



POTENTIAL MACROPHYTES AS BIOINDICATOR OF
HEAVY METALS IN RUNOFF FROM AREAS WITH
ACID SULFATE SOIL

BY

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ABSTRACT

The oxidation of pyrite produces high concentrations of ferrous ions and sulfuric acid, which in turn attacks clay minerals and produces high concentrations of monomeric Aluminum (Al) and other acid-soluble metals. Subsequent leaching of these toxic products into adjacent water bodies is rapidly increasing the stress on ecosystems. High concentrations of metals are usually associated with acidic drainage. Most metals are more water-soluble in acidic conditions and therefore metal accumulation in plants depends on the plant species, types of soil, environment and agricultural practice. The aim of the study is to monitor heavy metal runoff from acid sulfate fresh water body through plant-based technology. Therefore, objectives have been set up as follow: 1) to study physico-chemical properties of acid sulfate soil fresh water bodies, 2) to assess amounts of five (5) toxic metals (Al, As, Fe, Mn, Ni) in acidic fresh water bodies in Selangor and 3) to identify potential macrophytes as phytoindicator in acid sulfate soil fresh water bodies. The study has been conducted at fourteen (14) different sites in Selangor in areas of acid sulfate soil. Methodology of water sampling, nutrient analysis using HACH Salicylate method and ICP-MS for testing heavy metal was used. Comparing all the sampled plant species from research areas, it can be concluded that the pH observed were high and less acidic (5 – 6). The DO is low (3.5 - 4mg/L) with high level of Ammoniacal nitrogen that leads to excessive nutrient and water pollutants. The growth of the macrophytes was also affected by other environmental parameters, such as temperature, pH and DO resulting with *I.aquatica* > *N.stellata* > *P.stratiotes* > *L.palustris* > *U.aurea* as potential biomonitoring agents for unhealthy aquatic ecosystem environment. The concentration of Ammoniacal nitrogen ($\text{NH}_3\text{-N}$) was found substantially higher for *N.stellata*, *L.palustris* and *U.aurea*, which are classified under class III according to NWQS. *P.stratiotes* generates a great potential to be a phytoindicator for the run off of Al, Fe and Mn from acid sulfate soil. The potential macrophytes for biomonitoring for heavy metal run-off (Al, Fe and Mn) were *P.stratiotes*. As for the concentration of Ni, the significant phytoindicators were *N.stellata* and *P.stratiotes*; and for As the indicator was *L.palustris*. Among these six species analyzed, the most potential macrophytes to indicate unhealthy environment of acid sulfate soil are *P.stratiotes* and *N.stellata*, as they are present in low DO level, high pH, high concentration of $\text{NH}_3\text{-N}$ and tolerant of Al, Fe, Mn, and Ni.

Keywords: heavy metal, phytoindicator, bioindicator, acid sulfate soil.

خلاصة البحث

تنتج أكسدة البيريت تركيزات عالية من الأيونات الحديدية وحمض الكبريتيك، والتي بدورها تهاجم المعادن الطينية وتنتج تركيزات عالية من الألومنيوم الأحادي وغيرها من المعادن القابلة للذوبان في وسط حمضي. إن الترشيح المتكرر لهذه المنتجات السامة في المسطحات المائية المجاورة أدى إلى تزايد سريع للضغط على النظم الإيكولوجية. ترتبط التركيزات العالية للمعادن عادة بالتصريف الحامض، كما تعتمد معظم المعادن أكثر على الظروف الحمضية للذوبان في الماء، ولذلك فإن تراكم المعادن في النباتات يعتمد على الأنواع النباتية، وأنواع التربة، والبيئة، والممارسات الزراعية. الهدف من هذه الدراسة هو رصد جريان المعادن الثقيلة من مسطح المياه العذبة لحمض الكبريتات من خلال التكنولوجيا ذات الأصل النباتي. وبذلك، فقد تم وضع الأهداف على النحو التالي: (1) دراسة الخصائص الفيزيائية والكيميائية لمسطحات المياه العذبة للتربة ذات حمض الكبريتات، (2) تقييم كميات خمسة من المعادن السامة (الألمنيوم، الزرنيخ، الحديد، المنغنيز، النيكل) في مسطحات المياه العذبة الحمضية في ولاية سيلانجور، (3) تحديد النباتات ذات الأوراق الكبيرة المحتملة كمؤشر نباتي في مسطح المياه العذبة للتربة ذات حمض الكبريتات. وقد أجريت هذه الدراسة في أربعة عشر (14) موقعا مختلفا في ولاية سيلانجور، وبالضبط في مناطق تتكون من تربة ذات حمض الكبريتات. وقد تم استخدام منهجية أخذ عينات المياه، و تحليل المغذيات باستخدام طريقي "HACH Salicylate" و "ICP-MS" لاختبار المعادن الثقيلة، وبعد مقارنة جميع عينات الأنواع النباتية من مناطق البحث، فإنه يمكن استنتاج أن الرقم الهيدروجيني الملاحظ كان عاليا وأقل حامضية (5-6)، كما كان الأكسجين المذاب منخفضا (3.5-4 mg/L) مع وجود مستوى عال من النيتروجين النشادر الذي يؤدي إلى إفراز المواد الغذائية المفرطة والمياه الملوثة. وقد تأثر نمو النباتات ذات الأوراق الكبيرة أيضا بالعوامل البيئية الأخرى؛ مثل درجة الحرارة، ودرجة الحموضة والأكسجين المذاب، ما نتج عنه ما يلي: (*I.aquatica* > *N.stellata* > *P.stratiotes* > *L.palustris* > *U.aurea*) كعوامل رصد بيولوجي محتملة لوسط نظام بيئي مائي غير صحي. وقد وجد أن تركيز النيتروجين النشادر لـ "*N.stellata, L.palustris* and *U.aurea*" كان أعلى بكثير، والتي تصنف تحت الفئة الثالثة وفقا للمعيار الوطني لجودة المياه. وقد أنتج "*P.stratiotes*" احتمالا عاليا لأن يكون مؤشرا نباتيا لجريان الألمنيوم، والحديد، والمنغنيز، والنيكل من تربة ذات حمض الكبريتات. كما أن احتمالات النباتات ذات الأوراق الكبيرة للرصد البيولوجي لجريان المعادن الثقيلة (الألمنيوم، والحديد، والمنغنيز، والنيكل) كانت "*P.stratiotes*". أما بالنسبة لتركيز النيكل فإن المؤشرات النباتية الدالة كانت "*N.stellata*" و "*P.stratiotes*". أما بالنسبة للزرنيخ "As" فإن المؤشر كان "*L.palustris*". إن من بين هذه الأنواع الستة التي تم تحليلها، فإن النباتات ذات الأوراق الكبيرة الأكثر احتمالا للإشارة إلى وجود بيئة غير صحية لتربة حمض الكبريتات هي: "*P.stratiotes*" و "*N.stellata*" كما كانتا موجودتان في الأكسجين المذاب ذات المستوى المنخفض، ودرجة الحموضة العالية، وارتفاع تركيز "NH₃-N"، وبتساخا مع الألمنيوم، والحديد، والمنغنيز، والنيكل.

الكلمات المفتاحية: المعادن الثقيلة، المؤشر النباتي، المؤشر البيولوجي، تربة حمض الكبريتات.

APPROVAL PAGE

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DECLARATION

I hereby declare that this dissertation is the result of my own investigation, except where otherwise stated. I also declare that it has not been previously or concurrently submitted as a whole for any other degrees at IIUM or other institutions.

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METALS IN RUNOFF FROM AREAS WITH ACID SULFATE SOIL**

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CHAPTER 1

INTRODUCTION

The soils of the humid tropics have been shown to be managerially problematic, particularly with regard to their fertility. In an undisturbed environment, these soils are inherently infertile. Like all acid soils of the humid tropics, these soils are low in soil pH, which brings with it many potential associated problems, including Hydrogen (H), Aluminium (Al), and Manganese (Mn) toxicity, Calcium (Ca) deficiency, low Cation Exchange Capacity (CEC), (Phosphorus) P fixation and low microbial activity (Tessens and Shamshuddin, 1983; Foy, 1984). Acid sulfate soils are weak mechanically and therefore highly erodible, if drain banks are not properly stabilized, they are prone to collapse, dumping into the drains eroded soil and sediments, which are highly acidic and loaded with heavy metals and nutrients (Paul, 2003). The consequences of acid sulfate soils and acidic drain waters have adverse environmental effects on vegetation and aquatic life in terms of fish kills, reduced crop harvest and changes in water quality. In particular, the coastal plains of some countries including Australia, Thailand, Indonesia, Malaysia, and New Zealand have been affected (Indraratna, 1999). Reviews on the characteristics and management of these soils did not take into account the effect of terracing in exposing saprolites or C horizon. With the surface soils and subsoils already being considered problematic, one could only imagine what impact the saprolites pose to the fertility of these soils. As the Tasnee, (1986) has mentioned, their low productivity may be due to one or more of the following unfavourable factors; soil acidity, salinity, aluminium toxicity, low content of major nutrients, low base status, and hydrogen sulfide toxicity.

This research attempts to identify the changes in soil physico-properties that contribute to the release of heavy metal runoff by assessing the potential of vegetation as a phytoindicator for acid sulfate soil. To achieve this, the soil-water-plants profile in relation to acid sulfate soil environment in fourteen (14) identified locations in Selangor were selected for further investigation in order to develop plant-based technology for monitoring heavy metal runoff by soil chemical analysis. Geological aspects of these locations were also taken into consideration as they were named as areas that contain large amounts of acid sulfate soil.

1.1 THE STUDY

The research explores an alternative means of cleaning contaminated acid sulfate soil and the surrounding water body from heavy metal runoff by using plant-based technology with suitable aquatic plants as phytoindicator.

1.2 RESEARCH BACKGROUND

Acid Sulfate Soils (ASS) is extensive in this Asean region (Dent, 1986). The utilization and management of these soils appear to be strongly related to the depth of the sulfuric horizon, the amount of organic matter in the B horizon and the depth at which unripe marine clay is encountered. As a consequence of all these properties, acid sulfate soils can be considered problem soils, and the potential of eroded and contaminated water bodies are high. Recognition of the potential hazard caused by heavy metal and the needs to protect the environment has resulted in greater investment into research, legislating and enforcing permissible limit of the metals by developed countries. The decrease in the number of clean rivers were attributed to an

increase in the number of polluting sources, such as sewage treatment plants, manufacturing industries and palm oil mills, which contributed to a high pollution loading (Wan, 2013).

The application of plants in environmental protection strategies is called phytotechnology. Phytoremediation is an emerging technology that utilizes plants and then associated rhizosphere microorganisms to remove, transform or contain toxic chemicals located in soils, sediments, ground water, surface water and even the atmosphere (Sridhar et al., 2002). Currently, phytoremediation is used for treating many classes of contaminations, including petroleum hydrocarbons, chlorinated solvents, pesticides, explosives, heavy metals and radionuclides, and landfill leachates that might appear in most acid sulfate soil. This strategy may be seen as a final polishing step following the initial treatment of high level contamination; however, when contaminations are in low concentration, phytoremediation alone may be the most economical and effective remediation strategy. An important principle of phytoremediation is to match the proper plant species and subspecies to the contaminated site with planned applications. Matching the plant to the site often requires research and testing (Lynne, 2001).

The use of aquatic macrophytes, such as *Azolla* with hyper accumulating ability is known to be an environmentally friendly option to restore polluted aquatic resources (Sood, 2012). Microphytes and macrophytes are well-known biological filters and they carry out purification of the water bodies by accumulating dissolved metals. The ability to hyperaccumulate heavy metals makes them interesting research candidates, especially for the treatment of industrial effluents and sewage waste water. Macrophytes are excellent indicators of watershed health because they can respond to nutrients, light, toxic contaminants, metals, herbicides, turbidity, water level change,

and salt, and are easily sampled through the use of transects or aerial photography. Their abundance metrics are easily to calculate and indicate as integrators of environmental condition. The natures of macrophytes that are unchangeable biological filters play an important role in the maintenance of aquatic ecosystem with long period monitoring. Some species have expressive ability of bioconcentration and, therefore, increased accumulation of nutrients and heavy metals (Stankovic et al., 2000). Hyperaccumulator plants are usually found on metalliferous soils, where the natural exposure to a surplus of various metals has driven the evolution of metal hyperaccumulation, as well as plant resistance to heavy metals (Ernst, 1998). Therefore, macrophytes can be used as bioindicators or phytoindicators.

1.3 PROBLEM STATEMENT

Contaminated sites exist throughout Malaysia and elsewhere that require cleanup to protect human health and the environment. Acid sulfate are an almost unique case where the soil problems are so severe that they can dominate most other aspects of land development from engineering works to agricultural system, economic and social planning at regional and local levels, as well as environmental impact and reclamation. When acid sulfate soil is disturbed and oxidised it may generate a large amount of acidity. One tonne of iron sulfide can produce 1.5 tonnes of sulfuric acid when oxidized (Department of Environment and Conservation Australia, 2009). Poor fertility of the acid sulfate soil is more complex, and could impose a serious limitation to crop production in the upland areas. However, their chemical and physical properties and the potential problems related to these properties are a greater cause for concern. Unlike ordinary soil materials, which can be amended and improved to suit crop requirements, acid sulfate soils are more difficult. Oxidation of acid sulfate soils

can also lead to the release of metals like Cadmium (Cd) and Lead (Pb), and metalloids such Arsenic (As) in the environment (e.g. Corkhill et al. 2008). At present, a little work has been done that deals with the properties, utilization, problems and management of exposed acid sulfate soil in water bodies. Eswaran and Wong (1978) noted that in such steep terraced areas where horizon C are exposed, their characterization and interpretation of agricultural potential based on soil information become less meaningful. Among the problems that have been identified are:

- i. Sulfide oxidation along highway corridors resulted in severe problematic roadside management conditions.
- ii. Sulfuric acid and dissolved Aluminum (Al) corrodes urban infrastructure.
- iii. Metal toxicity in water and soil caused loss in the sustainability of agriculture production and quality.
- iv. Pollution caused problems to related ecology.
- v. Inadequate information on the management of acid sulfate soil.
- vi. Preventing heavy metal pollution is critical and expensive.

This acidic soil caused degradation of road construction materials, which require high maintenance and need special treatment and management. In addition to its nature, acid sulfate soil tends to decline the local surface water quality due to input of acidity and metals which mainly contain Aluminium (Al) and Iron (Fe). Vegetations are found poorly established along acid sulfate soil due to iron staining. Most plants will find it hard to grow on acidified sediments. As for the agricultural practices, there is loss of rural productivity, and loss of commercial and recreational fisheries. Acid sulfate soils cause significant environmental problem due to release of

acidity and metal during oxidation of naturally occurring sulfur species (Linda, 2006). The discharge of acidic water into waterways and wetlands may cause fish kills and loss of aquatic biodiversity, and the infiltration of water through the soil profile may contaminate groundwater with acid, arsenic, metals and other contaminants. Careful testing program and monitoring requirement is needed for prediction of potential limitation of acid sulfate soil for any development. Future work on the amelioration of exposed acid sulfate materials to improve their sustainability is also necessary.

1.4 RESEARCH QUESTIONS

1. What are the physico-properties of acid sulfate soil that contribute to the contamination of heavy metal in the soil and water bodies?
2. What are the types of heavy metal associated with the run-off from acid sulfate soil?
3. What are the criterias needed by an aquatic plant to be indicated as phytoindicator for cleaning contaminated soil and water from a definite type of heavy metal?

1.5 OBJECTIVES

The aim of the study is to monitor heavy metal runoff from acid sulfate fresh water body through plant-based technology.

1. To study physico-chemical properties of acid sulfate soil in fresh water bodies.
2. To assess amounts of five (5) toxic metals (Al, As, Fe, Mn, Ni,) in acidic fresh water bodies in Selangor.

3. To identify the potential macrophytes as phytoindicator in acid sulfate soil fresh water bodies.

1.6 RESEARCH SIGNIFICANCE

The study is attempting on developing a set of significance to the environment and human life such as:

1. Highly efficient technology, as proved by many researchers and other developed countries.
2. New knowledge of ecological engineering approach using aquatic plants as water purifier and water quality indicator or plant-based green technology.
3. Cost-effective treatment for unhealthy environment.
4. Chemical free and subtle approach to remove contaminants.
5. Conservation of natural resources.
6. Reduction of heavy metal runoff.
7. Increase public awareness about environment.
8. Creation of wildlife habitat and aesthetic resources.
9. Long-term technology that is imperative to achieve economically viable and socially acceptable decontamination.

CHAPTER 2

LITERATURE REVIEW

2.1 NATURE OF ACID SULFATE SOIL

2.1.1 Formation of Acid Sulfate Soil

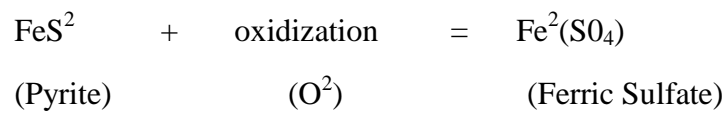
Acid sulfate soil develops when the production of acid from the oxidation of pyrite exceeds the neutralizing capacity of parent material and the pH level drops below 4 (Naylor, 1993). These soils are most likely to occur in coastal regions of Australia, New Zealand, Netherland, Thailand, Indonesia and Malaysia, but can also be associated with dry land salinity in some inland agricultural areas. It occupies worldwide an area of ca. 17 million ha (Andriensse and van Mensvoort, 2002). The lack of details given in many papers and the lack of an accepted definition of acid sulfate soils makes it difficult to decide when acid sulfate soils were first recognized in Peninsular Malaysia (Shamsuddin, 2006). According to worldwide studies, the term acid sulfate soil applies to estuarine sediment deposits laid down in the late Pleistocene era by rising sea levels caused by the melting of polar ice caps at the end of the last ice age about 20,000 years BP. The EPA (Environmental Protection Agency) of Victoria Government defined the soil as;

‘... any soil, sediment, unconsolidated geological material or disturbed consolidated rock mass containing metal sulfides which exceeds criteria for acid sulfate soils specified in Publication 655 entitled ‘Acid Sulfate Soil and Rock’ published by the Authority in 1999 as amended from time to time or republished by the Authority’.

The metal sulfides are pyrite (FeS_2) and its exposure to oxygen and water can generate sulfuric acid. This may result in acidification of soil, sediment, rock, surface

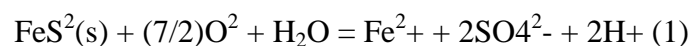
water and groundwater. Acid sulfate soil develops when the production of the pyrite exceed the neutralizing capacity of the parent materials. It also causes pH level to drop <4.0 (Nylon, 1993). They are commonly found less than five metres above sea level and may not be obviously seen on the soil surface as they are often buried beneath layers of more recently deposited soils and alluvial sediments.

Iron sulfide (FeS^2) is not stable when exposed to oxygen (O^2), thus rapidly changing to Iron oxides (FeSO^4) and sulphuric acid which dissolves Aluminium (Al).

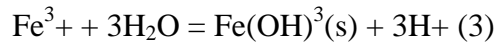
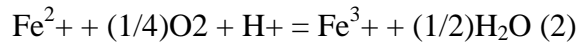


It also contains Aluminium (Al) and Iron (Fe) toxicities and causes nutrient deficiencies, particularly of Phosphate (P). The oxidation of pyrite often results in yellow mottles of jarosite (2.5Y 8/6). Kyuma et al, (2003) stated that the general conditions that lead to the formation of sulfide-containing sediments are; (1) the presence of marine or brackish water as the source of sulfate, (2) stagnation of water as typically found in lagoons and bays, and (3) a supply of decomposable organic matter. This process is mainly anaerobic, alternated with a limited aerobic process. Once formed, it may persist as a stable solid phase. Thus, solid elemental sulfur is quite common in recent marine sediments.

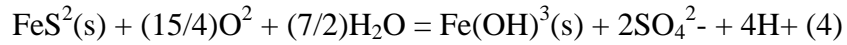
Upon exposure to the air, pyrite undergoes oxidation as follows:



The ferrous iron is further oxidized to ferric iron. This is precipitated if the environmental pH is higher than about 3.

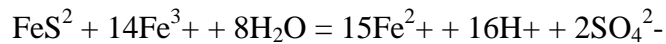


Thus, the overall reaction is:



It is known that the reaction (ferrous iron to ferric iron) is a slow process if it proceeds in a purely chemical fashion. At a pH of 3, the half life of this reaction is around 1000 days (Stumm and Morgan 1970). In the soil, however, this reaction is mediated by autotrophic iron bacteria, *Thiobacillus ferrooxidans* and *Ferrobacillus ferrooxidans*, and proceeds much faster.

Another important reaction is the oxidation of pyrite by Fe^{3+} ,



This produces even more acidity. The reaction runs quite rapidly. The half life of this reaction is from 20 to 1000 minutes. The only key to define acid sulfate soil is the presence of sulfuric horizon and sulfidic material which is pyrite and jarosite minerals, which slightly differs the soil from other soils. As being mentioned earlier, the major difficulty in interpreting published data is the lack of uniformity of the definitions of acid sulfate soil (Paramannathan, 1986). Today the criteria used in Peninsular Malaysia is based on those given in Soil Taxonomy (Soil Survey Staff, 2005) which contain:

i. Sulfidic Materials

Sulfidic materials are waterlogged mineral or organic soil materials that contain 0.75% or more Sulfur (S) (dry weight) mostly in the form of sulfides and have

less than three times as much carbonate (CaCO_3 equivalent) as Sulfur (S) (Noordin et al., 1986). Pyrite (FeS_2) is considered as sulfidic material.

ii. Sulfuric Horizon

According to Soil Survey Staff, (1999) et.al, the sulfuric horizon is composed either of mineral or organic soil material that has both a pH of less than 3.5 (1:1 by weight in water or in a minimum of water to permit measurement) and the presence of jarosite mottles (the colour of fresh straw that has a hue of 2.5 Y 8/6 or yellower and a chroma of 6 or more). The layer is about 15cm or more thick and consists of about 0.05 % or more water-soluble sulfate.

2.1.2 Classification of Acid sulphate soil

There are two types of acid sulphate soil, which are actual acid sulphate soil and potential acid sulphate soil. Actual and potential acid sulfate soils are often found in the same soil profile, with actual acid sulfate soils generally overlying potential acid sulfate soil horizons. Both of these types present similar criteria and slightly differ in terms of pyrite oxidation and physical properties. The three common ways in which acid sulphate are identified are through site inspection, subsurface inspection and using ground water quality as indicators (Sullivan, 1995).

1. Actual acid sulfate soil

Actual acid sulfate soil (ASS) is a coastal sedimentary material that once contained iron pyrites, and may still contain some, but which has been exposed to the atmosphere by drainage or disturbance so that the pyrite has been oxidised to form sulfuric acid, thereby decreasing the pH of the soil to less than

3.5 (Thomas, 2003). The oxidation process produces hydrogen ions in excess of the sediment's capacity to neutralize the acidity, resulting in soils of pH of 4 or less when measured in dry season conditions. ASS can be characterized by jarosite concentration which are bright yellow or straw-coloured mottles of the mineral jarosite and often contain dark reddish-coloured streaks of iron oxide.

2. Potential acid sulfate material

Potential acid sulfate soil (PASS) is a coastal sedimentary material that contains iron pyrites that have not been oxidized (Thomas et al. 2003). These soils are poorly drained and pH is usually near neutral (approximately 7) or slightly acidic reaction under field conditions. It was described as environmentally unfriendly when are exposed to air by disturbance or over drainage and once disturbed, will produce acid and become actual acid sulfate soil with toxic elements that can kill fish, contaminate shell fish, drinking water and ground water.

3. Classification of Acid sulphate soil by taxonomy

According to soil classification, acid sulphate soil and potential acid sulphate soil can be grouped into three:-

i. Sulfaquent

Mineral soils which have sulfidic material within 50cm of the soil surface are classified as Sulfaquent. This group is poorly drained, high in pyrite and is neutral or slightly acid under field condition (Attanandana, 2007). When oxygen penetrates the soil upon draining, it becomes acid sulphate due to oxidation of pyrite. The problem encountered in this soil