ELSEVIER

Journal of Hazardous Materials B103 (2003) 263–277

Journal of Hazardous Materials

www.elsevier.com/locate/jhazmat

Effects of adsorbents and copper(II) on activated sludge microorganisms and sequencing batch reactor treatment process

S.A. Ong*, P.E. Lim, C.E. Seng

School of Chemical Science, Universiti Sains Malaysia, Penang 11800, Malaysia

Received 13 March 2003; received in revised form 25 July 2003; accepted 29 July 2003

Abstract

Wastewater treatment systems employing simultaneous adsorption and biodegradation processes have proven to be effective in treating toxic pollutants present in industrial wastewater. The objective of this study is to evaluate the effect of Cu(II) and the efficacy of the powdered activated carbon (PAC) and activated rice husk (ARH) in reducing the toxic effect of Cu(II) on the activated sludge microorganisms. The ARH was prepared by treatment with concentrated nitric acid for 15 h at 60–65 °C. The sequencing batch reactor (SBR) systems were operated with FILL, REACT, SETTLE, DRAW and IDLE modes in the ratio of 0.5:3.5:1:0.75:0.25 for a cycle time of 6 h. The Cu(II) and COD removal efficiency were 90 and 85%, respectively, in the SBR system containing 10 mg/l Cu(II) with the addition of 143 mg/l PAC or 1.0 g PAC per cycle. In the case of 715 mg/l ARH or 5.0 g ARH per cycle addition, the Cu(II) and COD removal efficiency were 85 and 92%, respectively. ARH can be used as an alternate adsorbent to PAC in the simultaneous adsorption and biodegradation wastewater treatment process for the removal of Cu(II). The specific oxygen uptake rate (SOUR) and kinetic studies show that the addition of PAC and ARH reduce the toxic effect of Cu(II) on the activated sludge microorganisms.

Keywords: Sequencing batch reactor; Simultaneous adsorption and biodegradation; Copper(II); Rice husk; Biological wastewater treatment

1. Introduction

Through mining, industrial activities and fossil fuels combustion, people, each year, spew thousands of metallic pollutants into air and water [1]. Unlike most organic

* Corresponding author. Present address: Department of Applied Chemistry, Oita University, Oita 870-1192, Japan.
E-mail address: ongsoonan@yahoo.com (S.A. Ong).

0304-3894/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2003.07.008

pollutants, heavy metals are generally refractory and cannot be degraded biologically. The removal of toxic metals from wastewater may be obtained in different ways as precipitation, ionic exchange, adsorption, electro-deposition, etc. [2–4]. Since its first introduction for heavy metals removal, activated carbon has undoubtedly been the most popular and widely used adsorbent in wastewater treatment applications. In spite of its prolific use, activated carbon remains an expensive material since higher the quality of activated carbon, the greater its cost. Research interest in the production of alternative adsorbents to replace the costly activated carbon has intensified recent year such as chitosan, fly ash, saw dust, rice husk (RH), peat soil, etc. [5]. Rice husk, an agricultural waste, has been reported to be a good adsorbent for metal ions and dyes [6,7]. Raw rice husk must undergo pretreatment such as pyrolysis, acid or steam activation to improve its adsorption capacity.

Heavy metals are toxic to most microorganisms at specific concentrations and often cause serious upsets in biological waste treatment plants. The toxicity of heavy metals in activated sludge mixed liquor depends mainly upon two factors, namely, metal species and concentration [8]. The concentration of heavy metals in wastewater should be reduced at a certain level before the application of the biological processes [9,10]. It was reported that microorganisms in activated sludge were inhibited by copper and zinc at concentration above 1 and 10 mg/l, respectively [11]. The use of conventional activated sludge system and PACT to treat Cr(VI) containing wastewater has been carried out by Lee et al. [12]. The result shows that the powdered activated carbon (PAC) additions in activated sludge system can reduce the toxicity of Cr(VI) on activated sludge microorganisms due to the adsorption of Cr(VI) on PAC. This will increase the bioactivities of microorganisms and the efficiency of COD and Cr(VI) removal will be increased.

The objective of this research is to evaluate the efficacy of the simultaneous adsorption and biodegradation processes under sequencing batch reactor (SBR) operation in treating copper(II)-containing wastewater with powdered activated carbon or activated rice husk (ARH) addition.

2. Materials and methods

2.1. Preparation of rice husk and biomass for adsorption

Raw rice husks were collected from a rice mill located at Permatang Pauh, Butterworth. Initially, the rice husks were washed by tap water several times to remove the dirt, and then rinsed with distilled water. The rice husks were dried in an oven at 103 °C, then blended and sieved into sizes of 250 μm or less. Acid-activated rice husks were prepared by treating the sieved raw rice husks with concentrated HNO_3 (AR grade) at temperatures of 60–65 °C for 15 h. Then, the acid treated rice husks were washed by tap water and finally rinsed with distilled water until the pH was neutral. It was then dried in an oven again.

The deactivated biomass for adsorption study was prepared by autoclaving the live biomass at 1.5 atm pressure and at 121 °C for 30 min.

2.2. Adsorption study

The adsorbents used in the adsorption study were PAC, RH, ARH and the biomass. This study was conducted to determine the adsorption capacity for each adsorbent with Cu(II). A weight of 0.03 g PAC was shaken with 100.0 ml Cu(II) solutions with concentrations varying from 5 to 90 mg/l for a contact time of 5 h. Then, the solution was centrifuged at the speed of 240 rpm, filtered, and then the supernatant analyzed for Cu(II) concentration by using flame atomic adsorption spectrophotometer (Perkin-Elmer, Model 3100). For RH and ARH, the weight used was 0.4 and 0.2 g, respectively. In the case of the deactivated biomass, the volume used was 5.0 ml.

2.3. Determination of specific oxygen uptake rate (SOUR)

This study was conducted to assess the effect of different concentrations of Cu(II) and adsorbents on the activities of activated sludge microorganisms. To determine the effect of Cu(II) on activated sludge microorganisms, 50 ml of activated sludge was collected from the SBR reactor and placed in a BOD bottle, which was subsequently filled with a fully aerated Cu(II)-containing base mix solution with the Cu(II) concentrations varying from 7 to 49 mg/l. For each Cu(II) concentration, the dissolved oxygen (DO) in the BOD bottle was measured using DO meter (YSI Model-57) at interval of 10 s until it reached about 1 mg/l. After the DO measurement, the sample was filtered for the determination of MLSS concentration. In the case for the study of effect of adsorbent on the activities of activated sludge microorganisms, adsorbents like PAC and RH with concentrations varying from 0 to 5000 mg/l were added into the BOD bottle, which was filled with a fully aerated Cu(II)-containing base mix solution with Cu(II) concentration of 10 mg/l. The SOUR was calculated using the following equation:

$$\text{SOUR}\left(\frac{\text{mg O}_2}{\text{g MLSS h}}\right) = -60\frac{G}{X} \tag{1}$$

where G is the slope of the linear portion of the DO decline curve in mg/l, and X is the MLSS concentration in g/l.

2.4. Treatment process with and without PAC or ARH

Two identical reactors with a total liquid volume of 10 l built from plexiglass with dimensions of 30 cm × 25 cm × 20 cm were operated in parallel for a cycle time of 6 h. The operation mode for FILL, REACT, SETTLE, DRAW and IDLE were in the ratio of 0.5:3.5:1.0:0.75:0.25. Aeration was applied to the SBR reactor during the FILL and REACT modes by using submerged aeration stones. This operating scheme was adopted based on the good settleability of the sludge with the sludge volume index (SVI), consistently less than 100 ml/g when treating the synthetic wastewater. In each cycle, 7 l of feed solution was introduced continuously into the SBR reactor during the FILL mode and then the same amount of treated effluent was drawn during the DRAW mode after settling for 1 h.

The activated sludge seed was obtained from a sewage treatment plant in Batu Ferringgi, Penang. The activated sludge was acclimatized in the laboratory for 2 months by feeding

it with a synthetic wastewater consisting of a base mix of peptone, sucrose, nutrients and buffer solution in the following composition (concentrations in mg/l): bacto-peptone (188), sucrose (563), NH_4Cl (344), $MgSO_4$ (49), $FeCl_3$ (11.3), KH_2PO_4 (250), K_2HPO_4 (318) and $NaHCO_3$ (100) giving an equivalent COD of 550–650 mg/l. Once the SBR reactor had achieved a steady state by monitoring the performance in terms of COD removal (less than 10% variation), Cu(II) was spiked into the synthetic wastewater at 5 mg/l and then increased to 10 mg/l. Adsorbent, PAC or ARH, will be added into the SBR reactor with the synthetic wastewater during FILL mode. Dosages of PAC tested were 71.5 mg/l or 0.5 g per cycle and 143 mg/l or 1.0 g per cycle for Cu(II) concentration of 10 mg/l. In the case for ARH, 429 mg/l or 3.0 g per cycle, 572 mg/l or 4.0 g per cycle and 715 mg/l or 5.0 g per cycle, respectively for Cu(II) concentration of 10 mg/l.

The treated effluents collected from the DRAW mode in each cycle were analyzed for COD and Cu(II) concentrations. The COD concentration was determined by using Method 5220 C [13], whilst Cu(II) concentration was determined by using flame atomic adsorption spectrophotometer (Perkin-Elmer, Model 3100). The determination of MLSS and MLVSS concentrations followed the Standard Methods [13]. However, the mixed liquor carbon suspended solid (MLCSS) and mixed liquor biomass suspended solid (MLBSS) were determined by using the differential heating method described by Arbuckle and Grigg [14].

2.5. Kinetic study

This study was conducted to investigate the effect of Cu(II) and adsorbent additions on the rate of COD removal during the REACT mode in a cycle. Once the REACT mode had started, the mixed liquor sample was collected at 1, 3, or 5 min intervals from SBR reactor. The sample was immediately acidified to stop the reaction and allowed to settle for half an hour. The supernatant was then analyzed for COD concentration.

3. Results and discussion

3.1. Adsorption study

3.1.1. Contact time

Fig. 1 shows that most of the curves have a sharp increase in the amount of Cu(II) adsorbed on adsorbents up to around 1 h, followed by a slower rate of adsorption for about 3 h of contact time. Most of the adsorbents had already achieved maximum uptake of the Cu(II) at the end of 3 h and beyond this time adsorption was negligible. Therefore, a contact time of 5 h was used for all subsequent experiments. Besides adsorption studies, the determination of contact time is important for the selection period of the REACT mode in the SBR reactor.

3.1.2. Adsorption isotherms

The data for the uptake of Cu(II) by PAC, RH, ARH and biomass have been analyzed in light of Langmuir mode of adsorption. The Langmuir equation may be described as

$$q_e = \frac{Q^0 b C_e}{1 + b C_e} \quad \text{(non-linear form)} \tag{2}$$

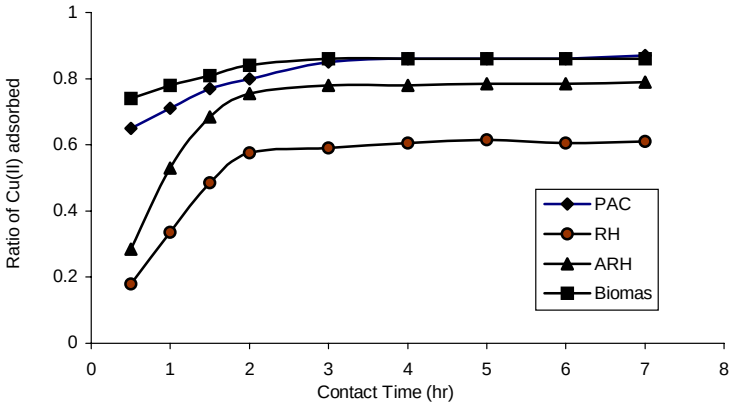

Fig. 1. Adsorption of Cu(II) ions on PAC, RH, ARH and biomass.

$$\frac{C_e}{q_e} = \frac{1}{bQ^0} + \frac{C_e}{Q^0} \quad \text{(linear form)} \tag{3}$$

where q_e is the mass metal adsorbed per unit mass of adsorbent (mg/g), C_e the equilibrium metal concentration (mg/l), Q^0 is the limiting amount of metal adsorbed per unit mass of adsorbent to form a complete monolayer on the surface and b is a constant related to the energy of adsorption. The plot of C_e/q_e against C_e gives a straight line (Fig. 2) for the adsorption of Cu(II) on PAC, RH, ARH and biomass showing that applicability of Langmuir isotherm. The values of Q^0 and b for each adsorbent are given in Table 1. The adsorbents arranged in the increasing order of adsorption capacities according to the Langmuir Q^0

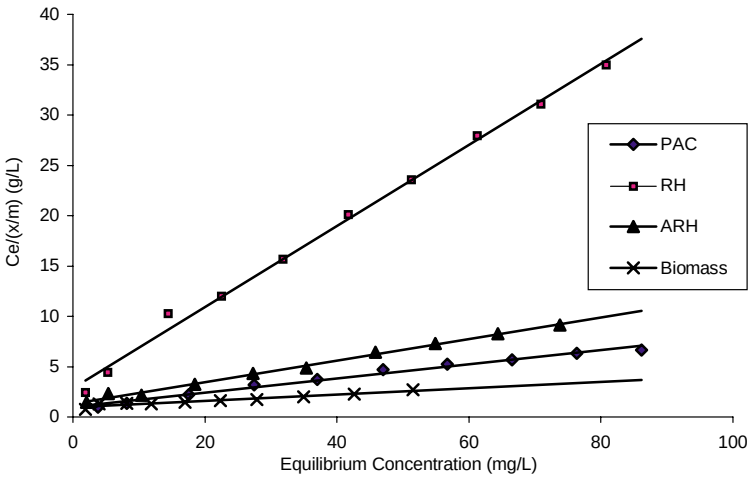

Fig. 2. Langmuir plot for the adsorption of Cu(II) on PAC, RH, ARH and biomass.

Table 1
Langmuir parameters

Adsorbate	Adsorbent	Q^0 (mg/g)	b	R^2
Cu(II)	PAC	14	0.0814	0.9837
	RH	2	0.1477	0.9956
	ARH	9	0.0803	0.9937
	Biomass	36	0.0255	0.9501

parameter were:

biomass > PAC > ARH > RH

The adsorption capacity Q^0 indicates that the adsorption of Cu(II) by biomass was comparable to PAC adsorption. This means that the biomass will play an equally important role as the PAC in reducing the added Cu(II) concentration in the SBR reactor. The adsorption capacity for biomass was high because metal ions were adsorbed on the binding sites present on the surface bacterial solids or formed complexes with bacterial exocellular polymers [9,10,15–18]. After activated by concentrated HNO_3, the adsorption capacity for RH was increased. The ARH will be used as adsorbent in the SBR reactor due to the good settleability during SETTLE mode and it will not contribute any COD to the base mix solution if compared to the RH.

3.2. Determination of specific oxygen uptake rate

3.2.1. Effects of Cu(II) on activated sludge microorganisms

This study was conducted to investigate the toxicity level of Cu(II) on the activated sludge microorganisms. Fig. 3 shown that the SOUR for biomass without Cu(II) addition was 142 mg O_2/(g MLSS h), which means that the microorganisms in activated sludge were very active in oxygen consumption to degrade the substrates. However, after 7 mg/l Cu(II) were added, the SOUR decreased drastically, by 69% if compared to the SOUR without Cu(II) addition. The addition of Cu(II) in the base mix solution inhibits the activities of microorganisms in substrate degradation and subsequently the oxygen uptake rate by microorganisms will be decreased. When higher Cu(II) concentrations were introduced to the activated sludge, the SOUR became lower until it reached a quite constant level, 7 mg O_2/(g MLSS h). This study showed that Cu(II) was very toxic to the activated sludge microorganisms although the concentrations of Cu(II) were low.

3.2.2. Effects of adsorbents on activated sludge microorganisms

3.2.2.1. Effects of PAC on microorganisms SOUR with and without Cu(II) addition. This study was conducted to investigate how the PAC affects the activities of microorganisms in activated sludge. Fig. 4 shows that SOUR was increased until it reached a quite constant level after addition of PAC with concentrations varying from 100 to 5000 mg/l. Before the PAC was added into the mix base solution, the degradation of substrates by microorganisms

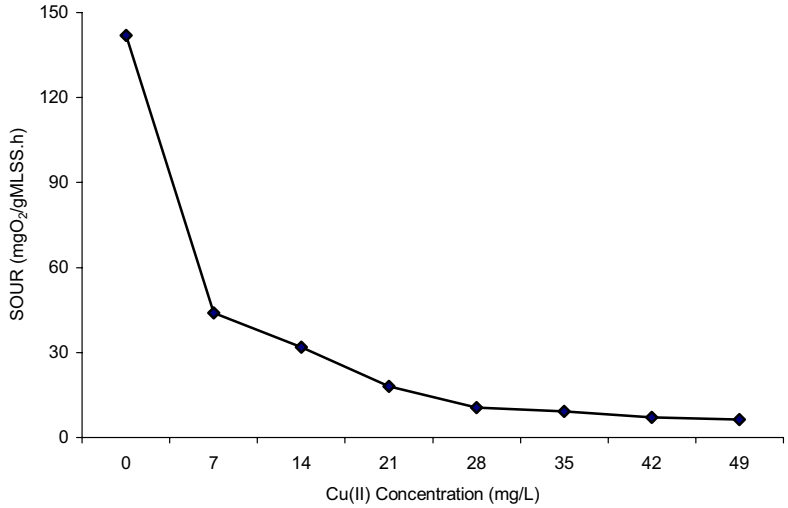

Fig. 3. Effect of Cu(II) concentration on microorganism SOUR.

was in a suspended form. It means that the substrate degradation depended on the probabilities of microorganisms and substrates coming across one another or meeting together. The additions of PAC can increase these probabilities by acting as reaction sites between microorganisms and substrates. Both microorganisms and substrates were attached on the PAC, so the substrate could be degraded by microorganisms easily.

In the case of 10 mg/l Cu(II) in the mix base solution, the microorganisms SOUR was lower if compared to the study without Cu(II) addition. It was due to the toxic effect of Cu(II), which has been explained in Section 3.2.1. Fig. 4 shows that the increase of the PAC concentrations in the 10 mg/l Cu(II)-containing mix base solution increased the

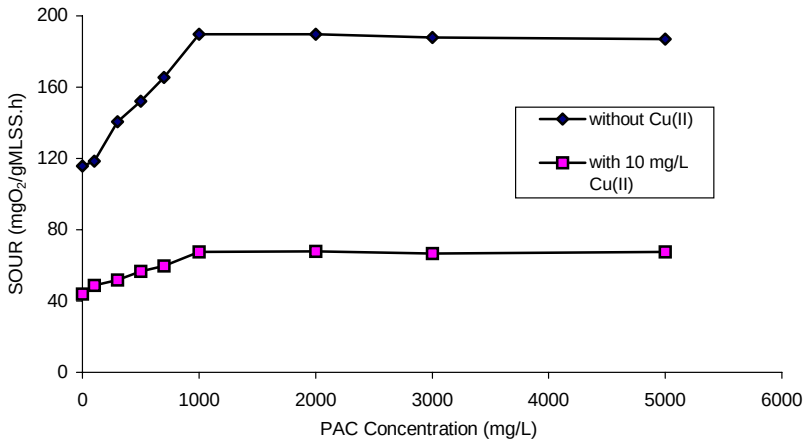

Fig. 4. Effect of PAC on microorganisms SOUR with 10 mg/l Cu(II) and without Cu(II) in the mix base solution.

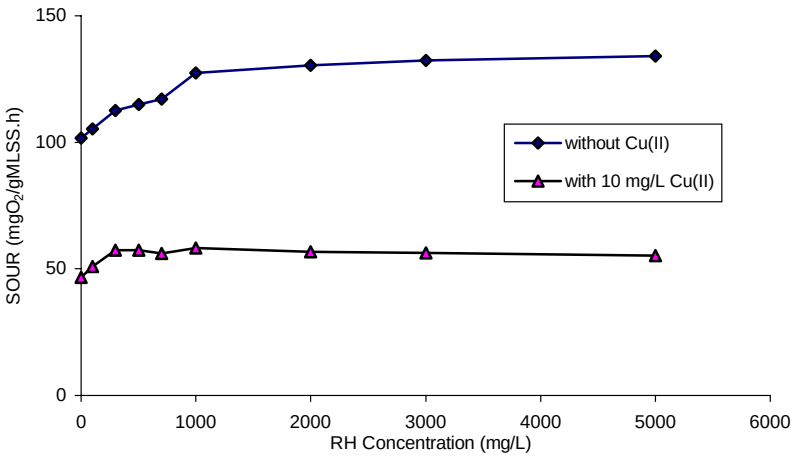

Fig. 5. Effect of RH on microorganisms SOUR with and without Cu(II).

microorganisms SOUR. The PAC additions reduced the toxic effects of Cu(II) on activated sludge microorganisms by Cu(II)-PAC adsorption. The increase of SOUR by the additions of PAC concentrations varying from 100 to 5000 mg/l were due to the Cu(II) adsorption by the PAC and the increase in reaction sites, which was provided by PAC.

3.2.2.2. Effects of RH on microorganisms SOUR with and without Cu(II) addition. Fig. 5 shows that the addition of RH increased the microorganisms SOUR for both mix base solution with 10 mg/l Cu(II) and without Cu(II) addition. The increases in oxygen uptake rates by activated sludge microorganisms were due to the ability of RH in Cu(II) adsorption and react as reaction sites between microorganisms and substrates. In the mix base solution without Cu(II) addition, the SOUR was increased around 30% for RH addition (Fig. 5) and 60% for PAC addition (Fig. 4), respectively. However, in the case of the mix base solution with 10 mg/l Cu(II) addition, the SOUR increased around 20% for RH addition (Fig. 5) and 50% for PAC addition (Fig. 4). This was due to the higher adsorption capacity of Cu(II) on PAC than RH and hence the toxic effect of Cu(II) was reduced.

3.3. Sequencing batch reactor (SBR) process with and without adsorbent

3.3.1. Treatment process with and without PAC

This study was conducted to investigate the effects of Cu(II) and PAC on the activated sludge microorganisms in SBR reactor. The performance of SBR reactor was accessed by monitoring the COD and Cu(II) concentrations in the treated effluent. Fig. 6(a) shows the change of COD removal efficiency in the SBR reactor with and without Cu(II) addition and at different PAC dosages. The addition of Cu(II) into the SBR reactor deteriorated the percentage of COD removal from 92 to around 70% on the addition of 5 mg/l Cu(II) and furthered decreased to 60% after the concentration of Cu(II) was increased to 10 mg/l. The addition of Cu(II) inhibits the bio-oxidation of activated sludge microorganisms in substrates

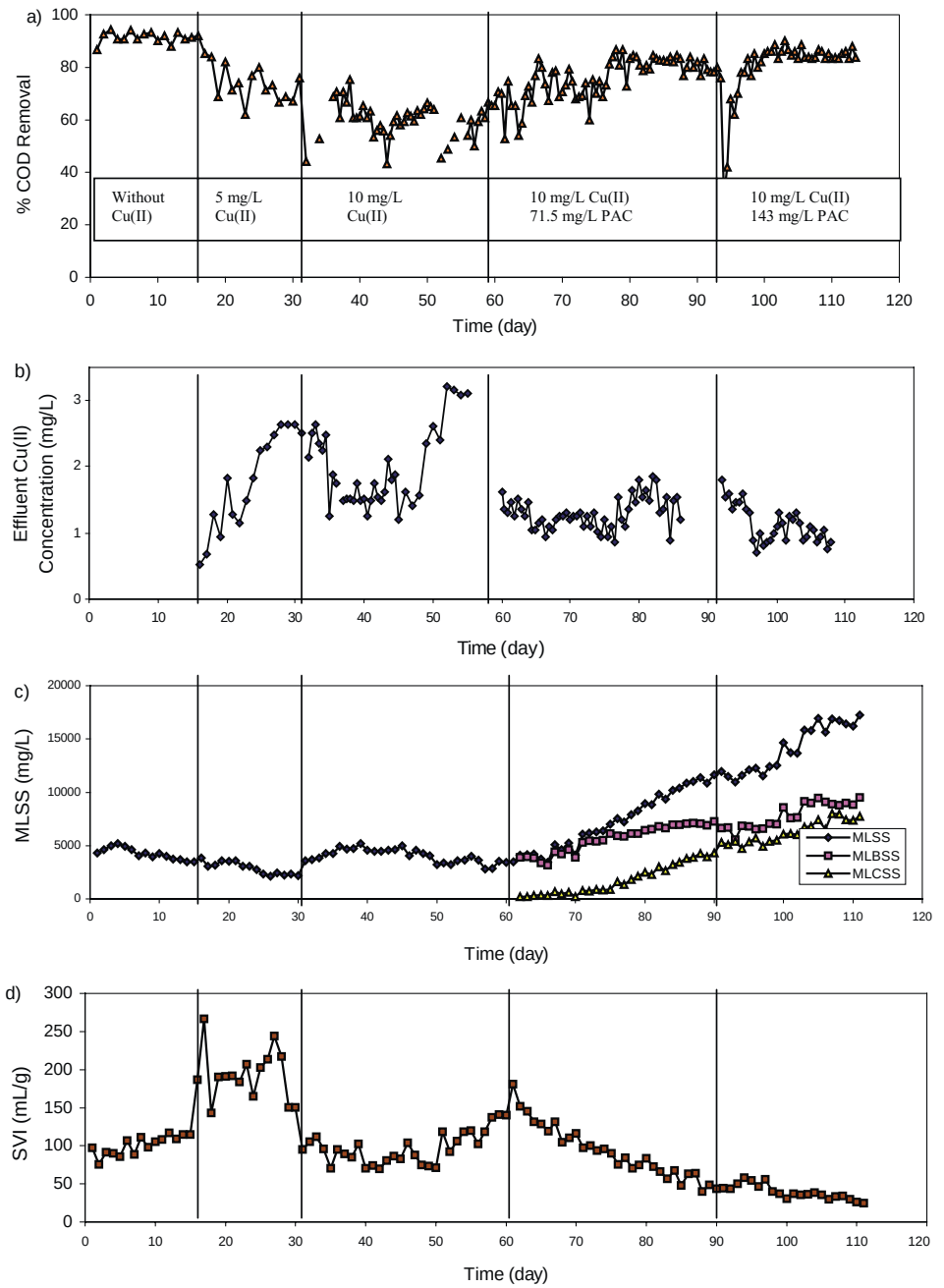

Fig. 6. The (a) COD removal efficiency, (b) effluent Cu(II) concentration, (c) MLSS concentration and (d) SVI for Cu(II)-containing wastewater before and after PAC addition.

degradation. The dissolved oxygen used by microorganisms was reduced and subsequently the SOUR was decreased after Cu(II) addition, which was explained in Section 3.2.1. The additions of 71.5 mg/l PAC or 0.5 g PAC per cycle increased the performance in the SBR reactor by reducing the COD effluents until below 100 mg/l or around 85% COD removal was achieved. The increases in PAC additions until 143 mg/l or 1.0 g PAC per cycle maintained the COD removal efficiency at 85%. The addition of PAC into the SBR reactor reduced the toxicity of Cu(II) on microorganisms by Cu(II)-PAC adsorption and hence enhanced the bio-oxidation.

Before the PAC additions, the effluent Cu(II) concentrations were consistently maintained below 3.5 mg/l (Fig. 6(b)) due to the Cu(II)-biomass adsorption, which was discussed in Section 3.1. The ability of activated sludge to retain Cu(II) to the tune of 70–80% of Cu(II) input in the range of 10–45 mg/l had been previously reported [19]. Fig. 6(b) shows that after the Cu(II) concentration was increased from 5 to 10 mg/l in synthetic wastewater, the effluent Cu(II) concentration was decreased. This was due to the increase in MLSS which is shown in Fig. 6(c). After the addition of 10 mg/l Cu(II), the sludge settleability was good and SVI was reduced until around 80 ml/g (Fig. 6(d)) during SETTLE mode in SBR reactor. The increase in MLSS would increase the binding sites for Cu(II)-biomass adsorption. The effluent Cu(II) concentration could be maintained at around 1 mg/l due to Cu(II)-PAC and Cu(II)-biomass adsorption after the PAC had added. The addition of PAC reduced the Cu(II) toxic effects on the microorganisms and hence increased the MLBSS in the SBR reactor (Fig. 6(c)). Besides, the sludge age of the biomass in the SBR reactor was quite long due to a very little sludge wastage during DRAW mode. The increase of the sludge age of the biomass enhanced the affinity of Cu(II) on the activated sludge microorganisms.

During FILL mode, the synthetic wastewater without Cu(II) additions was degraded immediately by activated sludge microorganisms, which is shown, by low DO in the DO profiles (Fig. 7). However, in the cases of 5 and 10 mg/l Cu(II) additions, this bio-oxidation period was prolonged until the REACT mode. The DO profiles in Fig. 7 show that after the Cu(II) addition, a longer period was required for bio-oxidation due to the Cu(II) toxic effects compared to the synthetic wastewater without Cu(II) addition.

3.3.2. Treatment process with and without ARH

The COD and Cu(II) concentrations of the treated effluents from SBR reactor were monitored to ascertain the effects of Cu(II) additions and the efficacy of the ARH in reducing the toxic effects of Cu(II). Fig. 8(a) shows the change of COD removal efficiency in SBR reactor with and without Cu(II) additions and at different ARH dosages. The additions of 286 mg/l ARH or 2.0 g ARH per cycle into the 5 mg/l Cu(II)-containing synthetic wastewater increased the percentage of COD (Fig. 8(a)) and Cu(II) (Fig. 8(b)) removal from around 75 and 66 to around 85 and 86%, respectively. The increases in Cu(II) and ARH concentrations to 10 and 429 mg/l or 3.0 g ARH per cycle, respectively, resulted in poorer COD and Cu(II) removal efficiency. However, the further increases of ARH addition to 715 mg/l or 5.0 g ARH per cycle and maintaining the 10 mg/l Cu(II) concentration, successfully reduced the COD and Cu(II) concentration in treated effluent to below 100 mg/l or a removal efficiency of about 85% and 0.8 mg/l or a removal efficiency of about 92%, respectively. These results indicated that ARH addition into the SBR reactor reduced the toxicity of Cu(II)

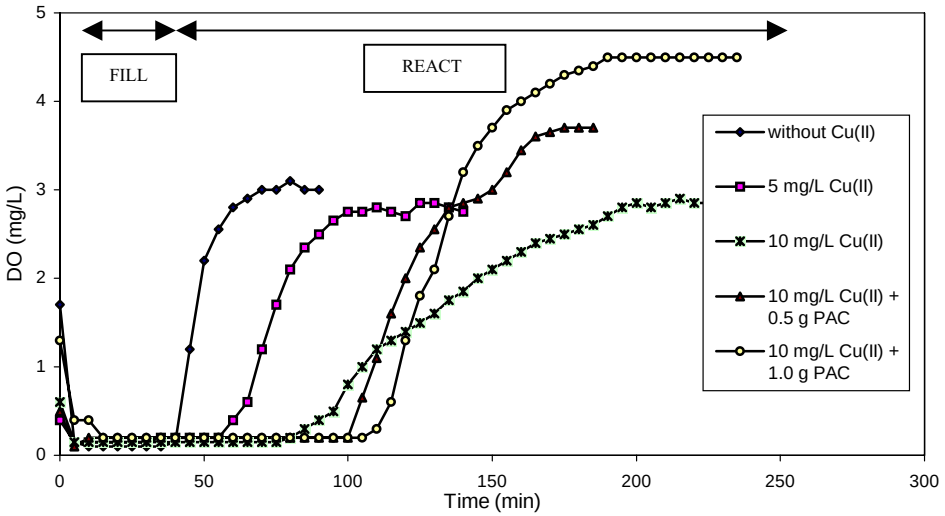

Fig. 7. Dissolved oxygen profiles during FILL and REACT modes, respectively, for base mix solution with and without Cu(II) and PAC addition.

on microorganisms by Cu(II)-ARH adsorption and hence enhanced the bio-oxidation. The Cu(II)-ARH adsorption alone cannot explain the percentage of Cu(II) removal efficiency at 92%, which was achieved in this study. The Cu(II)-biomass adsorption, which was explained in Section 3.3.1 also plays an important role in achieving the 92% Cu(II) removal efficiency. Fig. 8(c) shows that the MLSS in the SBR reactor increased from around 7000 to 19,000 mg/l and MLBSS was fairly constant with 8000 mg/l throughout the study. The good sludge settleability (Fig. 8(d)) allowed the accumulation of MLSS and little sludge wastage during the DRAW mode in the SBR reactor after ARH addition. The longer sludge age of the biomass produced more exocellular polymers and hence greater Cu(II) affinity [10].

Fig. 9 shows that the DO profiles during FILL and REACT modes for the Cu(II)-containing synthetic wastewater with and without ARH addition. The low DO values in FILL and REACT modes indicated that the bio-oxidation process was aggressively carried out by activated sludge microorganisms. The increases in ARH additions shortened this period due to the reducing of Cu(II) toxic effects on activated sludge microorganisms.

3.4. Kinetic study

The Monod equation has been widely used to describe substrate removal in biological wastewater treatment processes:

$$r_c = \frac{\mu_m X_v C}{K_m + C} \tag{4}$$

where r_c is the substrate removal rate, X_v the MLVSS concentration, μ_m and K_m the maximum and half velocity constants and C is the substrate concentration. At low substrate

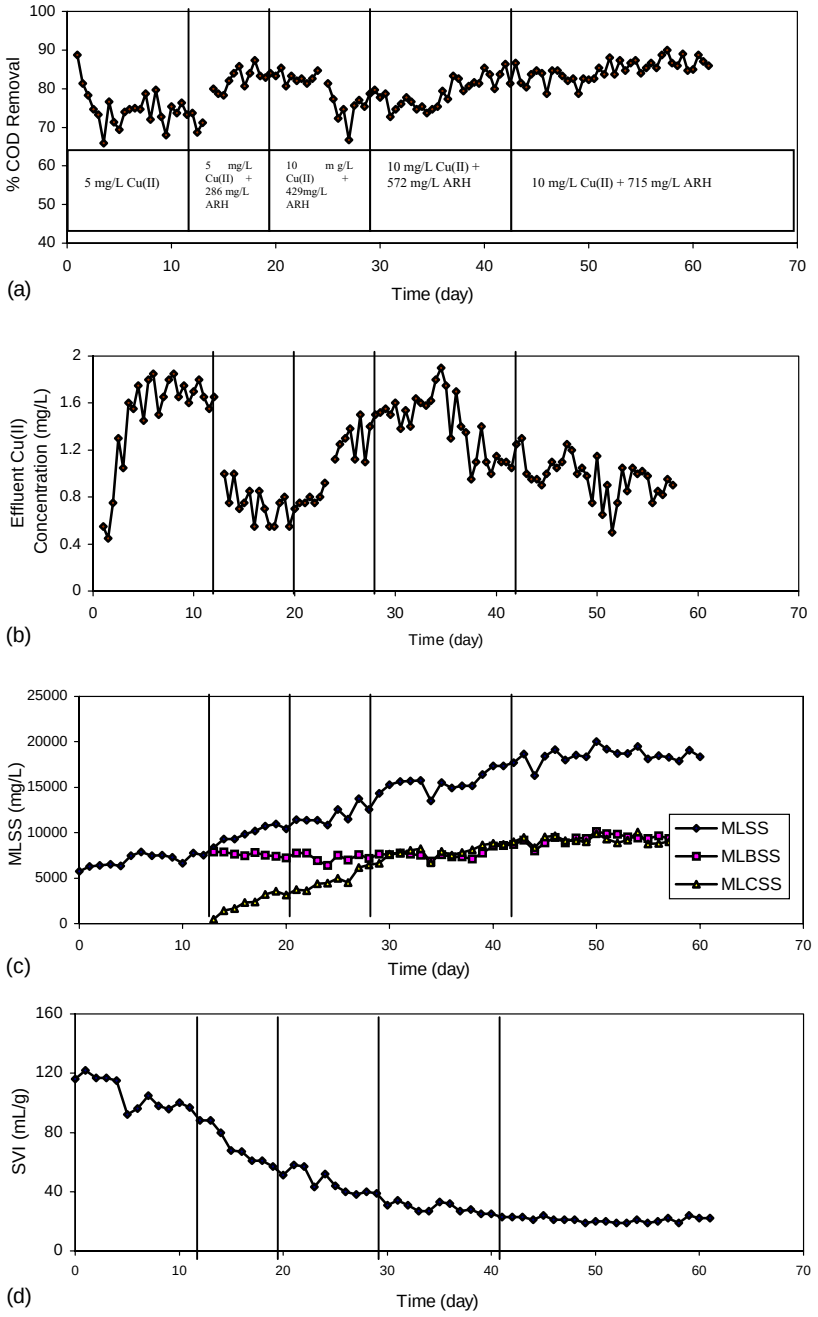

Fig. 8. The (a) COD removal efficiency, (b) effluent Cu(II) concentration, (c) MLSS concentration and (d) SVI for Cu(II)-containing wastewater before and after RH addition.

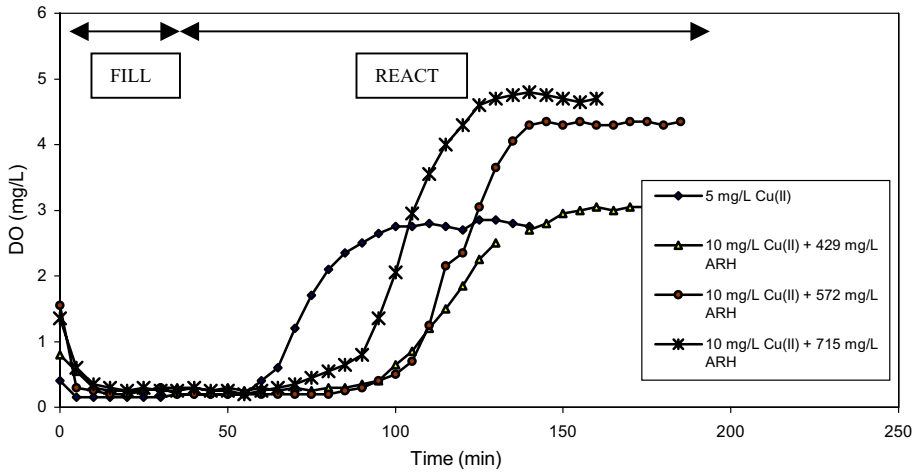

Fig. 9. Dissolved oxygen profiles during FILL and REACT mode, for base mix solution with and without Cu(II) and ARH addition.

concentration ($K_m \gg C$), Eq. (4) will reduce to a first-order formulation:

$$r_c = \frac{\mu_m X_v C}{K_m} \tag{5}$$

For SBR process, a mass balance on substrate in the reactor during the REACT mode can be shown to be:

$$-\left(\frac{dC}{dt}\right) = \frac{\mu_m X_v C}{K_m} = kC \tag{6}$$

where k is the pseudo first-order rate constant and t is the reaction time. In this case, k is the pseudo first-order rate constant for the REACT mode and C is the residual COD in the mixed liquor. By plotting n (COD) versus time, relatively good fit ($R^2 > 0.8$) for all cases was obtained indicating that the first-order formulation provides a reasonable correlation of kinetic results [20]. The apparent pseudo first-order rate constant k was determined from the gradient of the linear plot and the mean values of k for all cases are shown in Table 2.

Table 2
Comparison of pseudo first-order kinetic constants (per day)

Wastewater	k (per day)
Base mix	67 ± 10
Base mix + 5 mg/l Cu(II)	23 ± 1
Base mix + 10 mg/l Cu(II)	7 ± 1
Base mix + 10 mg/l Cu(II) + 71.5 mg/l PAC	32 ± 4
Base mix + 10 mg/l Cu(II) + 143 mg/l PAC	25 ± 2
Base mix + 10 mg/l Cu(II) + 429 mg/l ARH	19 ± 1
Base mix + 10 mg/l Cu(II) + 715 mg/l ARH	24 ± 1

In the presence of 5 mg/l Cu(II), the *k* value was decreased by 66% if compared to the base mix solution and further reduced to about 70% after 10 mg/l Cu(II) addition. The lower *k* values in the presence of Cu(II) indicate the toxic effect of Cu(II) on the activated sludge microorganisms. The increase in Cu(II) concentrations increased the toxic effects on the bio-oxidation process in microorganisms. The results in the kinetic study with the Cu(II) addition agreed with the earlier results of the effect of Cu(II) on SOUR activated sludge microorganisms.

It is observed that the addition of adsorbent, PAC and ARH, has resulted in an increase of the *k* value though the value still much lower than the case without Cu(II) addition. The *k* value in 71.5 and 143 mg/l PAC addition were 32 ± 4 and 25 ± 2 per day, respectively. If the uncertainties of the *k* value taken into account, it can be interpreted that the quantum of increase of PAC dosage was too small to result in a further observable reduction of the toxic effect of Cu(II) [20]. However, in the case of ARH additions, the increase in ARH from 429 to 715 mg/l did increase the *k* value by 26%. The increases of the *k* values in the PAC and ARH additions indicate the reduction of Cu(II) toxic effects and hence enhanced bio-oxidation by activated sludge microorganisms. The PAC and ARH should be added into biological treatment system before the activated sludge microorganisms are not highly intoxicated by heavy metals. It can be seen by drastic drop in *k* or SOUR value.

4. Conclusion

- The addition of the PAC and the RH increased the SOUR microorganisms in the base mix solution with and without the presence of Cu(II) by reducing the toxic effects of Cu(II) and provide a reaction site for microorganisms and substrates.
- The addition of 5 and 10 mg/l Cu(II) in the base mix solution decreased the performance of SBR reactor in terms of COD and Cu(II) removal efficiency in treated effluents.
- The addition of PAC and ARH in the SBR reactor reduced the inhibitory effect of Cu(II) on the activated sludge microorganisms partially.
- ARH can be used as an alternate adsorbent to PAC in the simultaneous adsorption and biodegradation wastewater treatment process for the removal of Cu(II).
- The biomass played an important role in the uptake of Cu(II) in the SBR reactor.

References

[1] D.N. Jenkins, Flow of toxic metals in environment, Int. Conf. Environ. Sens. Assess. 1 (1976) 1–5.
[2] N.A. Curry, Philosophy and methodology of metallic waste treatment, in: Proceedings of the 27th Industrial Waste Conference, Purdue University Engineering Ext. Series No. 141, 1972, pp. 85–94.
[3] J.G. Dean, F.L. Bosqui, K.H. Lanouette, Removing heavy metals from wastewater, Environ. Sci. Technol. 6 (1972) 518–522.
[4] J.V. Rouse, Removal of heavy metals from industrial effluents, J. Environ. Eng. Div., Am. Soc. Civ. Eng. 102 (EE5) (1976) 926–936.
[5] B. Sandhya, A.K. Tonni, Low-cost adsorbents for heavy metals uptake from contaminated water: a review, J. Hazard. Mater. B27 (2003) 219–243.
[6] K.S. Low, C.K. Lee, Quaternized rice husk as sorbent for reactive dyes, Biores. Technol. 61 (1997) 121–125.

[7] A.J. Mmari, A.A. Zainal, K.Y. Liew, Characterisation of pyrolysed rice husks and their adsorptive activities for Cu^{2+} ions, Malays. J. Chem. 1 (1998) 36–42.
[8] P. Madoni, D. Donatella, G. Gessuca, V. Luciano, Toxic effects of heavy metals on the activated sludge protozoan community, Water Res. 30 (1) (1996) 135–141.
[9] M.H. Cheng, J.W. Patterson, R. Minear, Heavy metals uptake by activated sludge, J. Water Pollut. Control Fed. 47 (1975) 362–376.
[10] P.O. Nelson, A.K. Chung, M.C. Hudson, Factors affecting the fate of heavy metals in the activated sludge process, J. Water Pollut. Control Fed. 53 (1981) 1323–1333.
[11] H. Chua, P.H.F. Yu, S.N. Sin, M.W.L. Cheung, Sub-lethal effects of heavy metals on activated sludge microorganisms, Chemosphere 39 (15) (1999) 2681–2692.
[12] S.E. Lee, H.S. Shin, B.C. Paik, Treatment of Cr(VI)-containing wastewater by addition of powdered activated carbon to the activated sludge process, Water Res. 23 (1989) 67–72.
[13] APHA, Standard Methods for the Examination of Water and Wastewater, 17th ed., American Public Health Association, Washington, DC, 1989.
[14] W.B. Arbuckle, A.A. Grigg, Determination of biomass MLVSS in PACT sludges, J. Water Pollut. Control Fed. 54 (1982) 1553–1557.
[15] K.R.K. Alibhai, I. Mehrotra, C.F. Forster, Heavy metal binding to digested sludge, Water Res. 19 (1985) 1483–1488.
[16] B.R. Fristoe, P.O. Nelson, Equilibrium chemical modeling of heavy metals in activated sludge, Water Res. 17 (1983) 771–778.
[17] T. Rudd, R.M. Sterritt, J.N. Lester, Stability constants and complexation capacities of complexes formed between heavy metals and extracellular polymers from activated sludge, J. Chem. Technol. Biotechnol. 33a (1983) 374–380.
[18] T. Rudd, R.M. Sterritt, J.N. Lester, Formation and conditional stability constants complexes formed between heavy metals and extracellular polymers from activated sludge, Water Res. 18 (1984) 379–384.
[19] E.Q. Moulton, K.S. Shumate, in: Proceedings of the 18th Conference on the Purdue Industrial Waste, vol. 18, 1963, pp. 607–615.
[20] P.E. Lim, S.A. Ong, C.E. Seng, Simultaneous adsorption and biodegradation processes in sequencing batch reactor (SBR) for treating copper and cadmium-containing wastewater, Water Res. 36 (3) (2002) 667–675.