

TREATMENT OF ACIDIC RAW WATER USING LIMESTONE

NADIAH BINTI MOKHTAR

A project report submitted in partial fulfillment of the
requirements for the award of the degree of Master of Engineering
(Civil - Wastewater)

Faculty of Civil Engineering
Universiti Teknologi Malaysia

NOVEMBER 2006

*To my beloved abah and mak;
Tuan Haji Mokhtar Omar & Pn Hjh Jasnin Abd Malek,*

ACKNOWLEDGMENT

I would like to express my gratefulness to Allah S.W.T for giving me strength and wisdom in my project work. In preparing this thesis, I was in contact with many people, researchers, academicians and technicians. They all have contributed to my understanding and valuable thoughts during my project.

First and foremost, I wish to express my sincere appreciation to my project supervisor, Dr. Azmi Aris, for encouragement, guidance and critics. His ideas enlighten my curiosity. Without his continued support and interest, this thesis would not have been the same as presented here.

My fellow postgraduate students, Ain and Kam should also be recognized for their support. My sincere appreciation also extends to all SAJ members, En. Aliman and Pn. Fadzlin and not forgotten Environmental Laboratory technicians, Pak Usop, En. Ramli and En. Muzaffar who have provided assistance at various occasions. Their views and tips are useful indeed. Unfortunately, it is not possible to list all of them in this limited space.

ABSTRACT

Sg. River is the only raw water source for Yong Peng 2 and 3 treatment plants which supply treated water for domestic, institutional, commercial and industrial use in Batu Pahat. Between the months of January to May 2005, Sg. Bekok registered a low pH of between 2.89 – 3.06. The acidic water hence, escalated the cost for water treatment in Yong Peng. (Southern Water Corporation Sdn. Bhd., 1999). In several extreme cases, the plants were incapable to supply sufficient water to the consumers in Batu Pahat area. The present study attempts to investigate the viability of limestone in treating acidic raw water with high concentration of iron and manganese. Sample of water was collected from tributary of Parit Ngamarto, Bekok Intake and Semberong Lagoon. A lab-scale study using plug-flow reactor system that consists of four limestone-drains was used to treat the raw water. The pH reading was monitored at inflow, outflow and three intermediate points within limestone reactor while effluent was collected for Fe and Mn analysis. Parit Ngamarto, Bekok Intake and Semberong Lagoon raw water sample was recorded an initial pH of 2.5, 2.89 and 3.12 with acidity of 530 mg/L as CaCO₃, 75 mg/L as CaCO₃ and 51mg/L as CaCO₃, respectively. The pH rise gradually as the water flow through limestone-drain at different flow rates (88 mL/min, 42 mL/min and 21 mL/min). The rate of pH rise varies depending on the acidity of the water. The rise of pH was also affected by the amount of limestone used. As pH increased, Fe and Mn concentration was found to decrease. By using statistical analysis i.e Analysis of Variance (ANOVA), a significant increase in pH could be related to the quantity of the limestone used, acidity and flow rate (contact time).

ABSTRAK

Sungai Bekok merupakan satu-satunya sumber air bagi Loji Rawatan Air Yong Peng 2 dan 3 yang membekalkan air terawat untuk kegunaan domestik, institusi, komersil dan peindustrian di Batu Pahat. Di antara bulan Januari 2004 hingga Mei 2005, Sungai Bekok telah mencatatkan bacaan pH yang rendah di antara 2.89 – 3.06. Keadaan air yang menjadi terlalu berasid ini seterusnya meningkatkan kos rawatan air di Yong Peng (Southern Water Corporation Sdn. Bhd., 1999). Kos meneutralkan air telah meningkat dan penjadualan rawatan menjadi bertambah rumit. Pada kes-kes tertentu, loji tersebut tidak mampu menyediakan air mengikut keperluan penduduk. Kajian ini dijalankan bagi mengkaji keupayaan batu kapur dalam merawat air mentah yang berasid dengan kepekatan unsur Besi dan Mangan yang tinggi. Sampel air diambil dari anak Parit Ngamarto, *Intake* Bekok dan lagun Semberong. Ujikaji makmal menggunakan sistem reaktor yang mengandungi empat parit yang dipenuhi dengan batu kapur digunakan untuk merawat air mentah. Bacaan pH dipantau pada salur masuk, salur keluar dan tiga titik pemantauan di dalam reaktor. Efluen dikumpulkan untuk analisis unsur Fe dan Mn. Air mentah dari anak Parit Ngamarto, *Intake* Bekok dan lagun Semberong di rekodkan dengan pH awal 2.5, 2.89 dan 3.12 dan keasidan 530, 75 dan 51 mg/L CaCO₃. Nilai pH di dapati meningkat secara perlahan-lahan apabila air mengalir melalui reaktor pada kadar alir yang berbeza (88 mL/min, 42 mL/min dan 21 mL/min). Kadar peningkatan pH meningkat secara berbeza bergantung kepada keasidan air. Apabila pH meningkat, kepekatan Fe dan Mn didapati menurun. Dengan menggunakan analisis statistik seperti Analysis of Variance (ANOVA), peningkatan pH dapat dikaitkan dengan kuantiti batu kapur yang digunakan, keasidan dan kadar alir (masa dedahan).

TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
	DECLARATION	ii
	DEDICATION	iii
	ACKNOWLEDGEMENTS	iv
	ABSTRACT	v
	ABSTRAK	vi
	TABLE OF CONTENTS	vii
	LIST OF TABLES	x
	LIST OF FIGURES	xi
	LIST OF SYMBOLS	xii
	LIST OF APPENDICES	xiv
I	INTRODUCTION	1
	1.1 Preamble	1
	1.2 Problem Statement	3
	1.3 Aim of Study	4
	1.4 Objectives of Study	4
	1.5 Scope of Study	5
II	LITERATURE REVIEW	6
	2.1 Water Catchment of Sg. Bekok	7
	2.2 Theoretical background of acidic water development	7

2.2.1	Peat soil	7
2.2.1.1	Characteristic of peat soil	7
2.2.1.2	Oxidation of pyrite	8
2.2.1.3	Biological sulphur retention	9
2.2.2	Organic acid	11
2.2.3	Agricultural activities	12
2.3	Metal leaching	13
2.3.1	Ferum	13
2.3.2	Manganese	14
2.3.3	Aluminum	15
2.4	Limestone treatment	15
2.4.1	Characteristic of limestone	16
2.4.2	Mechanism of pH adjustment	16
2.4.3	Previous study of limestone treatment	18
III	METHODOLOGY	22
3.1	Materials and equipments	22
3.2	Water quality analysis	24
3.2.1	Acidity measurement	24
3.2.2	Iron and Manganese	25
3.3	Experimental procedure	26
3.3.1	Batch-mode test	26
3.3.2	Continuous flow test	27
3.3.3	Aeration test	29
IV	RESULTS AND DISCUSSIONS	31
4.1	Batch-mode study	31
4.2	Continuous flow study	32
4.2.1	pH	33
4.2.1.1	Parit Ngamarito tributary	34
4.2.1.2	Bekok Intake	36

4.2.1.3	Semberong lagoon	36
4.2.2	Comparative analysis	38
4.2.3	Statistical analysis	39
4.2.4	Iron (Fe)	40
4.2.5	Manganese	42
4.3	Aeration	46
V	CONCLUSIONS AND RECOMMENDATIONS	47
5.1	Conclusions	47
5.2	Recommendations	48
	REFERENCES	49
	APPENDICES A - D	53

LIST OF TABLES

TABLE NO.	TITLE	PAGE
2.1	Effect of pH on the present of metal	13
2.2	Previous study on water/wastewater treatment using limestone	22
3.1	Characteristic of water sampling location	23
3.2	Reagent used in metal analysis	24
4.1	Characteristic of the raw water sample	36
4.2	pH reading for Parit Ngamarto's tributary at every sampling point	37 38
4.3	pH reading for Bekok Intake at every sampling point	39
4.4	pH reading for Semberong Lagoon at every sampling point	49
4.5	ANOVA for sample of Parit Ngamarto tributary	43
4.6	ANOVA for sample of Bekok Intake	45
4.7	ANOVA for sample of Semberong Lagoon	48
4.8	ANOVA for acidity	49
4.9	Fe removal at different contact time	49
4.10	Mn removal at different contact time	

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
1.1	Population growth projections 1950-2025 (Data from World Population prospect 1990,UN)	2
2.1	Simplified sulphur cycle in the soil	10
3.1	HACH DR/4000 Spectrophotometer	25
3.2	The set-up of batch mode test	26
3.3	The set-up of limestone-drain reactor	28
3.4	Continuous flow-mode test	28
3.5	Batch-mode treatment test conducted under aeration	30
4.1	Effect of limestone size on neutralizing acidic raw water	32
4.2	Profile of pH increase at different contact time for Parit Ngamarto tributary water sample	35
4.3	Profile of pH increase at different contact time for Bekok Intake water sample	36
4.4	Profile of pH increase at different contact time for Semberong Lagoon water sample	37
4.5	Effect of acidity on pH adjustment	39
4.6	Armoring occur at the last limestone drain	43
4.7	Removal of iron in the water samples at different contact time	44
4.8	Removal of Mn in the water samples at different contact time	45
4.9	Effect of aeration to pH	47

LIST OF SYMBOLS

A	-	Area
Al	-	Aluminum
Al _t	-	Acid-mobilized Aluminum
Al _o	-	Organic bound Aluminum
Al _i	-	Dissolved inorganic Aluminum
ALD	-	Anoxic Limestone drain
AMD	-	Acid Mine Drainage
ANC	-	Acid-neutralizing capacity
APS	-	Alkalinity Producing Systems
Ca ²⁺	-	Calcium ion
CaCO ₃	-	Calcium Carbonate
Cu	-	Cuprum
Cr	-	Chromium
DOC	-	Dissolved organic carbon
Fe	-	Ferum
FeS ₂	-	Pyrite
H ⁺	-	Hydrogen ion
H ₂ O	-	Water
HCO ₃ ⁻	-	Bicarbonate ion
M _s	-	Mass of limestone
Mn	-	Manganese
n	-	Porosity
Ni	-	Nickel
OA	-	Organic acid
OLD	-	Oxic Limestone Drainage
OPC	-	Open Limestone Channel
Pb	-	Lead

Q	-	Volumetric flow rate
S	-	Sample
t_R	-	Contact time
v	-	Velocity
W	-	Weight
Zn	-	Zinc
ρ_b	-	Bulk density

LIST OF APPENDICES

APPENDIX	TITLE	PAGE
A	Experimental form for batch mode test	53
B	Experimental form for aeration test	54
C	Acidity data	55
D	Malaysia National Water Quality Standards (Revised December 2004)	58

CHAPTER I

INTRODUCTION

11 Preamble

The importance of a dependable water supply has been recognized since ancient times. The digging of wells dates back to early Chinese and Egyptian history and aqueducts of the ancient Romans are considered today to be remarkable engineering achievement.

Water is a key component of socio-economic systems. It is the basis for agricultural, essential for many industries and for energy production. Its importance for human health and welfare is critical and thus supply of water for drinking and sanitation is of major concern everywhere.

The world of the late twentieth century is a place subject to many dynamic forces. Change is evidenced everywhere and in many different ways. Global population has expanded remarkably. Figure 1.1 shows the population growth projections between year 1950-2025 for Former USSR, Europe, America, Asia and Africa. As the population expands and as living standards rise, albeit unequally in different parts of the world, so do the demands for increased exploitation of natural resources. Henceforth, water pollution increase as well as water demand rises for fulfilling living necessity.

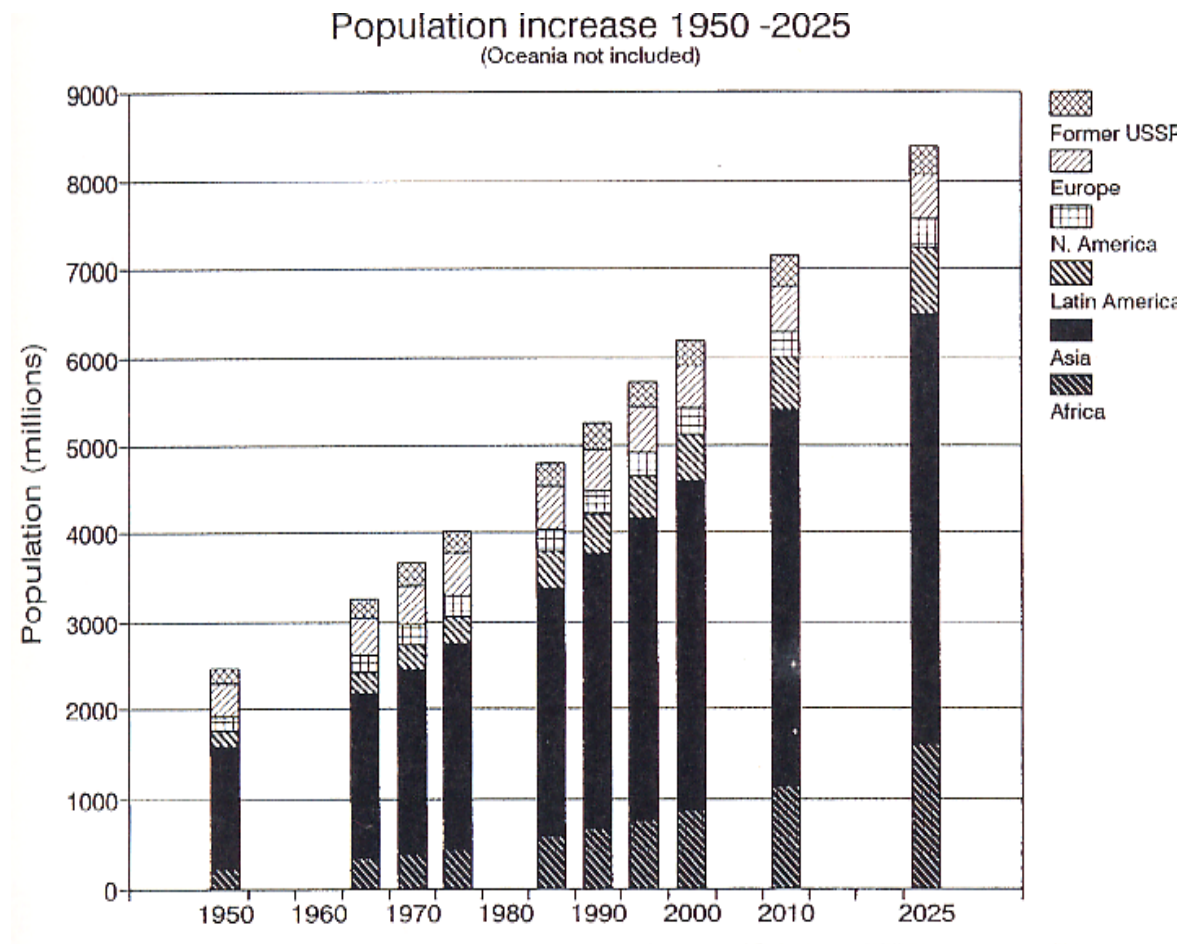


Figure 11 Population growth projections 1950-2025 (Data from World population prospect 1990,UN.)

Between the years of 1900-1995, world population has increased two times meanwhile water demand increased by six times (WHO, 1993). Eventhough the total amount of water has finite limit, the freshwater portion is limited and contaminated by point and nonpoint sources. As this happen, many countries are rapidly reaching condition of water scarcity.

In Malaysia, water demand was expected to be around 3.8 bilion m^3 in 2000 as compared to 0.8 bilion m^3 in 1980 and 3.1 m^3 in 1998 (Malaysia Water Industry Guide 2001). While water is readily abundance in Malaysia, its quality is deteriorates due to human activities and partly, natural phenomena. .

12 Problem statement

Stream water contamination from non-point source is currently an important issue in river system management of agricultural area. The sources of the problem are normally due to the agricultural activities such as use of fertilizer and pesticide which eventually are carried away into the river by surface runoff.

Additionally, the water quality problem can also be attributed to the natural phenomena aggravated further by human activities such as those experienced at Sg. Bekok, Batu Pahat. The Sg. Batu Pahat basin has a total catchment area of 1944 km². It has two main tributaries, namely Sg. Simpang Kiri and Sg. Simpang Kanan. Sg. Simpang Kanan is further subdivided into two main tributaries namely, Sg. Bekok (catchment area 645 km²) and Sg. Semberong (catchment area 273 km²). There are about four water treatment plants operating along Sg. Bekok.

Identified as among the raw water resources to the domestic water supply system in the Batu Pahat area, Sg. Bekok supply raw water directly to two water treatment plants, namely Yong Peng 2 and 3 Treatment Plant. Another two treatment plants, Sri Gading and Semberong Treatment Plant get raw water resources from an artificial lagoon which is also supplied by Sg. Bekok. The lagoon act as a reservoir and also for water quality stabilization before the water is pumped into the treatment plant. The Sg Bekok river basin is covering more than 100 km² area.

Sg. Bekok in recent years is facing severe water quality problem in term of pH. Between the months of January 2004 to May 2005, Sg. Bekok registered a low pH of between pH 2.89 – 3.06. The latest monitoring programme conducted by Institute of Environmental and Water Resources Management (IPASA), between the months of February to May 2006 also confirmed the readings. This has caused operational problems to the water treatment plant that completely depending on the raw water supply from the Sg. Bekok. The acidic water has caused corrosion of plant turbine and pipeline. Burst of pipe line has occasionally been reported resulting in water supply disturbance and shortages. The cost to neutralise the water has also increased and treatment scheduling became more complicated. The high

level of acidity in the water has also resulted in higher metals content (Fe, Al and Mn) concentrations, which exceeded the allowable limit set by the National Standard for Drinking Water Quality.

Others factor to be considered causing pollution problem to Sg Bekok is point and nonpoint sources pollutant created by the land use development adjacent to the river. There are pollution point sources that obviously can be found along the river bank such as palm oil industry, paper mill industry and chicken farm. Besides, pollution non point sources such as sediments, pesticides and agricultural fertilizer and pathogens transported across the land surface by runoff and through the soil by percolating water can also be observed. These activities may also contribute to the presence of heavy metal in river water body.

The common method of neutralizing pH at the treatment plant is through the use of limes slurry. However, as the pH of the water is too low, the use of lime slurry has become too expensive. Use of limestone has been reported to be one of the cheap methods in neutralizing pH (Muslim, 2005). Thus, this study investigates the feasibility of limestone as an in-situ pH treatment.

13 Aim of study

To provide an alternative solution to the acidic water problem of Sg. Bekok, Batu Pahat.

14 Objectives of study

The objectives of the study are:

- i. To determine the effectiveness of in-situ limestone treatment in adjusting the pH and reducing the acidity of the acidic raw water.
- ii. To determine the minimum contact time required for the limestone process.

- iii. To explore the effect of limestone treatment on the removal of iron and manganese.

15 Scope of study

The study consists of a thorough experimental work using a laboratory scale plug flow reactor. The limestone is of about 30 mm diameter and is obtained locally. Actual raw water from Sg. Bekok is used in the experiment. The efficiency of treatment is evaluated based on pH adjustment and removal of iron and manganese.

- i) To study the effect of aeration on the limestone treatment process.
- ii) To explore the feasibility of using ALD and OLD as the in-situ treatment process.
- iii) To enhance the surface area of the limestone.

REFERENCES

- Anderson,D.O. (2005). Labile aluminium chemistry downstream treated lake and an acid tributary: Effects of warm winters and extreme rainstorms. *Science of the Total Environment*.
- APHA (2002). *Standard Method for Examination of Water and Wastewater*. 21st Edition. Washington: American Public health Association.
- Asia Water & Environment Sdn Bhd (2005). *Kerja-kerja Pemulihan Sistem Saliran Kg.Ngamarto dalam Kawasan Tadahan Sg Bekok: Conceptual Integrated River Basin Management Plan*. Johor: Syarikat Air Johor Sdn Bhd.
- Aizah, H.A., Yusoff, M. S., Adlan, M. N. Adnan, N.H. Alias, S. (2004). Physico-chemical removal of iron from semi-aerobic landfill leachate by limestone filter. *Water Management*. 24:353-358.
- Biswas, A. K (1997). *Water resources: environment planning, management and development*. McGraw-Hill.
- Charlotte, A.N. and Paul, L.Y (2000). Zinc removal from hard, circum-neutral mine waters using a novel closed-bed limestone reactor. *Water Resources*. 34(4): 1262-1268.
- Cheremisinoff, P. N. (1993). *Water management & supply: water and wastewater treatment guidebooks*. Englewood Cliffs, N. J. Prentice-Hall.

- Cravotta III, C.A. (2003). Size and performance of anoxic limestone drains to neutralize acidic mine drainage. *Journal of Environmental Quality* 32(4): 1277-1289.
- Cravotta III, C. A. and Trahan, M.K. (1999). Limestone drain to increase pH and remove dissolved metals from acidic mine drainage, *Applied Geochemistry*. 14:581-606.
- Donahue, R. L. (1958). *Soils, an introduction to soils and plant growth*. Prentice-Hall Inc.
- Frank, A.P.C. and McCorquodale, J.A. (1992). *Chemical dynamics in freshwater ecosystems*. Lewis Publisher.
- Hammarstrom, J.M. Sibrell, P.L. and Harvey, B. (2003). Characterization of limestone reacted with acid-mine drainage in a pulsed limestone bed treatment system at the Friendship Hill Historical Site, Pennsylvania, USA. *Applied Geochemistry*. 18:1705-1721.
- Henrikson, L. and Brodin, W. (1995). *Liming of acidified surface water: A Swedish synthesis*. Swedish: Springer.
- Howells, G. and Dalziel, T.R.K. (1992). *Restoring acid waters: Loch Fleet 1984-1990*. London and New York: Elsevier Applied Science
- Kimion, A. Kssim, M. A. Solihin, J. Othman, F. Latif, A.A. and Kim, A. T. (2001). Impact of agricultural drainage on stream water quality, *Jurnal Teknologi*, 31(F): 67-77.
- Kushish, F. G. (1987). *Design practices for covered drains in an agricultural land drainage system, a worldwide survey*. India: International commission on irrigation and drainage India.

- Kelly, M. (1988). *Mining and the freshwater environment*. London & N. Y: Elsevier Applied Science.
- Kein, L. (1959). *River pollution; chemical analysis*. London Butterworths.
- Kenig, A. and Liu, L.H. (2002). Use of limestone for pH control in autotrophic denitrification: continuous flow experiments in pilot-scale packed bed reactors. *Journal of Biotechnology*. 99:161-171.
- Lipp, P., Schmitt, A. and Baldauf, G. (1997). Treatment of soft reservoir water by limestone filtration in combination with ultrafiltration. *Desalination*. 113:285-292
- Norotny, V. and Chesters, G. (1981). *Handbook of nonpoint pollution sources & management*. Van Nostrand Reinhold company.
- North, F. (1930) *Limestones: The origins, distribution, and uses*. Guildford: The Woodbridge Press, Ltd.
- Malaysia Water Industry Guide (2004), *Malaysia National Water Quality Standards (Revised December 2004)*, International Water Association.
- Muslim, R. (2006). *Pelarasan pH air mentah dengan menggunakan batu kapur*. Skudai, Johor: Universiti Teknologi Malaysia.
- Rump, H.H. and Kist, H. (1988). *Laboratory Manual for the Examination of water, Wastewater and soil*. German: Federal Republic of Germany.
- Shih, S.M., Lin, J.P. and Shiau, G.Y. (2000). Dissolution rates of limestones of different sources. *Journal of Hazardous Material*. B79:159-171.
- Steinberg, C.E.W. and Wright, R.F. (1992). *Acidification of freshwater ecosystems implications for future*. London: Wiley Publisher.

- Thibodeaux, L.J. and Aguilar, L. (2005). Kinetics of peat soil dissolved organic carbon release to surface water. Part 2: A chemodynamic process model. *Chemosphere*. 60: 1190-1196.
- Thornton, F. C. (1995). Manganese removal from water using limestone-filled tanks, *Ecological Engineering*. 4:11-18.
- W. van Loon, G. and Duffy, S.J. (2005). *Environmental chemistry a global perspective*. 2nd Edition : Oxford University Press
- Warburton, J. Joseph, H. and Andrew, J. M. (2004). Hydrological Controls of surficial mass movements in peat. *Earth-science*. Reviews 67: 139-156.
- Yung, G. J., Dooge, J.C.I., and John, C.R. (1994). *Global water resources issues*. Cambridge University Press.
- Zemkiewicz, P.F. Skousen, J.G. Brant, D.L. Sterner, P.L. and Lovett, R.J. (1997). Acid mine drainage treatment with armoured limestone in open limestone channels. *Journal of Environmental Quality*. 26(4): 1017-1024.