Evaluation of copper removal using MIRHA as an adsorbent in a continuous flow activated sludge system

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Abstract

The efficiency of copper removal from an aqueous solution was investigated in a continuous flow activated sludge system. Two identical biological reactors made of acrylic were used to carry out the research. Reactor one (R1) was used as control and contained only biomass. Reactor two (R2) contained biomass and microwave incinerated rice husk ash (MIRHA). Different concentrations of copper dosages in the range of 0.5 mg/L, 1 mg/L, 2 mg/L, 5 mg/L, 10 mg/L and 15 mg/L were used. Activated sludge was allowed an acclimatization time of 15 days in both reactors. Microwave incinerated rice husk ash (MIRHA) was then added to reactor two (R2) from day 16. It was allowed to acclimatize with the activated sludge until day 25. The reactors were subsequently fed with an aqueous solution containing copper of various doses from day 26 onwards. The results show that the effluents from both reactor one (R1) and reactor two (R2) have a minimum removal efficiency of about 86% for all the copper doses investigated. The maximum average copper removal efficiency for reactor one (R1) and reactor two (R2) is 93% and 97% respectively. Reactor two (R2) had higher copper removal efficiency for all the concentrations investigated. The mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) of reactor two (R2) significantly increased from phase 2 to phase 6 whereas in reactor one (R1), mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) stabilized from phase 2 to phase 4. This implies that using microwave incinerated rice husk ash (MIRHA) as an adsorbent in an activated sludge system can increase the reactor performance.
Keywords: activated sludge, copper, microwave incinerated rice husk ash (MIRHA).

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1 Introduction

The discharge of copper and other heavy metals into the environment from various industries are strictly been regulated due to the toxicity of these pollutants even at extremely low concentrations. Industries such as photographic, refineries, abandoned metal mines, metal plating operations, battery manufacturing processes, production of paints and pigments, ceramic and glass industries generate wastewater containing dissolved heavy metals [1, 2]. These pollutants can accumulate in the environment when present in excessive concentrations, cause various illnesses and threaten human health [3]. In biological treatment, copper and some other heavy metals can represent toxic effects which can reduce process efficiency and deteriorate effluent quality [4]. The copper concentration threshold of inhibitory effect on microorganisms is 1.0 mg/L [5]. The copper discharge limits set by the United States Environmental Protection Agency (EPA) is 0.0049 mg/L, while Malaysia's Department of Environment (DOE), Environmental Quality Act (1974) has set the copper discharge limit as 0.2 mg/L (Standard A) [6].

Various technologies have been developed for the removal of heavy metals from wastewater. These techniques include membrane filtration, electroplating, precipitation, ion exchange, electrodialysis, solvent extraction. However, these techniques may present significant demerits, which include high energy input, high chemical requirements and high cost [7, 8]. Due to the stringent environmental regulations and ecological requirements, the search for more treatment options with low energy, low labor, and low capital costs is of interest.

The addition of powdered activated carbon as adsorbent to wastewater (leachate) in an activated sludge process shows tremendous toxicity reduction and improved treatment process performance [9]. These adsorbents can add their adsorptive properties to the activated sludge to improve the process performance. The objective of this study is to evaluate copper removal efficiency using reactor one (R1) containing biomass only and reactor two containing biomass and microwave incinerated rice husk ash (MIRHA), monitor the average removal efficiency of organic matter (biochemical oxygen demand (BOD_5) and total chemical oxygen demand (TCOD)) during the research process.

2 Methodology

2.1 Adsorbent preparation

Rice husk was collected and washed with distilled water to remove impurities. It was subsequently dried at 105°C for 2 hours until constant weight is attained. It was then subjected to Microwave Incinerator at 800ºC for 2 hours. The microwave incinerated rice husk ash (MIRHA) produced was used in this study. The adsorbent was then stored in a tight container before use.

2.2 Design and fabrication of biological reactors

Two identical biological reactors was fabricated using 5 mm thick acrylic glass. Reactor one (R1) contains biomass only while Reactor two (R2) contains a mixture of biomass and microwave incinerated rice husk ash (MIRHA). The designed reactors were installed with adequate numbers of tube diffusers to provide sufficient aeration to the biomass. The aeration tank has a total volume of 8.5L.

2.3 Synthetic wastewater

Synthetic wastewater was used in this study. It was prepared by dissolving grinded dog food (Purina Alpo High Protein Puppy Dog Meal) in distilled water to simulate a medium strength domestic wastewater. Synthetic wastewater was used in order to provide more consistent organic loadings. The dog food was grinded using a blender for approximately 5 minutes. 600 mg grinded dog food was prepared and added into the influent tank, together with 0.15 mL/L of phosphate buffer (same phosphate buffer used for the biochemical oxygen demand (BOD) dilution water). The carbon, nitrogen, phosphorus (C:N:P) ratio of synthetic wastewater was calculated to be 100:24:3, meeting the required minimum 100:5:1 ratio for domestic wastewater to provide sufficient nutrients for biomass. The characteristics of influent feed concentration are shown in Table 1.

Table 1: Characteristics of synthetic wastewater.

Parameters	Concentration (mg/L)
COD	500
BOD_5	250
TSS	300
TKN	70
Ammonia (NH_3)	2
Nitrate (NO_3)	1
Phosphorus	10

2.4 Operation and maintenance of reactors

During the operation stage, both Reactors were set up in the laboratory by using biomass from the aeration tank of an activated sludge treatment plant. The influent was pumped into the reactors continuously at the rate of 7 L/d using Masterflex Precision Pump with tubing L/S 16. Both reactors were operated at extended aeration (solid retention time (SRT) ≈ 30 days, design mixed liquor suspended solids (MLSS) ≈ 4000 mg/L), in order to promote the growth of slow growing bacteria such as Nitrosomonas and Nitrobacter. These slow growing bacteria are crucial in removing ammonia from wastewater. Copper was dosed in the form of Copper Sulfate ($CuSO_4$) solution. The experiment has a total of 8 phases comprising of different copper doses as enumerated below.

Phase 1: Acclimatization (Day 1–15)
Phase 2: Addition of MIRHA (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)
Phase 8: Copper dosage 15.0 mg/L (Day 73–76).

The reactors were allowed an acclimatization period of 15 days respectively to stabilize the biomass. 2000 mg/L of microwave incinerated rice husk ash (MIRHA) adsorbent was added to reactor two (R2) on day 16 and was allowed another 10 days to enable the biomass adapt to it without causing any shock effect. During Phase 1 and 2 of laboratory work, the sludge age was controlled through daily sludge recycling and wasting. However, from Phase 3 onwards, biomass is only recycled without wasting to ensure maximum growth of biomass to cushion for copper toxicity. The concentration of microwave incinerated rice husk ash (MIRHA) in the mixed liquor of reactor two (R2) was maintained at 2000 mg/L throughout Phase 2, by adding MIRHA to the aeration tank daily, taking into consideration the MIRHA wasted daily in the waste sludge (by knowing the MIRHA concentration and volume wasted) and MIRHA discharged into the effluent (from effluent Total Suspended Solids (TSS) measurement). From Phase 3 onward, 100 mg/L MIRHA was added daily into aeration tank of reactor two (R2). The purpose was to prevent MIRHA adsorbent from reaching the exhaustion point, where all the adsorbent becomes saturated with adsorbate. The influent and effluent samples were collected daily and the performance of both reactors was monitored for 76 days continuously.

2.5 Analytical methods

Copper test was carried out according to U.S Environmental Protection Agency (USEPA) Bicinchoninate method for powder pillows (Method 8506). Mixed liquour suspended solids (MLSS), and mixed liquor volatile suspended solids (MLVSS) were analyzed according to the 21st edition of standard methods for the examination of water and wastewater. Total Chemical Oxygen Demand (TCOD) was analyzed through Hach method using DR 2000 spectrophotometer. Biochemical oxygen demand (BOD_5) was determined by standard method number 5210.

3 Results and discussion

3.1 Copper removal

The process flow for the reactor operation and Influent copper concentration at different dosing and time is summarized in Figure 1.

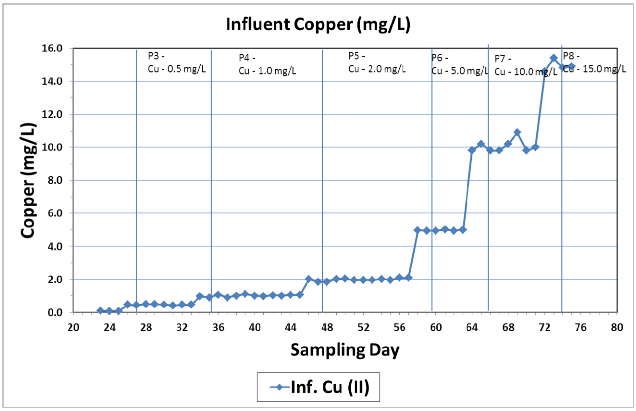

Figure 1: Influent copper (mg/L).

The results presented in Figure 2 shows that reactor two (R2) had higher average copper removal efficiency than reactor one (R1) in all phases. During phase 3 (Day 26–33; copper concentration of 0.5 mg/L), average removal efficiency for reactor one (R1) and reactor two (R2) was 91% and 97% respectively. This indicates that microwave incinerated rice husk ash (MIRHA) adapted with the biomass in reactor two (R2) and improved the reactor performance. At phase 4, (Day 34–45; copper concentration of 1 mg/L), an average removal efficiency of 93% and 95.1% was observed for both reactor one (R1) and reactor two (R2) respectively. In phase 5 (Day 46–57; copper concentration of 2 mg/L), reactor two (R2) has a better average removal efficiency of 92% as compared with reactor one (R1) 89%. At phase 6, (Day 58–63; copper concentration of 5 mg/L), average removal efficiency for both reactor one (R1) and reactor two (R2) was 88% and 96% respectively whereas at phase 7, (Day 64–72; copper concentration of 10 mg/L), average removal efficiency for both reactor one (R1) and reactor two (R2) was 92% and 94.3% respectively. In phase 8, there was no significant difference between the average removal efficiency for both reactor one (R1) and reactor two (R2). The average removal efficiencies for both reactor one (R1) and reactor two (R2) in phase 8 were 87% and 88% respectively.

As shown in Figure 2, there was no significant difference between average removal efficiency of reactor one (R1) and reactor two (R2) except in phase 3 and 6. For reactor one (R1), effluent copper concentration from phases 3–5 meets the Malaysia's DOE Environmental Quality Act (1974) Standard "A" copper discharge limit of 0.2 mg/L while phases 6–8 violated the Environmental Quality Act. Effluent copper concentration decreased from phase 3–4 and slightly increased from phase 4–6. There was however, sharp decrease in phase 7 and a slight increase in phase 8 due to increase in influent copper concentration. For reactor two (R2), effluent copper concentration from phases 3–6 meets the Malaysia's DOE Environmental Quality Act (1974) Standard "A" copper discharge limit of 0.2 mg/L whereas phases 7–8 violated the Environmental Quality Act. Effluent copper concentration increased from phases 3–5 and decreased in phase 6. There was also an increase in effluent copper concentration from phase 7–8. The decrease in effluent copper concentration in phase 6 of reactor two (R2) can be attributed to gradual acclimatization as well as adaption of biomass to microwave incinerated rice husk ash (MIRHA) adsorbents whereas the increase in effluent copper concentration from phase 7–8 can be attributed to toxicity of copper at high concentration.

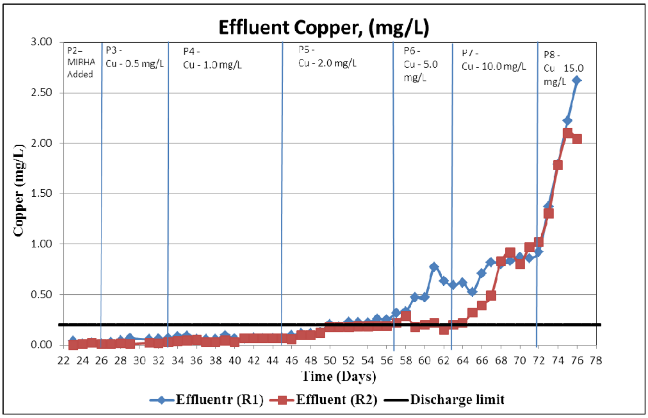

Figure 2: Effluent copper (mg/L).

From the obtained result, it was obvious that reactor two (R2) was able to reduce influent copper concentration of 5 mg/L (phase 6) below the Malaysia's DOE Environmental Quality Act (1974) Standard "A" copper discharge limit of 0.2 mg/L. This implies that microwave incinerated rice husk ash (MIRHA) can be effectively added as an adsorbent to an activated sludge process to improve the process performance.

3.2 Removal of organic matter (total chemical oxygen demand TCOD)

The result obtained from the analysis of total chemical oxygen demand (TCOD) is depicted in Figure 3. During the acclimatization period of phase 1 and phase 2, the effluent total chemical oxygen demand (TCOD) for both reactor one (R1) and reactor two (R2) show significant improvement from day 1 to day 25. Phase 2 is considered to be the stabilization phase due to the acclimatization of biomass to its new environment. The average effluent total chemical oxygen demand (TCOD) removal efficiency from reactor one (R1) in phase 2 was 92% and maintained a decreasing trend until phase 8. For reactor two (R2), similar decreasing trend of average total chemical oxygen demand (TCOD) removal efficiency was observed from phase 3 until phase 8. The average effluent total chemical oxygen demand (TCOD) removal efficiency for both reactor one (R1) and reactor two (R2) is tabulated in Table 2.

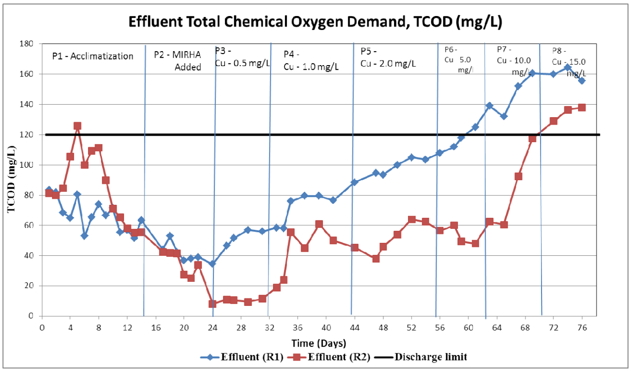

Figure 3: Effluent total chemical oxygen demand (TCOD) (mg/L).

Table 2: Average effluent total chemical oxygen demand (TCOD) for reactor one (R1) and reactor two (R2).

Phase	Day	Influent. copper (mg/L)	R1 (%)	R2 (%)
1	1–15	0.0	87	85
2	16–25	0.0	92	94
3	26–33	0.5	89	97
4	34–45	1.0	84	90
5	46–57	2.0	80	89
6	58–63	5.0	75	88
7	64–72	10.0	70	80
8	73–76	15.0	68	75

As shown in Figure 3, Average effluent total chemical oxygen demand (TCOD) concentration from reactor one (R1) was found to have exceeded the DOE Malaysia Standard "A" limit of 120 mg/L as the research proceeded into Phase 6 (day 58–63; copper concentration of 5 mg/L). However, for reactor two (R2), average effluent total chemical oxygen demand (TCOD) concentration was found to exceed the DOE Malaysia Standard "A" limit of 120 mg/L at phase 8 (day 73–76; Copper concentration 15.0 mg/L). Generally, for reactor two (R2), microwave incinerated rice husk ash (MIRHA) adsorbent helped to delay copper toxicity effect and also assisted in total chemical oxygen demand (TCOD) removal, by helping to extend microbes copper inhibitory level, from 2.0 mg/L to 10.0 mg/L.

3.3 Removal of organic matter (Biochemical Oxygen Demand, BOD_5)

The effluent biochemical oxygen demand (BOD_5) result for reactor one (R1) and reactor two (R2) is depicted in Figure 4. Average effluent biochemical oxygen demand (BOD_5) concentrations for reactor one (R1) and reactor two (R2) are presented in Table 3. For reactor one (R1), average biochemical oxygen demand (BOD_5) removal efficiency was significantly high between Phases 1–5. During these phases, the removal efficiency of biochemical oxygen demand (BOD_5) was closely stable. This can be attributed to the acclimatization of the biomass within the reactor which enables the microbes to tolerate toxicity within low copper concentration. However, at phases 6–7, average biochemical oxygen demand (BOD_5) removal efficiency decreased. This can be attributed to the toxicity of high copper concentration to the microbes in the reactor resulting to a shock effect. The average biochemical oxygen demand (BOD_5) removal efficiency from phase 1 to phase 5 in reactor one (R1) meets the limit set by DOE Malaysia standard "A" guideline of 20 mg/L. The average biochemical oxygen demand (BOD_5) removal efficiency from phases 6–7 violated the DOE Malaysia standard "A" guideline of 20 mg/L.

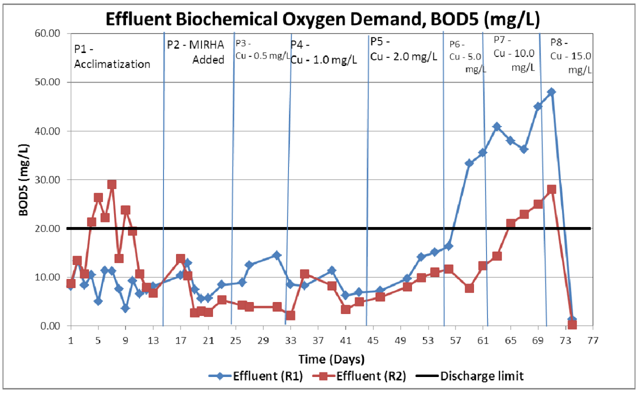

Figure 4: Effluent BOD_5 (mg/L).

For reactor two (R2), average biochemical oxygen demand (BOD_5) removal efficiency of phases 1–6 was significantly high. This implies that addition of microwave incinerated rice husk ash (MIRHA) to the reactor enhanced the acclimatization of the microbes and improved their resistance ability against toxicity and shock effect. At phase 7 (day 64–72; copper concentration 10.0 mg/L), the average biochemical oxygen demand (BOD_5) removal efficiency decreased. This could be explained that the microbes may have attained their shock resistant threshold which results in shock effects and can lead to death of such microbes. The removal efficiency at phases 1–6 in reactor two (R2) meets the DOE Malaysian Standard "A" guideline of 20 mg/L. However, at phase 7 (day 64–72; Copper concentration 10.0 mg/L), the removal efficiency violates the DOE Malaysia Standard "A" guideline of 20 mg/L as shown in Figure 4. It can be concluded that the addition of microwave incinerated rice husk ash (MIRHA) to reactor two (R2) enhanced the resistivity of microbes against toxicity of high copper concentration more than 5 mg/L but less than 10 mg/L.

Table 3: Average effluent BOD_5 for RI and R2.

Phase	Day	Inf. Cu (mg/L)	R1 (%)	R2 (%)
1	1–15	0.0	96	95
2	16–25	0.0	96	97.5
3	26–33	0.5	95	98
4	34–45	1.0	97	96.4
5	46–57	2.0	94	96.2
6	58–63	5.0	85	95.2
7	64–72	10.0	83	84
8	73–76	15.0	–	–

3.4 Monitoring of mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS)

The mixed liquor suspended solids (MLSS) in reactor one (R1) was approximately 2000 mg/L, after stabilization in Phase 2. It remained nearly the same until Phase 5 as shown in Figure 5. There was a gradual decline of the mixed liquor suspended solids (MLSS) in reactor one (R1) from Phase 6 (Day 58–63; Copper concentration 5.0 mg/L), due to the reduction of microbes, which is one of the elements that contributes to MLSS. However, there was increase of mixed liquor suspended solids (MLSS) in reactor two (R2) to approximately 4000 mg/L in Phase 2 (day 16–25; MIRHA addition). The increase of mixed liquor suspended solids (MLSS) in reactor two (R2) was due to the addition of 2000 mg/L of microwave incinerated rice husk ash (MIRHA) adsorbents in the reactor.

The mixed liquor suspended solids (MLSS) in reactor two (R2) maintained an upward trend from Phase 2 to Phase 5, because the daily addition of 100 mg/L microwave incinerated rice husk ash (MIRHA) contributed to the increase in solids content. The mixed liquor suspended solids (MLSS) in reactor two (R2) reached a maximum value in Phase 6, but gradually declined afterward, probably due to dying of microbes as a result of increased copper toxicity.

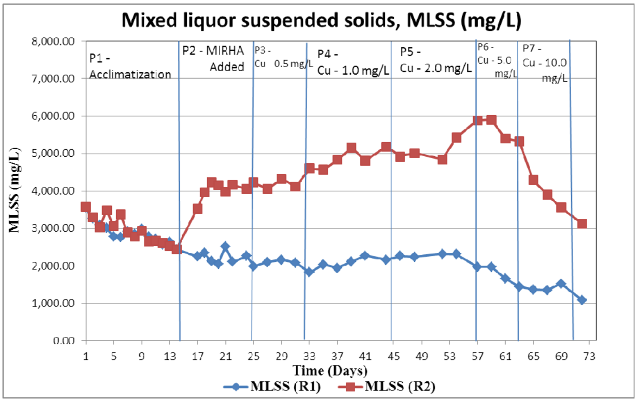

Figure 5: Effluent MLSS (mg/L).

Figure 6 shows the effluent mixed liquor volatile suspended solids (MLVSS) in reactor one (R1) and reactor two (R2). For reactor one (R1), the mixed liquor volatile suspended solids (MLVSS) stabilized at approximately 1500 mg/L throughout Phase 2 and 3. The mixed liquor volatile suspended solids (MLVSS) in reactor one (R1) continued to grow in Phase 4 (day 34–45; Copper concentration 1.0 mg/L), reaching the peak on Day 46, recording a value of 1833 mg/L. Although the copper inhibitory concentration to microbes is 1.0 mg/L [5], acclimatization assisted microbes to cope with copper concentration of 1.0 mg/L in Phase 4 (day 34–45; Copper concentration 1.0 mg/L). There was no sign of reduction of mixed liquor volatile suspended solids (MLVSS) in reactor one (R1) at Phase 4. The mixed liquor volatile suspended solids (MLVSS) in reactor one (R1) stabilized in Phase 5 (day 46–57; Copper concentration 2.0 mg/L). However, the mixed liquor volatile suspended solids (MLVSS) showed a gradual decline in phase 6 (day 58–63; Copper concentration 5.0 mg/L) due to toxicity of

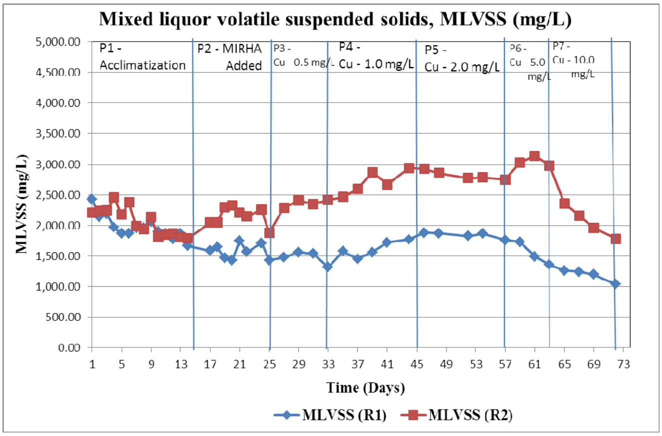

Figure 6: Effluent MLVSS (mg/L).

copper at high concentration. As for reactor two (R2), it gradually increased from 2000 mg/L in Phase 1 (day 1–15; acclimatization), to approximately 3100 mg/L in Phase 6 (day 58–63; Copper concentration 5.0 mg/L). There was higher growth rate of mixed liquor volatile suspended solids (MLVSS) in reactor two (R2) compared to reactor one (R1). This can be referred to a combination of bacteria growth media in reactor two (R2). As compared to sole suspended growth in reactor one (R1), microwave incinerated rice husk ash (MIRHA) provided a medium for attached growth in reactor two (R2), apart from the suspended growth. Thus, microwave incinerated rice husk ash (MIRHA) adsorbent also helped in the growth of biomass in activated sludge system.

Mixed liquor volatile suspended solids (MLVSS) in reactor two (R2) was at its highest in Phase 6 (day 58–63; Copper concentration 5.0 mg/L), recording a value of 3100 mg/L in day 61. However, mixed liquor volatile suspended solids (MLVSS) in reactor two (R2) gradually declined afterwards, implying the death of microbes at copper dosage of 10.0 mg/L during Phase 7.

4 Conclusion

This study shows that microwave incinerated rice husk ash (MIRHA) can be used as an adsorbent to improve the process performance of activated sludge system. MIRHA was able to enhance the removal efficiency of copper concentration of 5 mg/L. MIRHA also serves as an attach growth media for the microbes in the reactor as well as help enhance the resistant of the microbes against shock effect and toxicity of copper. MIRHA adsorbent generally improved the overall removal of organic matters (TCOD and BOD) and copper, and improved the growth of microbes in the activated sludge system. It is also concluded that acclimatization is capable to improve microbes' tolerance towards copper toxicity in extended aeration activated sludge system.

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