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COPPER REMOVAL FROM BIOLOGICAL TREATMENT SYSTEM USING MODIFIED ADSORBENT DERIVED FROM GROUNDWATER TREATMENT PLANT SLUDGE AND RICE HUSK

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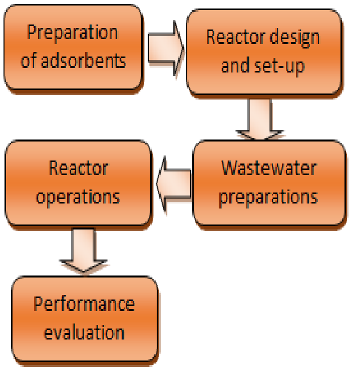
Graphical abstract



Abstract

Copper removal from synthetic wastewater by biomass assisted adsorbents was evaluated in this study. Three different biological reactors of the same size (8.5 L) were aerobically operated at solid retention time (SRT) of 30 days and hydraulic retention time (HRT) of 0.8 day. The first reactor was operated with biomass alone as the control reactor. The second reactor consist of biomass and ground water treatment plant sludge (GWTPS) whilst the third reactor consist of biomass and hybrid adsorbent (HA), which comprises 50% of microwaved incinerated rice husk ash (MIRHA) and 50% of GWTPS. The reactors were operated in eight different phases (Phase 1 – 8). Phases 1 – 2 were operated as acclimation period during which the biomass were allowed to stabilize within the reactor without copper addition. From phase 3 – phase 8, copper was added to the influent of the reactors at various concentrations and the reactor performance was monitored every two days. Results revealed that copper removal with the control reactor (RC) was markedly inferior compared with the reactors supported with GWTPS and HA adsorbents. The copper removal in the control reactor was in the range 0.47 – 2.62 mg/L from phase 5 to phase 8. Copper removal in the GWTPS reactor was in the range 0.19 – 0.83 mg/L from phase 5 to phase 8 whereas copper removal in the HA reactor was in the range 0.27 – 1.09 mg/L at the same conditions. Percentage removal of copper was 85 %, 94 % and 95 % for the control, GWTPS and HA reactors, respectively. The adsorbents, GWTPS and HA reactors removed copper effectively. This study demonstrates that solid waste materials such as GWTPS and HA can be beneficially utilized to improve biomass tolerance towards heavy metal toxicity and yields a significant removal of copper.

Keywords: Adsorbents, sludge, rice husk, Copper, Biomass, Heavy metal

1.0 INTRODUCTION

The presence of various toxic compounds such as cyanides, degreasing solvents, oil and heavy metals in wastewater have become a subject of concern due to their associated dangers [1, 2]. Heavy metal contaminated wastewater can present severe health and environmental challenges when discharged into water bodies such as lakes and rivers at concentrations higher than the specified limits [3]. Most government regulating bodies has subjected residual effluent heavy metal concentration to frequent amendments due to the toxicity they present. Long time exposure and consumption of copper contaminated wastewater at high concentrations could cause stomach and intestinal distress, kidney and liver damage [4]. Compliance of the stringent limits set out by regulating bodies has been harassing wastewater operators in terms of heavy metal removal. Industrial wastewater are large volume production and could be beneficially used to supplement limited freshwater resources when properly treated [5]. Thus, there is dire need for the development of low cost and yet, effective treatment methods for heavy metal removal. Various methods have been developed to treat copper contaminated wastewater. However, some demerits have been reported. Biological treatment process is cost effective but its efficiency is hindered by copper toxicity on the biomass consortium [6]. Chemical precipitation is effective towards copper removal but can produce a high volume of sludge [7-9]. Solvent extraction, membrane processes and ion exchange method are hindered by incomplete metal removal, high energy consumption, high capital investment and membrane fouling problem [8, 10].The use of adsorbent to enhance the removal capacity of biological treatment systems is gaining wider interest. Although the research in this area is still in infancy, few adsorbents have been reportedly used to enhance biomass tolerance towards toxicity. Such study include powdered activated carbon [11] and microwave incinerated rice husk ash (MIRHA) [6]. The utilization of these adsorbents derived from solid and agricultural waste precursors are useful in reducing the problems associated with solid waste disposal. These adsorbents provide adequate stability for the biomass adaptation to copper toxicity even at high concentration. Few processes such as biosorption, bioaccumulation and bio reduction has been associated with the mechanism of the combination of adsorbent and biomass [12].

The objective of this study is to investigate the performance of a biological wastewater treatment reactor with and without the addition of adsorbent materials (GWTPS and HA) for the removal of copper from synthetic wastewater. Experiments were conducted in eight different phases and copper removal was monitored every two day

2.0 EXPERIMENTAL

2.1 Reactor Design and Setup

Three rectangular reactors of equal volume (8.5 L) were fabricated using acrylic glass with thickness of 5 mm and height of 200 mm. The reactor is designed with an influent point towards the top in a downflow process. A baffle was inserted towards the effluent point to prevent biomass washout into the effluent. Few openings were designed on the reactor cover for easy insertion of air diffusers towards the bottom of the reactor.

The three reactors were set up in the laboratory using a seed sludge from a domestic sewage treatment plant (STP). The solid retention time (SRT) was 30 days for the three reactors to promote the growth of slow growing bacteria such as Nitrosomonas and Nitrobacter. The mixed liquor suspended solid (MLSS) concentration was 4000 mg/L. Air diffusers were installed at the bottom of the reactor.

2.2 Wastewater Preparation

The synthetic wastewater used in this study was prepared with Purina Alpo substrate. The wastewater was prepared on a daily basis to provide fresh carbonaceous matter to the biomass. The use of synthetic wastewater was important to provide consistent organic loading for a better assessment of the reactors. A 0.15 mL/L of phosphate buffer (same phosphate buffer used for the BOD dilution water) was added to the influent tank containing the synthetic wastewater. The C: N: P ratio of synthetic wastewater was calculated to be 100:24:3, respectively which meets the required minimum 100:5:1 ratio for domestic wastewater to provide sufficient nutrients for biomass of the respective reactors. Copper was added to the synthetic wastewater according to the experimental plan.

2.3 Adsorbent Materials and Preparation

Groundwater Treatment Plant Sludge (GWTPS) was collected from Air Kelantan Sdn. Bhd., groundwater treatment plant in muddy sludge form. GWTPS was dried at 105°C for 24 hours according to Standard Methods for the Examination of Water and Wastewater, number 2540B [8]. It was then grounded into powder form and stored in a closed container.

Hybrid adsorbent (HA) consists of equal mixture of GWTPS and MIRHA. MIRHA was produced from rice husk precursor. Rice husk was collected and washed with distilled water to remove impurities. It was subsequently dried at 105 oC for 2 hours until a constant weight was attained. It was then subjected to microwave incinerator at 800°C 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 prior to experiment.

HA was then prepared by weighing out and mixing an equal amount of GWTPS and MIRHA in the ratio of 1:1 respectively.

2.4 Reactor Operation

The three reactors were operated at hydraulic retention time (HRT) of 0.8 days. Air was supplied to the reactors by means of air pumps. The influent was pumped into the reactors by means of a Master flex peristaltic pump. Fresh synthetic wastewater was applied to the reactors at fixed HRT. The experiments were conducted in eight different phases (Table 1). Phase 1 was primary acclimation period for the biomass to adapt to the reactors. Phase 2 was secondary acclimation period during which the adsorbents (GWTPS and HA) were added to their respective reactors. From phase 3 – 8, copper was added to the influent wastewater in different concentrations. Sludge age was controlled in phase 1 and 2 through daily recycling and wasting. GWTPS and HA concentrations in the mixed liquor were maintained at 2000 mg/L in phase 2 through daily addition to the reactors, taking into consideration the (GWTPS and HA) wasted daily in the waste sludge and discharged into the effluent (from effluent Total Suspended Solids measurement). In phase 3, Cu (II) concentration of 0.5 mg/L was added to the reactors. Sludge was only recycled without wasting to ensure maximum growth of biomass to cushion for Cu (II) toxicity. Henceforth, 100 mg/L of GWTPS and HA was added daily into their respective reactors. The purpose was to prevent the adsorbents from reaching the exhaustion point, where all the adsorbent becomes saturated with adsorbate. In phase 4, Cu (II) concentration was increased to 1.0 mg/L. In phase 5, 6, 7 and 8, Cu (II) concentration was increased to 2, 5, 10 and 15 mg/L respectively for all reactors. The influent and effluent samples were collected daily and the performance of the reactors was monitored for 11 weeks continuously. Cu (II) concentration was measured using Hach spectrophotometric method while MLVSS was analyzed according to the 21st edition of standard methods for the examination of water and wastewater number 2540E.

Table 1 Experiment plan of eight different phases

Phase	Concentration	Days
1	Acclimation	1-15
2	Addition of GWTPS and HA	16-25
3	Cu(II) dosage 0.5 mg/L	26-33
4	Cu(II) dosage 1.0 mg/L	34-45
5	Cu(II) dosage 2.0 mg/L	46-57
6	Cu(II) dosage 5.0 mg/L	58-63
7	Cu(II) dosage 10.0 mg/L	64-72
8	Cu(II) dosage 15.0 mg/L	73-76

3.0 RESULTS AND DISCUSSION

Figure 1 illustrates the experimental plan with copper concentration and sampling days. Phase 1 and 2 were primary and secondary acclimation periods, respectively. Copper concentration was increased in the influent wastewater sequentially from phase 3 – 8.

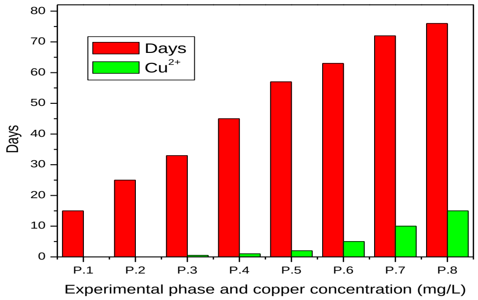


Figure 1 Copper concentrations and sampling days

Addition of copper in Phase 3 (copper concentration 0.5 mg/L) did not show any significant toxicity effect on all three reactors (Figure 2). A copper removal efficiency of about 72 %, 84 % and 86 % was observed for HA, GWTPS and the control reactors respectively in Figure 3. The mixed liquor volatile suspended solids (MLVSS) were observed to drop slightly due to the effect of heavy metal. This was more significant in the control reactor (Figure 4). The HA reactor was more tolerant to heavy metal addition. The MLVSS pattern in Figure 4 shows that the GWTPS and HA reactors were yet to stabilize. In phase 4 (copper concentration 1.0 mg/L), all three reactors were observed to exhibit high copper removal and significant tolerance towards toxicity.

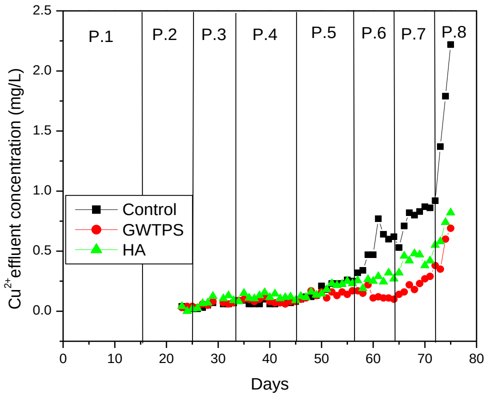


Figure 2 Copper removals in all reactors

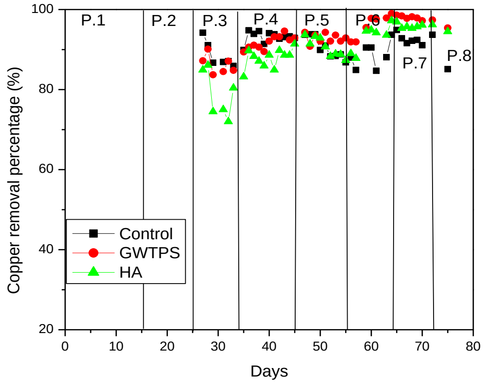


Figure 3 Copper percent removals in all three reactors

Residual copper concentration in this phase was below 0.09 mg/L for all three reactors. Copper removal exceeded 90 % for GWTPS and HA reactors, but was about 89.8% for the control reactor (Figure 3). Copper removal increased for all reactors when concentration was raised from 0.5 mg/L to 1.0 mg/L. This could be due to the adaptation of microorganisms to the reactors, which reflected in the increase of MLVSS for all reactors (Figure 4). HA reactor had a higher MLVSS increase in phase 4. It is important to note that HA is a combination of adsorbents of rice husk and GWTP and could contribute the properties of these adsorbents.

In phase 5 (copper concentration 2.0 mg/L), copper toxicity was observed most significant in the control reactor which resulted to a decrease of MLVSS in Figure 3. The residual copper concentration increased for all three reactors (Figure 2). The effluent copper concentration in this phase was in the range of 0.32 mg/L, 0.17 mg/L and 0.25 mg/L (Figure 2) corresponding to percent removal of 85 %, 92 % and 88 % (Figure 3) for the control, GWTPS and HA reactors, respectively. The mixed liquor volatile suspended solids (MLVSS) for the control and HA reactors increased, but decreased for the GWTPS reactor (Figure 4). The control reactor was found to be in steady state in this phase.

In phase 6 (copper concentration of 5.0 mg/L), residual copper concentration (Figure 2) increased to 0.6 mg/L for the control reactor, decreased in the GWTPS reactor to 0.11 mg/L and was near constant for the HA reactor (0.3 mg/L) corresponding to percent removal of about 88 %, 98 % and 94 % (Figure 3) respectively.

Increase in percent removal of copper was observed when copper concentration was raised from 2 – 5 mg/L. The MLVSS for the control reactor decreased, increased for the GWTPS reactor and was near constant for the HA reactor (Figure 4).

In phase 7 (copper concentration 10 mg/L), residual copper concentration increased for all three reactors (Figure 2). The residual copper concentration was in the range 0.9 mg/L, 0.3 mg/L and 0.4 mg/L corresponding to percent removal of 91 %, 97 % and 96 % (Figure 3) for the control, GWTPS and HA reactors respectively. The MLVSS for all reactors decreased in this phase (Figure 4). However, the decrease was more significant for the control reactor. The GWTPS and HA reactors improved the biomass tolerance towards copper toxicity.

In phase 8 (copper concentration 15 mg/L), residual copper concentration increased for all three reactors (Figure 2). The residual copper concentration was 2.62 mg/L, 0.8 mg/L and 1.1 mg/L corresponding to percent removal of 85 %, 95 % and 94 % for the control, GWTPS and HA reactors respectively. In similar trend, the MLVSS for all reactors (Figure 4) decreased. This suggests that the reactors have attained their toxicity threshold.

The addition of small amounts of heavy metals to biological systems usually support cell growth, up to the point at which the optimum concentration is surpassed, and a relative decrease of the stimulation effect is observed [13].

Further increase of heavy metal concentration will adversely affect the cell growth until the complete decrease of microbial activity and system failure [13]. The critical point for the control reactor (Phase 5), GWTPS reactor (Phase 8) and HA reactor (Phase 8) did not depend on microbial type or acclimation since the biomass can adapt with time to higher concentrations of Cu (II).

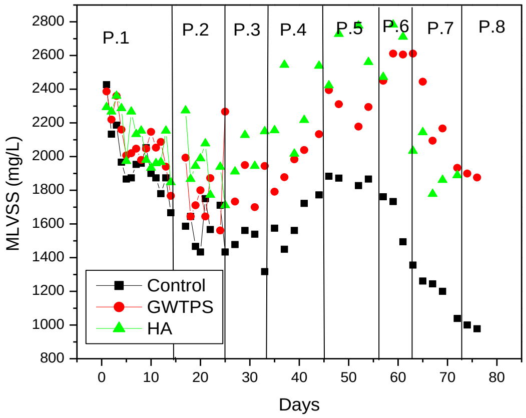


Figure 4 MLVSS concentrations in various reactors

However, in Phase 5 (control reactor) and Phase 8 (GWTPS and HA reactors), heavy metal inhibitory effect at higher concentration was observed and resulted to decrease in bio reduction of Cu (II) [12]. Thus, there was significant inhibition on the biosorption, bioaccumulation and bio reduction processes of Cu (II) in control reactor (Phase 5) and GWTPS/RHA reactors (Phase 8). The build-up of toxic Cu (II) in both reactors might have caused damage on the living cells, resulting to partial loss of sorption abilities and the release of accumulated metal into the solution in the later phases [12]. Heavy metals can damage surfaces of living cells and leach accumulated compounds into the solution [14]. GWTPS and HA was able to sustain the biomass against toxicity which was evident in the drastic reduction of Cu (II) up to Phase 8. Cu (II) reduction in Phase 8 was high (95 % and 94 % for GWTPS and HA reactors) indicating that the reactors has not reached the critical point and could still withstand higher Cu (II) concentrations. Thus, GWTPS and HA provided significant support for activated sludge in biosorption, bio reduction, bioaccumulation and defence against heavy metal toxicity.

The effect of copper on the various reactors was investigated by monitoring the growth of biomass (Figure 4). After the two acclimation periods of phase 1 and 2, copper toxicity was slightly visible in all reactors in phase 3. Increase in biomass concentration was observed from phase 4 – 5 for the control reactor, phases 3 – 6 for the MIRHA and HA reactors respectively. Between phases 7 – 8, significant decrease of biomass below 1000 mg/L was observed for the control reactor whereas the MIRHA and HA reactors have MLVSS concentration of 1830 mg/L ad 1880 mg/L, respectively.

Thus, the difference in the concentration of MLVSS between the control reactor and the MIRHA/HA reactors could be attributed to the addition of adsorbents to the reactors. Although copper toxicity was observed mostly in the control and MIRHA reactors, their bio reduction capacity suggests they can tolerate copper of higher concentrations (> 15 mg/L). The MLVSS content is enhanced with the presence of adsorbents. Meanwhile, in control reactor without adsorbents, the MLVSS content is low. This plausibly indicates that adsorbent preferably facilitate the biomass attachment on the surface and enhance the MLVSS content.

4.0 CONCLUSION

The performance of a biological system was examined for copper removal with and without the addition of adsorbents. Two adsorbents (GWTPS and HA) derived from waste materials was utilized as support materials to enhance biomass tolerance towards toxicity. Three reactors were set up. One reactor served as control and was operated without the addition of adsorbents. GWTPS and HA were added to the other two reactors respectively. The experiment was conducted in eight different phases. The initial two phases were acclimation period for biomass stabilization. Results show that all three reactors were effective for copper removal. However, their efficiency had a limit. For the control reactor, copper removal was significant up to phase 5 and beyond that, residual copper concentration increased significantly. The GWTPS has better copper removal than the HA reactor. A copper removal of 95% and 94% was observed for the GWTPS and HA reactors at phase 8 respectively. MLVSS was higher in the GWTPS reactor (1899 mg/L) than the HA reactor (1866 mg/L) Both the GWTPS and HA reactors showed significant resistance and tolerance toward copper toxicity from phase 3 up to phase 8. It was observed that when influent copper concentration was increased, residual copper concentration and percent copper removal increases. This study demonstrates that solid and agricultural waste materials are efficient to enhance biomass resistance and tolerance towards copper toxicity. Thus, these two adsorbents are cost effective, and easily available, which further adds its value to be utilized as adsorbents.

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