THE EFFECTIVENESS STUDY OF COCKLE SHELL IN TREATING ACIDIC SURFACE WATER

NURUL AIN BINTI ZAINODIN

A thesis submitted in fulfillment of the requirements for the award of the degree of Bachelor of Civil Engineering

Faculty of Civil Engineering and Earth Resources
University Malaysia Pahang

JUNE 2012

ABSTRACT

Malaysia was reported to produce 13,000 metric ton of cockle shell during Ninth Malaysia Plan (2006-2010). In 2007, Malaysia has a number of 1055 of farmers working on cockle cultivation agriculture with 6000 hectare of cultivation area (Izura, 2008). These figures do not only indicate the vast availability of cockles but also the amount of waste generated. This project was run in attempt to study the potential of cockle shell in ameliorating surface water acidification. A lab-scale study of different sizes and volumes of cockle shell and limestone was used. The values of pH were measured continuously at interval time until the pH remains constant. The effectiveness of cockle shell to increase the pH of acidic water to circum-neutral was then compared to limestone. Thus, it is believed that the cockle shell would be able to replace limestone in liming process. Moreover, the availability of cockle is high and low cost.

ABSTRAK

Malaysia telah menghasilkan 13,000 metrik tan kulit kerang semasa Rancangan Malaysia Ke-9 (2006-2010). Pada 2007, Malaysia mempunyai 1055 pekerja di dalam bidang perusahaan kerang dengan keluasan 6000 hektar (Izura, 2008). Angka ini menunjukkan terdapat banyaknya jumlah sisa kulit kerang dihasilkan. Projek ini dijalankan untuk mengenalpasti potensi kerang sebagai produk rawatn air berasid. Satu kajian makmal dijalankan dengan menggunakan dua saiz dan beberapa berat kulit kerang dan batu kapur yang berbeza Bacaan pH di ambil secara berterusan pada satu tempoh masa sehingga bacaannya tidak berubah atau stabil. Keberkesanan kulit kerang untuk meningkatkan bacaan pH air berasid kepada keadaan neutral dibandingkan dengan keberkesanan batu kapur. Kulit kerang dipercayai mampu menggantikan batu kapur dalam proses peneutralan air. Lebih-lebih lagi kulit kerang mudah diperolehi dan mempunyai kos yang rendah.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

CERRM	-	Centre for Earth Resources Research & Management
INWQS	-	Interim National Water Quality Standard
BS	-	British Standard
$CaCO_3$	-	Calcium Carbonate
Ca^{2+}	-	Calcium
Mg^{3+}	-	Magnesium

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Research Background

In University Malaysia Pahang at Pekan Campus, there are four lakes and in this study, we named all lake as Lake A, Lake B, Lake C and Lake D. The area of each lakes is different which is Lake A has 37.20 acre, Lake B has 44.26 acre, Lake C has 8.11 acre and Lake D 21.16 acre.

In general, the four lakes in UMP require preservation and conservation in order to enable the dynamic natural ecosystems to be maintained. Development project nearby the lakes has contributed the negative impact to the water quality. According to the study done by Centre for Earth Resources Research & Management (CERRM), they had found that one of the lakes is acidic with the pH below 4. Acidic surface water is harmful to plant life, aquatic life and humans.

Recently, UMP management has already allowed the students to use the lakes as a medium for recreational activities such as kayaking. However, according to Interim National Water Quality Standards (INWQS) by the Department of Environmental (DOE) Malaysia, the lakes water quality does not meet the standards of class II B; the water quality standards which is a must for a water regulator to achieve as there is a close contact between human and water body. Due to this problem, this study is initiated. This study is focusing on the ability of cockle shell as a physical treatment in terms of the effectiveness of its sizes and volumes of limestone and shell in increasing the pH to the level of circum-neutral.

1.2 Problem Statement

The problems of lakes at University Malaysia Pahang, may classify as common problems. The water is acidic and according to INQWS the range doesn't meet the standard for recreational purposes and the students supposedly could not use the lakes for water activities. According to the study done by the CERRM (UMP), the current pH of water is less than 4. Based on effluent standards of conventional and other pollutants in protected waters for category II class B, the water are safe for human when the pH in the range of 6.0 to 9.0. But, in this study, we intended to achieve at least pH 5.8 in order to obtain green algae environment which are the predecessors for the start of an ecosystem.

1.3 Objectives of Research

1. To study the effectiveness of cockle shell in treating acidic surface water in terms of sizes and volume.
2. To study the effectiveness of limestone in treating acidic surface water in terms of sizes and volume.
3. To compare the performance of cockle shell and limestone in treating acidic surface water in terms of sizes and volumes.

1.4 Scope and Limitation of the Study

The study comprises of an experimental study of using a laboratory scale in order to evaluate the effectiveness of limestone and shell in treating acidic surface water. The efficiency of limestone and shell had been evaluated in relation to their respective pH adjustment to their sizes and volumes.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

On a global scale, acidification is one of the major issues of freshwater pollution. Acidification of fresh waters has been identified as among of water quality deterioration as a result of multiple intensive land use and management or naturally occurring factors. In large regions of Europe and eastern North America, thousands of lakes, rivers and stream have been damaged through acidification. But only this last decade have the effects on the ecosystem been analyzed.

Acidification of surface waters can result from direct deposition of pollutants into lakes and streams which is through runoff and soil through flow from the surrounding catchment. The acidity of water is typically expressed by the pH or proton activity which an intensity factor that reflects the relative balance between ion hydrogen (H^+) sources and sinks at any given point and space.

2.2 Acidification Effect to Aquatic Life

Biological organisms and the environment in which they live are called an ecosystem. Because of the connections between the fishes, plants, and other organisms living in an aquatic ecosystem, changes in pH or aluminum levels affect the biodiversity. Thus, as lakes and streams become more acidic, the numbers and types of fish and other aquatic plants and animals that live in these waters decrease (U.S Environmental Protection agency, 2008). Most freshwater lakes, streams, and ponds have a neutral pH in the range of 6 to 9 (INWQS). When the pH of water falls below 6 and especially below 5, there had effects on aquatic life.

As the pH approaches 5, non desirable species of plankton and mosses may begin to invade and population of smallmouth bass disappears. But, when the pH is below than 5, fish populations begin to disappear and the bottom is covered with undecayed material, and mosses may dominate near shore areas and if the pH is below 4.5, the water is essentially devoid fish. Aluminum ions (Al^{3+}) that attached to the minerals in soils can be released into lakes where they can kill many fish by stimulating excessive mucus formation. It can also leads the fish to lower body weight and smaller size makes fish less able to compete for food and habitat. The most serious effect of increasing acidity of surface water is interference with the fish reproductive cycle. Calcium level in the female fish may be lowered to the point where she cannot produce eggs or the eggs fail to pass from the ovaries.

2.3 Theoretical Background of Water Acidification

Acidification of freshwater occurs can be caused by many things. It can occur naturally and also caused by other things such as development, agriculture activities, and global climate. The natural acidification usually comes from acidic soil and natural organic acids.

2.3.1 Acidification of Soil

Acidic soils can modify the surface water chemistry and may be responsible for defining a large part of surface water acidity (C.Krug, S.Letohn, 1990). The mechanism by which increased strong acid concentration can acidify surface waters related to an alkalinity depression in the soil which results in a pH reduction in water after the dissolution of carbon dioxide (CO_2) (Frank and McCorquodale, 1992). The natural processes contributing to acidification of soil are introduction of carbonic acid from precipitation, microbiological and root respiration, acidic decaying products like humic acids, coming from vegetation decay, nitrification from natural sources of nitrogen and formation of sulphuric acid during oxidation of iron sulphides.

The acidification of soil generates damaging agents to fresh water quality, the pH of water getting lower, concentration of aluminum ion and heavy metal increases, and the deficiency of base cations (Ca^{2+}, Mg^{2+}, K^{+}) and nutrients (L.Powlowski, 1996). Hydrogen ions generated by natural and anthropogenic biogeochemical processes dissolve aluminums from soils and leach exchangeable cations.

2.3.2 Effects of Organic Acids

Organic acid are important agents of freshwater acidity that must be considered in watershed acidification. Extensive surveys during past decade suggest that a significant fraction, perhaps as much as one-third, of acidic waters in temperate zones are acidic because of organic acids (Hemond, 1992).

The behavior of natural organic acids in the anthropogenic acidification process depends on the concentration of total organic carbon, the activity of natural organic acids, pH based on background acid neutralization capacity and the magnitude of acid deposition (A.Clair, F.Dennis, A.Scraton, Gilliss, 2007). Natural organic acids are also efficient complexes' of metal. Water with the significant of natural organic acids concentration, there is a little aluminums toxity as this metal is complexes with organic acid (Peterson, 1989).

Although complexity and variability hinder precise measurement and characterization, natural organic acids have a substantially strong acidic character and may reduce runoff pH. The extent of this pH reduction in surface waters and organic anion contributions as a function of dissolved organic carbon (DOC) and pH have been recognized. Increased of DOC may reduce the pH below 5.0.

2.3.3 Metal Leaching

Metals are introduced in freshwater or aquatic life systems as a result of the weathering of soil and rocks from volcanic eruptions and variety of human activities that involves metal pollutants. The concentration of trace metal in fresh waters is a result of complex competition between processes of adsorption or precipitation and also formation of soluble complexes.

All heavy metals exist in surface waters in colloidal, particulate, and dissolved phases, although dissolved concentrations are generally low (Kennish, 1992). The colloidal and particulate metal may be found in hydroxides, oxides, silicates, or sulfides or adsorbed to clay, silica, or organic matter. The solubility of trace metals in surface waters is predominately controlled by the water pH, the type and concentration of metal could adsorb, and the oxidation state of the mineral components and the redox environment of the system (Connell et al., 1984). When the pH of water was dropped, the metal particles become more mobile since the metal solubility increases. Aluminium, iron and manganese are usually found in surface water and groundwater. Acidity is also generated from the oxidation of these metals ions which increased the amount of hydrogen ions in water.

Aluminium (Al): $$Al^{3+} + 3H_2O \longrightarrow Al(OH)_3 + 3H^+ \quad (2.1)$$

Manganese (Mn): $$Mn^{2+} + H_2O + 1/2O_2 \longrightarrow MnO_2 + 2H^+ \quad (2.2)$$

Iron (Fe): $$Fe^{2+} + 1/4O_2 + 5/2H_2O \longrightarrow Fe(OH)_3 + 2H^+ \quad (2.3)$$

2.4 pH

The pH is a measure of the amount of free hydrogen ions (H^+) in water. The pH ranges from 0 to 14, with a pH of 7 being neutral and indicating water that is neither acidic nor basic. Water with a pH below 7 is acidic; water with a pH greater than 7 is basic. The most common natural control of the pH of water is the bicarbonate buffering system, which depends on the amount of calcium carbonate dissolved in the water. pH is an important water quality variable because aquatic animals are sensitive to changes in pH, especially when these changes are sudden or large.

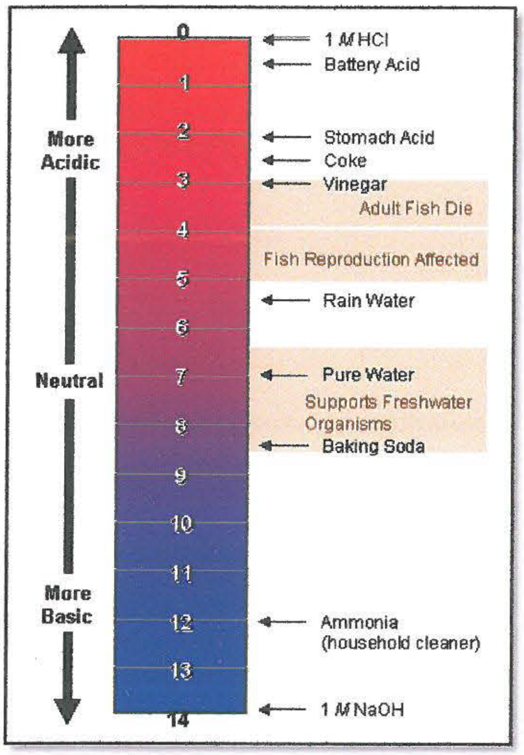

Figure 2.1: pH range

2.4.1 Alkalinity

Alkalinity was often defined as his capacity of a solution to neutralize acidity. The important property of alkalinity is that it acts as a buffer. One aim of treatment for acid-impacted water is to increase alkalinity by dissolving substances with calcium carbonate ($CaCO_3$) into the water. While many different substances can add alkalinity, calcium carbonate is most often the major contributor in natural waters. For this reason, alkalinity is usually shown as an equivalent amount of $CaCO_3$.One confusing aspect of alkalinity is that a solution can be mildly acidic but also contain some alkalinity. In fact, this can often happen as a result of treatment of acidic water. Having water with high alkalinity, particularly when there is a likelihood of this water mixing with more acidic water at some point downstream, is usually desirable.

2.4.2 Acidity

Acidity is a measures the capacity of water to neutralize alkalinity. An acid mine drainage stream that has an acidity of 100 mg/L $CaCO_3$ would require that much carbonate to neutralize the acid.

2.4.3 Acid Neutralizing Capacity (ANC)

Acid Neutralizing Capacity (ANC) is another measurement similar to alkalinity. The difference between ANC and alkalinity is that ANC measures the net condition of the water. For example, an ANC below 0 means the water is acidic and has no buffering capacity. If the ANC is above 0, the water has some buffering ability.

2.4.4 Acid Mine Drainage

Iron (Fe), manganese (Mn), and aluminium (Al) are common in acid mine drainage. Aluminium (Al) is the most common toxic metal in streams affected by acid rain. During treatment, pH and alkalinity must be high enough so that when metals precipitate, sufficient alkalinity remains to buffer any additional acid inputs .In AMD treatment; iron and manganese precipitate at different pH. Manganese requires a higher pH generally around 8.0 compared to the 6.5 needed for iron to precipitate. Often, many passive treatments are unsuccessful at removing manganese due to this high pH requirement. Metals are an important factor to consider because they are toxic to aquatic life and harm their habitats. For example, metal precipitate on the bottom of streams covers and destroys habitat for many types of aquatic insects. Dissolved aluminium is toxic to fish and can cause fish kill.

2.5 Limestone as a Treatment Product for Surface Water Acidification

2.5.1 Introduction

Liming is one of the most cost-effective methods of slowing the effects of acidification, restoring acidic waters, and enhancing the abundance and diversity of aquatic life (Helfrich,J.Neves,Parkhurst 2009). Limestone was use widely in freshwater and wastewater treatment.

In recent years, a variety of passive treatment system have been developed that do not require continuous chemical inputs and that take advantage of naturally occurring chemical and biological processes to cleanse contaminated fresh water (Skjelkvåle, J.Mannio, A.Wilander, T.Andersen, 2001). The primary passive technologies make use of limestone layer in neutralize acid and removing metals which include Anoxic. Limestone Drain (ALD), Alkalinity Producing Systems (APS), Limestone Pond, Open Limestone Channel (OPC) and Oxic Limestone Drainage (OLD). Several investigators have studied the effectiveness of limestone in treating various types of waters and wastewaters (J.Metesh, Jarell, Oratez, 1998). These include treatment of acidic mine drainage (AMD), removal of heavy metal and neutralization of river and lake waters. Limestone is widely use as treatment product since several decades. It's the most popular and effective in treating acidic water and sediments until now.

Figure 2.2 Limestone

2.5.2 Characteristics of Limestone

Limestone is a sedimentary rock composed primarily of calcium carbonate ($CaCO_3$) in the form of the mineral calcite. The rock which contains more than 95% of calcium carbonate is known as high-calcium limestone. It most commonly forms in clear, warm, shallow marine waters. It is usually an organic sedimentary rock that forms from the accumulation of shell, coral, algal and fecal debris. It can also be a chemical sedimentary rock formed by the precipitation of calcium carbonate from lake or ocean water.

2.5.3 Types of Limestone

There have several types of limestone which are agriculture limestone (aglime, $CaCO_3$), dolomite lime ($MgCO_3$), quicklime (CaO), hydrated lime ($CaOH_2$) and soda ash (Na_2CO_3). These types of limestone had different characteristics or effects after being applied to acidic water.