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Effects of Cu(II) and Cd(II) on the performance of sequencing batch reactor treatment system

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Abstract

The effects of Cu(II) and Cd(II)-containing wastewater on activated sludge microorganisms were investigated. The addition of Cu(II) and Cd(II) affected significantly the activities of activated sludge microorganisms in the bio-oxidation process, as indicated by drastic reduction in the specific oxygen uptake rate (SOUR) values. The sequencing batch reactor (SBR) system was operated with FILL, REACT, SETTLE, DRAW, and IDLE modes in the time ratio of 0.5:3.5:1.0:0.75:0.25 for one cycle time of 6 h. The addition of Cu(II) and Cd(II)-containing synthetic wastewater into the SBR system decreased the chemical oxygen demand (COD) and metals removal efficiencies. The examination of the pseudo first-order rate constant, k', providing a quantitative estimate of the inhibitory effect of the metal, showed that the k' value with the metals addition was around 10 times lower than that without metals addition.

Keywords: Wastewater treatment; Sequencing batch reactor; Heavy metals; SOUR

1. Introduction

Heavy metals are commonly found in effluents from electroplating and other metal-processing industries. Conventional methods of heavy metal removal from aqueous solutions usually involve physico-chemical treatments such as precipitation, filtration, ionic exchange, adsorption, electron-deposition, reverse osmosis etc. [1–4]. Although the mechanisms by which heavy metals affect biological treatment processes are not well defined, the general response of these processes to varying concentrations of metals is well documented [5]. It was reported that activated sludge microorganisms and process efficiency were inhibited by cadmium, chromium and nickel at concentration above 10 mg/l [6,7]. However, trace amounts of heavy metals are still required by microorganisms for optimum growth [8]. The deleterious effects of toxic compounds on biological processes are complex and are generally related to the species, and the solubility of the metal concentration of the toxicant [9].

Sequencing batch reactors (SBRs) are an attractive alternative to conventional biological wastewater treatment systems, mainly because of their simplicity and flexibility of operation. A numbered of papers providing a good description and evaluation of the SBR systems had been published [10,11]. The SBR is a periodically operated, fill-and-draw reactor [10,12]. Each reactor in a SBR system has five discrete periods in each cycle: FILL, REACT, SETTLE, DRAW, and IDLE. Reactions imitated during FILL and completed during REACT. After REACT, the mixed liquor suspended solids (MLSSs) are allowed to separate by sedimentation during SETTLE in a defined time period; the treated effluent is withdrawn during DRAW. The time period between the end of the DRAW and the beginning of the new FILL is termed IDLE [13]. SBRs have been successfully used to remove various types of pollutant including dyes [14] and chlorinated compounds [15]. Moreover, filamentous bacteria growth can be easily controlled by varying the FILL:REACT ratio or varying the operating strategies during FILL mode [16,17].

In fact, a single metal species exists very seldom in wastewater. The presence of more than one metal often gives rise to interactive effects. Although the interactive effects of a mixture of heavy metals are extremely complex, it has been shown that the final expression of heavy metal toxicity in

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a biological treatment process depends on types and concentration levels of metals, order of metal addition, types of microorganisms present in the medium, mean cell residence time, type and strength of the influent wastewater and the pH of the medium [18]. The objective of this research was to investigate the effects of Cu(II) and Cd(II)-containing wastewater on the performance of SBR system. The efficacy of powdered activated carbon (PAC) in reducing the toxic effects of Cu(II) and Cd(II) on the activated sludge microorganisms' activities was investigated. Cu(II) and Cd(II) were used for the study because of their widespread industrial use and known toxicity to organisms.

2. Materials and methods

2.1. Batch sorption tests

Sorption tests were conducted in plastic bottles (120 ml) using an orbital shaker in a constant room temperature. The adsorbents used were PAC and biomass. An appropriate amount of PAC or biomass was shaken with 100.0 ml Cu(II) or Cd(II) solutions with concentrations varying from 5 to 90 mg/l for a contact time of 5 h. The sorption mixture was centrifuged and the supernatant was analyzed for Cu(II) or Cd(II) concentration using flame atomic adsorption spectrophotometer (Perkin Elmer, Model 3100).

The metal sorption data were fitted to the Langmuir isotherm model:

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

where q_e is the mass of metal adsorption per unit mass of adsorbent (mg/g), C_e, the equilibrium concentration of metal in solution (mg/l), Q^0 is the maximum metal adsorption per gram of biomass (mg/g) and b is the constant related to affinity (l/mg).

2.2. Specific oxygen uptake rate (SOUR) study

The effects of Cu(II) and Cd(II) on the activated sludge were investigated by measuring the change of SOUR of activated sludge by increasing the concentration of heavy metals. A sample of 50 ml activated sludge was collected from the SBR reactor and placed in a biochemical oxygen demand (BOD) bottle, which was subsequently filled with a fully aerated of Cu(II) and Cd(II)-containing base solution with the concentrations varying from 7 to 35 mg/l. The ratio of Cu(II) and Cd(II) concentration was 1:1 at all run. The dissolved oxygen (DO) concentration was monitored with an YSI DO meter Model-57 at 10 s interval until it reached about 1 mg/l. In the case for studying the effect of adsorbent on the activated sludge microorganisms activities, powdered activated carbon with concentrations varying from 0 to 5000 mg/l were added into the BOD bottle, which was filled with a fully aerated of combined Cu(II) and Cd(II)-containing base solution with the heavy metals concentration of 10 mg/l. The SOUR can be calculated according to the following equation:

$$\text{SOUR}(\text{mg O}_2/\text{g MLSS} \cdot \text{h}) = -\left(\frac{60G}{X}\right) \tag{2}$$

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

2.3. SBR process with and without PAC

A 10 l sequencing batch reactor was used to simulate the operation of the activated sludge process. The SBR system was operated for a cycle time of 6 h. The operation modes for FILL, REACT, SETTLE, DRAW, and IDLE were in the time 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 using submerged aeration stones. In each cycle, 7 l of feed solution was introduced continuously into the SRR 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 wasting of sludge was achieved during the DRAW mode. A schematic diagram of the reactor is shown in Fig. 1.

The activated sludge seed was obtained from municipal wastewater treatment plant and was acclimatized in the laboratory by feeding it with a synthetic wastewater consisting of (mg/l) bacto-peptone (188), sucrose (563), NH_4Cl (344), $MgSO_4$ (49), $FeCl_3$ (11.3), KH_2PO_4 (250), K_2HPO_4

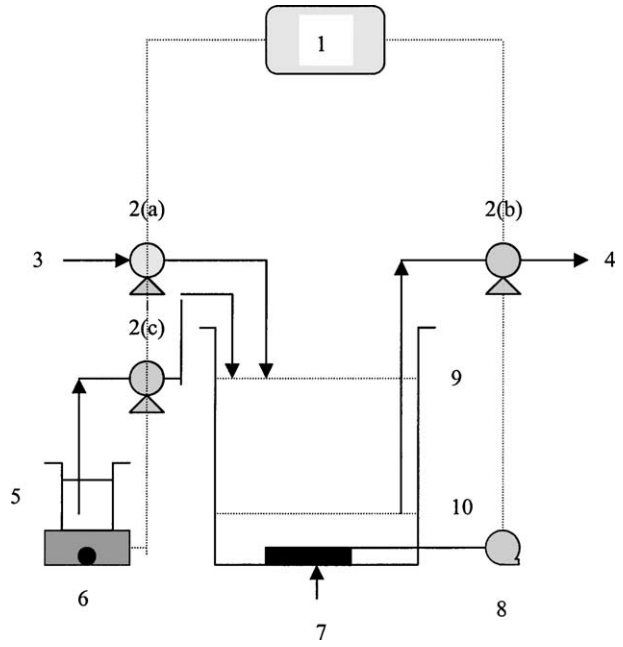

Fig. 1. Sequencing batch reactor. (1) Timer; (2) pumps; (3) synthetic wastewater; (4) treated effluent and desludge; (5) PAC slurry; (6) magnetic stirrer; (7) submerged aeration stone; (8) air pump; (9) maximum water level; and (10) minimum water level.

(318) and $NaHCO_3$ (100). This composition contributed 550–650 mg/l of chemical oxygen demand (COD) concentration. Once the SBR reactor achieved a steady state by monitoring the performance of COD removal and mixed liquor suspended solid concentration (less than 10% variation), 5 mg/l Cu(II) and 15 mg/l Cd(II) were spiked into the synthetic wastewater and then increased to 10 mg/l Cu(II) and 30 mg/l Cd(II). PAC was added into the SBR reactor with the synthetic wastewater during FILL mode. Dosage of PAC tested was 143 mg/l or 1.0 g/cycle.

The treated effluents collected from the DRAW mode in each cycle were analyzed for COD, Cu(II) and Cd(II) concentrations. The COD concentration was determined by using Method 5220C (APHA, 1992), whilst Cu(II) and Cd(II) concentration were determined by using flame atomic adsorption spectrophotometer (Perkin Elmer, Model 3100). The determination of mixed liquor suspended solid (MLSS) and mixed liquor volatile suspended solid (MLVSS) concentrations followed the standard methods [19]. However, the mixed liquor carbon suspended solid (MLCSS) and mixed liquor biomass suspended solid (MLBSS) were determined by using the differential heating method proposed by Arbuckle and Grigg [20].

2.4. Kinetic study

This study was conducted to investigate the rate of COD removal in the SBR reactor. The pseudo first-order kinetic constants of biological oxidation during the REACT mode were determined for reactor treating Cu(II) and Cd(II)-containing wastewater before and after the addition of metal ions by monitoring the residual soluble COD in the mixed liquor. Mixed liquor sample was collected in a flask at 1, 3 or 5 min intervals from SBR reactor once the REACT mode began. The sample was immediately acidified to stop the reaction and allowed to settle for half an hour. The supernatant was analyzed for COD concentration.

3. Results and discussion

3.1. Adsorption Isotherms

Data for the uptake of Cu(II) and Cd(II) by PAC and biomass, respectively, were tested with the Langmuir isotherm. The plot of C_e/q_e against C_e (Eq. (1)) gives a straight line for the adsorption of Cu(II) and Cd(II) on PAC and biomass showing the applicability of Langmuir isotherm. The Langmuir constants evaluated from the isotherm with the correlation coefficient are shown in Table 1. The adsorption capacity Q^0 indicates that the adsorption of Cu(II) and Cd(II) by biomass was higher than PAC adsorption. The high adsorption capacity of biomass was due to the metals adsorbed on the surface of bacterial solids or formed complexes with bacterial exocellular polymeric substances.

Table 1
Langmuir parameters

Adsorbate	Adsorbent	Q^0 (mg/g)	b	R^2
Cu(II)	PAC	14	0.0814	0.9837
	Biomass	36	0.0255	0.9501
Cd(II)	PAC	36	0.0152	0.9151
	Biomass	53	0.0277	0.9743

3.2. Effects of Cu(II) and Cd(II) on microorganisms SOUR

This was conducted to investigate the toxicity level of mixed Cu(II) and Cd(II) on the activated sludge microorganisms. The addition of Cu(II) and Cd(II) affected significantly the activities of microorganisms in the processes degrading organic matters, as indicated by a drastic reduction in the SOUR values (Fig. 2). The SOUR values decreased about 90% when Cu(II) and Cd(II) concentrations were higher than 20 mg/l, respectively. During this stage, almost all the activities of microorganisms were inhibited by the toxic effects of Cu(II) and Cd(II).

3.3. Effects of PAC on microorganisms SOUR

This was conducted to investigate how the PAC affects the activities of activated sludge microorganisms. The addition of PAC into the base solution with and without the presence of Cu(II) and Cd(II) increased the oxygen uptake rate of activated sludge microorganisms, as indicated by a gradual increase in the SOUR values (Fig. 3). PAC reduced the toxic effects of Cu(II) and Cd(II) on the activated sludge microorganisms by Cu(II)–PAC and Cd(II)–PAC adsorption processes. Besides, the addition of PAC could increase the probabilities of microorganisms and substrates come closer

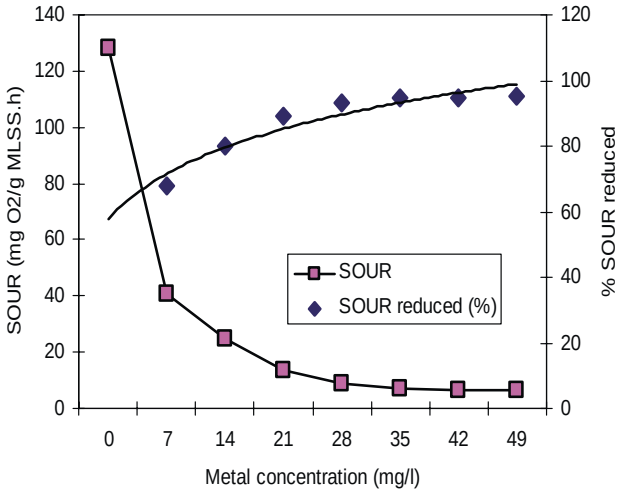

Fig. 2. Effect of combined Cu(II) and Cd(II) concentration on microorganisms SOUR.

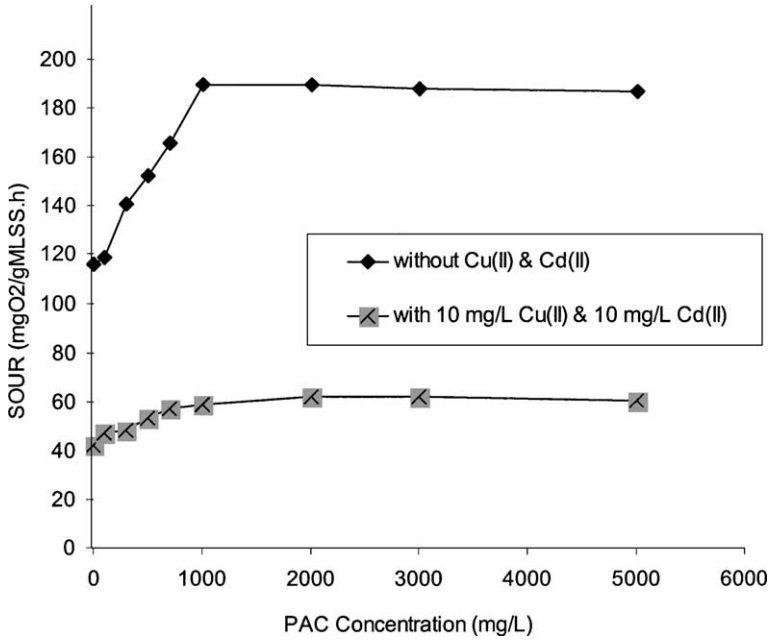

Fig. 3. Effect of PAC on microorganisms SOUR with and without Cu(II) and Cd(II) in the mix base solution.

to each another by supplying many reaction sites between microorganisms and substrates. Both microorganisms and substrates adhered on the PAC surface, so the substrate could be degraded by microorganisms easily. The increase of reaction sites and the decrease of the metal toxicity by adding PAC enabled the activated sludge microorganisms to perform the biodegradation process effectively. Consequently, the oxygen consumption by activated sludge microorganisms was increased.

3.4. Treatment process with and without PAC

The effects of combined Cu(II) and Cd(II) on the performance of SBR system was measured by monitoring the COD, Cu(II), and Cd(II) concentrations in the treated effluent. Fig. 4a shows the change of COD removal efficiency in the SBR system with and without Cu(II), Cd(II) and PAC addition. The addition of 5 mg/l Cu(II) and 15 mg/l Cd(II) into the SBR reactor decreased the percentage of COD removal from 90 to 75%. The addition of Cu(II) and Cd(II) inhibited the bio-oxidation of activated sludge microorganisms in substrates degradation. The dissolved oxygen used by the microorganisms diminished and subsequently the SOUR decreased after Cu(II) and Cd(II) addition. After 20 days of the addition of 10 mg/l Cu(II) and 30 mg/l Cd(II), the COD removal efficiency decreased drastically until around 40%. The added metals had serious effects on the bio-oxidation of activated sludge microorganisms in COD removal. The additions of 143 mg/l PAC or 1.0 g PAC/cycle only slightly improved the COD removal efficiency. By the time the PAC was added, the intoxicated microorganisms hardly performed the biodegradation process effectively.

During the period of addition of 5 mg/l Cu(II) and 15 mg/l Cd(II) into the SBR system, the average removal efficiency of Cu(II) and Cd(II) were 80 and 73%, respectively (Fig. 4b). This was due to the Cu(II) and Cd(II) adsorption by biomass. The adsorption ability of activated sludge had been previously reported as to retain Cu(II) removal ratio at 70–80% of the range of 10–45 mg/l influent [21]. Fig. 4b shows that the effluent Cu(II) and Cd(II) concentration increased drastically after the Cu(II) and Cd(II) concentration were increased from 5 to 10 mg/l and 15 to 30 mg/l, respectively. This could be due to the binding sites on the activated sludge being almost saturated and could not further retain the metals from the synthetic wastewater. After the addition of PAC, the Cu(II) and Cd(II) concentration in the treated effluent were reduced to 1.5 and 2.5 mg/l, respectively, due to the Cu(II)–PAC and Cd(II)–PAC adsorption.

Fig. 4c shows that after the addition of mixed Cu(II) and Cd(II), the MLSS in the SBR system increased until around 9000 mg/l. The addition of metal ions killed the filamentous bacteria in the activated sludge. The decrease in the filamentous bacterial population improved the settling ability of the activated sludge in the SBR system which was shown by low sludge volume index (SVI) in the Fig. 4d. The increase in MLSS concentration would increase the binding sites for metal-biomass adsorption. However, after 20 days with the addition of 10 mg/l Cu(II) and 30 mg/l Cd(II), the treated effluents became very cloudy and contained high concentrations of suspended solids in treated effluents. The washout of suspended solids caused the decrease of biomass in the SBR system. The addition of PAC able lead to maintenance of about 7000 mg/l of biomass due to the agglomeration process between biomass and PAC. This action prevented

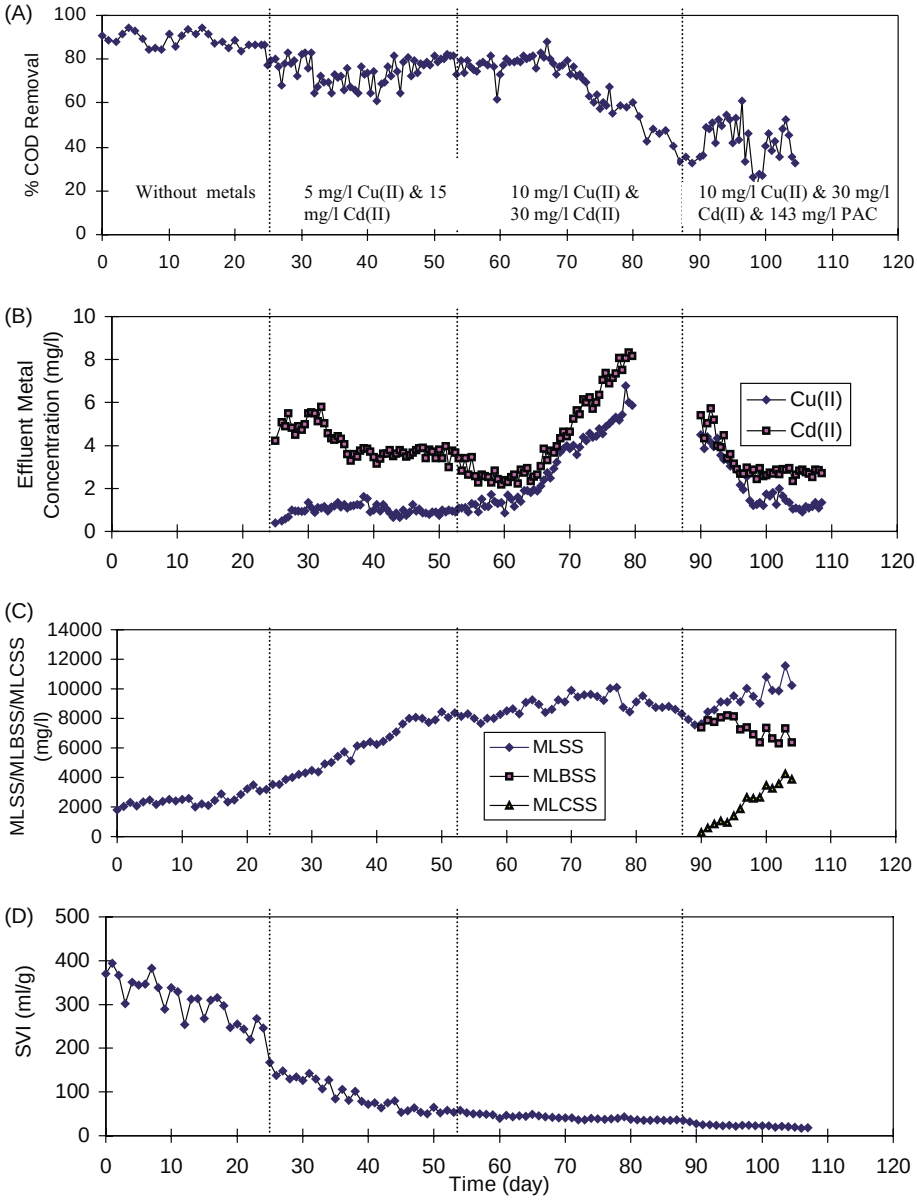

Fig. 4. The (a) COD removal efficiency; (b) effluent Cu(II) and Cd(II) concentration; (c) MLSS concentration; (d) SVI in SBR treating Cu(II) and Cd(II)-containing wastewater before and after the addition of PAC.

continues washout of biomass from SBR system. The accumulation of PAC in the SBR system was shown in the increase of MLCSS in Fig. 4c. The sludge age of the biomass was quite long (about 35–50 days) due to little sludge wastage. The increase of the sludge age of the biomass enhanced the affinity of metals on the activated sludge [22].

Fig. 5 shows the DO profiles during FILL and REACT modes for the SBR treating Cu(II) and Cd(II)-containing wastewater. During FILL mode, activated sludge microorganisms degraded the synthetic wastewater without metals addition immediately. This is shown by low DO in the DO profile. The low DO values in FILL and REACT modes indicated that activated sludge microorganisms aggressively carried out the bio-oxidation process. However, in the cases of metals addition, the bio-oxidation period was prolonged until the REACT mode due to the toxic effects of metals. After 35 days with the addition of 10 mg/l Cu(II) and 30 mg/l Cd(II), the DO in the SBR reactor was increased rapidly during FILL mode. This indicated that the oxygen consumed by activated sludge microorganisms was low due to the low bioactivity in substrate degradation. The DO profile for the system with PAC addition was quite similar to the system without PAC addition. This is because the SBR system was placed under too toxic conditions and the activated sludge microorganisms could not carry out the biodegradation process effectively by the time the PAC was added.

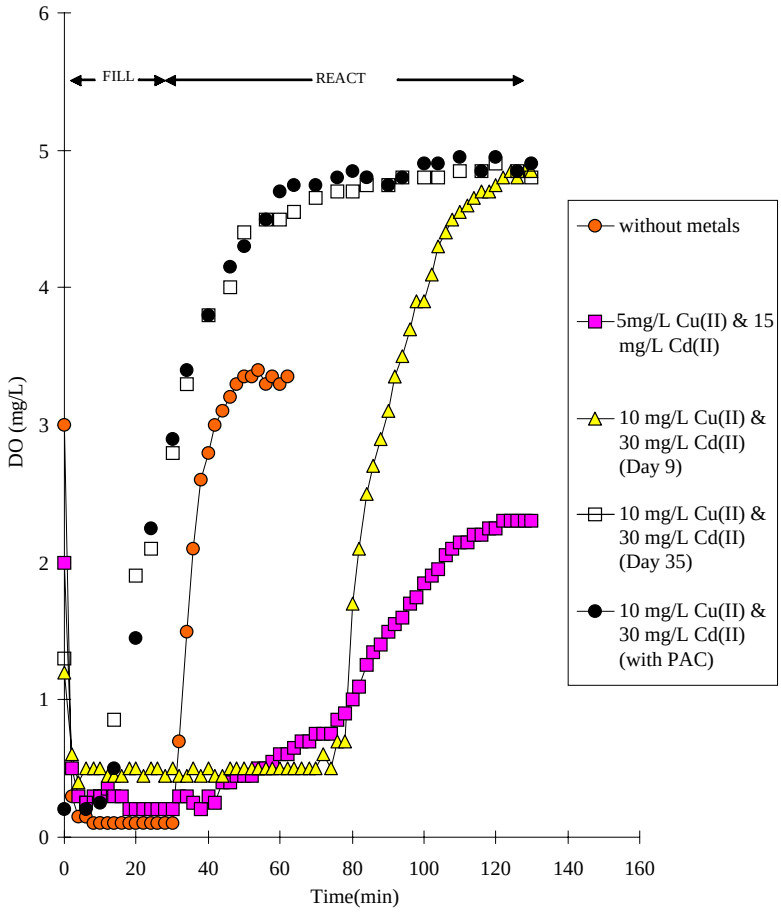

Fig. 5. DO profiles during FILL and REACT modes in the SBR reactor with and without metals and PAC containing wastewater.

3.5. Kinetic study

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

$$r_c = \frac{\mu_m X_v C}{K_m + C} \quad (3)$$

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 concentration ($K_m \gg C$), Eq. (3) will reduce to a first-order formulation:

$$r_c = \frac{\mu_m X_v C}{K_m} \quad (4)$$

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

$$-\left(\frac{dC}{dt}\right) = \frac{\mu_m X_v C}{K_m} = kC \quad (5)$$

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 ln (COD) versus time, the k value can be determined (Fig. 6). A relatively good fit ($R^2 > 0.9$) for all cases was obtained indicating that the first-order formulation provides a reasonable correlation of kinetic results. The pseudo first-order rate constant k was determined from the gradient of the linear plot and the value

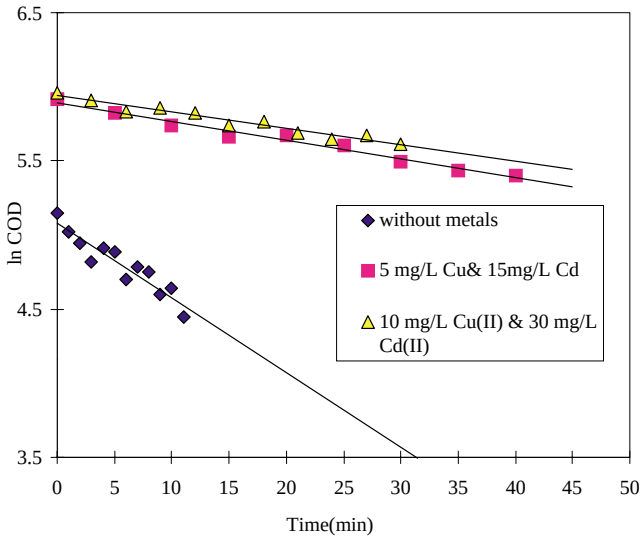

Fig. 6. Plots of ln COD vs. time for first-order kinetic constant determination for combined Cu(II) and Cd(II) wastewater.

Table 2
Comparison of pseudo first-order kinetic constants (day MLVSS)$^{-1}$

Wastewater	k'	MLVSS (mg/l)
Without metals	0.0228	3182
5 mg/l Cu(II) and 15 mg/l Cd(II)	0.0044	4156
10 mg/l Cu(II) and 30 mg/l Cd(II)	0.0020	8154

of k was then divided by MLVSS, giving the value for the pseudo first-order rate constant, k', in day^{-1} MLVSS^{-1}.

The change in the k' value provides a quantitative estimate of the inhibitory effects of the metal on the bioactivity. Table 2 shows that after the addition of metals, the k' value became lower. This indicated that the Cu(II) and Cd(II) inhibited the bioactivity of the activated sludge microorganisms in SBR reactor. The increase of the metals concentration had increased the inhibitory effects on the activity of the microorganisms.

4. Conclusion

The addition of PAC increased the oxygen uptake rate of activated sludge microorganisms by reducing the toxic effects of metals and supplying reaction sites for the access of microorganisms and substrates.

The COD removal efficiency in the SBR system decreased from 90 to 75% after the addition of 5 mg/l Cu^{2+} and 15 mg/l Cd^{2+} in the base solution. This was due to the inhibitory effects of the metals on bio-oxidation of activated sludge microorganisms. These results were confirmed by the kinetic study showing that the microbial activity in the SBR system with the metals addition was around 10 times lower than the system without metals addition.

The addition of 10 mg/l Cu(II) and 30 mg/l Cd(II) in the base solution seriously affected the bio-oxidation of microorganisms and the addition of PAC failed to improve the bio-activity of microorganisms. The addition of PAC into SBR reactor to reduce the toxic effects of metals should be carried out as early as possible before the microorganisms were seriously impaired.

The Cu^{2+} and Cd^{2+} removal ratio in the SBR systems was above 80 and 70%, respectively, which was attributed to the metals-PAC and metals-biomass adsorption process.

Appendix A. Nomenclature

b	constant related to affinity (l/mg)
BOD	biochemical oxygen demand (mg/l)
COD	chemical oxygen demand (mg/l)
C	substrate concentration (mg/l)
C_e	equilibrium concentration of metal in solution (mg/l)
DO	dissolved oxygen (mg/l)
G	slope of the linear portion of the DO decline curve (mg/l min)
k	pseudo first-order rate constant (day^{-1})
k'	pseudo first-order rate constant (min MLVSS)$^{-1}$
K_m	half velocity constant
MLBSS	mixed liquor biomass suspended solid (mg/l)
MLCSS	mixed liquor carbon suspended solid (mg/l)
MLSS	mixed liquor suspended solid (mg/l)
MLVSS	mixed liquor volatile suspended solid (mg/l)
PAC	powdered activated carbon
q_e	mass of metal adsorption per unit mass of adsorbent (mg/g)
Q^o	maximum metal adsorption per gram of biomass (mg/g)
r_c	substrate removal rate
SBR	sequencing batch reactor
SOUR	specific oxygen uptake rate (mg O_2/g MLSS h)
SVI	sludge volume indics (ml/g)
X	MLSS concentration (g/l)
X_v	MLVSS concentration (mg/l)
μ_m	maximum velocity constant

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