Faculty of Resource Science and Technology

USE OF *TENUALOSA MACRURA* SCALES AS BIOSORBENT FOR THE REMOVAL OF MANGANESE AND CADMIUM IN WATER

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Use of *Tenualosa macrura* scales as biosorbent for the removal of Mn and Cd in water

NUR INANI BINTI HISHAMUDDIN

This project is submitted in partial fulfillment of the requirements for the Degree of Bachelor of Science with Honours

(Aquatic Resource Science and Management program)

Supervisor: Dr Farah Akmal Idrus

Aquatic Resource Science and Management

Department of Aquatic Science

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DECLARATION

I hereby declare that no portion of this dissertation has been submitted in support of an application for another degree of qualification of this or any other university or institution of higher learning.

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Λ	Wavelength
µm	Micrometer
AAS	Atomic Absorption Spectroscopy
Cd	Cadmium
G	Gram
HA	Hydroxyapatite
HCl	Hydrochloric acid
HNO_3	Nitric acid
M	Molar
mL	Milliliter
Mn	Manganese
Min	Minute
NaOH	Sodium hydroxide
Nm	Nanometer
Ppm	Parts per million
Rpm	Rate per minute
spp.	Species

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Use of *Tenualosa macrura* scales as biosorbent for the removal of Manganese and Cadmium in water

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ABSTRACT

Heavy metals contamination has become the major environmental problems in water pollution. Manganese and cadmium are the examples of heavy metals that can cause hazards to human and other forms of life. Removal of manganese and cadmium using *Terubok* fish scales as biosorbent was studied. This study was focused under various parameters such as varying pH, contact time, amount of biosorbent dosage and initial metal ion concentration. The absorption rates of manganese and cadmium was obtained by flame Atomic Absorption Spectroscopy (AAS). The optimum pH for both manganese and cadmium removal is achieved at pH 8 with the lowest concentration left in the sample, 5.83 ± 0.50 ppm and 0.63 ± 0.55 ppm respectively. The maximum removal of manganese and cadmium under best absorption conditions: biosorbent dosage = 0.10 g for both Mn and Cd; concentration = 30 ppm (Mn), 50 ppm (Cd) and contact time = 60 min (Cd). The finding showed that promising biosorption of manganese and cadmium using *Terubok* fish scale as potential biosorbent.

Keywords: Biosorption, fish scales, cadmium, manganese, *Tenualosa* spp.

ABSTRAK

Pencemaran logam berat telah menjadi masalah utama alam sekitar dalam pencemaran air. Mangan dan kadmium adalah contoh logam berat yang boleh menyebabkan bahaya kepada manusia dan hidupan lain. Penyingkiran mangan dan kadmium menggunakan sisik ikan terubuk sebagai penyerap telah dikaji. Kajian ini dijalankan di bawah pelbagai parameter seperti pH yang berbeza-beza, tempoh masa, jumlah sisik ikan dan kepekatan ion logam. Kadar penyerapan mangan dan kadmium diuji menggunakan alat Atomic Absorption Spectroscopy *(AAS). pH yang optimum untuk penyingkiran mangan dan kadmium ialah pH 8 masing-masing dengan kepekatan terendah dalam sampel iaitu* 5.83 ± 0.50 ppm and 0.63 ± 0.55 ppm. *Keadaan yang paling optimum untuk penyingkiran maksimum mangan dan kadmium ialah seperti berikut: jumlah sisik ikan yang diguna = 0.10 g bagi mangan dan kadmium; kepekatan ion logam = 30 ppm bagi mangan, 50 ppm bagi kadmium dan tempoh masa = 60 min untuk kadmium. Dapatan kajian menunjukkan bahawa sisik ikan Terubok boleh menjadi penyerap yang berpotensi bagi menyerap mangan dan kadmium.*

***Kata kunci** : Serapan, sisik ikan, kadmium, mangan, Tenualosa* spp.

1.0 INTRODUCTION

Heavy metals are a group of pollutants which present naturally in the earth's crust (Das *et al.,* 2007). Rapid urbanisation and industrialisation has substantially enhanced the metal contamination in aquatic ecosystems. Due to the fact, the presence of heavy metals in large quantities will cause harm to human and other living organisms (Aziz *et al.*, 2008; Witek-Krowiak *et al.*, 2011). Chin (2006) stated that metals are presence in aquatic ecosystems by many processes such as atmospheric deposition, weathering of soils and rocks and variety of human activities.

Manganese (Mn) and cadmium (Cd) are the examples of heavy metals that responsible for water pollution. Mn is an important metal for human development, metabolism, and antioxidant system. However, excessive exposure of manganese may lead to neurodegenerative disorder. According to Lewinsky (2007), the harmful effects of Cd include acute and chronic disorders, for instance 'itai-itai' disease, renal damage, hypertension, and testicular atrophy.

The heavy metal contaminants need to be removed from water in order to protect the environment. Recently, the use of conventional method has been conducted to remove heavy metal from wastewater. Rorrer (1998) stated conventional methods for heavy metal removal from aqueous solution include chemical precipitation, electrolytic recovery, ion exchange and solvent extraction/liquid membrane separation. But these methods are often cost prohibitive having inadequate efficiencies at low metal concentrations.

Biosorption has emerged as a new technology which is cost effective. According to Drake and Rayson (1996), biosorption is a physico-chemical adsorption whereby metal ions become attached to the biomass surface. It has the natural potential of the biomass to immobilize dissolved components for example, heavy metal ions on its surface (Witek-Krowiak *et al.*, 2011).

Several biosorbents have been used by using low cost biomaterials for removing heavy metal such as rice husk, crab shell, egg shell, cocoa shell and black tea leaves. The feasibility of using fish scale as an adsorbent to remove heavy metals was examined by Mustafiz (2003). The fish scales of *Catla catla*, *Cyprinus carprio* and *Tilapia mossambica* had been reported and give promising results for the heavy metal removal. Little research is known to remove Mn and Cd by using *Tenualosa macrura* fish scales. Therefore, *Tenualosa macrura* fish scales are used in this research as the biosorbent. The objective of this study is:

1. To measure the biosorption activity of *Tenualosa macrura* fish scales under various parameters such as varying pH, contact time, amount of fish scales dosage and initial metal ion concentration.

2.0 LITERATURE REVIEWS

2.1 Heavy metals

Metals cannot be degraded to non-toxic forms. Once they contaminate the ecosystems, they remain a potential threat for many years. Heavy metals are elements that have high densities and belong largely to the transition group in the periodic table.

Cadmium (Cd) is a possible carcinogen and its chronic exposition to high concentration can result in respiratory illness (Karar *et al.*, 2005). Cd is being used in the industry as stabilizers, electroplating, alloys for telegraph and telephone wires. Cd is released in tiny particulates as dust; the small size allows these toxic metals to rise on the wind to be inhaled, or transported onto topsoil or edible plants. Cd is being used widely in industrial applications such as electroplating.

Manganese (Mn) is not found as a free element in nature. It is always found in combination of iron and other minerals. Karar *et al.* (2005) stated that Mn is a neurotoxic element whose prolonged exposure leads to neurological disease called ‘manganism’. The industrial uses of Mn are fertilisers, pharmaceuticals, catalysts, dyes, paint, dryers and disinfectants. Besides, Mn is a metal that being used widely in the preparation of alloys.

2.2 Heavy metals contamination in aquatic ecosystem

In order to improve the living conditions and comforts of human life, people has made great steps towards the urbanisation and industrialisation without notice the bad impacts of it. According to Karar *et al.* (2005), rapid urbanisation and industrialisation has increased the air pollution level worldwide. Polluted air can either be deposited directly onto the surface of water or be deposited onto land and carried to water bodies via runoff.

Bem *et al.* (2003) and Wang *et al.* (2001) mentioned that the trace elements are released both by natural and anthropogenic sources into the atmosphere. However, manmade activities gave more dramatic effects to our ecosystems. It has long been known that many metals are essential to life and ecosystems in the right concentrations (Morgan *et al.,* 1964; Yunice *et al.,* 1968; Salanki *et al.,* 1992).

Heavy metals are non-biodegredable thus they will tend to accumulate in the environment, especially aquatic environments. Besides, metals can be transported from one environment compartment to another (Christensen *et al.*, 1994).

Only bioavailable chemicals may be bioaccumulated by aquatic organisms, possibly leading to biomagnifications in the food webs and may cause threat to human that consume those. The toxic effects of heavy metals may affect growth, reproduction and mortality of fishes. Human activity has brought about degradation of the natural environment from all aspects; biological, chemical, physical and social.

2.3 Biosorption

There is an urgent need for removal of heavy metal contaminants because it can affect our life and ecosystems. In recent years, biosorption has emerged as a new technology which has distinct advantages over current treatments methods (Zayadi and Othman, 2013). Biosorption of heavy metals occurs as a result of physicochemical interactions, mainly ion exchange or complex formation between metal ions and the functional groups present on the cell surface (Tunali *et al.*, 2006). In addition, biosorption has a natural potential to immobilize heavy metal ions on its surface.

Das *et al.* (2007) mentioned that there are many types of natural products act as biosorbents that have been applied for removing heavy metal. However, biosorption process needs only biomass with high metal binding and selectively for heavy metal. The advantages of biosorption over conventional methods not only low cost and high efficiency but it also can minimize chemical and biological sludge and not require additional nutrient (Huang, 2007).

2.4 *Tenualosa* spp.

The important estuarine fishes locally known in Malaysia as ikan *Terubok* or the tropical shad of genus *Tenualosa* (family Clupidae) are commercially and culturally in many Asian countries including Malaysia (Khairul Adha *et al.*, 2014). Blaber *et al.* (1996) stated that these clupeids are unique because they are protandrous hermaphrodite. Table 1 showed five *Tenualosa* spp. which can be found in Asian region. However, only two species can be found along the coastal waters of Sarawak that is *T. toli* (*Terubok Sungai*) and *T. macrura* (*Terubok Laut*).

Table 1: The variety of *Tenualosa* spp. in tropical Asian region

Common name	Scientific name	Origin
Terubok	*Tenualosa toli*	Malaysia
Terubuk	*Tenualosa macrura*	Indonesia
Hilsa	*Tenualosa ilisha*	India
Pha Mak Pang	*Tenualosa thibaudeaui*	Mekong
Nd	*Tenualosa reevesii*	Southern China

Source: Blaber *et al.*, 1999

A number of fish scale namely *Labeo rohita, Catla catla* and Atlantic cod had been reported and give promising results of heavy metal removal (Zayadi and Othman, 2013). The application of using fish scales as biosorbent for heavy metals removal is a recent innovation (Begum and Kabir, 2012) since the fish scales are less used.

2.4.1 *Tenualosa toli*

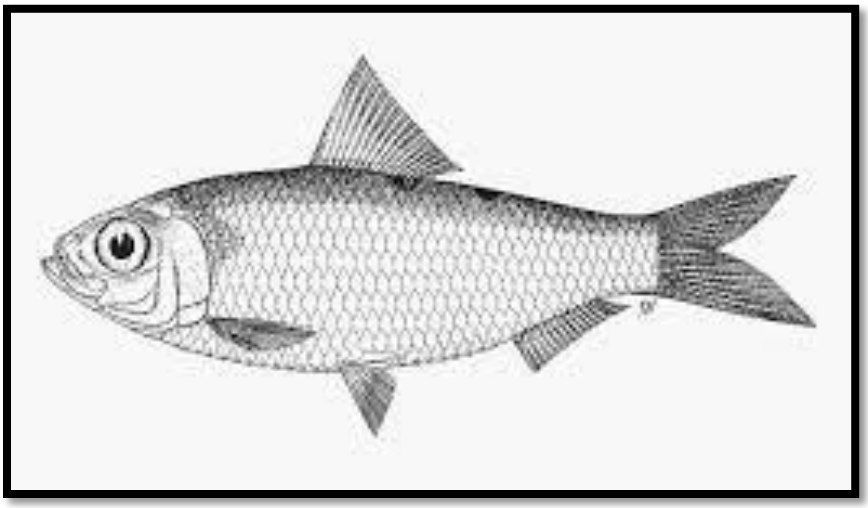

Figure 1 *Tenualosa toli*

Tenualosa toli (Figure 1) can be found in the estuary and adjacent coastal areas of Sarawak which comprises the estuaries of Batang Sadong, Batang Lupar, Batang Lassa and Batang Saribas (Rajali, 1991; Milton *et al.*, 1997; Philip, 2001; Blaber *et al.*, 2003).

Toli shad can be easily distinguished from other *Tenualosa* spp because it lacks the series of black spots on the side which can characterize the species. It can grow to about 400 mm SL (standard length) and can live from 2 to 3 years (Milton *et al.*, 1997).

According to Rahman & Salimon (2006), *T. toli* rich in lipid and provide valuable fatty acids that plays an important role in human health and eventually become one of the important consumption tropical shad in Malaysia.

2.4.2 *Tenualosa macrura*

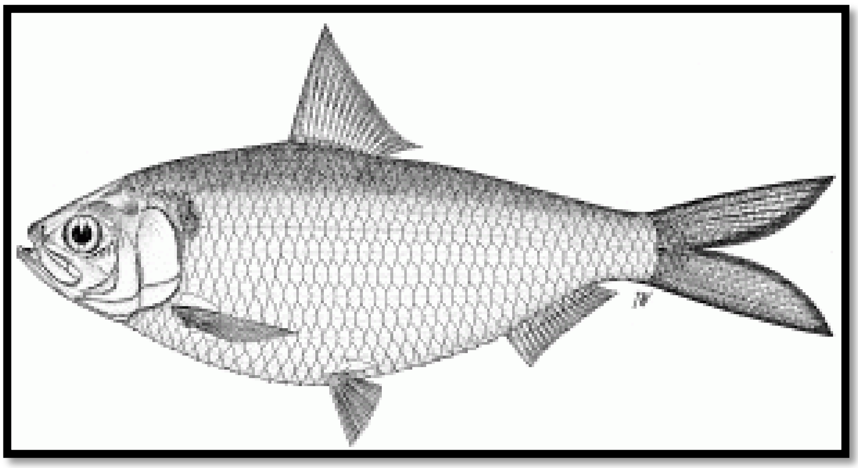

Figure 2 *Tenualosa macrura*

Tenualosa macrura (Figure 2) has long caudal fin, long and pointed lobes, but has no series of dark spots along flanks. It resembles *T. toli* which has longer head but shorter tail. According to Allsop and West (2003), *T. macrura* is a protandrous fish that changes from male to female mainly between 14 and 20 cm SL (Standard length) about six month to one year in age, after the male has spawned.

This longtail shad is schooling in coastal waters and ascending rivers to breed. Previously, *T. macrura* can be found widespread South-east Asia but now it can only be found in the coastal waters of Sumatra and Borneo (Blaber *et al.*, 2005).

2.5 *Tenualosa macrura* (*Terubok laut*) fish scales as biosorbent

Members of Clupeidae family usually have a body protected with shiny cycloid scales. The scales are circular and very smooth. The scales act like small transparent pieces of bone which protect the fish from minor cuts and scratches. Cycloid scales overlap from head to tail arrangement which can reduce drag as the fish swims. Figure 3 and Figure 4 show the cycloid scales of *Tenualosa macrura.*

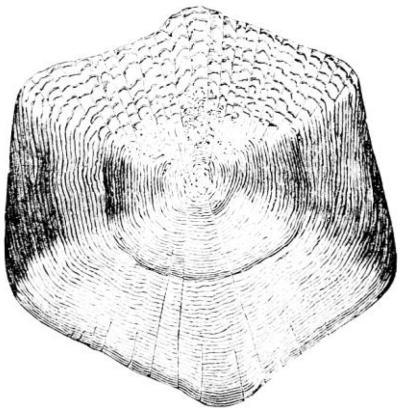

Figure 3 Cycloid scale of *Tenualosa* spp.

Figure 4 *Tenualosa macrura* scales

Bajic *et al.* (2013) stated FTIR analysis shows the important functional groups of fish scale, such as hydroxyl, amides, phosphate and carbonate, exists as available adsorptive sites for Cd and Mn removal. According to Gil & Ossa (2013), microstructural analysis revealed that the scale is composed by different layers associated with collagen and a top layer associated with hydroxyapatite. Hydroxyapatite (HA) is a mineral form of calcium apatite with the formula $Ca_5(PO_4)_3(OH)$ as shown in Figure 5.

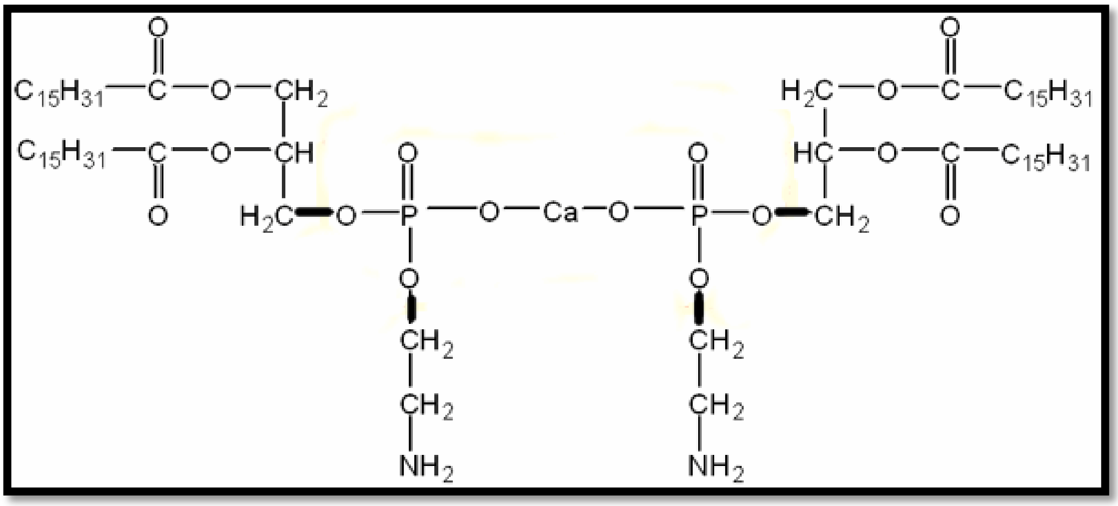

Figure 5 The chemical structure of hydroxyapatite

3.0 MATERIALS AND METHODS

3.1 Preparation of biosorbent

The adult *terubok* fish were obtained from local fish market. The fish scales were cleaned using 15% of nitric acid to remove adhering dust and soluble impurities (Zayadi and Othman, 2013). After that, the fish scales were soaked and washed repeatedly with distilled water for further clean up until neutral pH was obtained (Figure 6). The clean fish scales were allowed to dry at room temperature (Figure 7) for a day before kept in an oven at 100°C for 48 hours. The dried fish scales were ground using plastic mortar and pestle. Then the fish scales were sieved through 60 mesh to obtain 250 µm of particle size. The fish scales were kept in a plastic petri dish for further use as biosorbent (Figure 8).

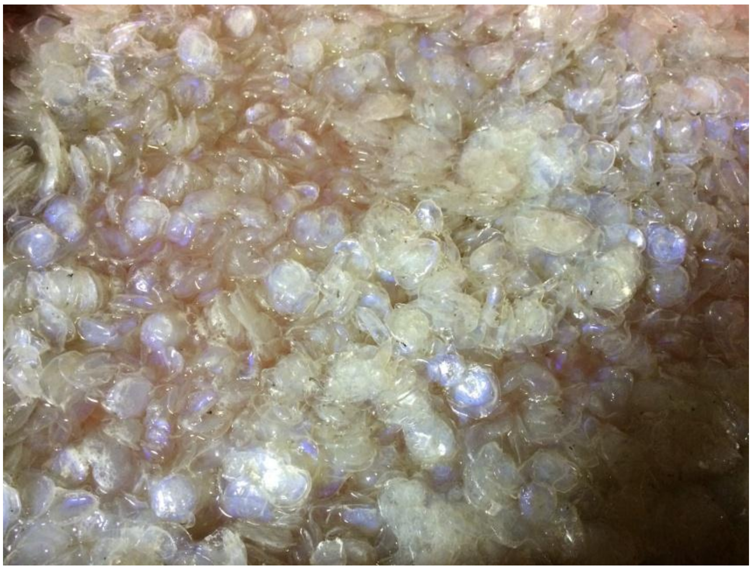

Figure 6 Fish scales soaked with distilled water

Figure 7 Dried fish scales

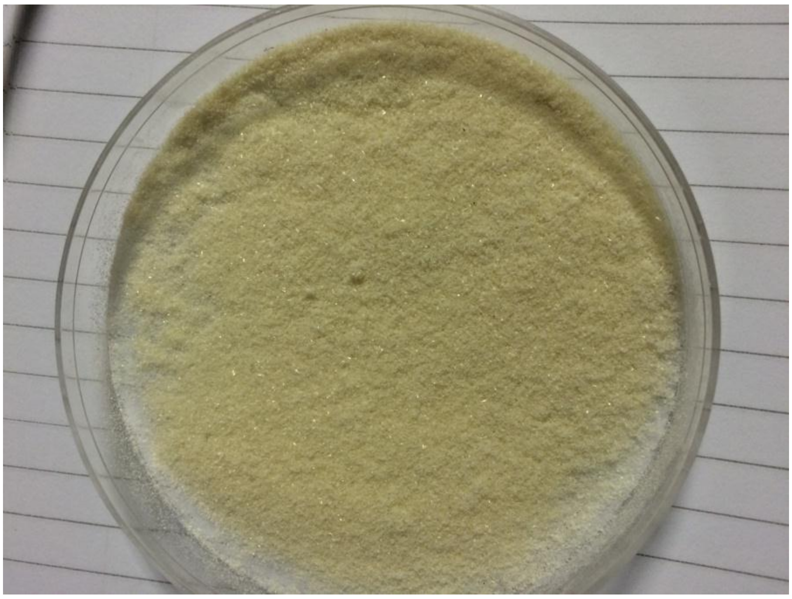

Figure 8 Fish scales as biosorbent