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Mathematical modeling of copper(II) ion inhibition on COD removal in an activated sludge unit

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Abstract

A mathematical model was developed to describe the Cu(II) ion inhibition on chemical oxygen demand (COD) removal from synthetic wastewater containing 15 mg l^{-1} Cu(II) in an activated sludge unit. Experimental data obtained at different sludge ages (5–30 days) and hydraulic residence times (HRT) (5–25 h) were used to determine the kinetic, stoichiometric and inhibition constants for the COD removal rate in the presence and absence of Cu(II) ions. The inhibition pattern was identified as non-competitive, since Cu(II) ion inhibitions were observed both on maximum specific substrate removal rate (k) and on the saturation constant (K_s) with the inhibition constants of 97 and 18 mg l^{-1}, respectively, indicating more pronounced inhibition on K_s. The growth yield coefficient (Y) decreased and the death rate constant (b) increased in the presence of Cu(II) ions due to copper ion toxicity on microbial growth with inhibition constants of 29 and 200 mg l^{-1}, respectively indicating more effective inhibition on the growth yield coefficient or higher maintenance requirements. The mathematical model with the predetermined kinetic constants was able to predict the system performance reasonably well especially at high HRT operations.

Keywords: Activated sludge; Biological treatment; Copper(II) ions; Inhibition; Mathematical model

1. Introduction

Heavy metal containing wastewaters cause detrimental effects on all forms of life upon direct discharge to the environment [1–4]. Copper, zinc, lead, mercury, chromium, cadmium, iron, nickel and cobalt are the most frequently found heavy metals in industrial wastewaters.

Trace amounts (μg l^{-1}) of some metal ions such as copper, zinc, iron, nickel, cobalt are required by some organisms as cofactors for the enzymatic activities. However, heavy metal ion concentrations at ppm (mg l^{-1}) level are known to be toxic to most of the organisms because of irreversible inhibition of many enzymes by the heavy metal ions. Toxicity of heavy metal ions on activated sludge bacteria vary depending on the type and concentrations of heavy metal ions and the organisms as well as the environmental conditions such as pH, temperature, dissolved oxygen (DO), presence of other metal ions, ionic strength and also the operating parameters such as, sludge age (solids retention time, SRT) and hydraulic residence time (HRT) [5].

Metal ions present in wastewaters are biosorbed onto the surfaces of activated sludge bacteria by fast passive adsorption followed by slow metal ion uptake [6]. In most of the cases passive adsorption onto the extracellular polymeric substances is the dominant mechanism. Both free and adsorbed metal ions are known to have toxic effects on the organisms by different mechanisms. The most widely known mechanism for heavy metal toxicity is the irreversible inhibition of extracellular or intracellular enzymes upon binding of metal ions [7]. Removal of heavy metals from wastewaters by biosorption has been studied extensively by many investigators [8–12]. However, there is limited number of studies on toxic effects of heavy metal ions on activated sludge processes [5,13–26].

There are no sound mathematical models describing the inhibitory effects of metal ions on performance of activated sludge units. In order to be able to predict the performance of an activated sludge unit treating Cu(II) ion containing wastewater, this study was designed to estimate the system performance under different experimental conditions with Cu-free and Cu-containing synthetic wastewater. Copper(II) ions were selected

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as model heavy metal in this study due to its common presence in metal industry wastewaters. Therefore, the major objective of this study is to develop a sound mathematical model describing the Cu(II) ion inhibition on COD removal in an activated sludge unit treating Cu(II) containing synthetic wastewater. The experimental data reported in our previous study [27] constituting variable HRT and sludge age (SRT) experiments were used to determine the kinetic, stoichiometric and the inhibition constants for COD removal in the developed model.

2. Mathematical model development

Activated sludge design equations were modified for Cu(II) ion containing wastewaters by considering Cu(II) inhibition on COD removal rate. Copper ion inhibitions on both the maximum specific substrate removal rate and on the saturation constant were considered.

In an activated sludge unit, a COD balance over the aeration tank yields:

$$Q(\mathrm{COD_o} - \mathrm{COD_R}) = U_{\mathrm{COD}} X V \tag{1a}$$

or

$$U_{\mathrm{COD}} = \frac{Q(\mathrm{COD_o} - \mathrm{COD_R})}{VX} = \frac{\mathrm{COD_o} - \mathrm{COD_R}}{\Theta_{\mathrm{H}} X} \tag{1}$$

where Q is the flow rate of wastewater to the aeration tank ($\mathrm{l\,h^{-1}}$), $\mathrm{COD_o}$ and $\mathrm{COD_R}$ are the COD concentrations in the feed and in the reactor (or effluent) at the steady-state ($\mathrm{mg\,l^{-1}}$); U_{COD} is the specific rate of COD removal ($\mathrm{mg\,COD\,mg^{-1}}\,X\,\mathrm{h^{-1}}$); X is the total biomass concentration in the aeration tank at steady-state ($\mathrm{mg\,l^{-1}}$); V is the volume of the wastewater in the aeration tank (7.6 l); Θ_{H} is the hydraulic residence time (V/Q, h).

In the presence of Cu(II) ions the specific rate of COD removal (U_{COD}) may be written as follows:

$$U_{\mathrm{COD}} = \frac{k_{\mathrm{app}}\,\mathrm{COD_R}}{K_{\mathrm{s,app}} + \mathrm{COD_R}} \tag{2}$$

where k_{app} and $K_{\mathrm{s,app}}$ are the apparent specific rate and saturation constants for COD removal which can be written as follows with the Cu(II) inhibition constants.

$$k_{\mathrm{app}} = \frac{k}{(1 + \mathrm{Cu}/K_{\mathrm{Cu}})} \quad \text{and} \quad K_{\mathrm{s,app}} = K_{\mathrm{s}}\left(1 + \frac{\mathrm{Cu}}{K'_{\mathrm{Cu}}}\right) \tag{3}$$

where k is the maximum specific rate constant for COD removal in the absence of Cu(II) ions ($\mathrm{h^{-1}}$); K_{Cu} is the Cu(II) ion inhibition constant for k ($\mathrm{mg\,l^{-1}}$); Cu is the total Cu(II) concentration in the feed and also in the aeration tank at steady-state ($\mathrm{mg\,l^{-1}}$); K_{s} is the saturation constant for COD removal in the absence of Cu(II) ($\mathrm{mg\,l^{-1}}$); K'_{Cu} is the Cu inhibition constant for K_{s} ($\mathrm{mg\,l^{-1}}$).

Combination of Eqs. (1)–(3) yields the following equation which may be used for design purposes.

$$U_{\mathrm{COD}} = \frac{k_{\mathrm{app}}\,\mathrm{COD_R}}{K_{\mathrm{s,app}} + \mathrm{COD_R}} = \frac{[k/(1 + \mathrm{Cu}/K_{\mathrm{Cu}})]\mathrm{COD_R}}{K_{\mathrm{s}}(1 + \mathrm{Cu}/K'_{\mathrm{Cu}}) + \mathrm{COD_R}} = \frac{\mathrm{COD_o} - \mathrm{COD_R}}{\Theta_{\mathrm{H}} X} \tag{4}$$

In the absence of copper(II) ions, Eq. (4) reduces to the following equation:

$$U_{\mathrm{COD}} = \frac{k\ \mathrm{COD_R}}{K_{\mathrm{s}} + \mathrm{COD_R}} = \frac{\mathrm{COD_o} - \mathrm{COD_R}}{\Theta_{\mathrm{H}} X} \tag{5}$$

or in double reciprocal form,

$$\frac{1}{U} = \frac{\Theta_{\mathrm{H}} X}{\mathrm{COD_o} - \mathrm{COD_R}} = \frac{1}{k} + \frac{K_{\mathrm{s}}}{k}\frac{1}{\mathrm{COD_R}} \tag{6}$$

A plot of $1/U$ versus $1/\mathrm{COD_R}$ (or $1/S$) yields a straight line with a slope of K_{s}/k and y-axis intercept of $1/k$.

Similarly, in the presence of Cu(II) ions Eq. (4) can be written in double reciprocal form as follows:

$$\frac{1}{U} = \frac{\Theta_{\mathrm{H}} X}{\mathrm{COD_o} - \mathrm{COD_R}} = \frac{1}{k_{\mathrm{app}}} + \frac{K_{\mathrm{s,app}}}{k_{\mathrm{app}}}\frac{1}{\mathrm{COD_R}} \tag{7}$$

In this case, a plot of $1/U$ versus $1/\mathrm{COD_R}$ (or $1/S$) yields a straight line with a slope of $K_{\mathrm{s,app}}/k_{\mathrm{app}}$ and y-axis intercept of $1/k_{\mathrm{app}}$.

The most important operating variable affecting the performance of an activated sludge unit or the effluent quality is the sludge age or the SRT. In the presence of Cu(II) ions, the steady-state effluent COD concentration (or the aeration tank COD) is related to the sludge age as follows:

$$\frac{1}{\Theta_{\mathrm{c}}} = Y_{\mathrm{app}} U_{\mathrm{COD}} - b_{\mathrm{app}} = Y_{\mathrm{app}}\left(\frac{\mathrm{COD_o} - \mathrm{COD}_R}{\Theta_{\mathrm{H}} X}\right) - b_{\mathrm{app}} \tag{8}$$

where Y_{app} is the apparent growth yield coefficient ($\mathrm{g}\,X\,\mathrm{g\,COD^{-1}}$); b_{app} is the apparent death rate constant ($\mathrm{d^{-1}}$) including Cu(II) inhibitions and Θ_{c} is the sludge age (SRT, d). A plot of $1/\Theta_{\mathrm{c}}$ versus U yields a line with a slope of Y_{app} and a y-axis intercept of b_{app} in the presence of Cu(II) ions.

Inhibition effects of Cu(II) ions on the growth yield coefficient and on the death rate constants can be expressed as follows:

$$Y_{\mathrm{app}} = \frac{Y_{\mathrm{M}}}{(1 + \mathrm{Cu}/K_Y)} \tag{9}$$

$$b_{\mathrm{app}} = b\left(1 + \frac{\mathrm{Cu}}{K_b}\right) \tag{10}$$

where Y_{M} is the maximum growth yield coefficient ($\mathrm{g}\,X\,\mathrm{g}\,S^{-1}$) and '$b$' is the death rate constant ($\mathrm{d^{-1}}$) in the absence of Cu(II) ions; K_Y and K_b are the inhibition constants on the growth yield coefficient and death rate constants in the presence of Cu(II) ions.

Combination of Eqs. (8)–(10) yields the following design equation:

$$\frac{1}{\Theta_{\mathrm{c}}} = \frac{\mathrm{Y}_M}{(1 + \mathrm{Cu}/\mathrm{K}_Y)} U_{\mathrm{COD}} - b\left(1 + \frac{\mathrm{Cu}}{K_b}\right) \tag{11}$$

In the absence of Cu(II) ions Eq. (8) can be written as follows:

$$\frac{1}{\Theta_{\mathrm{c}}} = Y_{\mathrm{M}} U_{\mathrm{COD}} - b = Y_{\mathrm{M}}\left(\frac{\mathrm{COD_o} - \mathrm{COD_R}}{\Theta_{\mathrm{H}} X}\right) - b \tag{12}$$

A plot of $1/\Theta_{\mathrm{c}}$ versus U yields a line with a slope of Y_{M} and a y-axis intercept of (b).

3. Materials and methods

3.1. Experimental set-up

A laboratory scale activated sludge unit was used throughout the study. The system consisted of an aeration tank of volume 8.5 l and a sludge settling tank of 1.5 l made of stainless steel. The aeration and sludge settling tanks were separated by an inclined plate which allowed passage of the wastewater from the aeration to the settling tank through the holes on the plate. The inclined plate had a 3 cm gap at the bottom which allowed the passage of the settled sludge from the settling to the aeration tank. Aeration tank was vigorously aerated by using an air pump and several porous diffusers. Synthetic wastewater was kept in a deep refrigerator at 4 °C to avoid any decomposition and was fed to the aeration tank with a desired flow rate by a peristaltic pump (Watson-Marlow 505 D_i/L). The effluent was removed from the top of the settling tank by gravitational flow. Temperature, pH, and dissolved air (DO) concentrations in the aeration tanks were kept at $T = 25 \pm 2$ °C, pH 7.0 ± 0.2 and DO = 2 ± 0.5 mg l^{-1}.

3.2. Wastewater composition

Synthetic wastewater composed of diluted molasses, urea, KH_2PO_4 and $MgSO_4$ with a COD/N/P ratio of 100/8/1.5 was used throughout the study. Typical composition of the feed wastewater was $COD_o = 2000 \pm 100$ mg l^{-1}, $N_T = 160 \pm 10$ mg l^{-1}, PO_4–P = 30 ± 1 mg l^{-1}, $MgSO_4$ = 50 mg l^{-1}, Cu(II) = 15 mg l^{-1}. pH was nearly 6.9 in the feed wastewater which increased to pH >7.5 in the aeration tank because of ammonia released from biodegradation of urea. pH of the aeration tank content was adjusted manually to pH 7 by addition of dilute sulfuric acid several times a day.

3.3. Organisms

The activated sludge culture obtained from PAK MAYA Bakers Yeast Company wastewater treatment plant in Izmir, Turkey was used as the seed culture. The activated sludge culture was grown in the aeration tank using the same synthetic wastewater in the absence of Cu(II) ions.

3.4. Experimental procedure

About 7 l of the synthetic wastewater was placed in the aeration tank which was inoculated with 1 l of the activated sludge culture. The system was operated in batch mode for three days to obtain a dense culture of the activated sludge before starting the continuous operation. Feed wastewater was fed to the reactor with a desired flow rate and removed with the same rate. Temperature, pH and DO were approximately $T = 25 \pm 2$ °C, pH 7.0 ± 0.2, DO = 2 ± 0.5 mg l^{-1} throughout the experiments. In variable sludge age experiments, sludge age (SRT) was varied between 5 and 30 days while HRT was constant at 10 h. Sludge age was adjusted by removing certain fraction of sludge from the aeration tank everyday. For example, 10% of the sludge was removed from the aeration tank everyday to adjust the sludge age to 10 days. In variable HRT experiments, HRT was varied between 5 and 25 h while the sludge age was constant at 10 days. Hydraulic residence times were adjusted to desired level by changing the flow rate of the feed wastewater. Feed COD and Cu(II) concentrations were constant at 2000 ± 200 mg l^{-1} and 15 mg l^{-1}, respectively, throughout the experiments. Experiments were performed in the order of increasing sludge age and HRT. The same set of experiments was performed with Cu(II)-free wastewater to determine the performance of the system in the absence of Cu(II) ions. Every experiment was continued until the system reached the steady-state yielding the same COD, and Cu(II) levels in the effluent for the last three days. Average time elapsed for each experiment was two to three weeks. Two experiments from each set were repeated twice to test the reproducibility of the results. Due to good reproducibility of the repeated experiments, the other experiments were not repeated. The samples collected from the feed and effluent wastewater at the steady-state were analyzed for COD, Cu(II) and biomass concentrations after centrifugation.

3.5. Analytical methods

Samples were withdrawn everyday for analysis and centrifuged at 8000 rpm ($7000 \times g$) for 20 min to remove biomass from the liquid phase. Clear supernatants were analyzed for COD and Cu(II) ion contents. COD was determined using the closed reflux method according to the Standard Methods [28]. The clear supernatants were analyzed for Cu(II) ion concentrations using an atomic absorption spectrometer (ATI Unicam 929 AA Spectrometer) at 324.8 nm wavelength. Biomass concentrations were determined by filtering the samples through 0.45 μm millipore filter and drying in an oven at 105 °C until constant weight. COD and Cu(II) analyses were carried out in triplicates with less than 3% standard deviations from the average.

4. Results and discussion

4.1. Performance of the system in the absence of Cu(II) ions

Experimental data obtained at different HRT (HRT = 5–25 h, SRT = 10 d) and the sludge ages (SRT = 5–30 d, HRT = 10 h) in the absence of Cu(II) ions are presented in Table 1. The data obtained at variable HRT (5–25 h) and constant SRT (10 d) were plotted in form of $1/U$ versus $1/S$ (or $1/COD_R$) in Fig. 1. From the slope and the intercept of the best-fit line the following constant were obtained by using Eq. (6).

$$k = 0.0625\,\mathrm{h}^{-1} = 1.5\,\mathrm{d}^{-1},$$

$$K_s = 254\,\mathrm{mg\,l}^{-1} \quad (R^2 = 0.85)$$

Similarly, the experimental data obtained with variable SRT (5–30 d) at constant HRT (10 h) were plotted in form of $1/\Theta_c$ versus U according to Eq. (12) and the following constants were determined from the slope and the intercept of the best-fit line (Fig. 2).

$$Y_M = 0.23\,\mathrm{g}\,X\,\mathrm{g}^{-1}\,\mathrm{COD}, \qquad b = 0.138\,\mathrm{d}^{-1} \quad (R^2 = 0.96)$$

Table 1
Data for variable SRT (Θ_c) and HRT (Θ_H) experiments in the absence of Cu(II) ions

Θ_c (d)	Θ_H (h)	COD_o (mg l^{-1})	COD_e (mg l^{-1})	%COD Rem	X (mg l^{-1})
30	10	2020	10	99	6900
25	10	2010	43	98	6300
20	10	2040	117	94	5600
15	10	2015	208	90	4700
10	10	2035	418	79	3500
5	10	2020	654	68	2200
10	25	2030	55	97	6600
10	20	2020	145	93	5700
10	15	2015	284	86	4450
10	10	2020	417	79	3020
10	5	2010	800	60	2200

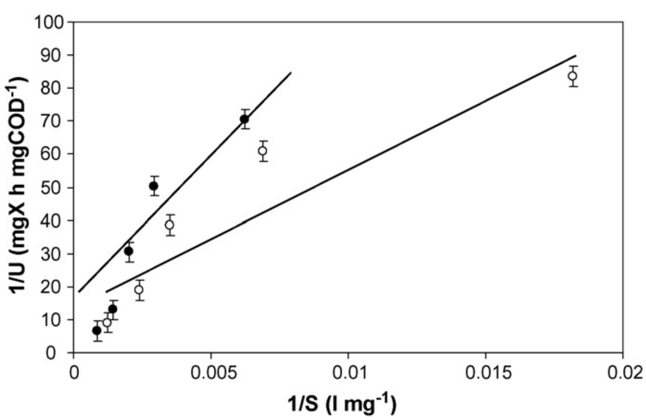

Fig. 1. Plots of $1/U$ vs. $1/S$ for variable HRT experiments in the presence and absence of Cu(II) ions. SRT = 10 d, COD_o = 2000 mg l^{-1}. (○) Cu-free experimental data, (●) experimental data with 15 mg l^{-1} Cu(II) in the feed. Continuous lines are the model predictions.

The kinetic and stoichiometric constants determined for Cu(II)-free wastewater are comparable with the literature reports where k is between 1 and 5 d^{-1}, K_s is 100–300 mg l^{-1}, Y_M is 0.2–0.5 g X g^{-1} S and b is 0.01–0.15 d^{-1}. The maintenance coefficient (m, g COD g X^{-1} h^{-1}) defined as $m = b/Y_{X/S}$ was calculated to be $m = 0.6$ g COD g^{-1} X d^{-1} = 0.025 g S g^{-1} X h^{-1}.

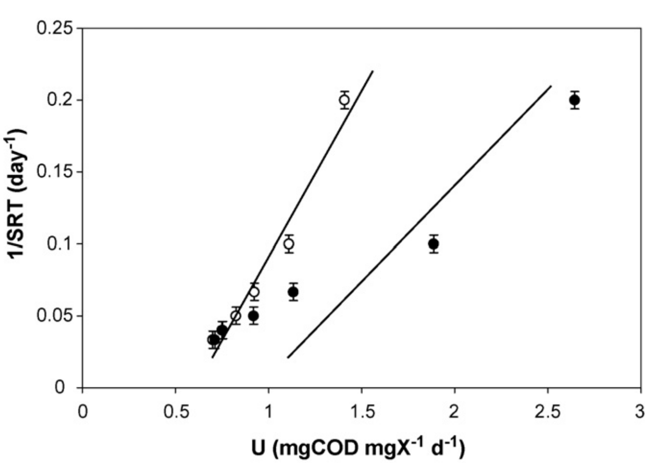

Fig. 2. Plots of $1/\Theta_c$ vs. U for variable SRT experiments in the presence and absence of Cu(II) ions. HRT = 10 h, COD_o = 2000 mg l^{-1}. (○) Cu-free experimental data, (●) experimental data with 15 mg l^{-1} Cu(II) in the feed. Continuous lines are the model predictions.

Specific rates of COD removal (U) were calculated using Eq. (5) with the predicted model constants and were depicted in form of $1/U$ versus $1/S$ as a continuous line along with the experimental data points in Fig. 1. The agreement between the model predictions (continuous line) and the experimental data (open circles) was reasonable in the absence of Cu(II). The experimental data and model predictions were compared in Fig. 2 in form of $1/\Theta_c$ versus U in the absence of Cu(II) ions. The model predictions were in good agreement with the experimental data.

4.2. Performance of the system in the presence of Cu(II) ions

The same experiments as listed in Table 1 were performed with 15 mg l^{-1} Cu(II) ions in the feed wastewater. Some Cu(II) ions were adsorbed onto the biomass in the activated sludge yielding aqueous Cu(II) ion concentrations lower than 15 mg l^{-1}. Since both the free and adsorbed Cu(II) would cause inhibition on microbial activities, the total Cu(II) ion concentration was considered in the model.

The experimental data obtained with the fed Cu(II) concentration of 15 mg l^{-1} are presented in Table 2 for variable HRT and SRT experiments along with effluent Cu(II) concentrations. The effluent Cu(II) decreased and percent biosorption of Cu(II) by microorganisms increased with increasing HRT and SRT. The experimental data obtained with variable HRT (5–30 h) and constant SRT (10 d) were plotted in form of $1/U$ versus $1/S$ (or $1/COD_R$) as shown in Fig. 1. From the slope and the intercept of the best-fit line the following apparent coefficients were obtained (Eq. (7)):

$$k_{app} = 0.054\,h^{-1} = 1.3\,d^{-1},$$

$$K_{s,app} = 463\,mg\,l^{-1} \quad (R^2 = 0.90)$$

By using the definitions of k_{app} and $K_{s,app}$ in Eq. (3) and substituting the values of $k = 1.5\,d^{-1}$, $K_s = 254$ mg l^{-1} and Cu = 15 mg l^{-1} into Eq. (3), the following inhibition constants were determined.

$$K_{Cu} = 97\,mg\,l^{-1}, \qquad K'_{Cu} = 18\,mg\,l^{-1}$$

Apparently, Cu inhibition on the saturation constant (K_s) was more pronounced than that on the rate constant (k), since K_{Cu}

Table 2
Data for variable SRT (Θ_c) and HRT (Θ_H) experiments in the presence of Cu(II) ions

Θ_c (d)	Θ_h (h)	Cu_o ($mg\,l^{-1}$)	Cu_e ($mg\,l^{-1}$)	%Cu biosorbed	COD_o ($mg\,l^{-1}$)	COD_e ($mg\,l^{-1}$)	%COD Rem	X ($mg\,l^{-1}$)
30	10	15	2.4	84	2017	27	99	6700
25	10	15	3.1	79	2050	198	90	5900
20	10	15	4.1	73	2015	349	83	4350
15	10	15	4.8	68	2043	484	76	3300
10	10	15	5.3	65	2032	657	68	1750
5	10	15	6.2	59	2025	945	53	980
10	25	15	3.2	79	2055	185	91	5350
10	20	15	3.9	74	2011	342	83	4200
10	15	15	4.6	69	2041	490	76	3150
10	10	15	5.3	65	2047	696	66	1750
10	5	15	6.2	59	2025	1175	42	1100

was larger than K'_{Cu}. The type of Cu inhibition on COD removal rate is non-competitive resulting in lower rate and higher saturation constants in the presence of Cu(II) ions. There are no similar kinetic modeling studies in the literature on Cu(II) ion inhibition in activated sludge operations with the determined kinetic and inhibition constants to compare our results with.

Similar to the experiments in the absence of Cu(II) ions, the experimental data obtained with variable sludge ages (SRT = 5–30 d) at a constant HRT of 10 h in the presence of $15\,mg\,Cu\,l^{-1}$ were used to estimate the inhibition constants on 'Y' and 'b'. Eq. (11) was used to correlate the experimental data using the values of $Y_M = 0.23\,g\,X\,g^{-1}\,S$, $b = 0.1385\,d^{-1}$, $Cu = 15\,mg\,l^{-1}$. STATISTICA 5 program was used for determination of the inhibition constants by iteration and the following constant were determined by using the Quasi Newton-Simplex approximation.

$$K_Y = 27\,mg\,l^{-1}, \qquad K_b = 210\,mg\,l^{-1} \quad (R^2 = 0.85)$$

Apparently, Cu(II) ion inhibition on the growth yield coefficient (Y) was more pronounced than that on the death rate coefficient (b) since K_Y was smaller than K_b. The growth yield coefficient decreased to $Y_{app} = 0.15\,g\,X\,g^{-1}$ COD and the death rate coefficient increased to $b_{app} = 0.15\,d^{-1}$ in the presence of $15\,mg\,l^{-1}$ Cu(II) ions. Therefore, the maintenance coefficient in the presence of $15\,mg\,Cu\,l^{-1}$ was $m_{app} = b_{app}/Y_{app} = 1\,d^{-1} = 0.041\,g\,COD\,g^{-1}\,X\,h^{-1}$. The maintenance coefficient increased by 64% in the presence of $15\,mg\,l^{-1}$ Cu(II) as compared to Cu-free wastewater. In the presence of Cu(II) ions, specific rates of COD removal (U) were calculated using Eq. (4) with the predicted model constants and were depicted in form of $1/U$ versus $1/S$ as a continuous line along with the experimental data points (closed circles) in Fig. 1. The agreement between the model predictions (continuous line) and the experimental data (closed circles) was reasonable at high $1/S$ or high HRT levels, but not that good at low $1/S$ or HRT values in the presence of Cu(II). The experimental data and model predictions were compared in Fig. 2 in form of $1/\Theta_c$ versus U in the presence of Cu(II) ions. Again the agreement between the model predictions and the experimental data was reasonable at low SRT or high U values, but not that good at high SRT levels in the presence of Cu(II).

With the determined kinetic and inhibition constants, the design equations (Eqs. (4) and (11)) in the presence of Cu(II) ions take the following form:

$$U_{COD} = \frac{[0.0625/(1+Cu/97)]COD_R}{254(1+Cu/18)+COD_R} = \frac{COD_o - COD_R}{\Theta_H X} \tag{13}$$

where Cu, COD_R, and biomass (X) concentrations are in $mg\,l^{-1}$, U is in $mg\,COD\,mg^{-1}\,X\,h^{-1}$ and Θ_H is in hours.

$$\frac{1}{\Theta_c} = \frac{0.23}{(1+Cu/27)}U_{COD} - 0.1385\left(1+\frac{Cu}{210}\right) \tag{14}$$

where Cu is in $mg\,l^{-1}$, U is in $mg\,COD\,mg^{-1}\,X\,d^{-1}$ and Θ_c is in days.

Eq. (13) was used to predict the variations of effluent COD (or COD_R) with HRT and the results are depicted in Fig. 3. The model predictions are in reasonable agreement with the experimental findings especially at high HRT (greater than 15 h) levels where inhibition is less pronounced due to high biomass concentrations.

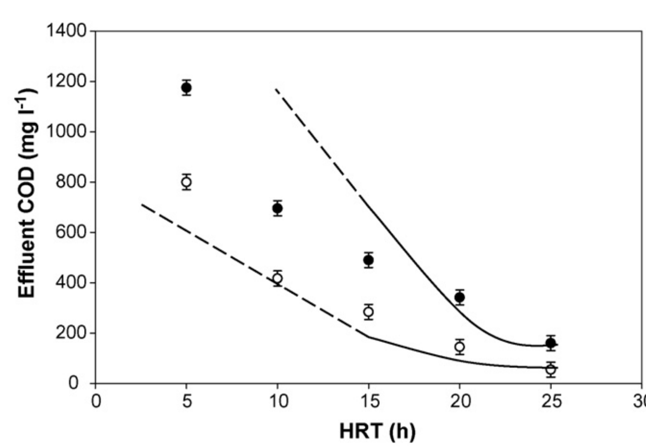

Fig. 3. Variations of effluent COD concentration with hydraulic residence time (HRT). (○) Cu-free feed, (●) Cu-containing feed ($15\,mg\,Cu\,l^{-1}$) experimental data. Continuous lines are the model predictions.

5. Conclusions

Design equations of activated sludge units were modified for Cu(II) containing wastewater to include Cu(II) ion inhibition on COD removal rate and the saturation constants. Activated sludge experiments were performed with synthetic wastewater containing $15\,\mathrm{mg\,l^{-1}}$ Cu(II) ions and $2000\,\mathrm{mg\,l^{-1}}$ COD at different solids (SRT) and HRT in order to quantify Cu(II) ion inhibition on COD removal rate at different operating conditions. The same experiments were repeated with Cu(II)-free wastewater. The kinetic and stoichiometric constants obtained in the absence of Cu(II) ions were, $k = 1.5\,\mathrm{d^{-1}}$, $K_s = 254\,\mathrm{mg\,l^{-1}}$, $Y_M = 0.23\,\mathrm{g}\,X\,\mathrm{g^{-1}}$ COD, $b = 0.1385\,\mathrm{d^{-1}}$ which are comparable with the literature values. Copper ions present in the feed wastewater ($15\,\mathrm{mg\,l^{-1}}$) affected both the rate (k) and the saturation constants (K_s) adversely yielding lower 'k' and higher 'K_s' values with a non-competitive inhibition pattern. The inhibition constants for the rate and the saturation constants were found to be $K_{Cu} = 97\,\mathrm{mg\,l^{-1}}$ and $K'_{Cu} = 18\,\mathrm{mg\,l^{-1}}$ indicating more pronounced inhibition on K_s. The growth yield coefficient decreased to $0.15\,\mathrm{g}\,X\,\mathrm{g^{-1}}\,S$ and the death rate constant increased to $0.15\,\mathrm{d^{-1}}$ in the presence of $15\,\mathrm{mg\,l^{-1}}$ Cu(II) ions. The inhibition constants on the growth yield (Y) and the death rate constant (b) were $K_Y = 27\,\mathrm{mg\,l^{-1}}$ and $K_b = 210\,\mathrm{mg\,l^{-1}}$ indicating more pronounced Cu(II) inhibition on the growth yield coefficient or higher maintenance requirements in the presence of Cu(II) ions. Model predictions were compared with the experimental data and a reasonable fit was observed especially at high SRT and HRT levels where Cu(II) inhibition was less pronounced due to high biomass concentrations.

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