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Journal of Hazardous Materials 143 (2007) 233–239
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

Mathematical modelling of 4-chlorophenol inhibition on COD and 4-chlorophenol removals in an activated sludge unit

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Received 13 July 2006; received in revised form 5 September 2006; accepted 6 September 2006
Available online 10 September 2006

Abstract

A mathematical model was developed for an activated sludge unit treating 4-chlorophenol (4-CP) containing synthetic wastewater composed of diluted molasses, urea, KH_2PO_4 and $MgSO_4$ with COD and 4-CP contents of 2500 and 500 mg l^{-1}, respectively. The model included 4-CP inhibition on COD and 4-CP removals. Experimental data obtained at different hydraulic residence times (HRT = 5–30 h) and sludge ages (SRT, 3–30 days) were used to estimate the kinetic and inhibition constants for COD and 4-CP removal rates. 4-CP inhibition on COD removal was negligible while the inhibition on 4-CP removal was significant. The specific rate constant (k), saturation constant (K_s) for COD oxidation were found to be 2.64 day^{-1} and 559 mg l^{-1}, respectively. A similar model was used for 4-CP oxidation in the activated sludge unit and the constants were found to be $k' = 1.44\ day^{-1}$, $K'_s = 25.7\ mg\ l^{-1}$, $K'_{CP} = 559\ mg\ l^{-1}$ and $K_{I,CP} = 17\ mg\ l^{-1}$. Increases in death rate constant because of 4-CP inhibition was also quantified and the inhibition constants were determined for both COD and 4-CP removals. Model predictions with the estimated kinetic constants were in good agreement with the experimental data. Developed model can be used to estimate the performance of an activated sludge unit treating 4-CP containing wastewater under the specified experimental conditions.

Keywords: Activated sludge; 4-Chlorophenol (4-CP); Mathematical model

1. Introduction

Some chemical industry effluents such as pulp and paper, petrochemicals and pesticides contain toxic concentrations of chlorophenols which have deleterious effects on the receiving environment upon direct discharge. Biological treatments of such wastewaters are usually difficult due to toxic effects of chlorophenols on the organisms. Different methods were developed for biological treatment of chlorophenol containing wastewaters in recent years since biological treatment methods result in complete mineralization of chlorophenols and are relatively inexpensive as compared to physical and chemical treatment methods [1–5].

Most of the investigations on biodegradation of chlorophenols focused on suspended pure culture studies using different bacteria and fungi [6–16]. Usually, a carbohydrate substrate was used as the primary metabolite and the chlorophenols were used as cometabolites [9,10,14]. Limited number of studies was reported on biological treatment of wastewaters containing chlorophenols [17–21]. Pre-adaptation of the activated sludge cultures to chlorophenols was reported to improve the rate and the extent of biodegradation of those compounds [5,17,18]. Recent investigations on biodegradation of chlorophenols focused on the use of immobilized cells or biofilm reactors [22–30]. Biofilm reactors are more resistant to high concentrations of chlorophenols, because of high biomass concentrations and diffusion barriers within the biofilm for the toxic compounds. However, suspended culture systems offer some advantages such as better control and easy operation as compared to the biofilm reactors and may result in high removal efficiencies for COD, chlorophenols and toxicity, if operated with high sludge recycle at high sludge ages.

Design and operation of activated sludge units treating chlorophenol containing wastewaters require sound kinetic models with pre-estimated kinetic and stoichiometric coefficients. There are very limited number of mathematical modelling studies on biodegradation of chlorophenols. Some of those studies were carried out with pure cultures in batch systems and some with activated sludge cultures in continuous systems [16,18–21,31–34]. Lack of sound kinetic models based on experimental studies in an activated sludge unit is the

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doi:10.1016/j.jhazmat.2006.09.015

major obstacle in understanding and design of systems treating chlorophenol containing wastewaters. For this reason the major objective of this study is to develop sound kinetic models for COD and 4-CP removals in an activated sludge unit and to determine the kinetic and stoichiometric coefficients using the experimental data. Experiments were performed at different hydraulic residence times (HRT = 5–30 h) and sludge ages (SRT = 3–30 days) while the fed COD and 4-CP concentrations were constant at 2500 ± 100 and $500 \pm 10\ mg\ l^{-1}$, respectively. The experimental data was used for determination of the model constants by iteration using the STATISTICA 5 program.

2. Materials and methods

2.1. Experimental system

A laboratory scale activated sludge unit was used throughout the study. The system consisted of an aeration tank of volume 7.6 l and a sludge settling tank of 1.6 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 inclined 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 diffusors. Synthetic wastewater was kept in a deep refrigerator at 4 °C in order 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, UK). 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 measured twice a day and were adjusted to desired levels. Temperature pH and DO levels throughout the study were $T = 25 \pm 2$ °C, pH 7.5 ± 0.5 and DO $= 2 \pm 0.5\ mg\ l^{-1}$, respectively.

2.2. Wastewater composition

Synthetic wastewater composed of diluted molasses, urea, KH_2PO_4 and $MgSO_4$ resulting in COD/N/P = 100/8/1.5 in the feed wastewater was used throughout the study. Typical composition of the feed wastewater was $COD_o = 2500 \pm 100\ mg\ l^{-1}$, $N_T = 200 \pm 20\ mg\ l^{-1}$, $PO_4\text{-}P = 38 \pm 2\ mg\ l^{-1}$, $MgSO_4 = 50\ mg\ l^{-1}$ and $4\text{-}CP_o = 500 \pm 10\ mg\ l^{-1}$ (with a COD content of $1.62\ g\ COD\ g^{-1}$ 4-CP). Major COD components in the feed wastewater were the carbohydrates (sucrose) and other carbonaceous compounds present in molasses and the 4-CP content. Feed wastewater pH was nearly 6.9 which increased to nearly 8 due to ammonia released from degradation of urea in the activated sludge unit. pH in the aeration tank was controlled manually around 7.5 by addition of dilute sulfuric acid several times a day.

2.3. Organisms

The activated sludge culture obtained from PAK MAYA Bakers Yeast Company (Izmir, Turkey) wastewater treatment plant was used as the seed culture. The activated sludge culture was grown in the aeration tank using the same synthetic wastewater in the presence of $50\ mg\ l^{-1}$ 4-CP for a week before inoculation of the experimental system.

2.4. Experimental procedure

Experiments were started batch wise. About 7 l of the synthetic wastewater containing $50\ mg\ l^{-1}$ 4-CP was placed in the aeration tank and was inoculated with 1 l of the inoculum culture. The system was operated in batch mode for several 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 7.5 ± 0.5, DO $= 2 \pm 0.5\ mg\ l^{-1}$, respectively, throughout the experiments. Sludge age (SRT) was changed by removing a certain fraction of the sludge from the aeration tank everyday. For example, 10% (1/10) of the sludge was removed from the aeration tank everyday to adjust the sludge age to 10 days. Hydraulic residence time (HRT) was changed by adjusting the flow rate of the feed wastewater. Hydraulic residence time (HRT) was varied between 5 and 30 h while the sludge age was constant at 10 days in the first set of experiments. Sludge age was varied between 3 and 30 days in the second set of experiments while the HRT was constant at 25 h. Every experiment was conducted until the system reached the steady-state yielding the same COD and 4-CP contents in the effluent for the last 3 days. Average time elapsed for each experiment was about 2–3 weeks. The samples collected from the feed and effluent wastewater at the steady-state were analyzed for COD, 4-CP and biomass concentrations after centrifugation.

2.5. 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 4-CP contents. Colorimetric method based on 4-aminoantipyrene was used as specified in the Standard Methods for determination 4-CP in terms of phenol index [35]. Chemical oxygen demand (COD) was determined using the closed reflux method according to the Standard Methods [35]. Biomass concentrations were determined by filtering the samples through 0.45 μm milipore filter and drying in an oven at 105 °C until constant weight. The samples were analyzed in triplicates with less than 3% standard deviations from the average.

3. Mathematical models

3.1. Mathematical model for COD removal

Activated sludge design equations used for COD removal were modified by considering 4-CP inhibition. The inhibition models were mainly used for biodegradation of phenols and chlorophenols in batch systems, but not for the activated sludge systems treating chlorophenol containing wastewaters [18,20].

A similar model was used by Eker and Kargi for biological treatment of 2,4-dichlorophenol containing synthetic wastewater in an activated sludge unit [21].

With the assumption that the aeration tank is completely mixed, a COD balance over the aeration tank yields:

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

or

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

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

In the presence of 4-CP inhibition, the specific rate of COD removal (U_{COD}) can be represented by the following equation:

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

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 4-chlorophenol (CP) inhibition constants:

$$k_{\mathrm{app}} = \frac{k}{(1 + \mathrm{CP_R}/K_{\mathrm{CP}})} \quad \text{and} \quad K_{\mathrm{s,app}} = K_{\mathrm{s}} \left(1 + \frac{\mathrm{CP_R}}{K_{\mathrm{I,CP}}}\right) \tag{3}$$

where, k is the maximum specific rate constant for COD removal ($\mathrm{h^{-1}}$); K_{CP} the 4-CP inhibition constant for k ($\mathrm{mg\,l^{-1}}$); $\mathrm{CP_R}$ the 4-CP concentration in the aeration tank at steady-state ($\mathrm{mg\,l^{-1}}$); K_{s} the real saturation constant for COD removal ($\mathrm{mg\,l^{-1}}$); $K_{\mathrm{I,CP}}$ is the 4-CP inhibition constant for K_{s} ($\mathrm{mg\,l^{-1}}$).

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

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

The experimental data obtained for COD removal at different hydraulic residence times were used to determine the kinetic constants (k, K_{CP}, K_{s}, $K_{\mathrm{I,CP}}$) in Eq. (4) by iteration using the STATISTICA 5 computer program with Quasi–Newton approximation.

In activated sludge systems, steady-state COD concentration in the aeration tank is related with the sludge age (solids retention time, SRT) as follows:

$$\frac{1}{\Theta_{\mathrm{c}}} = Y_{\mathrm{M}} U_{\mathrm{COD}} - b_{\mathrm{app}} = Y_{\mathrm{M}} \left(\frac{\mathrm{COD_o} - \mathrm{COD_R}}{\Theta_{\mathrm{H}} X}\right) - b_{\mathrm{app}} \tag{5}$$

where Y_{M} is the maximum growth yield coefficient on COD ($\mathrm{g\,X\,g\,COD^{-1}}$); b_{app} the apparent death rate constant ($\mathrm{day^{-1}}$) and Θ_{c} is the sludge age (SRT, days).

Inhibition effects of 4-CP on microorganisms can be described by an enhanced death rate coefficient at high $\mathrm{4\text{-}CP_R}$ levels as follows:

$$b_{\mathrm{app}} = b \left(1 + \frac{\mathrm{CP_R}}{K_{\mathrm{b}}}\right) \tag{6}$$

where 'b' is the real death rate constant ($\mathrm{day^{-1}}$); K_{b} is the 4-CP inhibition constant for the death rate constant.

Combination of Eq. (5) and (6) yields the following design equation:

$$\frac{1}{\Theta_{\mathrm{c}}} = Y_{\mathrm{M}} U_{\mathrm{COD}} - b_{\mathrm{app}} = Y_{\mathrm{M}} \left(\frac{\mathrm{COD_o} - \mathrm{COD_R}}{\Theta_{\mathrm{H}} X}\right) - b \left(1 + \frac{\mathrm{CP_R}}{K_{\mathrm{b}}}\right) \tag{7}$$

Experimental data obtained at different sludge ages (SRT) were used to determine the constants (Y_{M}, b, and K_{b}) in Eq. (7) by iteration using the STATISTICA 5 program.

3.2. Kinetic model for 4-CP removal

Similar to COD removal kinetics in the activated sludge unit, 4-CP inhibition on 4-CP removal kinetics can be modelled as follows.

4-CP balance around the aeration tank yields:

$$Q(\mathrm{CP_o} - \mathrm{CP_R}) = U_{\mathrm{CP}} X_{\mathrm{CP}} V \tag{8a}$$

or

$$U_{\mathrm{CP}} = \frac{Q(\mathrm{CP_o} - \mathrm{CP_R})}{V X_{\mathrm{CP}}} = \frac{\mathrm{CP_o} - \mathrm{CP_R}}{\Theta_{\mathrm{H}} X_{\mathrm{CP}}} \tag{8b}$$

where Q is the flow rate of wastewater to the aeration tank ($\mathrm{l\,h^{-1}}$), $\mathrm{CP_o}$ and $\mathrm{CP_R}$ the 4-CP concentrations in the feed and in the reactor at steady-state ($\mathrm{mg\,l^{-1}}$); U_{CP} the specific rate of 4-CP removal ($\mathrm{mg\,4\text{-}CP\,mg^{-1}\,X\,h^{-1}}$); X_{CP} the 4-CP degrading biomass concentration in the aeration tank at steady-state ($\mathrm{mg\,l^{-1}}$); V the wastewater volume in the aeration tank (7.6 l); Θ_{H} is the hydraulic residence time (V/Q, h).

The specific rate of 4-CP removal (U_{CP}) is can be written as follows:

$$U_{\mathrm{CP}} = \frac{k'_{\mathrm{app}} \mathrm{CP_R}}{K'_{\mathrm{s,app}} + \mathrm{CP_R}} \tag{9}$$

where k'_{app} and $K'_{\mathrm{s,app}}$ are the apparent specific rate and saturation constants for 4-CP oxidation which can be written as follows with the 4-CP inhibition terms:

$$k'_{\mathrm{app}} = \frac{k'}{(1 + \mathrm{CP_R}/K'_{\mathrm{CP}})} \quad \text{and} \quad K'_{\mathrm{s,app}} = K'_{\mathrm{s}} \left(1 + \frac{\mathrm{CP_R}}{K'_{\mathrm{I,CP}}}\right) \tag{10}$$

where, k' is the maximum specific rate constant for 4-CP removal ($\mathrm{h^{-1}}$); K'_{CP} the 4-CP inhibition constant for k' ($\mathrm{mg\,l^{-1}}$); $\mathrm{CP_R}$ the 4-CP concentration in the aeration tank at steady-state ($\mathrm{mg\,l^{-1}}$); K'_{s} the real saturation constant for 4-CP removal ($\mathrm{mg\,l^{-1}}$); $K'_{\mathrm{I,CP}}$ is the 4-CP inhibition constant for K'_{s} ($\mathrm{mg\,l^{-1}}$).

Table 1
Experimental data obtained at different hydraulic residence times (SRT 10 days, 4-CP_o = 500 mg l^{-1}, COD_o = 2500 mg l^{-1})

θ_H (h)	COD_o (mg l^{-1})	COD_e (mg l^{-1})	E_{COD} (%)	4-CP_o (mg l^{-1})	4-CP_e (mg l^{-1})	$E_{4\text{-}CP}$ (%)	X (mg l^{-1})	U_{COD} (mg COD mg^{-1} X^{-1} h^{-1})	$U_{4\text{-}CP}$ (mg 4-CP mg^{-1} X h^{-1})
30	2331	144	94	511	2	100	3560	0.0205	0.0048
25	2457	253	90	513	4	99	3492	0.0252	0.0058
20	2372	226	90	519	7	99	3345	0.0321	0.0077
15	2339	217	91	520	51	90	3270	0.0433	0.0096
10	2397	673	72	493	327	34	2800	0.0616	0.0059
5	2663	1487	44	503	428	15	1856	0.1267	0.0081

Combination of Eqs. (8b)–(10) yields the following equation which may be used for design purposes:

$$U_{CP} = \frac{k'_{app}CP_R}{K'_{s,app} + CP_R} = \frac{[k'/(1 + CP_R/K'_{CP})]CP_R}{K'_s(1 + CP_R/K'_{I,CP}) + CP_R} = \frac{CP_o - CP_R}{\Theta_H X_{CP}} \quad (11)$$

The experimental data obtained for 4-CP removal at different hydraulic residence times were used to determine the kinetic constants in Eq. (11), by iteration using the STATISTICA 5 program with Quasi-Newton approximation.

The sludge age is related to the specific rate of 4-CP removal by the following equation:

$$\frac{1}{\Theta_c} = Y'_M U_{CP} - b'_{app} = Y'_M \left(\frac{CP_o - CP_R}{\Theta_H X_{CP}}\right) - b'_{app} \quad (12)$$

where Y'_M is the maximum growth yield coefficient on 4-CP (g X g 4-CP^{-1}); b'_{app} the apparent death rate constant (day^{-1}) for 4-CP oxidizing organisms, Θ_c the sludge age (SRT, days) and X_{CP} is the 4-CP degrading biomass concentration in the aeration tank (mg l^{-1}).

Variation of death rate constant with the 4-CP concentration in the reactor can be expressed as follows:

$$b'_{app} = b'\left(1 + \frac{CP_R}{K'_b}\right) \quad (13)$$

where b' is the real death rate constant (d^{-1}); K'_b is the 4-CP inhibition constant for the death rate constant.

Combination of Eqs. (12) and (13) yields the following design equation:

$$\frac{1}{\Theta c} = Y'_M U_{CP} - b'_{app} = Y'_M \left(\frac{CP_o - CP_R}{\Theta_H X_{CP}}\right) - b'\left(1 + \frac{CP_R}{K'_b}\right) \quad (14)$$

Experimental data obtained at different sludge ages (SRT) were used to determine the constants (Y'_M, b', and K'_b) in Eq. (14) by iteration using the STATISTICA 5 program.

4. Results and discussion

4.1. Determination of kinetic and stoichiometric constants for COD removal

Experimental data obtained at different hydraulic residence times (HRT, Θ_H) and sludge ages (SRT, Θ_c) are summarized in Tables 1 and 2. Variations of effluent COD and 4-CP with HRT and SRT (sludge age) are depicted in Figs. 1 and 2. The effluent COD and 4-CP concentrations decreased steadily with increasing hydraulic residence time (HRT) from 5 to 30 h (Fig. 1). Similarly, increasing sludge ages from 3 to 30 days resulted in steady decreases in effluent COD and 4-CP as shown in Fig. 2.

In estimating the COD removal kinetic constants as presented in Eq. (4) the experimental data obtained for COD removal at different hydraulic residence times between 5 and 30 h were used (SRT = 10 days, $COD_o = 2500 \pm 100$ mg l^{-1}, 4-$CP_o = 500 \pm 10$ mg l^{-1}). The kinetic constants obtained from iteration using the STATISTICA 5 program with the

Table 2
Experimental data obtained at different sludge ages (HRT 25 h, 4-CP_o = 500 mg l^{-1}, COD_o = 2500 mg l^{-1})

θc (days)	COD_o (mg l^{-1})	COD_e (mg l^{-1})	E_{COD} (%)	4-CP_o (mg l^{-1})	4-CP_e (mg l^{-1})	$E_{4\text{-}CP}$ (%)	X (mg l^{-1})	U_{COD} (mg COD mg^{-1} X^{-1} h^{-1})	$U_{4\text{-}CP}$ (mg 4-CP mg^{-1} X h^{-1})
30	2630	175	93	498	6	99	6250	0.015712	0.003149
25	2670	174	93	498	7	99	5800	0.017214	0.003386
20	2535	102	96	504	5	99	4200	0.023171	0.004752
15	2323	238	90	497	6	99	3230	0.025820	0.006080
10	2300	295	87	489	9	98	3115	0.025746	0.006164
5	2390	600	75	495	340	31	1770	0.040452	0.003503
3	2685	1045	61	518	501	3	1530	0.042876	0.000444

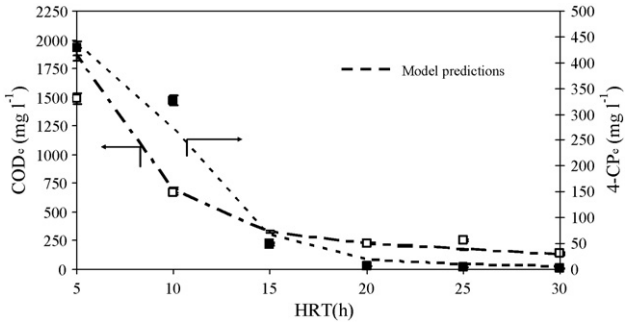

Fig. 1. Comparison of the experimental data with the model predictions for effluent COD and 4-CP concentrations in variable HRT experiments. (□) COD_{exp}, (■) 4-CP_{exp}, (- - -) model predictions.

Quasi-Newton approximation are as follows:

$k = 0.11\,h^{-1} = 2.64\,day^{-1}$,

$K_s = 559\,mg\,l^{-1}$ $(R^2 = 0.89)$

K_{DCP} and $K_{I,DCP}$ values were found to be 3.2×10^5 and 4.1×10^6, respectively, indicating almost no inhibition of 4-CP on COD removal kinetics. This is to be expected since the steady-state 4-CP concentrations in the aeration tank were lower than $300\,mg\,l^{-1}$ for HRT > 20 h while the IC_{50} value (4-CP concentration causing 50% activity loss) for 4-CP was $500\,mg\,l^{-1}$.

Experimental data obtained at different sludge ages (SRT = 3–30 days) for COD removal are presented in Table 2 at constant HRT = 25 h, $COD_o = 2500 \pm 100\,mg\,l^{-1}$ and 4-$CP_o = 500 \pm 10\,mg\,l^{-1}$. The data was used in estimating the constants of Eq. (7) by iteration using the STATISTICA 5 program. By excluding the data points at 25 and 30 days of SRT (since those were close to the data obtained at 15 and 20 days), the following constants were found for COD removal by Quasi-Newton approximation:

$Y_M = 0.347\,g\,X\,g\,COD^{-1}$,

$b = 0.136\,day^{-1}$ $(R^2 = 0.95)$

K_b (3.4×10^9) value was found to be very high indicating almost no 4-CP inhibition effects on the death rate constant for COD removal. The values of Y_M and (b) are close to those reported in literature [32].

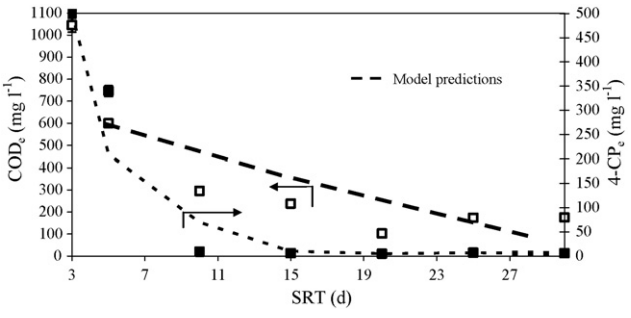

Fig. 2. Comparison of the experimental data with the model predictions for effluent COD and 4-CP concentrations in variable SRT experiments. (□) COD_{exp}, (■) 4-CP_{exp}, (- - -) model predictions.

4.2. Determination of kinetic and stoichiometric constants for 4-CP removal

Similar procedure was used for 4-CP removal kinetics. 4-CP removal data obtained at different hydraulic residence times (SRT = 10 days, $COD_o = 2500 \pm 100\,mg\,l^{-1}$, 4-$CP_o = 500 \pm 10\,mg\,l^{-1}$) between 5 and 30 h were used (Table 1). Percentage of 4-CP degrading organisms was varied between 20% and 50% of the total biomass and the kinetic constants were determined for each case. The best fit between the experimental and predicted effluent COD and 4-CP concentrations were obtained when 4-CP degrading organisms were 50% of the total biomass. Therefore, X_{CP} was considered as 50% of total biomass concentration in calculations (i.e., $X_{CP} = 0.50X$). The kinetic constants of Eq. (11) determined by using the STATISTICA 5 program with Hooke–Jeeves Pattern approximation were as follows for 4-CP removal ($R^2 = 0.79$):

$k' = 0.06\,h^{-1} = 1.44\,mg\,4\text{-}CP\,mg^{-1}\,X_{CP}\,day^{-1}$,

$K'_s = 25.7\,mg\,l^{-1}$, $K'_{CP} = 559\,mg\,l^{-1}$,

$K'_{I,CP} = 17\,mg\,l^{-1}$

As compared to the COD removal kinetic constants, specific rate constant for 4-CP removal ($1.44\,mg\,4\text{-}CP\,mg^{-1}\,X_{CP}\,day^{-1}$) was lower than that for the COD removal ($2.64\,mg\,COD\,mg\,X^{-1}\,day^{-1}$) indicating that COD compounds (mainly sucrose) present in molasses were degraded faster than 4-CP. Saturation constant for 4-CP oxidation rate ($25.7\,mg\,l^{-1}$) was also lower than that of COD oxidation ($559\,mg\,l^{-1}$) indicating effective oxidation of 4-CP by 4-CP oxidizing organisms. COD oxidation was not adversely affected by 4-CP since 4-CP concentrations in the reactor were much lower than the IC_{50} value of 4-CP ($500\,mg\,l^{-1}$) for most of the experimental points. However, 4-CP oxidation rate was inhibited by 4-CP. 4-CP inhibition on saturation constant ($K'_{I,CP} = 17\,mg\,l^{-1}$) was much more pronounced than that on the rate constant ($K'_{CP} = 559\,mg\,l^{-1}$) for 4-CP oxidation. Inhibition effects of 4-CP on 4-CP oxidation rate was found to be much more pronounced, probably due to the fact that 4-CP oxidizing organisms were more sensitive to 4-CP concentrations.

Similar to COD oxidation, the growth yield and death rate constants for 4-CP oxidation were determined by using the experimental data obtained at different sludge ages (3–30 days) as presented in Table 2 at constant HRT = 25 h, $COD_o = 2500 \pm 100\,mg\,l^{-1}$ and 4-$CP_o = 500 \pm 10\,mg\,l^{-1}$. Again the 4-CP degrading biomass concentration was considered to be 50% of the total biomass concentration ($X_{CP} = 0.50X$) yielding the best fit of the experimental data to the model predictions. The constants of Eq. (14) were determined by correlating the experimental data in Table 2 using the STATISTICA 5 program with Quasi-Newton-Simplex approximation. The following coefficients were found for DCP removal when data obtained at 15, 20 and 25 days were excluded since those

Table 3
Summary of estimated kinetic and stoichiometric constants

	Parameter						
	k (day^{-1})	K_s ($mg\,l^{-1}$)	K_{CP} ($mg\,l^{-1}$)	$K_{I,CP}$ ($mg\,l^{-1}$)	Y_M ($g\,X\,g\,S^{-1}$)	b (day^{-1})	K_b ($mg\,l^{-1}$)
COD oxidation	2.64	559	$3.2\,10^5$	4.1×10^6	0.347	0.136	3.4×10^9
4-CP oxidation	1.44	25.7	559	17	0.206	4.7×10^{-5}	0.071

data were close to each other ($R^2 = 0.99$):

$$Y'_M = 0.206\,g\,X\,g\,4CP^{-1}, \qquad b' = 4.7 \times 10^{-5}\,day^{-1},$$
$$K'_b = 0.071\,mg\,l^{-1}$$

The maximum yield coefficient for microbial growth on 4-CP was found to be much lower than that obtained for COD due to higher energy content of COD compounds present in molasses (mainly sucrose) as compared to 4-CP. The death rate constant (b') was very low indicating negligible death in the absence 4-CP in the reactor. However, the inhibition constant of 4-CP (K'_b) on death rate constant (b') was quite small ($0.071\,mg\,l^{-1}$) indicating significant increases on death rate constant (b') of 4-CP oxidizing organisms at high 4-CP concentrations.

The model predictions of the effluent COD and 4-CP were compared with the experimental data in Figs. 1 and 2 for variable HRT and SRT experiments. The model predictions were in good agreement with the experimental data indicating the validity of the model.

5. Conclusions

A mathematical model was developed for an activated sludge process treating 4-chlorophenol (4-CP) containing synthetic wastewater considering 4-CP inhibitions on both COD and 4-CP removals. Experimental data on COD and 4-CP removals obtained at different hydraulic residence times (HRT = 5–30 h) and sludge ages (SRT = 3–30 days) were used for determination of the kinetic and stoichiometric constants of the models. Estimated kinetic coefficients are presented in Table 3 for both COD and 4-CP removal in the activated sludge unit. Those constants are only valid for the wastewater composition and the experimental conditions used in this study and may not be valid for the real industrial wastewater treatment systems. However, the developed approach may be used in modelling real activated sludge systems treating 4-CP containing wastewaters.

On the basis of the estimated kinetic constants it can be said that 4-CP inhibition on COD oxidation rate was negligible. However, 4-CP oxidation was adversely affected from 4-CP due to inhibition on the organisms. Both the maximum rate constant (k') and saturation constants (K'_s) for 4-CP oxidations were affected by 4-CP inhibition with a greater inhibition effect on the saturation constant.The growth yield and the death rate coefficients were also affected from 4-CP inhibitions.

The maximum growth yield coefficient ($Y_M = 0.347\,g\,X\,g\,COD^{-1}$) and the death rate constant ($b = 0.136\,day^{-1}$) for COD oxidation were comparable with the literature reports [32]. Almost no 4-CP inhibition was observed on death rate constant for COD oxidation due to very high K_b value. The yield coefficient for growth on 4-CP ($Y'_M = 0.206\,g\,X\,g\,4-CP^{-1}$) was much lower than that of COD oxidation ($Y_M = 0.347\,g\,X\,g\,COD^{-1}$) because of lower energy content of 4-CP as compared to carbohydrates present in molasses. The death rate constant for growth on 4-CP was very low ($b' = 4.7 \times 10^{-5}\,day^{-1}$) indicating negligible death in the absence of 4-CP. However, the inhibition constant on death rate for 4-CP ($K'_b = 0.071\,mg\,l^{-1}$) was very low indicating strong inhibition effects of 4-CP (or high death rates at high reactor 4-CP concentrations) for microbial growth on 4-CP. Model predictions with the pre-determined kinetic constant were found to be in good agreement with the experimental data on effluent COD and 4-CP concentrations as shown in Figs. 1 and 2.

Acknowledgements

This study was supported by the research funds of the State Planning Organization of Turkey and Dokuz Eylul University, Izmir, Turkey.

References

[1] P.M. Armenante, D. Kafkewitz, G.A. Lewandowski, C.J. Jou, Anaerobic–aerobic treatment of halogenated phenolic compounds, Water Res. 33 (1999) 681–692.
[2] E.I. Atuanya, H.J. Purohit, T. Chakrabarti, Anaerobic and aerobic biodegradation of chlorophenols using UASB and ASG bioreactors, World J. Microb. Biotechnol. 16 (2000) 95–98.
[3] M.W. Jung, K.H. Ahn, Y. Lee, K.P. Kim, J.S. Rhee, J.T. Park, K.J. Paeng, Adsorption characteristics of phenol and chlorophenols on granular activated carbons, Microchem. J. 70 (2001) 123–131.
[4] A.P. Annachhatre, S.H. Gheewala, Biodegradation of chlorinated phenolic compounds, Biotechnol. Adv. 14 (1996) 35–56.
[5] U. Bali, F. Sengul, Performance of a fed-batch reactor treating a wastewater containing 4-chlorophenol, Process Biochem. 37 (2002) 1317–1323.
[6] S.Y. Dapaah, G.A. Hill, Biodegradation of chlorophenol mixtures by *Pseudomonas putida*, Biotechnol. Bioeng. 40 (1992) 1353–1358.
[7] K. Fahr, H.G. Wetzstein, R. Grey, D. Schlosser, Degradation of 2,4-dichlorophenol and pentachlorophenol by two brown rot fungi, FEMS Microbiol. Lett. 175 (1999) 127–162.
[8] A. Farrell, B. Quilty, Substrate-dependent autoaggregation of *Psedomonas putida* CP1 during the degradation of mono-chlorophenols and phenol, J. Ind. Microbiol. Biotechnol. 28 (2002) 316–324.
[9] G.A. Hill, B.J. Milne, P.A. Nawrocki, Cometabolic degradation of 4-chlorophenol by *Alcaligenes eutrophus*, Appl. Microbiol. Biotechnol. 46 (1996) 163–168.
[10] M.H. Kim, O.J. Hao, Cometabolic degradation of chlorophenols by *Acinetobacter* species, Water Res. 33 (1999) 562–574.
[11] D.Y. Li, J. Erberspacher, B. Wagner, J. Kuntzer, F. Ligens, Degradation of 2,4,6-trichloro-phenol by *Azotobacter* sp. strain GP1, Appl. Environ. Microb. 57 (1991) 1920–1928.

[12] P. Steinle, G. Stucki, R. Stettler, K.W. Hanselmann, Aerobic mineralization of 2,6-dichloro-phenol by *Ralstonia* sp. strain RK1, Appl. Environ. Microb. 64 (1998) 2566–2571.
[13] C.C. Wang, C.M. Lee, C.H. Kuan, Removal of 2,4-dichlorophenol by suspended and immobilized *Bacillus insolitus*, Chemosphere 41 (2000) 447–452.
[14] S.J. Wang, K.C. Loh, Facilitation of cometabolic degradation of 4-chlorophenol using glucose as an added growth substrate, Biodegradation 10 (1999) 261–269.
[15] D.C. Yee, T.K. Wood, 2,4-dichlorophenol degradation using *Streptomyces viridosporus* T7A lignin peroxidase, Biotechnol. Prog. 13 (1997) 53–59.
[16] F. Kargi, S. Eker, Toxicity and batch biodegradation kinetics of 2,4-dichlorophenol by pure *Pseudomonas putida* culture, Enzyme Microb. Technol. 35 (2004) 424–428.
[17] E. Sahinkaya, F.B. Dilek, Effects of 2,4-dichlorophenol on activated sludge, Appl. Microbiol. Biotechnol. 59 (2002) 361–367.
[18] E. Sahinkaya, F.B. Dilek, Biodegradation of 4-chlorophenol by acclimated and unacclimated activated sludge—evaluation of biokinetic coefficients, Environ. Res. 99 (2005) 243–252.
[19] E. Sahinkaya, F.B. Dilek, Effects of biogenic substrate concentration on the performance of sequencing batch reactor treating 4-CP and 2,4-DCP mixtures, J. Hazard. Mater. 128 (2006) 258–264.
[20] E. Sahinkaya, F.B. Dilek, Effect of biogenic substrate concentration on chlorophenol degradation kinetics, J Chem. Technol. Biotechnol. 81 (2006) 1530–1539.
[21] S. Eker, F. Kargi, Kinetic modeling and parameter estimation for an activated sludge unit treating 2,4-dichlorophenol containing synthetic wastewater, Environ. Eng. Sci. 23 (2006) 263–271.
[22] B.W.K. Shieh, J.A. Puhakka, E. Melin, T. Tuhkannen, Immobilized cell degradation of chlorophenols, J. Environ. Eng. ASCE 116 (1990) 683–697.
[23] K.H. Radwan, T.K. Ramanujam, Studies on organic removal of 2,4-dichlorophenol wastwaters using a modified RBC, Bioprocess Eng. 16 (1996) 219–223.
[24] H.S. Shin, K.S. Yoo, J.K. Park, Removal of polychlorinated phenols in a sequential anaerobic–aerobic biofilm reactors packed with tire chips, Water Environ. Res. 71 (1999) 363–367.
[25] G. Swaminathan, T.K. Ramanujam, Effect of substrate concentration on biodegradation of 2,4-dichlorophenol using modified rotating biological contactors, Bioprocess Eng. 18 (1998) 169–173.
[26] J.H. Kim, K.K. Oh, S.T. Lee, S.W. Kim, S.I. Hong, Biodegradation of phenol and chlorophenols with defined mixed culture in shake-flasks and packed bed reactor, Process Biochem. 37 (2002) 1367–1373.
[27] S. Eker, F. Kargi, Kinetic modelling and parameter estimation in biological treatment of 2,4-dichlorophenol containing wastewater using rotating perforated tubes biofilm reactor, Enzyme Microb. Technol. 38 (2006) 860–866.
[28] S. Eker, F. Kargi, Biological treatment of *para*-chlorophenol containing synthetic wastewater using rotating brush biofilm reactor, J. Hazard. Mater. B 135 (2006) 365–371.
[29] F. Kargi, S. Eker, Removal of 2,4-dichlorophenol and toxicity from synthetic wastewater in a rotating perforated tube biofilm reactor, Process Biochem. 40 (2005) 2105–2111.
[30] H. Zilouei, B. Guieysse, B. Matiasson, Biological degradation of chlorophenols in packed bed bioreactors using mixed bacterial consortia, Process Biochem. 41 (2006) 1083–1089.
[31] P. Beltrame, P.L. Beltrame, P. Carniti, D. Pitea, Kinetics of biodegradation of mixtures containing 2,4-dichlorophenol in a continuous stirred reactor, Water Res. 16 (1982) 429–433.
[32] J. Chudoba, J. Albokova, B. Lentge, R. Kummel, Biodegradation of 2,4-dichlorophenol by activated sludge microorganisms, Water Res. 23 (1989) 1439–1442.
[33] F. Kargi, S. Eker, Kinetics of 2,4-dichlorophenol degradation by *Pseudomonas putida* CP1 in batch culture, Int. Biodeter. Biodegrad. 55 (2005) 25–28.
[34] F. Kargi, I. Konya, COD, *para*-chlorophenol and toxicity removal from *para*-chlorophenol containing synthetic wastewater in an activated sludge unit, J. Hazard. Mater. B 132 (2006) 226–231.
[35] A.E. Greenberg, L.S. Clesceri, A.D. Eaton (Eds.), Standard Methods for the Examination of Water and Wastewater, 17th ed., American Public Health Association (APHA), Washington, DC, 1989.