Effect of phenol shock loads on activated sludge and active carbon batch reactors

M. T. Sorour, W. A. Ibrahim and F. Abdelrasoul
Sanitary Engineering Dept., Alexandria University, Alexandria, Egypt
Sorourt@hotmail.com

A simple experimental set-up was used to study the treatability aspects of phenolic wastewater. Three types of reactor systems: Activated Sludge (AS), activated sludge plus Granular Activated Carbon (GAC) and granular activated carbon, were experimented under different phenol shock loading. Phenol toxic effect on biomass was also investigated. Experimental results showed that under different phenol shock loads (100, 200, 300, and 400 mg/l), the AS plus GAC reactor gave the highest COD and phenol % removal comparing with the other two systems. Results also showed that increasing phenol shock loading had an adverse effect on treatment efficiency for all cases. Respirometric analysis indicated that, for AS reactor, μ^H decreased from 2.75 d^{-1} at 0.0 mg/l phenol concentration to 1.62 d^{-1} at 200 mg/l phenol concentration. Increasing phenol shock load to 400 mg/l resulted in decreasing μ^H to only 0.93 d^{-1}. In order to confirm these results, the toxic effect was measured by following the fraction of Specific Oxygen Uptake Rate (SOUR) loss between the sludge with zero phenol and the sludge dosed with phenol. Results obtained indicated an increasing of toxicity factor from 0.5 at phenol concentration of 200 mg/l to 0.73 at phenol concentration of 400 mg/l.

يهدف هذا البحث إلى دراسة قابلية إزالة الفينول من المخلفات السائلة في ٣ أنواع من المفاعلات: حماة منشطة ، حماة منشطة مع كربون نشط و كربون نشط فقط. وقد أجريت التجارب المعملية تحت تأثير تركيزات مختلفة من الفينول (صفر، ١٠٠، ٢٠٠، ٣٠٠، ٤٠٠ مجم/لتر).وقد وجد أن المفاعل الذي يعمل بالحماة المنشطة مع الكربون النشط يعطي أعلى كفاءة في إزالة ال COD و الفينول بالمقارنة بالمفاعلين الآخرين. كما اتضح أيضا أن زيادة تركيز الفينول في المخلفات السائلة له تأثير سلبي على كفاءة المعالجة في المفاعلات الثلاثة. ولدراسة التأثير السام للفينول على البكتيريا فقد تم قياس معدل نمو البكتيريا في مفاعل الحماة المنشطة وقد اتضح أن معدل نموها قد تناقص من ٢,٧٥ يوم$^{-1}$ عند تركيز فينول صفر في المخلفات السائلة إلى ١,٦٢ يوم$^{-1}$ عند تركيز فينول ٢٠٠ مجم/لتر والى ٠,٩٣ يوم$^{-1}$ عند تركيز فينول ٤٠٠ مجم/لتر.من اجل التأكد من هذه النتائج فقد تم قياس معامل السمية باستخدام تعيين SOUR وقد اتضح أيضا أن معامل السمية قد ارتفع من ٠,٥ عند تركيز فينول ٢٠٠ مجم/لتر إلى ٠,٧٥ عند تركيز فينول ٤٠٠ مجم/لتر.

Keywords: Activated sludge, Phenol, Toxicity, Oxygen uptake rate

1. Introduction

Phenol is an inhibitory and toxic compound present in wastewater from petroleum refining, petrochemical, coke conversion and pharmaceutical plants. Biological degradation of phenolic wastewaters has been documented by several authors [1-3].

In the majority of the literature reports, the general consensus is that although phenols can be degraded in the activated sludge process, the presence of phenol in wastewaters increases the susceptibility of a biological system to become upset [4-6].

Although inhibitory and toxic, phenol is also a carbon and energy source for some microorganisms. There is scant data on the biodegradation of high strength phenolic wastewaters, which can exceed 1000 mg/l [2,6].

Paulowsky and Howel [7] found that the maximum specific growth rates of mixed cultures grown on phenol as the sole carbon source occurred at a substrate concentration of less than 100 mg/l. The steady-state phenol removal from a continuous flow reactor reached 90%.

In addition to biological degradation, adsorption processes, and in particular those

using activated carbon, are finding increased use in wastewater treatment for phenol removal. Adsorption on granular activated carbon (GAC) is one of the best commercial proven methods for removing toxic organic chemicals, such as phenol, from waste steam.

Addition of activated carbon to aeration tanks of suspended growth systems has been used to improve activated sludge operation and performance [8]. A study by Ferguson [9] indicated that activated carbon addition to activated sludge systems provides exceptional resistance to shock loading by phenol, presumable due to large reservoir of carbon.

The aim of this research is to study the treatability aspect of phenolic wastewater in three types of reactors: i) activated sludge (AS), ii) activated sludge + granular activated carbon (AS + GAC), and iii) granular activated carbon (GAC) alone. In this study, a simple experimental set-up was used to determine the cause by which phenol affects the performance of the three mentioned reactors in the response to shock phenol loadings. The toxic effect of phenol on biomass growth was also investigated.

2. Materials and methods

2.1. Activated sludge laboratory unit

The activated sludge used in batch experiments was obtained from a laboratory unit. This unit was operated utilizing synthetic sewage prepared by diluting with tap water (1-100) a concentrated shock solution containing 48.6 g/l of glucose, 11.65 g/l of $Na_3Po_4.12H_2O$, 8.8 g/l of $(NH_4)_2SO_4$, the same synthetic sewage was used through the experiments. The diluted solution was introduced into an aeration tank with 80 l/d. A completely mixed Plexiglas reactor was assembled with 47 l aeration tank (surface area 1758 cm^2) connected by a silicon rubber tube to a 26.5 l settling tank having surface area of 1600 cm^2. Variable speed peristaltic pumps (Master flex L/S Easy-Load) were utilized to recycle settled sludge and to feed the solution to the aeration tank. Aeration was supplied through diffusers located at the bottom of the aeration tank, supplied diffused air (3:4 mg/l level of dissolved oxygen) and maintained complete mixing.

Initially, the activated sludge system was seeded with sludge waste from Kafer El-Dawar wastewater treatment plant. The waste sludge was collected from the return sludge sump. During start-up period the unit was fed with the synthetic sewage and all settled sludge in the final settler was returned into the aeration tank. The start-up period was about 14 days; steady-state condition was considered achieved by the constant measured parameters of the effluent and Mixed Liquor Suspended Solids (MLSS) in the reactor. After reaching steady-state conditions, the laboratory unit was operated at sludge age of 10 days, and sludge was wasted directly from the aeration tank. During steady-state period F/M ratio ranged between 0.31 to 0.37 d^{-1} with an average of 0.34 d^{-1}, the MLSS ranged between 2333 to 2714 mg/l, and the effluent COD ranged between 30 to 70 mg/l with an average value of 50 mg/l.

2.2. Experimental batch systems

Batch systems were used to study the treatability aspect of phenolic wastewater. The effect of shock loading of several phenol concentrations (100, 200, 300 and 400 mg/l) on COD and phenol removal efficiency was studied; the effect of reactor retention time was also investigated.

Waste sludge from the activated sludge laboratory unit was employed for batch experiments. Three types of experimental batch systems were studied: i) batch reactor of AS, ii) batch reactor of AS + GAC, and iii) batch reactor of GAC.

2.3. AS batch reactor

The activated sludge batch reactor tests were carried out in 5 flasks; the operating volume of each reactor was 3 liter. In each reactor 2.2 l of the synthetic sewage was added to 0.8 l of sludge resulting in F/M 0.57 d^{-1}. First reactor was used as a control unit with zero phenol concentration; in reactors from the second to the fifth phenol concentrations of 100, 200, 300 and 400 mg/l were added, respectively. Compressed air was

used to supply oxygen to each flask through porous diffuser stones, the air also served to provide good mixing of reactor contents.

Samples were taken from each reactor after 1, 2 and 6 hours of operation for measuring COD and phenol concentration. Respirometeric analyses were carried out on the biomass of reactors no. 1, 3 and 5 (zero, 200 and 400 mg phenol /l) in order to assess phenol toxic effect.

2.4. AS + GAC reactor

The addition of GAC to activated sludge was studied in batch system, 5 flasks of 3 l operating volume each were used. In each reactor 2.2 l of the synthetic sewage was mixed with 0.8 l of sludge resulting in F/M ratio of 0.6 d^{-1}, 1 g/l of GAC (AquaSorb™2000) was added into each reactor. First reactor was used as a control with zero phenol concentration, for reactors from the second to the fifth phenol concentrations of 100, 200, 300 and 400 mg/l were added respectively. Compressed air was used to supply oxygen to each flask through porous diffuser stones. Samples were taken from each reactor after 1, 2 and 6 hours of operation for measurements. Also respirometeric analyses were carried out on the biomass of reactors no. 1, 3 and 5 (zero, 200 and 400 mg phenol /l).

2.5. GAC reactor

The GAC reactor system was experimented in 5 flasks of 3 l operating volume. In each reactor 2.2 l of the synthetic sewage was used, 1 g/l of GAC (AquaSorb™2000) was added into each reactor. concentrations of phenol (100, 200, 300 and 400 mg/l) were added into the flasks to simulate phenol shock loading. Compressed air was used to supply oxygen to each flask through porous diffuser stones. Samples were taken from each reactor after 1, 2 and 6 hours of operation for measurements.

2.6. Analytical techniques

Parameters monitored during this study were chosen to determine the reactor performance due to phenol shock loading. Phenol concentration was determined with 4-aminoantipyrine method. COD was measured by colorimetric method using spectrophotometers (DR 100 Colorimeter Hach). Oxygen uptake rate (OUR), specific oxygen uptake rate (SOUR) and all other parameters were measured according to the Standard Method for the Examination of Water and Wastewater [10]. The maximum specific growth rate of heterotrophs (μ^H) was measured according to the method proposed by Ekama et al [11].

3. Results and discussion

3.1. Reactor efficiency

The effect of phenol shock loading on 3 types of reactor systems (A.S; A.S +GAC; and GAC) was studied. For each system 5 batch reactors were used, the first as a control unit with zero phenol concentration, shock phenol loading was simulated in the other 4 batch reactors [concentrations of 100, 200, 300, and 400 mg/l were added into reactors no. 2- 5, respectively]

A comparison between the 3 reactor systems regarding COD% removal is shown in fig. 1. For all cases it is obvious that A.S + GAC gave the highest COD% removal comparing with the other 2 systems. It is also clear that increasing the retention time in all reactors resulted in increasing the COD removal efficiency.

The adverse effect of phenol shock loading on COD% removal can be recognized for all cases. For example, the COD% removal was 92% in A.S + GAC system after 6 hours of operation with no phenol, adding 100 mg/l of phenol decreased the COD% removal to 90%, while adding 400 mg/l of phenol decreased it to 72%.

Fig. 2 shows a comparison between the 3 reactor systems regarding phenol removal efficiency. From this figure it is obvious that A.S + GAC reactor gave the highest % phenol removal. Also, increasing retention time in all reactors resulted in increasing phenol removal efficiency.

Increasing phenol shock loading has an adverse effect on its removal efficiency. For example, the phenol % removal decreased from 85% in the A.S + GAC system with 6

hours retention and phenol shock loading of 100 mg/l to 55% at phenol shock loading of 200 mg/l, and to only 39% at phenol shock loading of 400 mg/l for the same conditions.

3.2. Phenol toxicity

Respirometric analyses were carried out to evaluate phenol toxic effect on biomass. These analyses were conducted on sludge of both the AS and AS + GAC reactor systems.

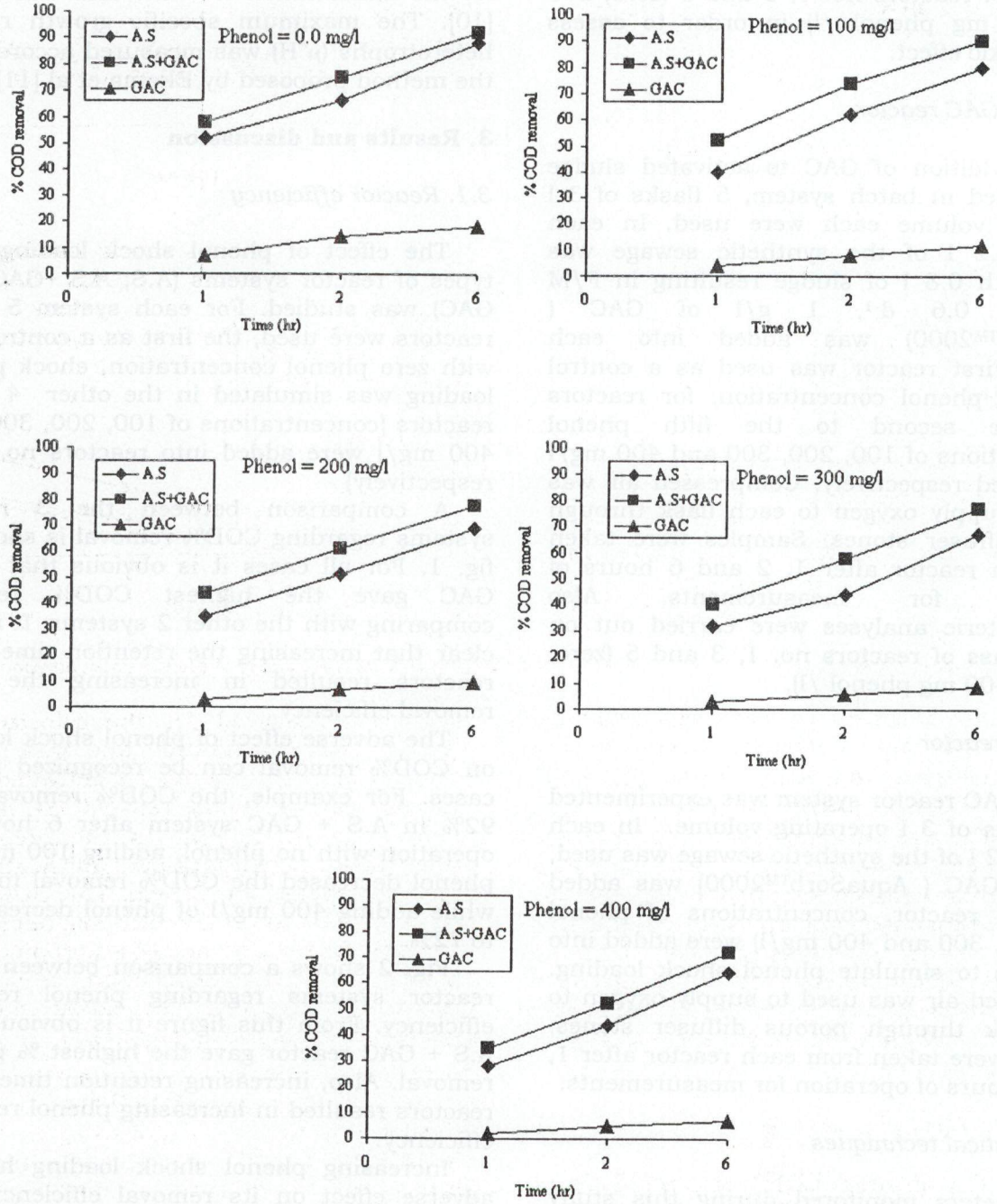

Fig. 1. Relation between % COD removal and the type of reactor for different phenol concentrations.

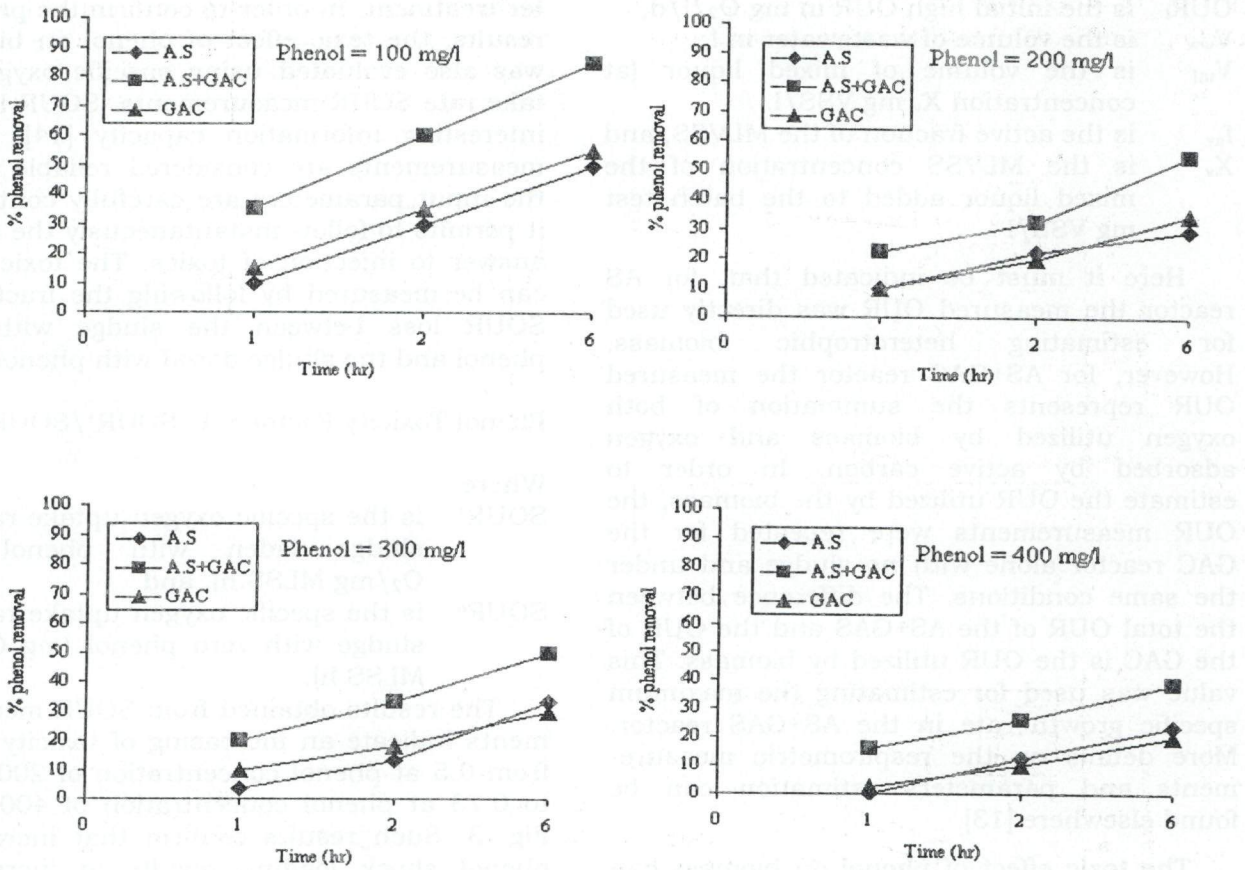

Fig. 2. Relation between %phenol removal and the type of reactor for different phenol concentrations.

The toxicity effect on biomass was evaluated by measuring the maximum specific growth rate of heterotrophs μ^H for the batches at 0, 200, and 400 mg/l phenol for both systems.

The μ^H was estimated using the method proposed by Ekama et al. [11] . They indicated that μ^H is usually specified as mg Active Volatile Suspended Solids (AVSS) synthesized per mg AVSS present per day i.e. mg AVSS/mg AVSS/d or simply d^{-1}. It is related to the maximum readily biodegradable substrate utilization rate K_{ms} (in units mg COD /mg AVSS/d),

$$\mu^{\wedge}H = K_{ms} \cdot Y_h \quad (1)$$

Now K_{ms} (in mg COD/ mg AVSS/d) is related to the initial high Oxygen Uptake Rate (OUR_i) at the beginning of the batch testes, OUR was measured for the selected batch after 10 min of operation and was repeated every 30 min. In general, for activated sludge process, carbonaceous removal is not only major sink for oxygen. In the presence of autotrophic microorganisms, nitrification also exerts a demand for oxygen. The OUR values can be attributed to heterotrophic microorganisms only in the absence of autorophic microorganisms or the application of 20 mg/l thiourea to suppress nitrification, moreover, phenol is toxic to nitrification [12].

$$K_{ms} = \frac{1}{1 - f_{cv} \cdot Y_h} \cdot OURi \frac{(V_{ww} + V_{ml})}{f_{av} \cdot X_v \cdot V_{ml}} . \quad (2)$$

Where:

f_{cv} is the COD/VSS ratio of the sludge (mg COD/mg VSS),

Y_h is the yield coefficient for hetrotrophs (mg VSS/ mg COD),
OUR_i is the initial high OUR in mg O_2/l/d,
V_{ww} is the volume of wastewater in l,
V_{ml} is the volume of mixed liquor (at concentration X_v mg VSS/l.
f_{av} is the active fraction of the MLVSS, and
X_v is the MLVSS concentration of the mixed liquor added to the batch test mg VSS/l .

Here it must be indicated that, for AS reactor the measured OUR was directly used for estimating heterotrophic biomass. However, for AS+GAC reactor the measured OUR represents the summation of both oxygen utilized by biomass and oxygen adsorbed by active carbon. In order to estimate the OUR utilized by the biomass, the OUR measurements were repeated for the GAC reactor alone with no sludge and under the same conditions. The difference between the total OUR of the AS+GAS and the OUR of the GAC is the OUR utilized by biomass. This value was used for estimating the maximum specific growth rate in the AS+GAS reactor. More details on the respirometric measurements and parameters estimation can be found elsewhere [13].

The toxic effect of phenol on biomass can easily be explained in table 1. For AS batches, the maximum specific growth rate μ^H was 2.75 d^{-1} in batch reactor no. 1 with zero phenol concentration, this value decreased to 1.62 d^{-1} in batch reactor no. 3 with phenol shock loading of 200 mg/l. Increasing phenol concentration in batch reactor no. 5 resulted in a reduction of μ^H to only 0.93 d^{-1}. For the AS+GAC batches, the maximum specific growth rate of heterotrophic was 2.57 d^{-1} with no phenol addition, using phenol shock loads of 200 and 400 mg/l resulted in decreasing this value to 1.38 and 0.79 d^{-1}, respectively. Comparing AS and AS+GAC systems, it is also clear that for all cases the maximum specific growth rates of hetrotrophic are higher in AS than in AS+GAC reactors. This may due the presence of active carbon which compete the biomass by adsorbing dissolved oxygen.

No doubt that phenol toxicity has an adverse effect on heterotrophs growth rate, this should be considered in designing biological unit process for phenolic wastewater treatment. In order to confirm the previous results, the toxic effect of phenol on biomass was also evaluated using specific oxygen up take rate SOUR measurements. SOUR has an interesting information capacity [14], SOUR measurements are considered reliable and if the input parameters are carefully controlled, it permits to follow instantaneously the sludge answer to injection of toxics. The toxic effect can be measured by following the fraction of SOUR loss between the sludge with zero phenol and the sludge dosed with phenol.

Phenol Toxicity Factor = $1- SOUR^+/SOUR^o$. (3)

Where:
$SOUR^+$ is the specific oxygen uptake rate for sludge laden with phenol (mg O_2/mg MLSS.h), and
$SOUR^o$ is the specific oxygen uptake rate for sludge with zero phenol (mg O_2/mg MLSS.h).

The results obtained from SOUR measurements indicate an increasing of toxicity effect from 0.5 at phenol concentration of 200 mg/l to 0.73 at phenol concentration of 400 mg/l Fig. 3. Such results confirm that increasing phenol shock loading results in increasing phenol toxicity and as a consequence decreases μ^H and activated sludge performance efficiency.

4. Conclusions

- Three batch systems were examined in order to study the treatability aspect of phenolic wastewater: AS, AS+GAC, and GAC. The effect of phenol shock loading on the performance of the three mentioned systems and phenol toxic effect on biomass were investigated.
- The AS+GAC gave the highest COD and phenol % removal under different phenol shock loads. The addition of GAC into the system provided exceptional resistance to shock loading by phenol. For the three type of reactors increasing phenol shock loading has an adverse effect on the removal efficiency of both COD and phenol.

Table 1
Maximum specific growth rate and phenol toxicity factor of AS and AS+GAC systems under different phenol shock loads

Phenol conc. (mg/l)	AS system		AS +GAC system	
	Maximum specific growth ratex(d^{-1})	Phenol toxicity factor	Maximum specific growth rate (d^{-1})	Phenol toxicity factor
0.0	2.75	0.00	2.57	0.00
200	1.60	0.50	1.38	0.54
400	0.93	0.73	0.65	0.79

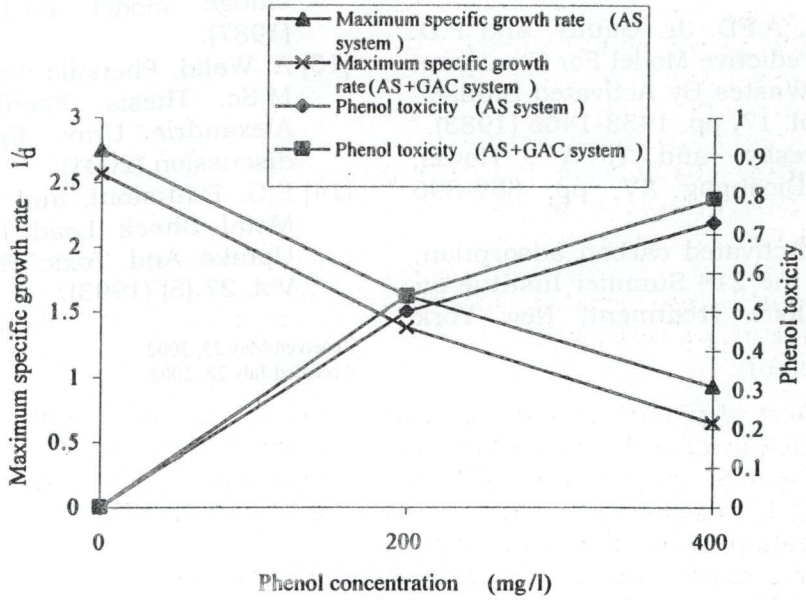

Fig. 3. Relation between maximum specific growth rate, phenol toxicity and phenol concentration.

• For all cases, increasing retention time improves the removal efficiency of both COD and phenol.

• Increasing phenol shock loading into both AS and AS+GAC systems results in decreasing the maximum specific growth rate of heterotrophic biomass.

List of abbreviations

A.S is the activated sludge,
COD is the chemical oxygen demand,
DO is the dissolved oxygen,
GAC is the granular active carbon,
MLSS is the mixed liquor suspended solids,
MLVSS is the mixed liquor volatile suspended solids,
OUR is the oxygen uptake rate,
OUR_i is the initial oxygen uptake rate
SS suspended solids, and
μ^H is the maximum specific growth rate of hetrotrophs biomass.

References

[1] A. lasllai and G. Mura, "Kinetics of Growth For Mixed Cultures Of Micro-

Organisms growing on phenol," Chem. Eng Biochem. J., Vol. 41(3), pp. 55-60 (1989).

[2] A. F. Rozich, A.FD. Jr. Gaudy and P. D. D`Adamo, "Selection Of Growth Rate Model Activated Sludge Treating Phenol," Wat. Res., Vol. 19, pp. 481-490 (1985).

[3] P. Kumaran, Microbial Degradation of Phenol in Phenol Bearing Industrial Wastes. Ph. D. Thesis, Nagur Univ. India, (1980).

[4] T. E. Short, "Controlling Phenols In Refinery Wastes," Oil Gas J., Vol. 72, pp. 119-124 (1974).

[5] K. H. Lanouette, " Treatment Of Phenolic Wastes," Chem. Eng. J., Vol. 84, pp. 99-106 (1977).

[6] A. F. Rozich, A.FD. Jr. Gaudy, and P.D. D`adamo, "Predictive Model For Treatment Of Phenolic Wastes By Activated Sludge," Wat. Res., Vol. 17, pp. 1453-1466 (1983).

[7] V. Paulowesky, and T. A . Howel, Biotechnol. Bioengng XV, pp. 889-896 (1973).

[8] J.A. Muller, Activated carbon adsorption, presented at the 21st Summer Institue on Biological Waste Treatment, New York (1976).

[9] J.F. Ferguson, "Combined Powdered Activated Carbon- Biological Stabilization Treatment Of Municipal Wastewater," 31st Purdue Industrial Conference (1976).

[10] American Public Health Association : Standard Methods for Examination of Water and Wastewater . 19th Edition, Washington (1995).

[11] A. Ekama, P.L Dold, and G. V. R. Marais, "Procedures For Determining Influent Cod Fractions And The Maximum Specific Growth Rate Of Heterotrophs In Activated Sludge Systems," Wat. Sci. Tech., Vol. 18 (1986)

[12] M. Henze, JR C.P.L. Grady, W. Gujer, G.V.R. Marais, and T. Matsuo, Activated sludge model no.1, IAWPRC Report (1987).

[13] A. Walid, Phenolic Wastewater Treatment. M.Sc. Thesis, Faculty of Engineering, Alexandria Univ. Egypt, Submitted to discussion (2001).

[14] F.G. Battistoni, and M.L. Ruello, "Heavy Metal Shock Load In Activated Sludge Uptake And Toxic Effects," Wat. Res., Vol. 27 (5) (1993).

Received May 25, 2002
Accepted July 28, 2002