Combined effects of cadmium and zinc on the activated sludge process

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The present research was undertaken to investigate the combined effects of cadmium and zinc on the activated sludge performance. The combined effects of cadmium and zinc shock loads were experimented on both i) normal sludge which was taken from a continuous flow activated sludge unit, and ii) acclimatized sludge which was taken from another continuous flow activated sludge unit. Both units were operated at steady state conditions, keeping all environmental and operational variables constant with the exception of continuous feeding of cadmium and zinc into the second unit. Steady- State operation of both units showed that the COD % removal efficiency was higher in Unit I than in Unit II, this may due to the continuous feeding of *cd/zn* into Unit II. It was also recognized that for both units increasing sludge age slightly improved COD % removal. Shock loads on batch tests showed that the higher the concentration of cadmium and zinc shock load the lower COD% removal at a given sludge age value. For both normal and acclimated sludges increasing cadmium and zinc shock loading resulted in decreasing the maximum specific growth rate of heterotrophs μ^{Λ}_{H}. However, for the same cadmium and zinc shock loading dosage, the μ^{Λ}_{H} of the acclimated sludge was always higher than the one of the normal sludge which confirms that the acclimated sludge is more capable to resist metal shock loads.

يهدف هذا البحث إلى دراسة التأثير المشترك للكادميوم والزنك على الحمأة المنشطة. وقد تمت الدراسة على وحدتى تجارب تعملان بطريقة الحمأة المنشطة الوحدة الأولى تم تغذيتها بمجاري تركيبة لا تحتوي على معادن ثقيلة والثانية تم تغذيتها بنفس المجاري مع إضافة كادميوم وزنك بتركيز ٥ مجم/لتر لكل عنصر بإستمرار. وقد تم تشغيل الوحدتين على التوازي مع تثبيت ظروف التشغيل على ٣ مراحل: المرحلة الأولى بعمر حمأة ٥ أيام والثانية ١٠ أيام والثالثة ١٥ يوم وقد استمرت كل مرحلة ٢٠ يوم. وفي نهاية كل مرحلة تم إجراء تجارب احمال الصدمة Shock Loads بالكادميوم و الزنك بتركيزات ٥/٥ و١٠/١٠ و٢٠/٢٠ مجم/لتر على Batch Reactors بها حمأة مأخوذة من وحدتي التجارب. وقد أظهرت النتائج الآتي: بالنسبة لتشغيل الوحدتين تحت ظروف Steady-State اتضح أن كفاءة إزالة COD أعلى في الوحدة الأولى والتي لم تتعرض للمعادن الثقيلة. وكذلك فأن زيادة عمر الحمأة يساعد على زيادة كفاءة إزالة COD زيادة طفيفة في كل من الوحدتين وبالنسبة لأحمال الصدمة على الـ Batch Reactors اتضح أن زيادة تركيز الكادميوم والزنك يسبب انخفاض في كفاءة إزالة COD وكذلك معدل نمو البكتريا بشكل عام غير أن الحمأة المأخوذة من الوحدة الثانية كانت اكثر مقاومة لأحمال الصدمة من حيث كفاءتها ومعدل نمو البكتريا الأعلى نظرا لاعتيادها على الكادميوم والزنك لفترات طويلة.

Keywords: Activated sludge, Heavy metals, Cadmium, Zinc, Metal toxicity

1. Introduction

It is well recognized that industrialization has resulted in the collection and discharge of heavy metals into the environment. Some of the heavy metals, for example, cobalt, copper, zinc are essential for the metabolism of many organisms, although others such as mercury, lead, and cadmium are not needed.

The presence of heavy metals in wastewater is of concern not only because heavy metal discharge into a receiving water course may be detrimental to the environment, but also because a reduced efficiency in biological wastewater treatment can occur. Greater emphasis on the efficient and effective treatment of wastewater has become necessary in recent years because of the passage of increasingly stringent effluent requirements, has led to a revived interest in the effects of various toxic materials on biological treatment processes. As a result, research has been undertaken to increase the level of understanding of the effects of heavy metals.

The mechanisms of metal removal in wastewater treatment plants have been widely discussed. Precipitation, adsorption on suspended solids during primary sedimentation [1, 2], adsorption on extracellular polymers and bacterial cells of activated sludge [2-4], have been shown to play an important role in metal uptake.

Activated sludge is the most commonly used biological treatment process employed in the removal of colloidal and soluble organic matter present in wastewaters. The deleterious effects of toxic compounds on biological processes are complex, and are generally related to the species, the solubility of the metal and concentration of the toxicant. Toxicity may also depend upon the influent matrix such as pH, concentration of other cations and/ or molecules present, suspended solids, and upon operational parameters such as sludge age [5-8].

Review of the relevant literature indicates that the extent of system acclimation also plays a major role in determining the toxicity of metals on activated sludge culture [9, 10]. A constant input level of heavy metal does not affect the biological treatment performance. Acclimatized sludges maintain high removal efficiency even if exposed to high concentrations of cadmium, zinc and mercury [11, 12]. An activated sludge process toward constant inputs of zinc has also been reported with high stability [13]. In contrast, shock loads manifest remarkable effects on activated sludges with major evidence for the non-acclimatized ones [14].

Moreover, the fact that municipal wastewater treatment systems often receive more than one metal simultaneously further complicates the picture. There has been little research on the combined effects of heavy metals on activated sludge to date. The combined effects of metals revealing synergistic or antagonistic effects have been hypothesized in the past, but have never actually been demonstrated.

A synergistic effect is one in which the effects of the metals in combination is greater than the summed effects of the individual metals. Conversely, an antagonistic effect is one in which the metals counteract each other diminishing the resulting effect [15].

The present research was undertaken to investigate the combined effects of cadmium and zinc on the activated sludge performance. The combined effects of cadmium and zinc shock loads were experimented on both
i) normal sludge which was taken from a continuous flow activated sludge unit, and
ii) acclimatized sludge which was taken from another continuous flow activated sludge unit. Both units were operated at steady state conditions, keeping all environmental and operational variables constant with the exception of continuous feeding of cadmium and zinc into the second unit.

2. Materials and methods

2.1. Laboratory apparatus

Two continuous activated sludge units were constructed and operated at the laboratory of the Sanitary Engineering Department, Alexandria University. Each unit was constructed with plexiglass and had 47 liter aeration tank volume, connected by a silicon rubber tube to a 26.5 liter settling tank. An influent flow rate of 80 l/d provided a hydraulic detention time of 7 hrs in the aeration tank and 4 hrs in the settling tank using activated sludge recycle ratio of 100 % of the influent flow rate.

Two variable speed peristaltic pumps (Master flex L/S Easy-Load) were used to transfer the feed solution (prepared daily and contained in two 150 liter feed tanks) to the activated sludge units. Another two variable speed peristaltic pumps (same model) were utilized to recycle settled sludge to the aeration tanks of each unit. Compressed air was used to supply oxygen to each process through porous diffusers stones. The air also served to provide good mixing of the Mixed Liquor Suspended Solids (MLSS).

2.2. Feed solution

The activated sludge process was simulated in the laboratory units utilizing a synthetic sewage prepared by diluting with tap water (1-100) a concentrated stock solution containing 48.6 g/l of glucose served as the carbon and energy source, 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 for both units with the exception of that cadmium and zinc were added in combination into the feed of one of the units (unit II) continuously with a constant concentrations of 5.0 mg/l for each.

2.3. Initial start-up

Unit I: The first activated sludge laboratory system (Unit I) was seeded with sludge wasted 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. Steady-state conditions were considered achieved by the constance of the measured parameter (MLSS ± 10%, and Specific Oxygen Uptake Rate, (SOUR) ± 15 %) [16]. The start-up period was about 21 days.

Unit II: The second activated sludge laboratory system (Unit II) was also seeded with the sludge wasted from Kafer El- Dawar wastewater treatment plant. The same previous procedure was followed, the unit was operated for about 21 days without any metal addition and then, metals (cadmium and zinc) in the feed were increased gradually and stepwise (0.5 mg/l of each at every step) until the desired concentrations of 5.0/5.0 mg/l were reached. At every step sufficient time was given for the culture to acclimatize to the increased metals concentration. Once the acclimatization procedure was complete, the MLSS concentration in both reactor and effluent and SOUR in reactor were monitored in order to determine whether steady-state conditions were reached.

2.4. Experimental plan

After reaching steady-state conditions, both units were operated at sludge age (θc) of 5 days, and sludge were wasted directly from aeration tanks (run I).

For both run II and run III all previously mentioned environmental and operational conditions were kept constant for both units with the exception of changing θc to be 10 d during run II and 15 d during run III. The duration of each run was 20 days.

At the end of each run sludge was taken from each unit to carry out batch tests in order to investigate the toxic effect of cadmium and zinc (*cd/zn*) shock loads, *cd/zn* doses of 5.0/5.0, 10.0/10.0, and 20.0/20.0 were experimented in batch tests for both sludge I and sludge II which were taken from units I and II, respectively.

2.5. Analytical methods

Parameters monitored during this study were chosen to determine the activated sludge performance under the combined effects of cadmium and zinc shock loads. COD was measured by colorimetric method using Spectrophotometer (DR 100- Colorimeter, Hach, USA). Oxygen uptake rate OUR, specific oxygen uptake rate SOUR, MLSS and all other parameters were measured according to the Standard Methods for the Examination of Water and Wastewater [17]. The maximum specific growth rate of hetertrophs ($\mu^{\wedge}{}_{H}$) was measured according to the method proposed by Ekama et al. [18]

3. Results and discussion

The experimental studies performed previously [19-24] show that there are some contradictory results on the effects of heavy metals; this may due to the fact that some experiments were performed by acclimated microorganisms and others used shock doses. In this research the combined effects of cadmium and zinc were studied on both normal sludge (sludge I) and acclimated sludge (sludge II). Batch systems were used to study the effect of cadmium and zinc shock loads on both normal and acclimated sludge.

3.1. Steady-state

As mentioned before, 3 steady-state runs were conducted on both units with 3 different sludge ages (5; 10; 15 days). The duration of each run was about 20 days. Fig. 1. shows the relationship between the COD % removal and the 3 different sludge ages for both Unit I and Unit II. The COD % removal efficiency is higher in Unit I than in Unit II, this may due to the continuous dosing of *cd/zn* (5.0/5.0 *mg*/l) into Unit II. It is also clear that for both units increasing sludge age slightly improves COD % removal efficiency.

In order to study the effect of combined *cd/zn* shock load on normal and acclimated

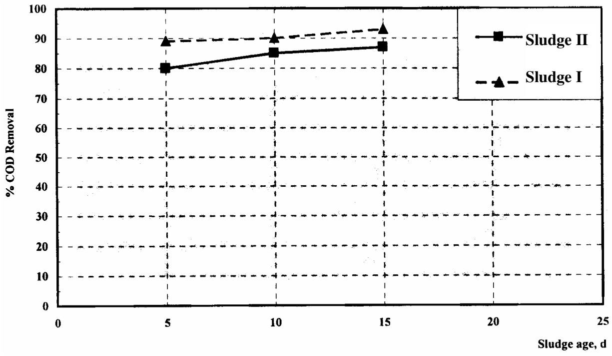

Fig. 1. Relation between COD% removal and sludge age for unit I & unit II.

sludge, the batch tests were conducted at the end of each steady-state run. At the end of run I (*θc*= 5*d*), the activated sludge batch reactor test was carried out in 8 flasks, the operating volume of each reactor was 3 liter. In each reactor 2.2 liter of synthetic sewage was added to 0.8 liter of sludge resulting in an average *F/M* ratio of 0.20 d^{-1}. The 8 flasks were divided into 2 groups, the sludge used for the first 4 flasks was taken from unit I (sludge I) and the sludge used for the second 4 flasks was taken from unit II (sludge II). The first reactor in each group served as a control and received the synthetic sewage void of cadmium and zinc. The remaining 3 reactors in each group received synthetic sewage with an influent concentration of *cd/zn*: 5.0/5.0; 10.0/10.0; and 20.0/20.0 mg/l, 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 4 hours of operation for measuring COD concentration. Fig. 2 shows COD % removal in the batch tests for normal and acclimated sludge after run I under *cd/zn* shock loads. In general, for both sludge I and II increasing *cd/zn* dosage causes a reduction in COD % removal efficiency. Comparing sludge I and II, it is obvious that sludge II (acclimated sludge) is more capable to resist shock loads of cd/zn, than sludge I (normal sludge). For example, adding *cd/zn* dosage of 20.0/20.0 mg/l resulted in COD % removal of 55% for sludge II, while this value was only 40% for sludge I.

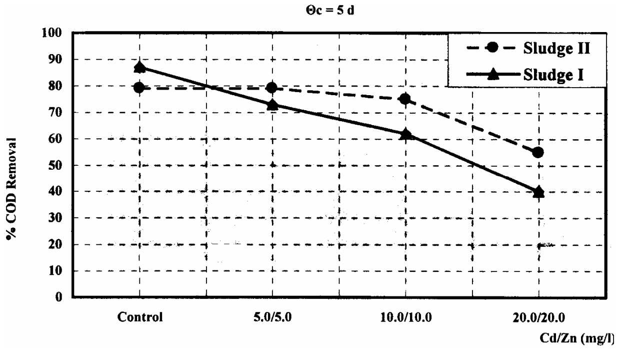

Fig. 2. COD% removal in batch reactors under shock loads (run I).

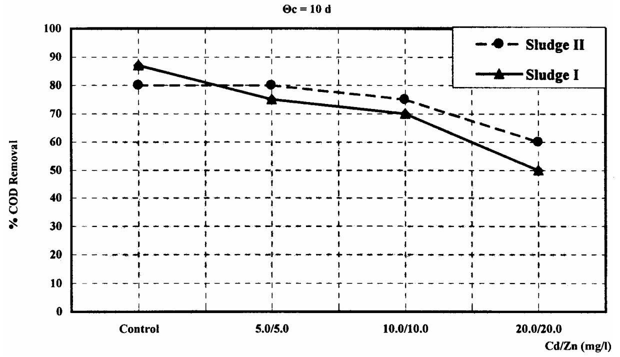

Fig. 3. COD% removal in batch reactors under *cd/zn* shock (run II).

The same batch test was repeated at the end of run II (*θc*= *10d*). Fig. 3 shows COD% in the batch tests for normal and acclimated sludge after run II under *cd/zn* shock loads. It is obvious that for both sludges increasing *cd/zn* dosage results in decreasing COD % removal. In general, acclimated sludge is more capable to resist shock loads of *cd/zn.*

Fig. 4 shows COD % in batch tests for normal and acclimated sludge after run III (*θc*= *15 d*). This figure also confirms that the acclimated sludge is more capable to resist shock loads of *cd/zn.* Accordingly, the same trend of COD % removal was observed for the 3 experimented sludge ages.

Fig. 5 shows the relationship between COD % removal and *cd/zn* shock load dosage for the 3 different sludge ages (sludge II). From this figure it is clear that increasing sludge age resulted in a slight improvement of COD % removal. For example, using *cd/zn* dosage of 20.0/20.0 mg/l and *θc*= *5* d, the COD % removal was 55%, increasing *θc* to 10 d improved COD % removal to 60 %.

Another increasing of *θc* to 15 d improved COD % removal to 63 %. The same trend was

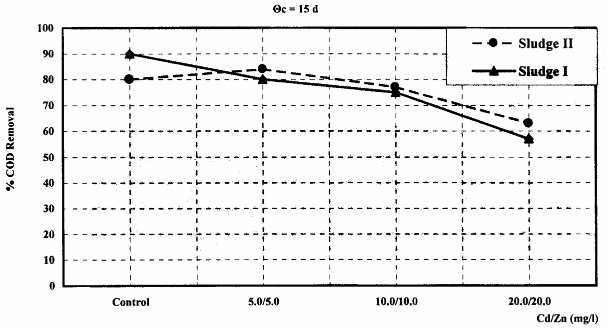

Fig. 4. COD% removal in batch reactors under *cd/zn* shock loads (run III).

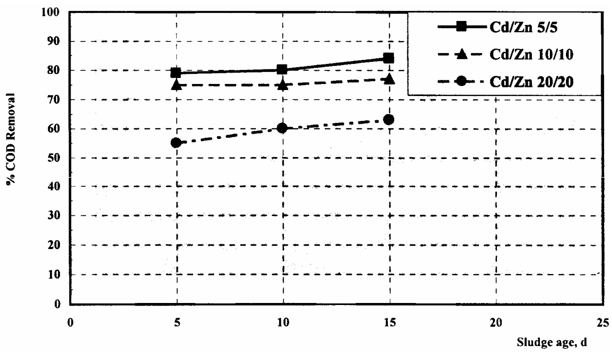

Fig. 5. Relation between COD% removal and sludge age under metal shock loads.

also observed for *cd/zn* shock loads of 5.0/5.0 and 10.0/10.0.

3.2. Metal toxicity

Respirometric analyses were carried out to evaluate the combined metal effect on biomass. The toxicity effect on biomass was evaluated by measuring the maximum specific growth rate μ^{A}_{H} for the batches at *cd/zn* 0.0/0.0; 5.0/5.0; 10.0/10.0; and 20.0/20.0 mg/l for both sludge I and sludge II at θc=15d.

The method proposed by Ekma et al. [18] was used to measure the μ^{A}_{H}. They indicated that aerobic batch tests can be used to obtain and evaluate the oxygen uptake rate OUR profile. The initial high OUR is a consequence of the utilization of the readily biodegradable COD from the wastewater as well as that derived from hydrolysis of the particulate biodegradable COD. The OUR is constant over this period because the concentration of readily biodegradable COD is so high that the growth rate of the heterotrophs is at maximum μ^{A}_{H} in accordance with Monod kinetics. Once the readily biodegradable COD from the influent is depleted, the OUR rapidly drops to the second level which is the rate associated with the utilization of the biodegradable COD. The readily biodegradable COD fraction and the maximum specific growth rate of the heterotrophs μ^{A}_{H} can be calculated using the OUR curve. Maximum specific growth rate of the heterotrophs μ^{A}_{H} proportional to the vertical height of the initial high OUR.

The maximum specific growth rate of the heterotrophs μ^{A}_{H} is usually specified as mg Active Volatile Suspended Solids (AVSS) present per day (mg AVSS/ mg AVSS/ d) or simply d^{-1}. The μ^{A}_{H} is related to the maximum readily biodegradable substrate utilization rate K_{ms} in unit mg COD utilized / mg active VSS/ d (mg COD/ mg AVSS/ d) through the yielded coefficient in units mg VSS synthesized/ *mg* COD utilized.

$$\mu^{A}_{H} = K_{ms} . Y_{h} . \qquad (1)$$

Now K_{ms} (in mg COD/*mg* AVSS/d) is related to the initial high OUR (OUR_i) at the beginning of the batch tests, 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 of 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 autotrophic microorganisms which can be achieved by the application of 20 mg/l thiourea to suppress nitrification [18].

$$K_{ms} = [1/ (1 - f_{cv} . Y_h)] . OUR_i . [(V_{ww} + V_{ml}) / (f_{av} . X_v . V_{ml})] . \qquad (2)$$

Where:

f_{cv}	is the COD/VSS ratio of the sludge (mg COD/mg VSS),
Y_h	is the yield coefficient for heterotrophs (mg VSS/mg COD),
OUR_i	is the initial high OUR in mg O_2/l/d,
V_{ww}	is the volume of wastewater (l),
V_{ml}	is the volume of mixed liquor (at concentration X_v mg VSS/l) (l),

f_{av} is the active fraction of MLVSS, and
X_v is the MLVSS concentration added to the batch reactor (mg VSS/l).

Fig. 6. shows the relationship between μ^{Λ}_{H} and metal shock loads for both normal and acclimated sludge ($\theta c = 20\ d$). The toxic effect of *cd/zn* on biomass can easily be noticed in fig. 6. For sludge I (normal sludge) μ^{Λ}_{H} was 4.61 d^{-1} with *cd/zn* dosage of 0.0/0.0 mg/l. μ^{Λ}_{H} decreased to 2.28 d^{-1} with *cd/zn* dosage of 5.0/5.0 mg/l, and 1.67 d^{-1} with *cd/zn* dosage of 10.0/10.0 mg/l. Finally, μ^{Λ}_{H} was only 0.83 d^{-1} with *cd/zn* dosage of 20.0/20.0 mg/l. Consequently, increasing metal shock loading causes sharp decrease in μ^{Λ}_{H} due to its toxic effect. From the same figure it can also be recognized that metal shock loading had also toxic effect on the acclimated sludge. However, the acclimated sludge is more capable to resist metal toxicity. For example, adding *cd/zn* dosage of 20.0/20.0 mg/l resulted in $\mu^{\Lambda}_{H} = 1.98\ d^{-1}$ in acclimated sludge, this value was only 0.83 d^{-1} in normal sludge.

4. Conclusions

Based on the results obtained from this research, the following conclusions can be made:

Steady- state:

- Comparing both continuous flow activated sludge units, the COD % removal efficiency was higher in Unit I than in Unit II. It is believed that the continuous feeding of cd/zn dosage of 5.0/5.0 mg/l in Unit II caused a reduction in the COD % removal of this unit.
- For both units, increasing sludge age slightly improved COD % removal. This result is in agreement with ref. [23].

Shock loads:

- From batch test experiments, and for all cases, the higher concentration of cadmium and zinc shock load the lower COD % removal at a given sludge age value.
- Higher sludge age values resulted in higher COD % removal at a given concentration of cadmium and zinc shock load.
- Generally, for both normal and acclimated sludges increasing cadmium and zinc shock loading resulted in decreasing the maximum specific growth rate of heterotrophs μ^{Λ}_{H}. However, for the same cadmium and zinc shock loading dosage, the μ^{Λ}_{H} of the acclimated sludge was always higher than the one of the normal sludge which confirms that the acclimated sludge is more capable to resist metal shock loads.

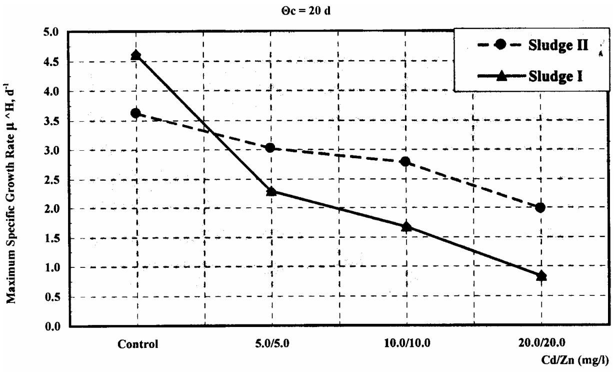

Fig. 6. The relationship μ^{Λ}_{H} and metal shock loads (run III).

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