Removal of Copper Using Microwave Incinerated Rice Husk Ash (MIRHA) In Continuous Flow Activated Sludge System

by

Khaw Seek Guan

Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
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CERTIFICATION OF APPROVAL

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Approved by,

(A.P. Dr. Shamsul Rahman B M Kutty)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

September 2011

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

(Khaw Seek Guan)

ABSTRACT

Copper is being widely used in a variety of textile, steel and dyes industries. Wastewater contains copper and organic matters need to be treated prior to discharge to the environment, else it could pose adverse health effects to human. Current heavy metals removal methods, such as adsorption by activated carbon, ion exchange, reverse osmosis, chemical precipitation and nanofiltration, are expensive, unable to completely remove heavy metals and involve high energy and chemical consumption. The purpose of this research is to propose the removal of copper and organic matters using biological treatment system, dosed with Microwave Incinerated Rice husk Ash (MIRHA) adsorbent. The objectives are to study if MIRHA is capable to delay the toxicity effect of copper and the feasibility of using MIRHA as low cost copper adsorbent in activated sludge system. The research is carried out by conducting experiments using 2 scaled down biological reactor. Medium strength wastewater dosed with copper at dosage of 0.5 mg/L, 1.0 mg/L, 2.0 mg/L, 5.0 mg/L and 10.0 mg/L is used as influent. The reactor is run in Extended Aeration Activated Sludge mode. The result shows that MIRHA adsorbent has improved the overall performance of biological treatment system in term of organic matters (TCOD & BOD) removal, copper removal and improved the growth of microbes in the activated sludge system. With MIRHA adsorbent and gradual acclimatization, microbes are capable to withstand copper concentration up to 5.0 mg/L, as compared to 2.0 mg/L without MIRHA. Besides, it is also concluded that acclimatization is capable to improve microbes' tolerance toward copper toxicity from 1.0 mg/L to 2.0 mg/L in Extended Aeration Activated Sludge system. In short, Extended Aeration Activated Sludge system dosed with MIRHA adsorbent is a new approach toward removal of copper and organic matters in wastewater that contains copper concentration up to 5.0 mg/L.

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CHAPTER 1: INTRODUCTION

1.1 Background Study

1.1.1 Wastewater Treatment

Wastewater is defined as a combination of the liquid or water-carried wastes removed from residences, institutions, commercial and industrial establishments [1].

When untreated wastewater accumulates and is allowed to go septic, the decomposition of the organic matter it contains will lead to nuisance conditions including the production of malodorous gases. Besides, untreated wastewater contains numerous pathogenic microorganisms that dwell in the human intestinal tract. Wastewater also contains nutrients, which can stimulate the growth of aquatic plants, and may contain toxic compounds or compounds that potentially maybe mutagenic or carcinogenic. For these reasons, the immediate and nuisance-free removal of wastewater from its sources of generation, followed by treatment, reuse or dispersal into the environment is necessary to protect public health and environment [1].

The constituents in the wastewater to be removed include suspended solids, biodegradable organics, nutrients (nitrogen and phosphorus), pathogens, volatile organic compounds, odors and occasionally heavy metals.

Wastewater treatment processes can be broadly categorized into 4 levels: preliminary, primary, secondary and tertiary treatment. The conventional wastewater treatment process is shown in Figure 1.

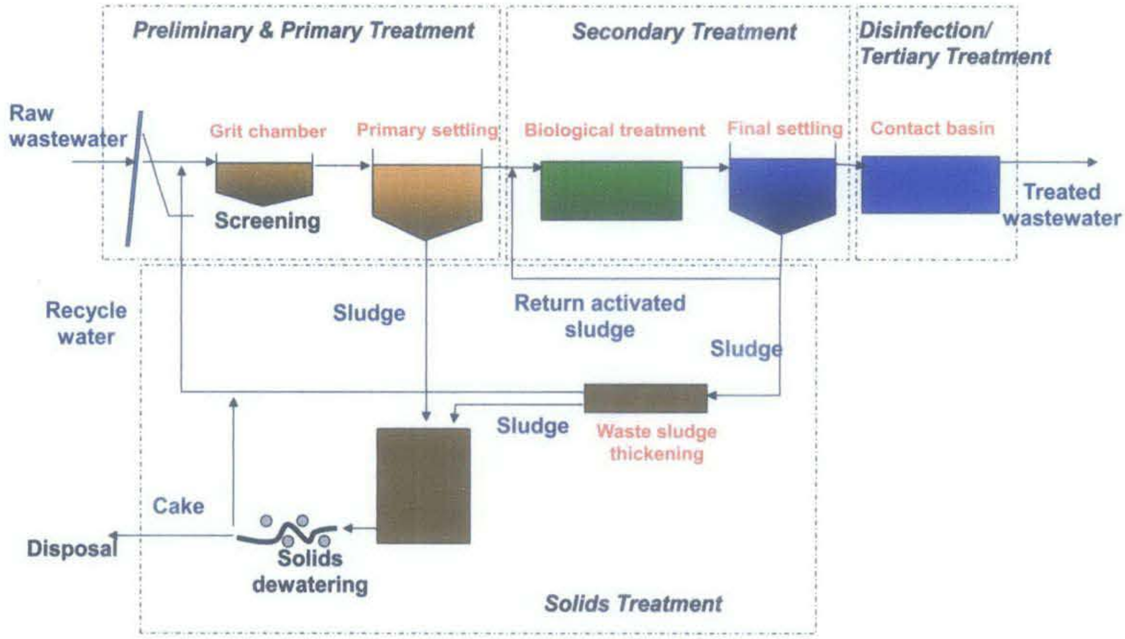

Figure 1: Conventional wastewater treatment process [2]

The levels of wastewater treatment and its function are presented in Table 1:

Table 1: Levels of wastewater treatment and its function [1]

Treatment level	Functions
Preliminary	Removal of wastewater constituents such as rags, sticks, floatables, grit, and grease that may cause maintenance or operational problems with the treatment operations, processes and ancillary systems.
Primary	Removal of a portion of the suspended solids and organic matter from wastewater.
Secondary	Removal of biodegradable organic matter and suspended solids.
Tertiary	Removal of residual suspended solids, usually by granular medium filtration or microscreens. Disinfection and nutrient removal is also included.

Treated wastewater should meet the regulations and standards set by respective local, state and federal authorities. For Malaysia, under Environmental Quality Act 1974: *Environmental Quality (Sewage) Regulations 2009*, the acceptable condition of sewage discharge for standard A and standard B are listed in Table 2.

Table 2: Acceptable conditions of sewage discharge for Malaysia Standard A and B [3]

Parameter	**Unit**	**Standard A**	**Standard B**
Temperature	°C	40	40
pH Value	-	6.0 – 9.0	5.5 – 9.0
BOD_5 at 20°C	mg/L	20	50
COD	mg/L	120	200
Suspended Solids	mg/L	50	100
Oil and Grease	mg/L	5	100
Ammoniacal Nitrogen (enclosed water body)	mg/L	5	5
Ammoniacal Nitrogen (river)	mg/L	10	20
Nitrate – Nitrogen (river)	mg/L	20	50
Nitrate – Nitrogen (enclosed water body)	mg/L	10	10
Phosphorous (enclosed water body)	mg/L	5	10

Note:

Standard A is applicable to discharge into any inland waters within catchment areas listed in the Third Schedule, while Standard B is applicable to any other inland waters or Malaysian waters.

1.1.2 Heavy Metals in Wastewater

Heavy metals are defined as metals, when in significant concentrations in water, that may pose detrimental health effects to human [4]. Heavy metals such as copper, zinc, cadmium and nickel are being widely used in a variety of electroplating, mining, smelters, tanneries, textile industry and chemical industries [5]. Various sources of heavy metals into water body are illustrated in Figure 2.

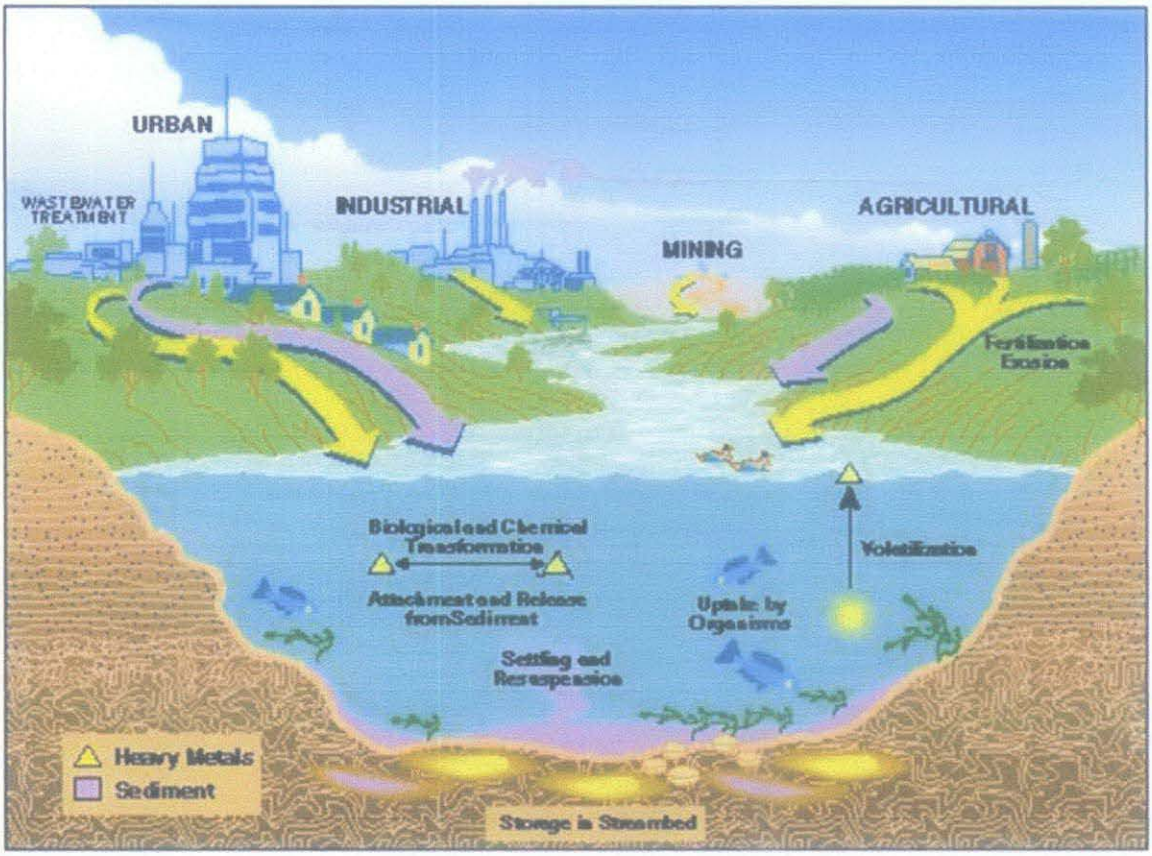

Figure 2: Sources of heavy metals into water body [6]

Copper is a type of heavy metal which is commonly found in wastewater discharged from textile processing, steel, pigments and dyes industries [3]. Copper is a major concern because it is highly toxic in aquatic environments and has effects in fish, invertebrates, and amphibians [7]. Excessive discharge of copper to the environment could lead to adverse health effects to human, such as anemia, liver and kidney damage, stomach and intestinal irritation [8].

Wastewater that contains copper has to undergo treatment processes prior to discharge to the environment. Copper concentration threshold of inhibitory effect on organisms and its discharge limits according to United States Environmental Protection Agency (EPA) and Malaysia Department of Environment (DOE) Environmental Quality Act (1974) are summarized in Table 3.

Table 3: Copper concentration threshold of inhibitory effect on organisms and its discharge limits

Metal	Symbol	Concentration threshold of inhibitory effect on organisms (mg/L) [1]	U.S. EPA Limit [1] (mg/L)	DOE M'sia EQA 1974 Standard A [3] (mg/L)
Copper	Cu	1.0	0.0049	0.20

1.2 Problem Statement

Many industries apply copper in their operation. The wastewater effluent from these industries contains organics matter as well as copper. One such industry is the textile industries. Effluent from textile industries contains biodegradable organic matters (ranging from 163 mg/L to 645 mg/L) and copper (ranging from 1.96 mg/L to 5.14 mg/L) [9].

Although various methods such as adsorption by activated carbon, ion exchange, reverse osmosis, chemical precipitation and nanofiltration have been employed to remove copper, these methods are expensive, unable to completely remove heavy metals and involve high energy and chemical consumption [10]. Besides, these methods are not capable to remove organics matter from wastewater satisfactorily.

Copper causes toxicity effects to microorganism [11]. The presence of copper reduces the efficiency of biological treatment system and causes effluent quality to deteriorate [11]. Excessive discharge of copper to the environment could lead to adverse health effects to human, such as anemia, liver and kidney damage, stomach and intestinal irritation [8].

1.3 Objectives

This research is aimed at proposing the use of biological treatment by Extended Aeration Activated Sludge (EAAS) system, dosed with Microwave Incinerated Rice Husk Ash (MIRHA) to remove copper from wastewater. Among the objectives include:

1. To evaluate the feasibility of MIRHA as heavy metal adsorbent in biological activated sludge system.

2. To determine if MIRHA can help in delaying the toxicity effects of copper in activated sludge system.

3. To investigate the impact of copper on Extended Aeration Activated Sludge system.

1.4 Scope of Study

The scope of this research is determined as below:

1. Medium strength synthetic wastewater with BOD 250 mg/L, dosed with copper (Cu) concentration ranging from 0.5 mg/L to 10.0 mg/L as influent.

2. MIRHA is made from rice husk obtained from BERNAS rice milling plant at Kg. Gajah, Perak, and incinerated in UTP microwave incinerator at 800°C for 2 hours.

3. The parameters of concern include influent and effluent COD, BOD, copper concentration, and biomass MLSS and MLVSS.

CHAPTER 2: LITERATURE REVIEW

Heavy metals are abundantly present in nature and are also added to water by man-induced activities such as manufacturing, construction, agriculture and transportation [12]. The present of potentially toxic heavy metals in the environment is very much a concern, primarily due to their non-biodegradability and persistence in the environment [13]. High concentrations of heavy metals in water supplies are undesirable as they may have potentially adverse effects on the health of organisms, the suitability of water for various purposes, the longevity of water and sewer networks, and the aesthetics of the environment [14]. Some metals are also known to be able to become concentrated in food chains through bioaccumulation [14]. Low concentrations of certain metals are harmless and traces are considered good for nutrition. Higher dosages of heavy metals may cause toxicity that is acute, chronic, synergistic, or mutagenic/ teratogenic [14].

2.1 Effects of Heavy Metals to Biological System

In a typical activated sludge system, microorganisms utilize organic matter in wastewater as substrates under aerobic conditions, removing the organic by microbial respiration and synthesis [12]. The microorganisms normally found in activated sludge system include bacteria (both single and multicellular), protozoa, fungi, rotifers and nematodes [12].

When the concentration of heavy metals increased in the wastewater, the activity of microorganism will decrease [12]. This is due to the toxicity effects of heavy metals to microorganism. Copper inhibitory concentration threshold to microorganism is 1.0 mg/L [1].

When dissolved heavy metals are present in sufficient concentration in the influent to a biological treatment system, the metals tend to accumulate in the system's biological treatment operations, and this may decrease the operating efficiency in removing organic matter and suspended solids [15]. This decrease in efficiency may also cause the metals concentration in the effluent to increase [12]. Thus the presence of heavy metal in biological treatment system will reduce the efficiency of the system in degrading organics and may cause effluent quality to deteriorate [15].

2.2 Heavy Metal Removal in Activated Sludge System

In conventional wastewater treatment, metal ions are removed through primary settling and in the activated sludge process. Primary settling removes a proportion of metals that are either insoluble or adsorbed onto the suspended solids [16].

In an activated sludge process, microorganisms biologically degrade materials and convert them into carbon dioxide, water, and cellular materials [17]. The microorganisms form aggregates or flocs and then pass into a settling tank for sedimentation [12]. Hence any metal that is adsorbed by the bacterial flocs may be partially removed from the water through a combination of microbial adsorption and sedimentation processes [12]. Factors which affect the settling properties of a mixed liquor such as loading rate, feed composition, mixing strength and sludge volume index will also affect its capacity to remove metals [17]. The concentration of metals in the solids sludge produced may be as much as twenty to thirty times greater than the concentration in the influent due to accumulation of metals [15].

Several heavy metal removal mechanisms in activated sludge system identified include:

a. Physical trapping or entrapment of precipitated metals in the sludge floc matrix [18, 19]

   At high metal concentrations, when most of the metal present in insoluble form, metal might be physically entrapped or entangled in the biological floc matrix [18]. However this does not differentiate between precipitated metals that settled independently and removed with the sludge fraction or precipitated metals that interact with the floc matrix and become physically entrapped during the settling of the flocs [18]. Metal retention in activated sludge is believed to occur through ion exchange, sorption, chelation or precipitation [19]. Most of the metals that are precipitated, adsorbed to the biological floc, or dissolved in the liquid fraction of the sludge would be removed during sedimentation in the final clarifier [19].

b. Binding of soluble metal to extracellular polymers [17, 20]

Many species of bacteria that are present in the mixed liquor of an activated sludge system produce extracellular polymers [17]. The polymers are in the form of slime or microcapsules that form a cohering layer and adhere to cell walls [17].

c. Accumulation of soluble metal by the cell [21]

Soluble metal can also be accumulated in living organisms and to varying degrees for different elements [21]. Activated sludge bacteria that do not produce capsules or extracellular materials accumulate the metals in their cytoplasm or by adsorption onto the cell wall [21]. The cell walls of most microorganisms will have slight negative charge, where positively charged metals will adsorb to the cell wall [21].

2.3 Heavy Metal Removal by Adsorption

Adsorption may be defined as adhesion, in an extremely thin layer, of gas molecules, dissolved substances, or liquids to the surface of solids with which they are in contact [22]. Adsorption may occur through physical, chemical, or ion-exchange processes [22].

Physical adsorption on the external surface of a particle is based in Van der Waals forces of attraction. Chemical adsorption is characterized by the formation of chemical associations or bonds between ions or molecules from solution and the surfaces of particles, which is mainly covalent [22, 23]. Ion exchange based adsorption is a chemical process whereby a negative or positive charge on a particle surface is equalized by ions possessing opposite charges [12].

Adsorption and precipitation are the most commonly used heavy metals removal methods in wastewater treatment. Studies [24-27] have found that most industries prefer precipitation over adsorption. However, hydroxide precipitation is not an effective heavy metal removal method [24]. A major drawback with hydroxide precipitation is sludge production [28], which requires post treatment and handling.

On the other hand, adsorption process has not been used extensively in wastewater treatment, but demands for a better quality of treated wastewater effluent, including toxicity reduction, have led to an intensive examination and use of the process of adsorption [1]. Studies on the treatment of effluent bearing heavy metal have revealed adsorption to be a highly effective technique for the removal of heavy metal from waste stream and activated carbon has been widely used as an adsorbent [29].

2.3.1 Activated Carbon

In the activated carbon metal adsorption process, metal contaminates waste could be "cleaned" by passing it through a series of packed bed filters containing activated carbon [15]. The carbon adsorbs the metal ions by a surface attraction / chemical bonding phenomenon [15].

Powdered activated carbon has also been used in Powdered Activated Carbon Treatment (PACT) systems where powdered activated carbon and bacteria are maintained in an aerobic or anaerobic treatment process [30]. In this process, physical adsorption and biological assimilation occur simultaneously, enabling synergistic treatment to occur [30]. The carbon "buffers" the biological system against the effect of toxic organics in the wastewater [30]. This buffering capacity ensures optimum performance of the biological system [30]. The PACT process may improve VOC / odour removal, sludge settleability / thickening / dewatering characteristics, and reduce effluent toxicity [30].

Activated carbon enhancement appears to include the mechanisms of improved buffering, increased biological surface area, decreased sensitivity to toxic substances, improved phase separation, and adsorption [31].

It is believed that the powdered adsorbent is able to absorb and desorb the organics in the wastewater and thereby dampen any load variations that may occur. Also, the adsorbent provides surface area for bacterial attachment and growth, resulting in a high concentration of biomass available for the conversion of the organics in the wastewater [31].

A major disadvantage of sludge process that is enhanced by powdered adsorbents is the cost of the adsorbent medium. Typically, for every pound of biomass an equivalent amount of powdered adsorbent is required [31]. Despite its extensive use in the water and wastewater treatment industries, activated carbon remains an expensive material [15, 32].

2.3.2 Agriculture By-products

In recent years, the need for safe and economical methods for the elimination of heavy metals from contaminated waters has necessitated research interest towards the production of low cost alternatives to commercially available activated carbon [32].

Various low cost agriculture by-products such as rice husk, sawdust, soybean hulls, cottonseed hulls, and sago waste have been studied to determine their capability to remove copper from wastewater [32]. The copper removal efficiency by these agriculture by-products is summarized in Table 4.

Table 4: Copper removal efficiency by various agriculture by-products [32]

Adsorbent	Cu (II) Removal Efficiency (%)
Rice Husk (Water and HCI washed)	80
Tartaric acid modified rice husk	>80
Rice husk carbon`	≈100
Tree sawdust	86
Soybean hulls	99.7
Cottonseed hulls	98.8
Sago waste	>75

The sorption capacity of various agriculture by-products is dependent on the type of adsorbent and the nature of the wastewater treated [32]. Study [32] concluded that these inexpensive, effective and readily available agricultural by-products hold great potential as adsorbents in heavy metals removal from wastewater.

2.3.3 Microwave Incinerated Rice Husk Ash (MIRHA)

Rice milling generates a byproduct known as husk that surrounds the paddy grain. During milling of paddy about 78 % of weight is received as rice, broken rice and bran. The other 22 % of the weight of paddy is received as husk. This husk is used as fuel in the rice mills to generate steam for the boiling process. During the burning process 75% of the organic volatile matter will be burned off while the remaining 25% is converted into rice husk ash (RHA) [33].

Rice husk have a very high silica content, and slow firing at a temperature of 500°C to 700 °C results in the formation of an amorphous material with a porous structure [34]. This RHA contains around 85% - 90% amorphous silica [35]. From the result of X-ray fluorescence (XRF) test [36], it is indeed concluded that MIRHA is having high silicon oxide (SiO_2) content (75.8%).

MIRHA is produced by burning rice husk ash at 800°C for 2 hours in a microwave incinerator. Study [36] has proved that MIRHA is capable to remove Cadmium (Cd), which is a type of heavy metal, from synthetic wastewater by batch adsorption process. Optimum pH for Cd removal is pH 4 (70% removal efficiency) [36].

In another research to study the effectiveness of MIRHA as adsorbent, MIRHA has been proven to be effective in removing Cu(II), Zn(II), COD and Color from treated POME wastewater with approximately 88%, 74%, 41%, and 88% removal, respectively[37].

Study [37] also concluded that the percentage removals of Cu(II), Zn(II) increased as dosage of MIRHA and contact time increased. The heavy metals removed by MIRHA and its optimum condition are summarized in Table 5.

Table 5: Heavy metals removed by MIRHA and its optimum condition

No.	Heavy metal	Removal Efficiency (%)	Optimum Condition	References
1	Cadmium	70	pH 4	[36]
2	Copper	88	50000 mg/L, 12 hour contact time	[37]
3	Zinc	74	50000 mg/L, 18 hour contact time	[37]
4	COD	41	40000 mg/L, 6 hour contact time	[37]
5	Colour	88	50000 mg/L, 6 hour contact time	[37]

Study [11] concluded that activated rice husk (ARH) can be used as an alternate adsorbent to powdered activated carbon (PAC) in the simultaneous adsorption and biodegradation wastewater treatment process for the removal of Cu(II).

2.4 Extended Aeration Activated Sludge (EAAS)

EAAS operates in the endogenous respiration phase of the growth curve, which requires a low organic loading and long aeration time [1]. The ideal growth curve of activated sludge at extended aeration phase is shown in Figure 3. An overview of the EAAS treatment system is presented in Figure 4.

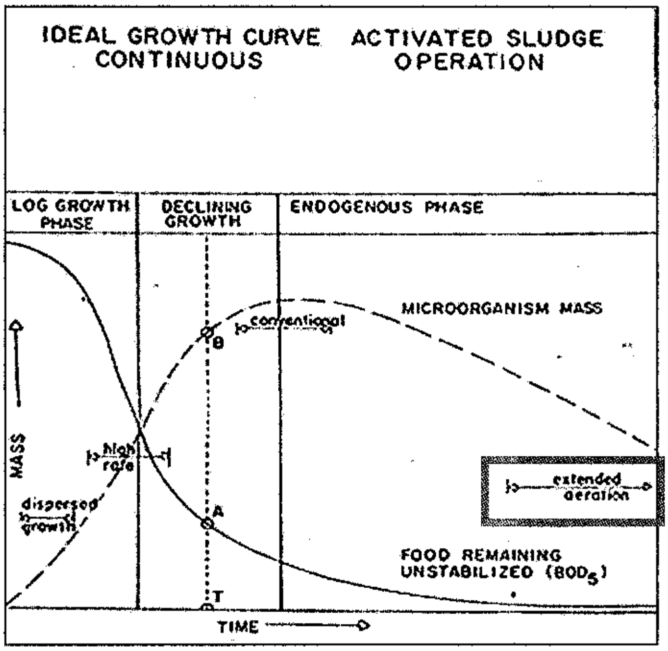

Figure 3: Ideal growth curve of activated sludge at extended aeration phase [38]

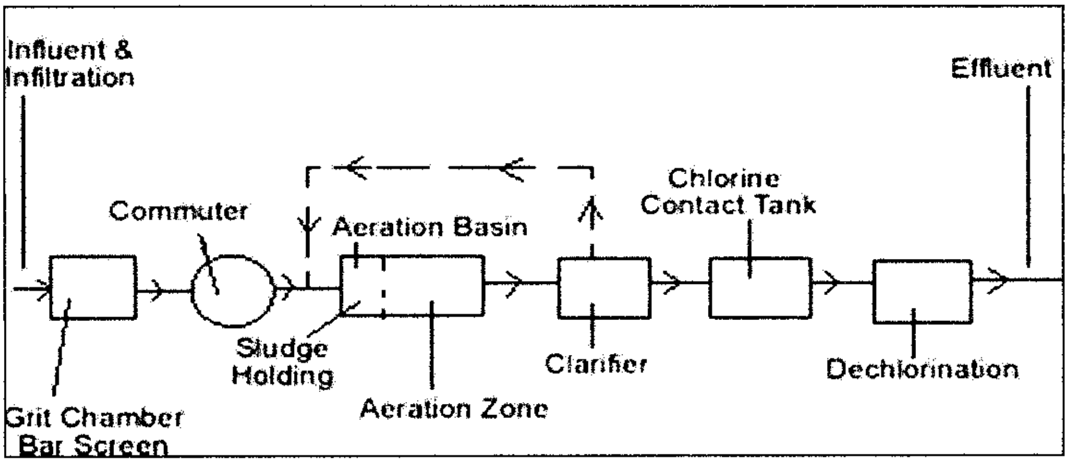

Figure 4: Overview of EAAS system [38]

Among the advantages of EAAS system include [39]:

a. Less sludge to be disposed
b. No further treatment needed for sludge
c. Excellent quality effluent (Suitable for ultimate reclamation)

Typical design parameters for EAAS are shown in Table 6.

Table 6: Typical design parameters for EAAS [1]

Design Parameters	Typical Value
Solid Retention Time, day	20-40
F/M ratio, MLVSS.d	0.04-0.10
Volumetric loading, kgBOD/ m^3.d	0.1-0.3
MLSS, mg/L	2000-5000
Hydraulic Retention Time, h	20-30
RAS, % of influent	50-150

The main reason for the system to be operated at long solid retention time is to promote nitrification and denitrification process, which encourages the rapid growth of slow growing bacteria such as *nitrosomonas* and *nitrobacter*.

The following conditions are essential to ensure that the microorganisms present in the floc or activated sludge are in a state of proper growth and, therefore, working at maximum efficiency [38]:

1. A continuous supply of sewage with a uniform and nutritionally adequate organic content. A highly variable organic load to the plant would be undesirable.

2. A complete mixing of incoming wastewater and the microorganisms present in the aeration basin (diffused aeration).

3. A continuous supply of dissolved oxygen as supplied by the blower (diffused aeration).

4. A settling tank (clarifier) where separation of mixed liquor solids from the liquid carrier is completely and efficiently carried forth.

CHAPTER 3: METHODOLOGY

3.1 Research Methodology

The purpose of this research is to assess the feasibility of MIRHA as potential adsorbent for the removal of copper in continuous flow activated sludge system. The research methodology is summarized in Figure 5 below:

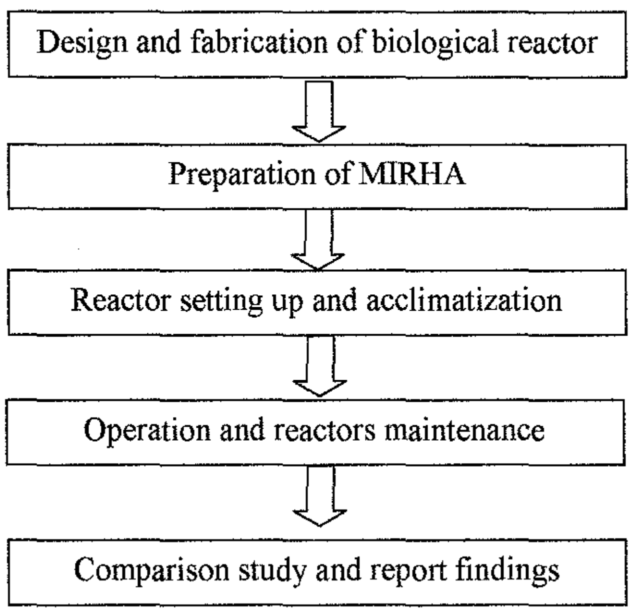

Figure 5: Research Methodology

3.2 Project Activities

3.2.1 Design and Fabrication of Biological Reactor

2 identical biological reactors made up of Perspex are used to carry out the research. One is for control purposes (Reactor A) and another as manipulation (Reactor B). The properties of biological reactor are tabulated in Table 7. Figure 6 and Figure 7 show the 3D perspective view and actual view of biological reactor respectively.

Table 7: Properties of Biological Reactor

No.	Properties	Parameter
1	Overall dimension	375mm (L) x 170mm (W) x 25mm (H)
2	Aeration compartment	300mm (L) x 160mm (W) x 180mm (H)
3	Freeboard	40mm
4	Aeration tank volume	8.0 L

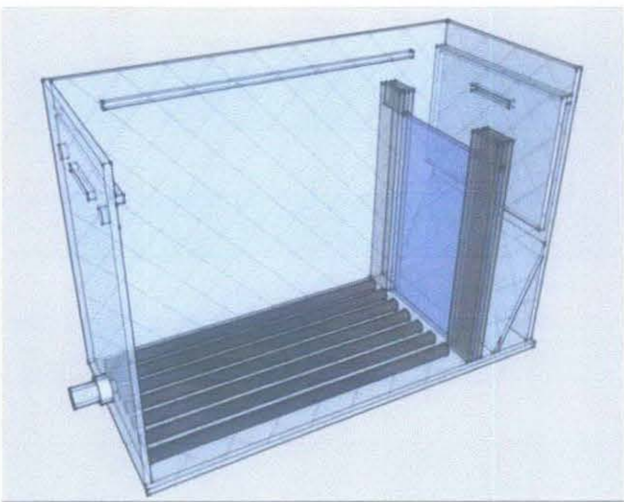

Figure 6: Reactor 3D perspective view

Figure 7: Reactor actual view

3.2.2 Preparation of MIRHA

Rice husk for producing MIRHA was obtained from BERNAS factory in Kg. Gajah. It was thoroughly washed with distilled water to remove dirt and was dried at $105^{0}C$ for 2 hours. It was then incinerated at 800°C for 2 hours in microwave furnace (Figure 8). Burning the rice husk at high temperature will increase the SiO_2 content but it is not suggested to burn rice husk above 800°C longer than one hour, because it tends to cause a sintering effect (coalescing of fine particles) and is indicated by a dramatic reduction in the specific surface [40].

Figure 8: Microwave furnace for the incineration of rice husk

Finally, the MIRHA was powdered by undergoing 3000 cycles of Los Angeles Abrasion machine (Figure 9) and stored in desiccators for future use. Figure 10 shows the final product of MIRHA.

Figure 9: MIRHA grinded by Los Angeles Abrasion machine

Figure 10: Final Product of MIRHA

3.2.3 Preparation of Synthetic Wastewater

In the continuous flow study, synthetic wastewater is used as the baseline wastewater to all reactors to ensure a consistent influent wastewater quality.

Purina Alpo High Protein Puppy Dog Meal is used to simulate raw municipal wastewater. The recipe involves grinding the Dog Meal in a blender for approximately 5 minutes. 600 mg/L grinded Dog Meal powder is then measured and added into the influent tank, together with 0.15 ml/L of phosphate buffer (same phosphate buffer used for the BOD dilution water). Several tests are conducted to verify the characteristics of synthetic wastewater. The characteristics of synthetic wastewater with comparison to typical medium strength wastewater are tabulated in Table 8.

The influent is kept suspended and well mixed in the influent tank using aquarium pump. Influent is pumped into biological reactors using Masterflex digital peristaltic pumps.

Table 8: Characteristic of Synthetic Wastewater

Parameter	Approximate Reading (mg/L)	Typical Medium Strength Wastewater Composition (mg/L) [1]
COD	500	430
BOD_5	250	190
TSS	300	210
TKN	73	70
Ammonia	2	25
Nitrate	1	0
Phosphorus	10	7
Minimum C : N : P	100 : 24 : 3	100:5:1

It is observed that the ammonia content in the synthetic wastewater is much lower than typical medium strength wastewater value. However since ammonia will be produced during the degradation of organic matters in biological treatment stage, the ammonia is predicted to be increase in aeration tank.

3.2.4 Experimental Methodology

Biological reactors were set up in UTP Environmental Engineering Laboratory, Block 14-02-10. The reactor setting up picture is shown in Figure 11. Hydraulic test were conducted to ensure all piping and connections are functioned properly without leaking.

Figure 11: Biological Reactor A (left) and B (right) setting up in laboratory

The operating parameters of biological reactors are listed in Table 9.

Table 9: Operating parameters of biological reactors

No.	Properties	Parameter
1	Influent flow rate	7 L/d
2	Mixed liquor temperature	20 °C
3	Minimum dissolved oxygen	2.0 mg/L
4	Sludge age	40 days
5	bCOD/BOD ratio	1.6
6	F/M ratio	0.085
7	BOD volumetric loading	0.2 kg BOD / m^3.d

There were a total of 7 phases involved in the research:

Phase 1: Acclimatization (Day 1 - 15)

Phase 2: Addition of MIRHA adsorbent (Day 16 - 25)

Phase 3: Copper dosage 0.5 mg/L (Day 26 - 33)

Phase 4: Copper dosage 1.0 mg/L (Day 34 - 45)

Phase 5: Copper dosage 2.0 mg/L (Day 46 - 57)

Phase 6: Copper dosage 5.0 mg/L (Day 58 - 63)

Phase 7: Copper dosage 10.0 mg/L (Day 64 - 72)

35L of influent synthetic wastewater was prepared every day and fed into reactor at flow rate of 7L / day. Copper is dosed in the form of copper sulfate ($CuSO_4$) solution. Effluent tank is cleaned every day after effluent samples have been collected.

During Phase 1 of acclimatization phase, biomass was fed with synthetic wastewater as described in Section 3.2.3 for 15 days.

During Phase 2, 2000 mg/L MIRHA adsorbents were added into the reactor. The purpose is to ensure that biomass is adapted to the presence of MIRHA adsorbents without causing shock effect. The concentration of MIRHA was maintained at 2000 mg/L throughout Phase 2, by adding MIRHA to the aeration basin daily, taking into consideration the MIRHA wasted daily in the waste sludge and MIRHA discharged into the effluent.

From Phase 3 onward, 100 mg/L MIRHA was added daily into aeration basin of Reactor B. The purpose is to prevent MIRHA adsorbent from reaching the break point, at which break point is defined as the time when the adsorbent has become saturated with adsorbate.

During Phase 1 and 2 the sludge age was controlled through daily sludge recycling and wasting. However from Phase 3 onward biomass is only recycled without wasting to ensure maximum growth of biomass to cushion for copper toxicity.

Parameters as outlined in Table 10 are monitored throughout the 7 phases.

Table 10: Parameters monitored and laboratory test frequency

No.	Parameter	Sample			Frequency
		Influent	Effluent	Biomass	
1	COD	Y	Y		Once every two days
2	BOD_5	Y	Y		
3	Cu (II)	Y	Y		
4	MLSS			Y	
5	MLVSS			Y	

All of the laboratory tests conducted are in accordance to Standard Methods for the Examination of Water and Wastewater (American Public Health Association 1995).

3.3 Key Milestone

Activities	Week																											
	FYP I														FYP II													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Topic Selection	■																											
Preliminary research (Literature Review, Methodology, Planning, Budget, Timing)		■	■	■	■																							
Submission of Extended Proposal						■																						
Proposal defence							■	■																				
Preparation of Interim Report									■	■	■	■	■															
Submission of Interim Report														■														
Project Work commences															■	■	■	■	■	■	■	■	■	■				
Submission of Progress Report																						■						
Pre-EDX																									■			
Submission of Draft Report																										■		
Submission of Technical Paper																											■	
Oral Presentation																												■
Submission of Project Dissertation																												■

3.4 Gantt Chart

Activities	Week																											
	FYP I														FYP II													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Preliminary planning	■	■	■	■																								
Reactor Design					■																							
Reactor Fabrication						■																						
Purchasing of chemicals, consumables							■																					
Setting-up of reactors in laboratory								■	■																			
Reactor commencement & acclimatization									■	■	■	■	■	■														
Characterization of synthetic wastewater										■	■	■																
Preparation of GWTPS & MIRHA													■	■														
Laboratory works: Vary dosage of adsorbents and heavy metals															■	■	■	■	■	■	■	■	■	■				
Results compilation and analysis																					■	■						
Pre-EDX																							■	■				
Report writing & Presentation																									■	■	■	■

3.5 Tools and Equipment

Tools used for the research works are summarized in Table 11.

Table 11: Tools used

No.	Tools	Quantity
1.	Masterflex digital peristaltic pumps	1 unit
2.	Masterflex tube size 16	4 meter
3.	Acrylic glass models – Biological reactors	2 units
4.	Influent tank mixer	1 unit
5.	Tube diffusers	48 units
6.	15 gallons sample containers	2 units
7.	Effluent containers	2 units

CHAPTER 4: RESULT AND DISCUSSION

4.1 Removal of Copper Heavy Metal

Copper test was carried out according to USEPA Bicinchoninate method for powder pillows (Method 8506). The influent copper level is presented in Figure 12.

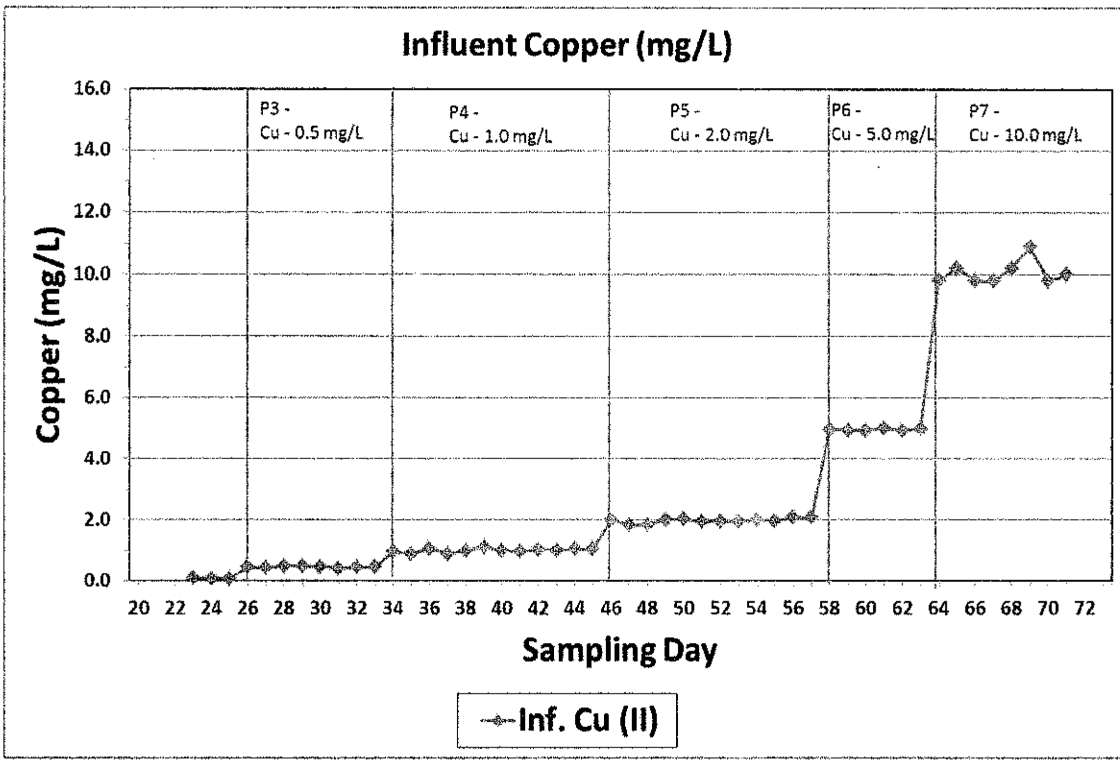

Figure 12: Influent Copper (mg/L)

Copper is dosed in the form of copper sulfate ($CuSO_4$) solution. Copper is dosed daily in the influent, and well mixed with synthetic wastewater. Copper is dosed starting from Phase 3 onwards, with increase in dosage gradually to ensure that microbes are acclimatized to the copper toxicity. This is to prevent shock effect due to sudden increase in copper toxicity which could result in dying of microbes.

Effluent copper result for Reactor A and B is presented in Figure 13. The average effluent copper and percent removal is presented in Table 12.

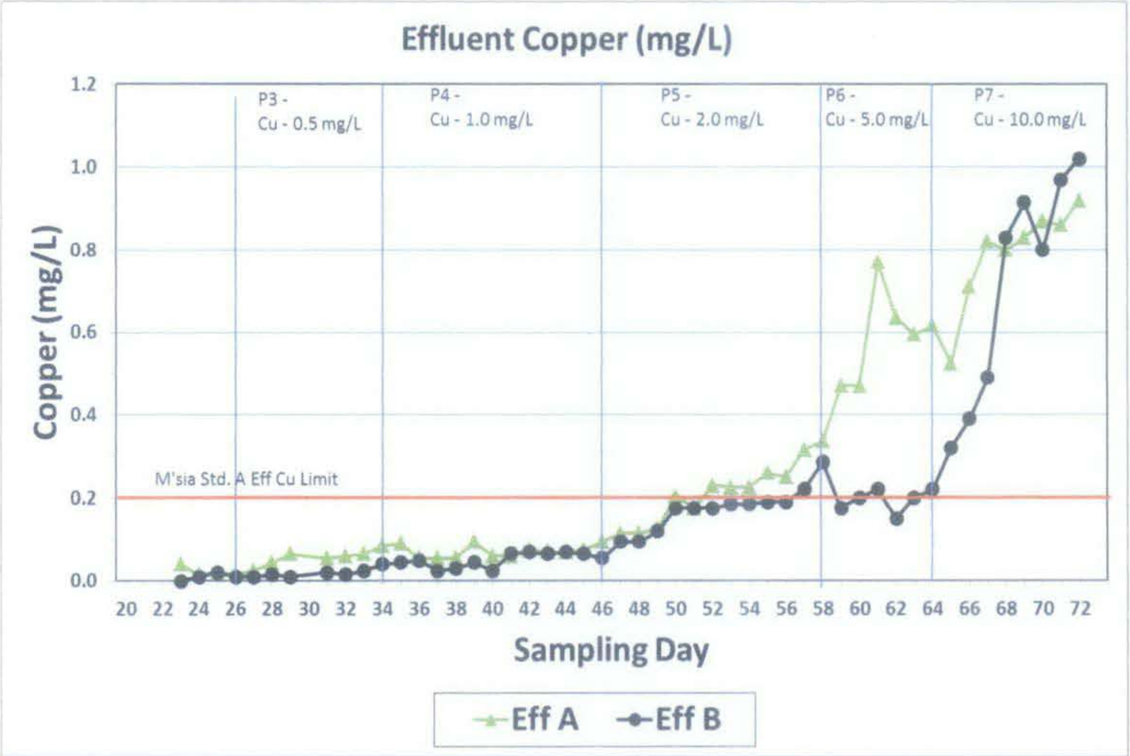

Figure 13: Effluent copper (mg/L)

Table 12: Average effluent copper value and removal efficiency

Phase	Day	Inf. Cu (mg/L)	Eff. A, mg/L (% removal)	Eff. B, mg/L (% removal)
3	26 - 33	0.5	0.047 (91%)	0.015(97%)
4	34 – 45	1.0	0.071 (93%)	0.051(95%)
5	46 – 57	2.0	0.215 (89%)	0.174 (91%)
6	58 – 63	5.0	0.593 (88%)	0.194 (96%)
7	64 – 72	10.0	0.792 (92%)	0.717 (93%)

It is observed that in Phase 3 where copper of 0.5 mg/L was added from day 26 – 33, the copper level in effluent A is always higher than B. Average copper in Eff. A is 0.047 mg/L, while Eff. B is 0.015 mg/L. This gives a 90.6% removal efficiency for A and 97% for B.

While in Phase 4 where 1.0 mg/L copper was added from day 34 – 45, average copper in Eff. A is 0.071 mg/L, and Eff. B is 0.051 mg/L. This gives a 92.9% removal efficiency for A and 94.9% for B. The improved performance in A may be attributed to the acclimatization of biomass, where the biomass has adjusted to the gradual increase in copper level. Note also that although the copper concentration threshold of inhibitory effect on organisms is 1.0 mg/L (Metcalf and Eddy, 2004), the acclimatization to copper certainly helped the survival of biomass in Reactor A at copper concentration 1.0 mg/L.

Reactor A started to show sign of stress during Phase 5 where 2.0 mg/L copper was added from day 46 – 57. Average copper in Eff. A is 0.215 mg/L, and Eff. B is 0.174 mg/L. This gives a 89.3% removal efficiency for A and 91.3% for B. It is observed that Eff. A has violated Malaysia's DOE Environmental Quality Act (1974) Standard A copper discharge limit of 0.2 mg/L.

Eff. A copper level rose steeply during Phase 6 where 5.0 mg/L copper was added from day 58 – 63. Average copper in Eff. A is 0.593 mg/L, and Eff. B is 0.194 mg/L. This gives a 88.1% removal efficiency for A and 96.1% for B. MIRHA adsorbents has indeed helped in the reduction of copper as evidenced in Reactor B, where Eff. B copper level is still within confinement of Malaysia's DOE Environmental Quality Act (1974) Standard A.

Both Reactor A and B effluent copper level shoot up during Phase 7 where 10.0 mg/L copper was added from day 64 – 70. Average copper in Eff. A is 0.792 mg/L, and Eff. B is 0.717 mg/L. This gives a 92% removal efficiency for A and 93% for B.

In conclusion, the result shows that MIRHA is capable to assist in removal of copper up to 5.0 mg/L Inf. Copper. This is comparatively better than control reactor, which already violated Malaysia's DOE Environmental Quality Act (1974) Standard A effluent copper limit of 0.2 mg/L when 2.0 mg/L influent copper is added during Phase 4. Thus, MIRHA adsorbent has prolonged the survival of microbes toward copper toxicity from 2.0 mg/L to 5.0 mg/L.

4.2 Removal of Organic Matters (TCOD)

The performance of the activated sludge processes in removing organic matters is measured in terms of Total Chemical Oxygen Demand (TCOD) and Biochemical Oxygen Demand (BOD). TCOD test was carried out by the Reactor Digestion method using Hach Method 8000. Throughout the 72 days of monitoring period, the average TCOD of influent is reported to be 485 mg/L. The influent TCOD result is presented in Figure 14. The influent TCOD value fluctuates between 400 mg/L to 600 mg/L throughout 72 days research period.

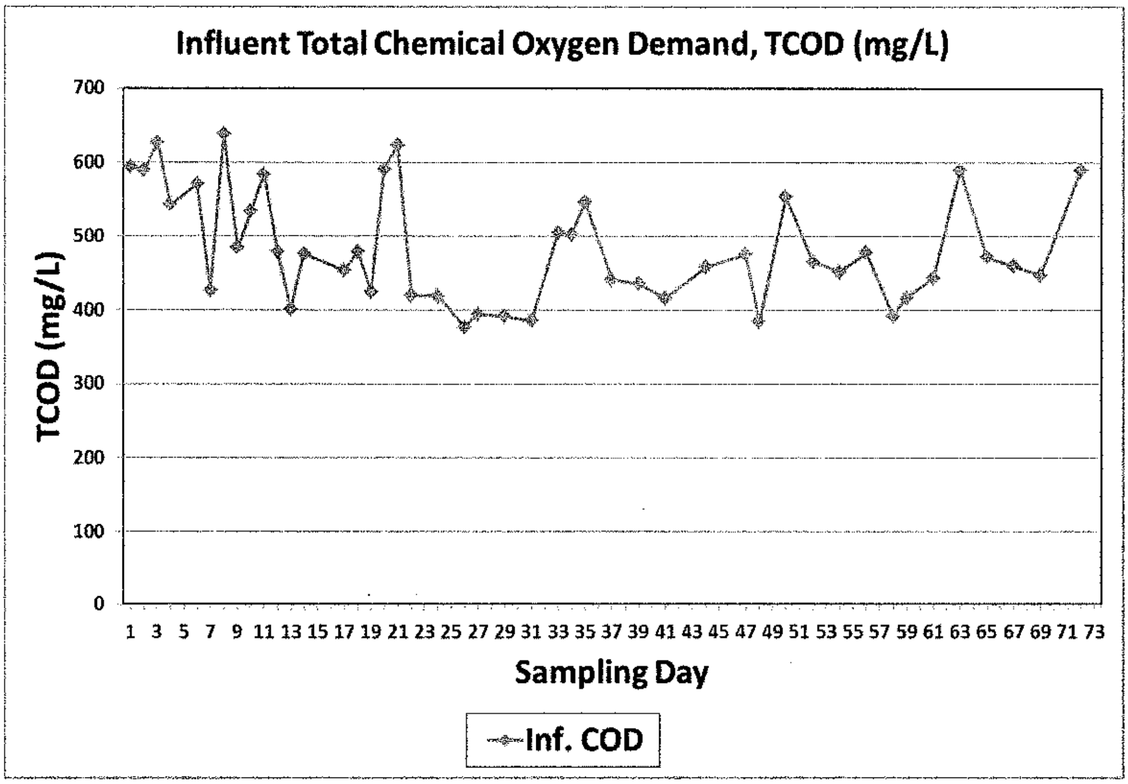

Figure 14: Influent TCOD (mg/L)

The effluent TCOD result for Reactor A and B is presented in Figure 15. Average Effluent TCOD value for Reactor A and B according to phases is presented in Table 13.

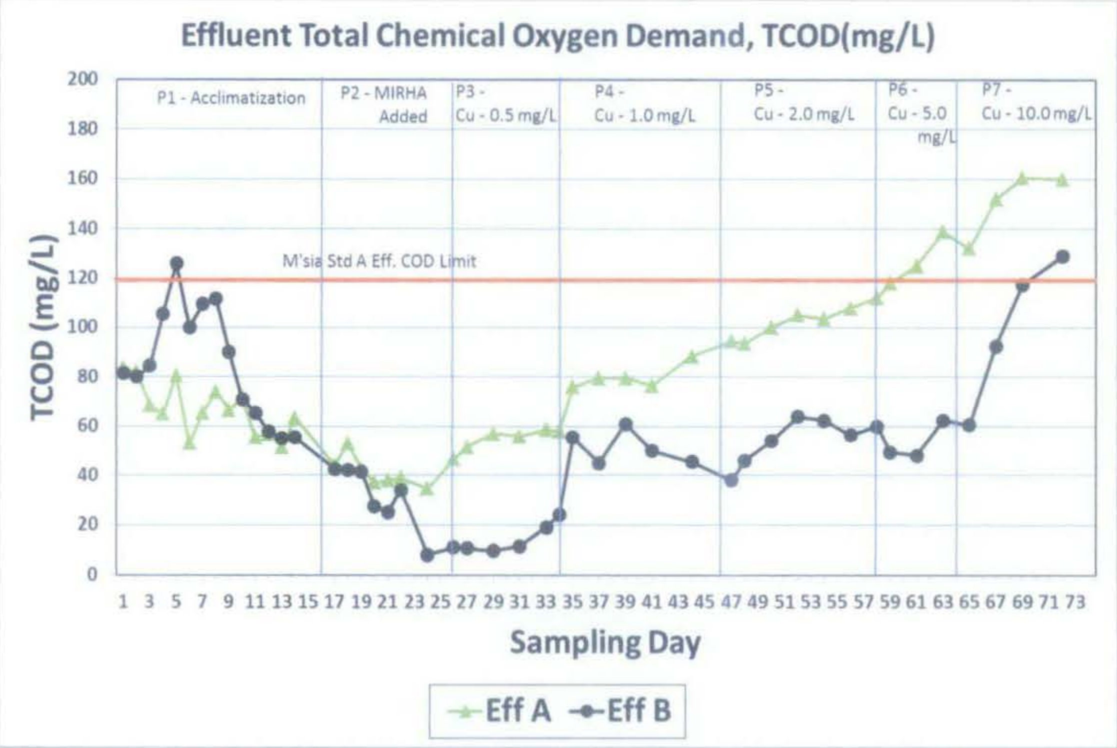

Figure 15: Effluent TCOD (mg/L)

Table 13: Average effluent TCOD value and removal efficiency

Phase	Day	Inf. Cu (mg/L)	Eff. A COD, mg/L (% removal)	Eff. B COD, mg/L (% removal)
1	1 – 15	0.0	67 (87%)	85 (83%)
2	16 - 25	0.0	42 (91%)	32 (93%)
3	26 - 33	0.5	56 (88%)	15 (97%)
4	34 – 45	1.0	80 (84%)	51 (89%)
5	46 – 57	2.0	102 (79%)	54 (89%)
6	58 – 63	5.0	127 (74%)	55 (89%)
7	64 – 72	10.0	151 (70%)	100 (80%)

During Phase 1 and Phase 2 of acclimatization phase, the Effluent COD for both Reactor A and B show significant improvement from Day 1 to Day 25. Phase 2 is considered stabilized phase where biomass has acclimatized to synthetic wastewater. The average Eff. A TCOD value in Phase 2 is 42 mg/L, which gives a 91% removal effieciency. While average Eff. B TCOD value is 32 mg/L during Phase 2, or 93% removal efficiency.

During Phase 3 where copper of 0.5 mg/L was added from day 26 – 33, average TCOD Eff. A rose to 56.2 mg/L (88% removal efficiency). In contrast, average COD Eff. B declined to 14.9 mg/L (97% removal efficiency). This has proven that MIRHA has indeed assisted in the TCOD removal in activated sludge in Phase 3.

During Phase 4 where 1.0 mg/L copper was added from day 34 – 45, average TCOD Eff. A continue to rise to 80 mg/L. This converts to 84% removal efficiency for Reactor A. On the other hand, Reactor B also saw an increase of effluent TCOD to 51.4 mg/L (89% removal).

As research proceeded to Phase 5 where 2.0 mg/L copper was added from day 46 – 57, average TCOD Eff. A rose to 102 mg/L (79% removal). While average COD Eff. B rose slightly to 54.4 mg/L (89% removal).

Average TCOD Eff. A exceeded Malaysia Standard A limit of 120 mg/L as the research proceeded into Phase 6, where 5.0 mg/L copper was added from day 58 – 63. Average TCOD Eff. A stood at 127 mg/L during Phase 6, or 74% removal efficiency. Interestingly, average TCOD Eff. B maintained at 55 mg/L, a mere increase of 0.6 mg/L from Phase 5, suggesting MIRHA has assisted microbes to cope well with the increase of Inf. Copper from 2.0 mg/L to 5.0 mg/L.

Both Effluent A and B COD value shoot beyond Standard A limit during Phase 7. Eff. B TCOD value increased drastically, suggesting MIRHA could not help in the TCOD removal when 10.0 mg/L influent copper is added. As of Day 72, the last day of research, Eff. A TCOD value stood at 160 mg/L, while Eff. B TCOD value stood at 129 mg/L.

In conclusion, MIRHA adsorbent has helped to delay copper toxicity effect, in term of TCOD removed, by helping to extend microbes copper inhibitory level, from 2.0 mg/L to 5.0 mg/L.

4.3 Removal of Organic Matters (BOD)

Biochemical oxygen demand (BOD) is the amount of dissolved oxygen needed by aerobic microorganism to break down organic matter presents in water sample. BOD value is expressed in milligrams of oxygen consumed per litre of sample during 5 days of incubation at 20 °C. The BOD_5 value for influent is presented in Figure 16.

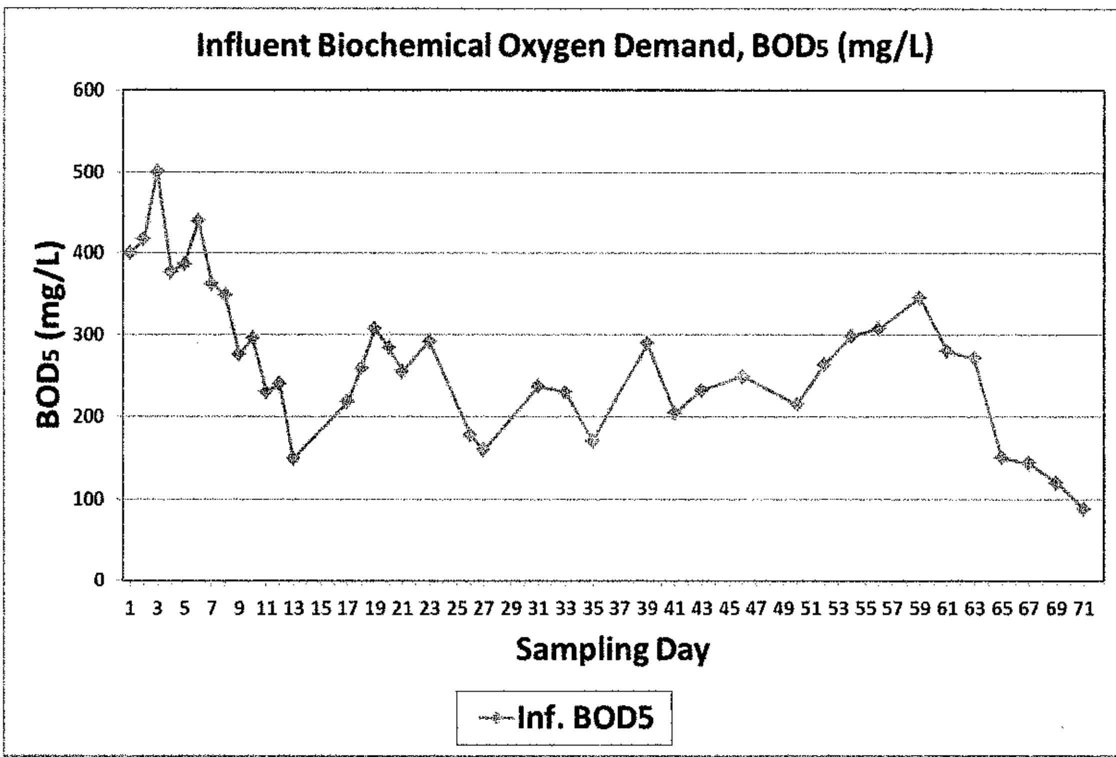

Figure 16: Influent BOD_5 (mg/L)

Average influent BOD_5 is recorded to be 250 mg/L, taking the average value recorded from Phase 2 (after stabilization) to Phase 6. Influent BOD_5 value saw a decrease in Phase 7 (Day 64 - 72), most probably caused by the toxicity of 10.0 mg/L copper. The copper toxicity has caused the dying of microbes in BOD bottle, resulting in the reduction of Dissolved Oxygen depletion, hence a lower BOD_5 value.

The effluent BOD_5 result for Reactor A and B is presented in Figure 17. Average effluent BOD_5 value for Reactor A and B according to phases is presented in Table 14.

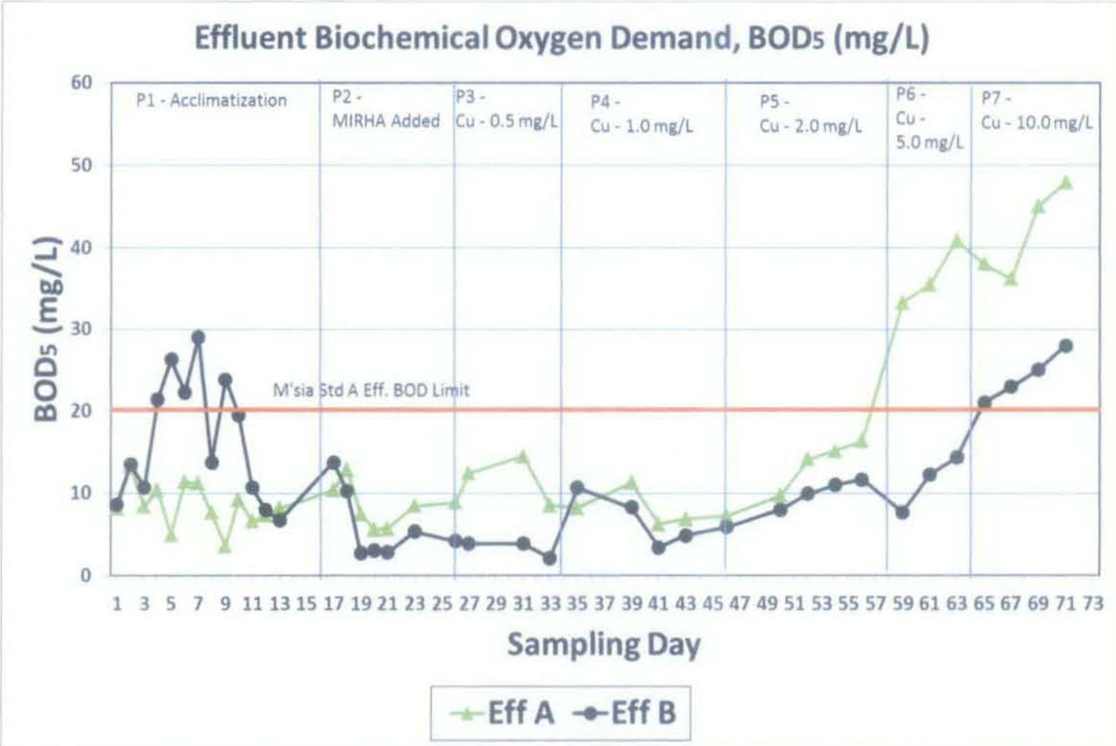

Figure 17: Effluent BOD_5 (mg/L)

Table 14: Average effluent BOD_5 value and removal efficiency

Phase	Day	Inf. Cu (mg/L)	Eff. A BOD_5, mg/L (% removal)	Eff. B BOD_5, mg/L (% removal)
1	1 – 15	0.0	9 (96%)	17 (93%)
2	16 - 25	0.0	9 (96%)	6 (98%)
3	26 - 33	0.5	12 (95%)	4 (98%)
4	34 – 45	1.0	8 (97%)	7 (97%)
5	46 – 57	2.0	14 (94%)	11 (96%)
6	58 – 63	5.0	37 (85%)	12 (95%)
7	64 – 72	10.0	42 (83%)	24 (90%)

Effluent BOD_5 value experienced a huge fluctuation in Phase 1, as the microbes were in the process of acclimatization to the synthetic wastewater. Effluent BOD_5 becomes stabilized in Phase 2. Reactor B slightly outperformed Reactor A in Phase 2, suggesting MIRHA assistance in microbes organic matter removal.

Eff. A BOD_5 rose to 12 mg/L in Phase 3, contributed by copper toxicity. In contrast, Eff. B BOD_5 declined to 4 mg/L, contributed by MIRHA adsorbent in Cu removal.

Eff. A BOD_5 dropped to 8 mg/L in Phase 4, implying microbes have been acclimatized to copper toxicity effect of 1.0 mg/L. Although theoretically microbes should have been dying at copper concentration of 1.0 mg/L, acclimatization throughout Day 1 – 33 has built the tolerance of microbes to copper toxicity effect.

Eff. A BOD_5 took a turn and rose to 14 mg/L in Phase 5; while Eff. B BOD_5 continue to rise to 11 mg/L.

Eff. A BOD_5 value violated the limit set by Malaysia DOE Standard A of 20 mg/L as the research progressed into Phase 6. Eff. A BOD_5 value stood at 37 mg/L. On the other hand, Eff. B BOD_5 value is still within acceptable limit, recorded a value of 12 mg/L.

Both Eff. A and Eff. B BOD_5 value shoot up above Standard A limit of 20 mg/L in Phase 7. Eff. A BOD_5 value stood at 42 mg/L; while Eff. B BOD_5 value stood at 24 mg/L.

In conclusion, MIRHA adsorbent has helped to prolong survivability of microbes toward copper toxicity from 2.0 mg/L to 5.0 mg/L.

4.4 MLSS and MLVSS

The mixture of solids resulting from combining recycled sludge with influent wastewater in the bioreactor is termed mixed liquor suspended solids (MLSS). MLSS variation is plotted in Figure 18.

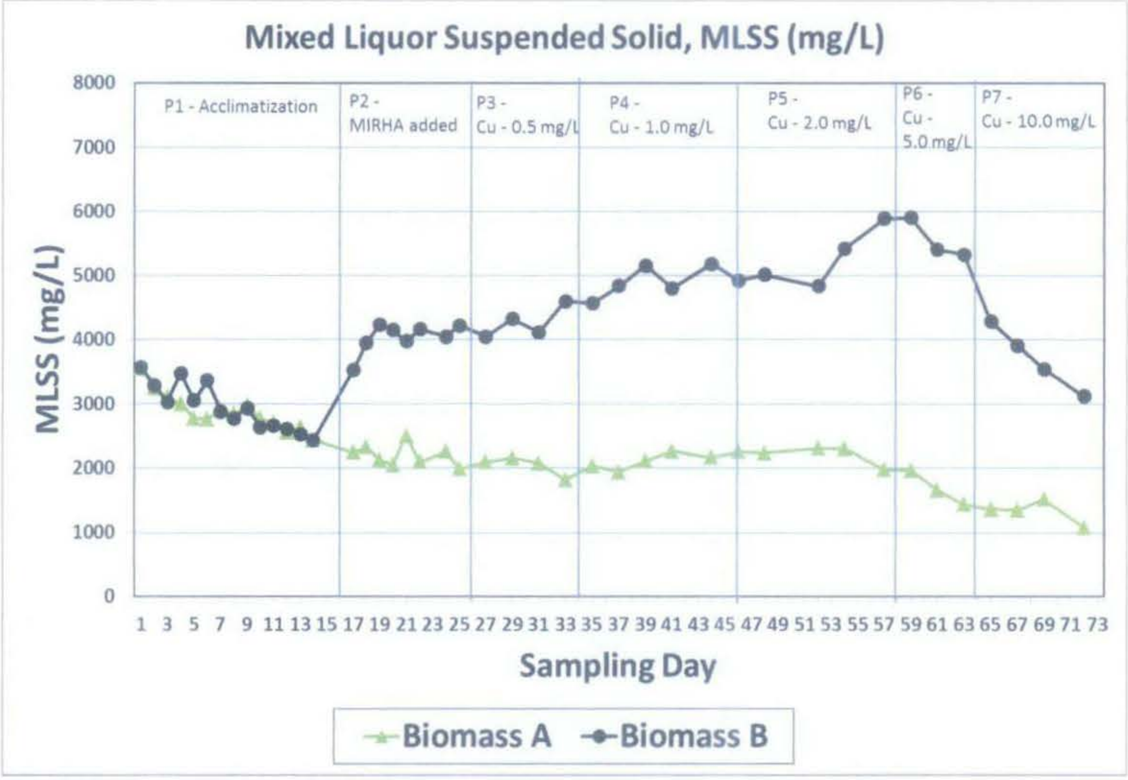

Figure 18: Biomass MLSS (mg/L)

Control reactor is having a MLSS of around 2000 mg/L, after stabilization in Phase 2 until Phase 5. MLSS Biomass A started to decline gradually from Phase 6, due to the decline of microbes, which is one of the elements contribute to MLSS.

While Reactor B saw an increase of MLSS to around 4000 mg/L in Phase 2. The increase of MLSS in Reactor B is due to the addition of 2000 mg/L of MIRHA adsorbents in reactor. MLSS Biomass B continue to rise gradually from Phase 2 to Phase 5, as the addition of 100 mg/L MIRHA daily contribute to the increase in solids content. MLSS Biomass B reached climax in Phase 6, and gradually declined afterward, again due to dying of microbes.

The amount of microorganisms in the biomass is denoted by the mixed-liquor volatile suspended solids (MLVSS). MLVSS Biomass A and B is presented in Figure 19.

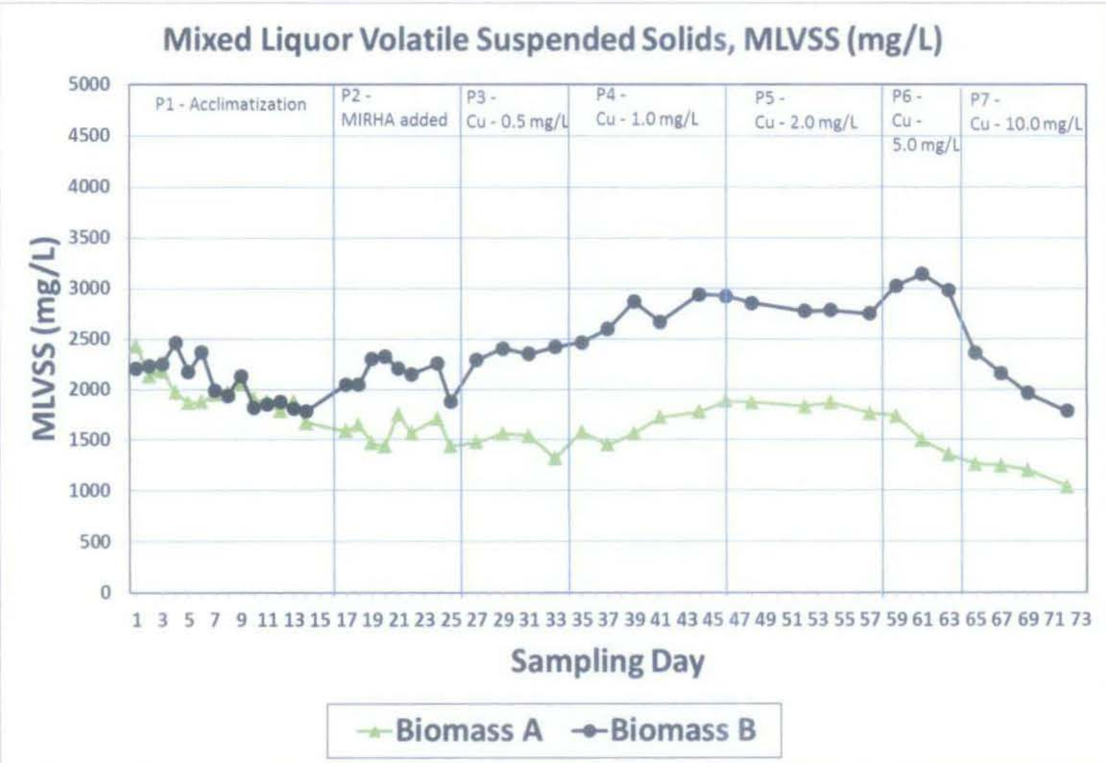

Figure 19: Biomass MLVSS (mg/L)

MLVSS Biomass A stabilized at around 1500 mg/L throughout Phase 2 and 3. MLVSS Biomass A continued to grow in Phase 4, reaching the peak in Day 46, recording a value of 1833 mg/L. Although the copper inhibitory concentration to microbes is 1.0 mg/L [1], the acclimatization has assisted microbes to cope with copper concentration of 1.0 mg/L in Phase 4. There is no sign of reduction of MLVSS in Reactor A in Phase 4. The

MLVSS Biomass A value stabilized in Phase 5. Only in Phase 6, where 5.0 mg/L copper is dosed, did the MLVSS Biomass A see a gradual decline.

As for MLVSS Biomass B, it gradually increased from 2000 mg/L in Phase 1, to around 2700 mg/L in Phase 5. The higher growth rate of MLVSS Biomass B, as compared to MLVSS Biomass A, can be attributed to suspended growth and attached growth in Reactor B. As compared to sole suspended growth in Reactor A, MIRHA provided a medium for attached growth in Reactor B, apart from the suspended growth. Thus MIRHA adsorbent helped in the growth of biomass in activated sludge system.

MLVSS Biomass B climaxed in Phase 6, recording a value of 3130 mg/L in Day 61. MLVSS Biomass B gradually declined afterward, implying the death of microbes for the copper dosage of 10.0 mg/L during Phase 7.

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

5.1 Recommendations for Future Work

This research only studies the effects of MIRHA to the removal of copper in activated sludge system. To further study on the suitability of MIRHA as heavy metal adsorbent in biological treatment, other heavy metals such as zinc and iron can be applied. It is even better if industrial wastewater, such as those from textile industries, be employed as influent to study the application the researched methodology in reality.

In addition to that, it is suggested that the ammonia level in the synthetic wastewater be adjusted to match the typical ammonia concentration in most of the domestic sewage. The ammonia level in the synthetic wastewater is only 2 mg/L, which is much lower than typical domestic sewage value of 25 mg/L. This can be rectified by adding ammonium chloride in influent.

Besides the 5 parameters studied (COD, BOD, Cu, MLSS and MLVSS), more parameters such as Total Suspended Solids, ammonia, nitrate, Sludge Volume Index, pH and temperature can be studied to cover a complete scope on the effects of MIRHA to the removal of heavy metals in activated sludge system.

5.2 Conclusion

Copper is commonly used in textile, steel and dyes industries. Effluent contains copper need to be treated prior to discharge to the environment, else it could pose danger to human health.

The purpose of this research is to propose the removal of copper using biological treatment system. Since copper concentration threshold of inhibitory effect on microbes is only 1.0 mg/L, MIRHA adsorbent dosed in the activated sludge system is proposed to study if MIRHA is capable to delay the toxicity effect of copper.

This research is carried out by conducting experiments using 2 scaled down biological reactor. Medium strength wastewater dosed with heavy metals (Cu) at dosage of 0.5 mg/L, 1.0 mg/L, 2.0 mg/L, 5.0 mg/L and 10.0 mg/L is used as influent. The reactor is run in Extended Aeration Activated Sludge mode.

The result shows that MIRHA adsorbent has indeed improved the overall performance of biological treatment system. With MIRHA adsorbent and gradual acclimatization, microbes are capable to withstand copper concentration up to 5.0 mg/L. MIRHA adsorbent generally improved the overall removal of organics matters (TCOD and BOD), copper, and improved the growth of microbes in the activated sludge system.

Apart from that, study also concluded that acclimatization is capable to improve microbes' tolerance toward copper toxicity in Extended Aeration Activated Sludge system. Acclimatization prolonged survivability of microbes from theoretical copper concentration threshold of 1.0 mg/L to 2.0 mg/L.

In conclusion, Extended Aeration Activated Sludge system dosed with MIRHA adsorbent is a new approach toward removal of copper in wastewater up to copper concentration of 5.0 mg/L.

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