

## POTENTIAL OF HIGH QUALITY LIMESTONE AS ADSORBENT FOR IRON AND MANGANESE REMOVAL IN GROUNDWATER

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### Abstract

Adsorption using low cost of media plays more attention to this current research. Previous literature found that high quality of limestone was effective in removing heavy metals in water and wastewater. In this study, the potential use of limestone media was investigated. Groundwater sample and limestone properties were characterized to determine the physical and chemical composition. The batch experiments were conducted to determine the effect of varied dosage and contact time. Analysis on isotherm and kinetic was carried out in this study. Batch study results showed that the maximum removal of both Fe and Mn was greater than 95 and 80% respectively which occurs at optimum dosage of 40g. Moreover, the optimum contact time of Fe and Mn was 90 and 120 minutes, respectively. At the optimum contact time, 96.8% of Fe and 87.4 % of Mn was removed using limestone adsorbent media. In isotherm study, the result revealed that Langmuir isotherm fitted the experimental data better than Freundlich isotherm for both Fe and Mn adsorption. In Langmuir isotherm, the maximum adsorption capacity for both Fe and Mn were 0.018mg/g and 0.011mg/g. Based on kinetic study, the removal of Fe and Mn followed the pseudo-second order kinetic model which  $R^2 (>0.99)$  greater than in pseudo-first order. This indicates that the chemisorption is the mechanism of adsorption, which contributed to the Fe and Mn removal from the groundwater sample. Thus, from these results, limestone could be used as an alternative for the removal of Fe and Mn from groundwater.

Keywords: Adsorption isotherm; limestone; chemisorption; Langmuir; Freundlich

### Abstrak

Penjerapan menggunakan bahan penjerap yang murah memainkan peranan penting dalam penyelidikan masa kini. Kajian sebelum ini menemukan batu kapur yang berkualiti tinggi sangat efektif untuk menyingkirkan logam berat dari air dan air sisa. Potensi menggunakan batu kapur dikaji dalam penyelidikan ini. Sampel air bumi dan ciri-ciri batu kapur dikaji untuk mengukur komposisi fizik dan kimianya. Ujikaji kelompok dijalankan untuk mengkaji kesan pelbagai dos dan masa aruhan. Analisis isoterma dan kinetik juga dilakukan dalam kajian ini. Keputusan ujikaji kelompok mendapati penyingkiran maksimum untuk ferum dan mangan adalah masing-masing melebihi 95% dan 80% dan berlaku pada 40g dose optimum. Masa optimum untuk penyingkiran ferum dan mangan adalah masing-masing 90 dan 120 minit. Pada masa optimum, 96.8% ferum dan 87.4% mangan telah disingkirkan melalui media batu kapur. Keputusan isoterma membuktikan isoterma Langmuir lebih berpadanan dengan data ujikaji daripada isoterma Freundlich. Dalam isoterma Langmuir, maksimum kapasiti penjerapan untuk kedua-dua ferum dan mangan adalah 0.018mg/g dan 0.011 mg/g. Keputusan kinetik pula menunjukkan penyingkiran ferum dan manganese bersepadanan dengan persamaan pseudo tertib kedua di mana nilai  $R^2 (>0.99)$  lebih besar dari persamaan pseudo tertib pertama. Ini membuktikan mekanisma penjerapan terhadap penyingkiran ferum dan manganese dari sampel air bumi adalah secara penjerapan kimia. Oleh itu, batu kapur boleh digunakan sebagai satu alternatif untuk penyingkiran ferum dan mangan dari air bumi.

Keywords: Isoterma penjerapan; batu kapur; penjerapan kimia; Langmuir; Freundlich

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## 1.0 INTRODUCTION

Iron (Fe) and Manganese (Mn) are heavy metals element found in the earth. Both Fe and Mn concentrations are normally higher in groundwater than in surface water due to the favorable redox condition prevailing in many aquifers [1] and also dissolution of iron bearing rocks and minerals, mainly oxides (hematite, magnetite, and limonite), sulphides, carbonates and silicates under anaerobic conditions [2]. However, their presence makes the water becomes brown-reddish color and indirectly causing the staining of plumbing fixtures and laundry problems. Thus, treatment of Fe and Mn is necessary to remove both Fe and Mn from groundwater.

Adsorption is a physico-chemical method that was very effective in treating heavy metals from water. There are many types of adsorbent used in treating heavy metal contaminated groundwater such as activated carbon [3:4], calcium carbonate based material, iron oxide minerals [5] and others. Natural geo-mineral including siderite [6], magnetite, hematite, goethite and laterite [7] and ferruginous manganese ore [8] are found to be very effective in heavy metal groundwater treatment. Based on previous works, limestone has the potential in removing more than 90% of heavy metals from water and wastewater [9, 10, 11, 12]. According to [13], the usage of limestone as reactive barrier is revealed as a potentially effective and inexpensive groundwater treatment method for iron removal. However, no study has been reported by proposing limestone as an adsorbent media in treating heavy metals in groundwater. Therefore, the application of limestone as a low cost media was proposed in this study.

In this research, batch adsorption experiments were conducted for various dosage (30, 35, 40, 45, 50 g of limestone media in 200mL of groundwater sample) and contact time (15, 30, 45, 60, 75, 90, 105, 120, 135 minutes). Adsorption isotherm and kinetic studies were enhanced using batch experimental results. The adsorption isotherm study was analysed to describe the adsorption isotherm and determine the adsorption capacity [14]. The sorption capacity was analysed using Langmuir and Freundlich model [15]. Furthermore, kinetic study was modelled using pseudo-first order and pseudo-second order to determine the adsorption rate and mechanism of limestone adsorbent onto metals.

This paper presents the potential use of limestone as a low cost adsorbent in treating heavy metal ions such as Fe and Mn from groundwater. The main objective of the present work is to establish the kinetic of heavy metals removal from groundwater using limestone adsorbent media. Thus, based on these results, limestone could be used as an alternative for the removal of heavy metals from groundwater.

## 2.0 METHODOLOGY

### 2.1 Characteristic of Groundwater Sampling

Groundwater sample was taken from USM borehole located near to School of Civil Engineering, USM Engineering Campus, Nibong Tebal Penang (5° 08' 50.5"N, 100° 29' 34.7"E). The characteristics of the groundwater sample were monitored for six months. For the analysis, Fe and Mn were measured using atomic adsorption spectrophotometer (AAS).

### 2.2 Properties of Limestone Media

Limestone was taken from marble industry located in Ipoh, Perak. It was rinsed several times using ultra-pure water (UPW) to remove dirt and dust. Then, the limestone was dried in oven at 105°C overnight. After that, it was sieved and ground in a powder form (size <0.75µm) to determine surface area using N<sub>2</sub> adsorption-desorption isotherm technique. The chemical composition of limestone media was also determined using X-Ray Fluorescence (XRF).

### 2.3 Adsorption Experiment

#### 2.3.1 Effect of Varied Dosage

Batch adsorption experiments were conducted to determine the effect of varied dosage ranging from 30 to 50g of limestone media in 200mL of groundwater sample. In this experiment, various dosage were put into conical flask and shaken using orbital shaker (shaking speed = 350 rpm, contact time = 180 minutes and settling time 90 minutes). After 90 minutes of settling time, 10mL of samples were drawn from supernatant for heavy metal analysis using Atomic Adsorption Spectrophotometer (AAS).

#### 2.3.2 Effect of Varied Contact Time

A series of batch adsorption experiment was conducted by shaking 40g limestone media in 200mL of groundwater sample (optimum dosage) in each 250mL of conical flasks. The aim of this experiment is to determine the optimum contact time required for maximum removal of Fe and Mn. The effect of various contact times (15, 30, 45, 60, 75, 90, 105, 120, 135 minutes) was studied. The samples were run in triplicates to obtain consistent results. The flasks were agitated at 350 rpm for 1 hour. After shaking process, the samples were allowed to settle for 90 minutes and thus were analysed using AAS.

The percentage removal, *R* (%) and adsorption capacity, *q<sub>e</sub>* (mg/g) of heavy metals can be expressed in the following equation.

$$R(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e)}{m} \times V \quad (2)$$

Where,  $C_0$  and  $C_e$ (mg/L) represent heavy metals concentration at initial and equilibrium,  $m$  is the mass of limestone adsorbent (g) and  $V$  is the volume of the groundwater sample (L).

For isotherm study, analysis was done using Langmuir and Freundlich isotherm model. Moreover, the kinetic study using pseudo- first order and pseudo-second order kinetics were modelled in this study. These two models describe the mechanism of the adsorption of heavy metals in groundwater sample [16].

**Table 1** Characteristic of groundwater sample at USM borehole

TEST PARAMETER	UNIT	USM BOREHOLE			STANDARD	
		MIN	MAX	AVE	RAW WATER	DRINKING WATER
<b>HEAVY METAL</b>						
IRON as FE	mg/L	0.13	10.65	2.27	1	0.3
MANGANESE as Mn	mg/L	0.42	1.04	0.7	0.2	0.1

\*Data for 6 months

### 3.2 Characterization of Limestone Media

$N_2$  adsorption-desorption analysis was used to determine the physical properties of surface area and porosity measurement of adsorbent media. The result shows that the multi-point BET surface area ( $S_{BET}$ ) was  $11.12m^2.g^{-1}$ . Using pore size distribution (BJH) method, the average pore diameter ( $D_p$ ) and total pore volume ( $V_t$ ) was  $3.688nm$  and  $0.01631cm^3.g^{-1}$ , respectively.

Table 2 shows the result of minerals and chemical composition of limestone media X-Ray Fluorescence analysis. The limestone used in this study contained 97.93% of  $CaCO_3$  and 0.87% of  $MgO$ . This indicated that the pure limestone (>97% of  $CaCO_3$ ) was used in this research work. The high concentration of  $CaCO_3$  influenced the removal of Fe and Mn in groundwater sample. The solubility of  $CaCO_3$  material might increase the adsorption capacity of Fe and Mn through the precipitation process.

**Table 2** Minerals and chemical composition of limestone media

oxide	Wt %	oxide	Wt. %
MgO	0.87	MnO	0.03
Al <sub>2</sub> O <sub>3</sub>	0.16	Fe <sub>2</sub> O <sub>3</sub>	0.05
SiO <sub>2</sub>	0.86	NiO	0.01
P <sub>2</sub> O <sub>5</sub>	0.02	CuO	0.01
SO <sub>3</sub>	0.01	SrO	0.04
K <sub>2</sub> O	0.03	CO <sub>2</sub>	41.57
CaO	56.36		

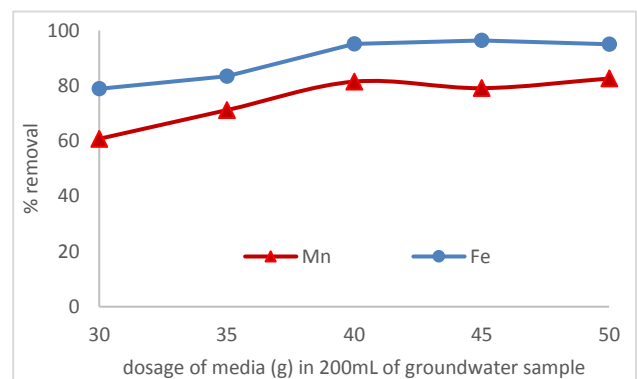
## 3.0 RESULTS AND DISCUSSION

### 3.1 Groundwater Characterization

Table 1 shows the characteristic of groundwater sampling taken from USM borehole for 6 months. From the data, it was found that the concentration of Fe and Mn in USM borehole were in the range of 0.13 - 10.65 mg/L and 0.42-1.04 mg/L respectively. The average of both Fe and Mn exceeded the acceptable limit of raw and drinking water standard.

### 3.3 Effect of Varied Dosage

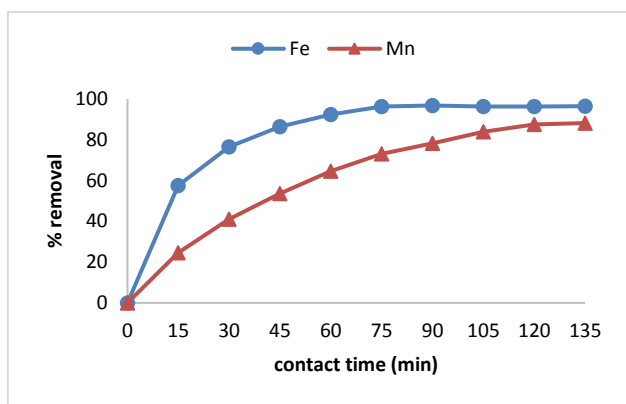
The removal of Fe and Mn increased parallel to the dosage of limestone media in groundwater samples. Figure 1 shows the plot of percentage removal of both metals versus varied dosage of limestone media. The removal of both metals increased when the dosage of media increased. The optimum removal of both metals was at 40g in 200mL of groundwater sample. The maximum percentage removal of Fe and Mn was 95% and 82%, respectively. After 40g of limestone dosage, the rate of sorption is equal to the rate of desorption and the equilibrium was achieved.



**Figure 1** Effect of dosage on the percentage removal of heavy metals

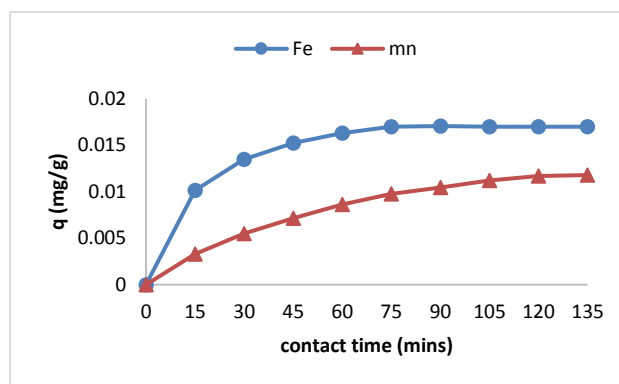
### 3.4 Effect of Contact Time

Figure 2 shows the effect of contact time on the removal of heavy metals using optimal dosage of 40g limestone in 200mL groundwater sample. The removal of Fe increased 57% at first 15 minutes. A rapid increment of Fe removal at first 15 minutes occurred due to the increase of driving force in groundwater solution that might increase the number of available active sites on the surface of limestone media. Moreover, it can be observed that the highest removal of Fe was 96.8% at an optimum contact time of 90 minutes. At 60 minutes of contact time, the removal of Fe was greater than 90% and achieved equilibrium after 90 minutes of contact time.



**Figure 2** Effect of contact time on the percentage removal of heavy metals

For Mn, the percentage of removal was gradually increased until the optimum contact time of 120 minutes. At the optimum contact time, 87.4 % of Mn was removed using limestone adsorbent media. Figure 3 shows the plot of adsorption capacity versus variation of contact time. From the plot, it could be observed that the adsorption capacity of Fe was drastically increased at initial stage and slowed after 60 minutes. Adsorption stopped and reached equilibrium after 90 minutes. The adsorption capacity at equilibrium of both Fe and Mn could reach until 0.017mg/g and 0.012mg/g, respectively. For Mn, the adsorption capacity increased gradually with contact time until achieved the equilibrium after 120 minutes.



**Figure 3** Effect of contact time on the adsorption capacity of heavy metals

### 3.5 Adsorption Isotherm

Adsorption isotherm can be analysed using Langmuir and Freundlich isotherm model. Langmuir isotherm refers to monolayer adsorption while Freundlich isotherm refers to multilayer adsorption [17]. The linear form of Langmuir and Freundlich equations are given in the equation (3) and (5).

Langmuir equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (3)$$

Where  $Q_0$  (mg/g) and  $b$  (L/mg) represents Langmuir constant related to adsorption capacity and energy of sorption.

The Langmuir isotherm characteristic can be expressed by equilibrium parameter,  $R_L$ .

$$R_L = \frac{1}{1 + bC_0} \quad (4)$$

The  $R_L$  shows that the isotherm is favorable ( $R_L < 1$ ), unfavorable ( $R_L > 1$ ) and linear ( $R_L = 1$ ).

Freundlich equation:

$$\log q_e = \frac{1}{n} \log C_e + \log K_f \quad (5)$$

Where  $K_f$  (mg/g)(L/mg) $^{1/n}$  is Freundlich constant and  $1/n$  is heterogeneity factor,  $q_e$  is the adsorption capacity at equilibrium (mg/g).

Table 3 shows the summary of isotherm results of both Langmuir and Freundlich models. The value of  $R^2$  for Fe and Mn removal using Langmuir model was 0.923 and 0.984, respectively. In Freundlich model, the value of  $R^2$  for Fe and Mn was 0.753 and 0.501. The results indicated that the value of  $R^2$  for both Fe and Mn followed the sequent: Langmuir > Freundlich. Thus, the monolayer Langmuir isotherm fitted the experimental data rather than Freundlich isotherm. In

Langmuir isotherm, the maximum monolayer adsorption capacity of Fe and Mn were 0.018 mg/g and 0.011 mg/g, while in Freundlich model, adsorption capacity were 0.029 mg/g and 0.010 mg/g. In Langmuir isotherm, the force of attraction between limestone adsorbent and heavy metal ions is very strong and chemically bonded (chemisorption) [4]. Moreover, Langmuir isotherm is favourable for Fe and Mn adsorption due to  $R_L$  value for both Fe and Mn adsorption is less than 1.

In Freundlich model, the value of intensity parameter,  $1/n$  for both Fe and Mn were in the range of 0.15- 0.22 (<1). This means that the adsorption in normal Freundlich and favourable.

**Table 3** Summary of isotherm results of both Langmuir and Freundlich models

Metal		Fe	Mn
Langmuir	$R^2$	0.923	0.984
	$Q_0$ (mg/g)	0.018	0.011
	$b$ (L/mg)	140.307	11.178
	Freundlich		
Freundlich	$R^2$	0.753	0.5011
	$K_f$	0.029	0.0104
	$1/n$	0.216	0.148

$K_f$  is the Freundlich constant related to the sorption intensity of the sorbent. The high value of  $K_f$ , the greater adsorption capacity of Fe and Mn. Based on Table 3, the value of  $K_f$  for Fe and Mn adsorption was in the range of 0.01 – 0.03.

### 3.6 Kinetic Study

Kinetic study can be modelled to determine the adsorption rate and mechanism on limestone adsorbent onto metals. Pseudo-first order and pseudo-second order kinetic are two kinetic models that commonly used in kinetic study. The equation for both models can be expressed as:

$$\log(q_e - q_t) = \log q_e - \frac{tk_1}{2.303} \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

Where  $q_e$  and  $q_t$  represent the amounts of heavy metals adsorbed (mg/g) at equilibrium and any time  $t$  (min).  $k_1$  is the rate constant adsorption and the value can be calculated from the slope of  $\log(q_e - q_t)$  versus  $t$  graph. For pseudo-second order,  $k_2$  is the rate constant adsorption. In this model, linear regression was obtained from the plot of  $t/q_t$  versus  $t$ .  $k_2$  is the rate constant adsorption that can be calculated from the intercept of the plot.

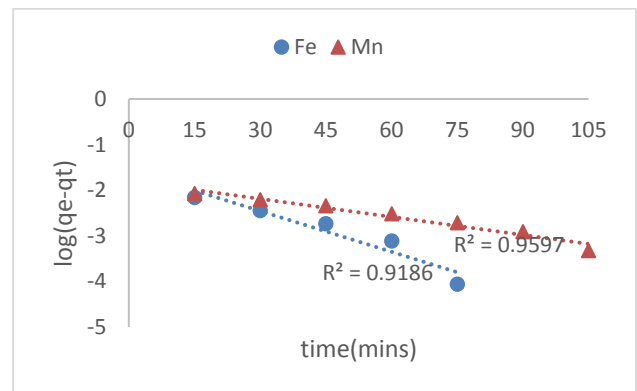
Figure 4 and Figure 5 show the linear plot of  $t/q_t$  versus  $t$ . The results indicated that  $R^2$  for both Fe and Mn were higher in pseudo-second order model rather than in pseudo first order model.  $R^2$  in pseudo-second order model were 0.997 and 0.996 for both Fe and Mn,

respectively. The higher value of  $R^2$  indicates that good applicability of the pseudo second order kinetic for Fe and Mn adsorption using limestone adsorbent [18]. Furthermore,  $q_{e, cal}$  for both Fe and Mn in pseudo-first order kinetic were 0.0275 and 0.0102 while in pseudo-first order kinetic model were 0.0189 and 0.0117mg/g, respectively as shown in Table 4. In the experiments, the values of adsorption capacity,  $q_{e, exp}$  for both Fe and Mn were 0.0171mg/g and 0.0117mg/g, respectively. The results found that the value of  $q_{e, cal}$  for Fe and Mn adsorption was very close to  $q_{e, exp}$  in pseudo-second order kinetic rather than in pseudo-first order kinetic model.

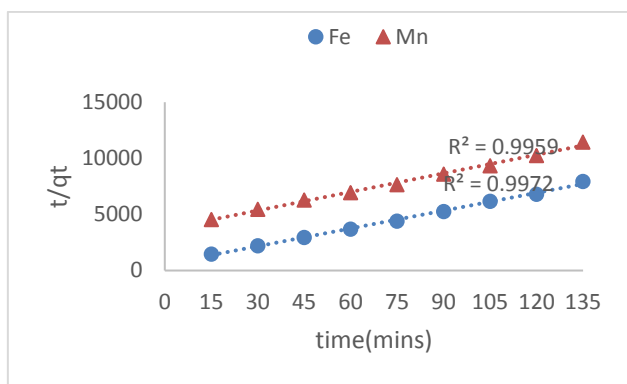
**Table 4** Kinetics model of limestone adsorption

Metal		Fe	Mn
Pseudo 1 <sup>st</sup> order	$q_{exp}$	0.01709	0.0117
	$q_{e, cal}$	0.028	0.010
	$R^2$	0.919	0.959
	$K_1$ (min <sup>-1</sup> )	0.069	0.030
Pseudo 2 <sup>nd</sup> order	$q_{e, cal}$	0.019	0.018
	$R^2$	0.997	0.996
	$K_2$ (min <sup>-1</sup> )	5.913	1.641

Therefore, in this study, it is suggested that the model follows the pseudo-second order kinetic. This shows that the adsorption process involved with chemisorption, which contributed to the Fe and Mn removal in the groundwater sample [19].



**Figure 4** Pseudo-first order kinetic model for heavy metals adsorption onto limestone media



**Figure 5** Pseudo-second order kinetic model for heavy metals adsorption onto limestone media

## 4.0 CONCLUSION

In this study, limestone has the potential in removing Fe and Mn in groundwater. The result showed that 40g of limestone media removed 95% and 82% of Fe and Mn in 200mL of groundwater sample. Moreover, adsorption isotherm study showed that the adsorption of both metals fitted the experimental data of the Langmuir isotherm rather than Freundlich isotherm due to higher  $R^2$  ( $> 0.9$ ) of Langmuir isotherm. In Langmuir model, the maximum adsorption capacity for both Fe and Mn were 0.018 and 0.011mg/g. Furthermore, adsorption kinetics study showed that adsorption of both metals followed the pseudo-second order kinetics model. This indicated that chemisorption was the mechanism of adsorption, which contributed to Fe and Mn removal from groundwater sample. As a result in this study, limestone was found to be very effective and a suitable alternative in removing heavy metals from groundwater due to the low cost of media.

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