were carried out on the at the same day of sampling. Agitation was set at 120 rpm for all experiments. All batch studies were performed triplicate with 100 ml of groundwater samples.

3. RESULTS AND DISCUSSIONS

PH reading fluctuated slightly with a maximum range was 0.46 standard unit. Initial pH value ranging from 7.5 to 7.45 and decrease slowly. The duration was between minute 50 and minute 55, shows pH drop drastically by maximum 0.2 pH standard unit for all purging test. Each purging test stabilized after 120 minutes of purging was taken as benchmark for all subsequent sampling. The pH value shows that the groundwater condition is circumneutral and this result is close to findings by researcher [42] with the range of pH only 0.5 standard unit.

Conductivity started to become stabilized in first 40 minutes for all purging test with initial values 9651 µS/cm (purging test 1), 9262 µS/cm (purging test 2) and 8941 µS/cm (purging test 3)(as shown in Figure 1). Similar to pH, at purging duration 50 to 55, the reading increases drastically with maximum reading of 13123 µS/cm (purging test 1). This phenomena can be described as a result of mix water skin formation that is caused by natural vertical flow, diffusion and dispersion. This condition induced temporal condition trends where concentrations adjacent to the upper part of the screen would be lower than in the surrounding aquifer. The concentrations adjacent to the lower part of the screen would be higher than in the aquifer [43]. At 120 minutes, the conductivity reading became steady with less 5% change throughout the purging process. Conductivity value stabilization is the most important factor in determining purging adequacy duration [15].
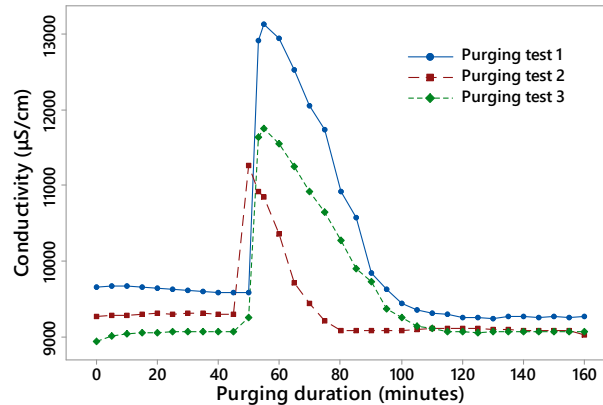
Fig. 1. Conductivity variation during purging process

Dissolved oxygen (DO) decreased drastically after purging started and stabilized after 40 minutes at very low concentration suggests the groundwater anoxic environment. In anoxic and reductive condition, heavy metals including manganese exist in soluble speciation hence the elevated concentration of manganese is expected [44]. Initial values of DO are 1.61 mg/L (purging test 1), 3.63 mg/L (purging test 2) and 1.02 mg/L (purging test 3). Higher concentration of initial DO was expected due to diffusion of oxygen from the atmosphere and the DO value gradually decrease with the increment of the depth of the well.
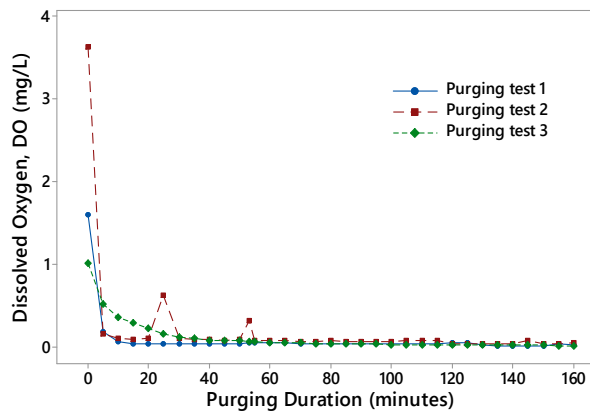

Fig. 2. Conductivity variation during purging process

Each purging test was executed continuously for at least 160 minutes and no significant change was observed. Similar drastic DO declination during purging in the first 100 minutes was also observed in other study [14]. DO concentration

decreases slowly then plateaus where stagnant water with high DO discarded leaving a mixture of stagnant water with low DO and aquifer water in the well. Depletion of DO in water bodies gives information that there are microorganism activities and organic matter degradation occurring in the water bodies or while recharge seeping through to the aquifer [45]. Based on the data plotted in Fig. 1 and Fig. 2 it is clear that all parameters stabilized at 120 minutes which can be concluded as suitable purging duration for subsequent sampling.

Total 53 (n=53) samples were collected and summarized in Table 3. The result shows elevated concentration of heavy metals such as iron, manganese and nickel. The groundwater pH is within circumneutral range between 6.8 to 7.1. Low DO value also contributed to the high value of heavy metals concentration in the groundwater Conductivity and TDS shows that the groundwater is classified as brackish water which is not suitable for drinking [46]. Natural organic matter content was measured as dissolved organic matter (DOC) and UV_{254}. It shows that high content of organic matter may increase the solubility of certain metals in water via NOM-metal complexation.

Table 3. Groundwater quality

Sample characteristic	Value
pH	6.8 – 7.1
Dissolved Oxygen, DO (mg/L)	0.04 – 0.68
Conductivity (μS/cm)	7854 – 11972
TDS (g/L)	5.69 – 7.30
Iron, Fe (ppb)	87.94 – 5389.45
Nickel, Ni (ppb)	128.81 – 227.39
UV_{254} (cm^{-1})	1.006 – 1.412
TOC (mg/L)	44.01 - 55.1

Fig. 3 shows the concentration of manganese for each sampling. National water quality standard sets acceptable value for manganese in raw water and drinking water are less than 200 ppb and 100 ppb respectively. The results shows that all 53 samples are exceeding both permissible limit for raw water and drinking water quality. Average concentration of manganese in sample is 444.0 ppb and ranged from 290.2 ppb to 760.2 ppb where the mean data is one fold higher compare to raw water maximum value (200 μg/L) and 4 fold higher that drinking water acceptable value (100 μg/L). The occurrence of elevated concentration of manganese in groundwater is common as reported by several researchers [17], [47], [48].

The elevation in manganese concentration resulted from anoxic environment is common in groundwater. Circumneutral pH helps to keep manganese in their reduced and soluble form and the solubility of manganese can be increased by high concentration of NOM in form of manganese-NOM complexation [30], [44].

Manganese can be introduced to water bodies naturally via bedrocks and soils weathering; and from anthropogenic sourced such as mining and agricultural activities, glass and paint industries as well as metal galvanization effluents [25], [37], [49].
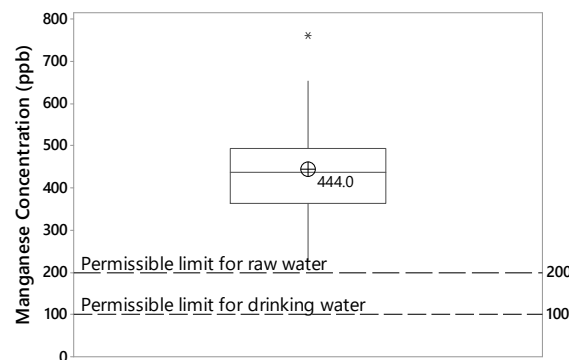

Fig. 3. Manganese concentration in groundwater (n=53)

Prior to correlation study, a normality test was performed for all parameter to comprehend the tabulation type of parameters. Both correlation and normality test were performed using Minitab 17.1.0. Normality test were performed using Anderson-Darling test to finalize which correlation to be used throughout this study. Based on the result obtained, manganese tabulation did not follow normal distribution thus Spearman's rank correlation is selected [50], [51]. In Spearman's approach, there are 5 ranks of correlation's association including very weak (0.00 – 0.19), weak (0.20 – 0.39), moderate (0.40 – 0.59), strong (0.60 – 0.79) and very strong (0.80 – 1.0) [52]. The correlation results for manganese are summarized in Table 4 and the correlations are significant at P-value of < 0.05.

Table 4. Correlation coefficient value for manganese and other groundwater quality parameter

Parameter	pH	DO	Conductivity	TDS	Iron	Nickel	UV_{254}
r_s	0.488	-0.532	0.690	0.649	0.661	-0.110	-0.095
P-value	0.091	0.000	0.000	0.000	0.000	0.477	0.538

Based on the result, manganese develops a significant correlation with DO, iron, conductivity and TDS value. Manganese concentration has a moderate negative correlation with dissolved oxygen value which explains that the decreasing value of dissolved oxygen could intensify the dissolved manganese in the groundwater. The positive strong correlation between iron and manganese ($r_s = 0.661$) indicates that the dissolution of both metals from the minerals as the natural condition of the groundwater exhibits reductive behaviour as the dissolved oxygen data is low

[18]. It is also suggested that a strong correlation between heavy metal contaminant is due a common source of the pollutant [53]. Conductivity and dissolved solids also had strong positive relationship with manganese with r_s value of 0.690 and 0.649 respectively. These results depict that manganese plays a major contribution in dissolved solid. Insignificant correlation coefficient value between manganese and pH was caused by small pH value distribution throughout sampling process. Insignificant values of manganese and nickel indicate that those contaminant are originated from different sources.

Fig. 4 shows the manganese removal efficiency using metakaolin. At 14 g, the performance of metakaolin is optimal which average removal rate of 30.2%. At optimum dosage, the equilibrium was achieved. This is due to overlapping or aggregation of adsorption sites [54]. Previous study by other researcher [42] using limestone as adsorbent managed to remove 70% of manganese. Low removal rate was due to adsorption site competition between manganese and other contaminant in the sample. It is proven that the sample also contains high concentrations of iron, nickel and natural organic matters (NOM) as in TOC and UV_{254} as stated in table 3. A number of studies [35], [55] also proved that competitive adsorption occurred in a sample that contains more than one type of heavy metal and other contaminant. Moreover, the existence of iron in significant amount in this particular groundwater affected the manganese removal efficiency. Theoretically, iron is more readily adsorbed compare to manganese due to smaller atomic weight [56], higher electronegativity value [57], smaller hydrated radius [58] and smaller ionic radius [59].
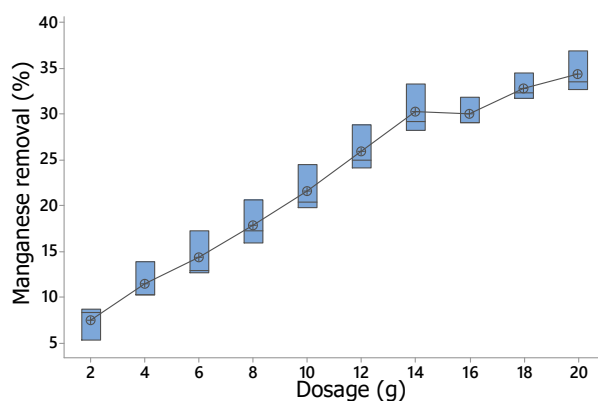

Fig. 4. Manganese removal (%) at various metakaolin dosage

Fig. 5 shows the removal percentages at different contact time. Optimum contact time based on the fig. 5 is at 120 minutes with average 33.2% removal. After 120 minutes the removal efficiency plateaus as the adsorption and desorption rate has

reached equilibrium state or the saturation of adsorption site occurred [36]. The slow rate of adsorption after 120 min could be due to agglemoration of heavy metals ion moleculs into metakaolin active sites and inteference of high concentration of electrolyte in waters [54, 57]. Therefore, in order to further understand the removal of manganese through adsorption-disorption process, synthetics manganese water is required.
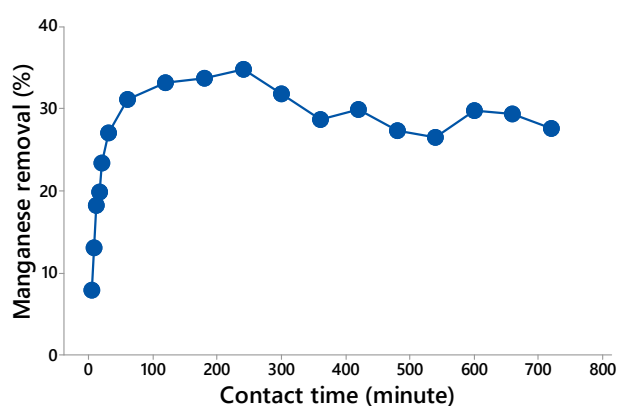

Fig. 5. Manganese removal (%) at various contact time

4. CONCLUSIONS

Groundwater purging duration is depending on the hydraulic conductivity which varies depending on the site of interest. In this study, 120 minutes of purging was assess to be adequate for chemical and physical characteristic of the groundwater. However, for study area such as microorganism, the purging duration might need to be revisited.

The groundwater sampled is not potable due to contaminants that possess organoleptic characteristic (iron, manganese, NOM) reduced the aesthetic value of the groundwater. High value of heavy metal concentrations directly affects the conductivity and TDS values. Furthermore, manganese content is higher than that of permissible limit for drinking and raw water. Long exposure with elevated concentration of manganese in drinking water can directly affected the consumer health.

Results show that metakaolin possess capability to immobilize manganese. An average of 30.2% of manganese from groundwater samples was removed at 14 g of metakaolin while optimum contact time was 120 minutes with 33.2% manganese removal. Adsorbate properties play a major factor in the adsorption

selectivity in a system with multiple contaminant, competitive adsorption significantly reduce the manganese removal efficiency.

Further study to improve metakaolin's performance such as geopolymerization need to be carried out. More actual waters should be studied using metakaolin to compare the performance between different samples such as surface water and samples from different wells.

5. ACKNOWLEDGEMENTS

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