

Elimination of Cu(II) toxicity by powdered waste sludge (PWS) addition to an activated sludge unit treating Cu(II) containing synthetic wastewater

M. Yunus Pamukoglu, Fikret Kargi*

Department of Environmental Engineering, Dokuz Eylul University, Buca, Izmir, Turkey

Received 21 November 2006; received in revised form 8 February 2007; accepted 9 February 2007

Available online 14 February 2007

Abstract

Copper(II) ion toxicity onto activated sludge organisms was eliminated by addition of powdered waste sludge (PWS) to the feed wastewater for removal of Cu(II) ions by biosorption before biological treatment. The synthetic feed wastewater containing 14 or 22 mg l⁻¹ Cu(II) was mixed with PWS in a mixing tank where Cu(II) ions were adsorbed onto PWS and the mixture was fed to a sedimentation tank to separate Cu(II) containing PWS from the feed wastewater. The activated sludge unit fed with the effluent of the sedimentation tank was operated at a hydraulic residence time (HRT) of 10 h and sludge age (SRT) of 10 days. To investigate Cu(II), COD and toxicity removal performance of the activated sludge unit at different PWS loadings, the system was operated at different PWS loading rates (0.1–1 g PWS h⁻¹) while the Cu(II) loading rate was constant throughout the operation. Percent copper, COD and toxicity removals increased with increasing PWS loading rate due to increased adsorption of Cu(II) onto PWS yielding low Cu(II) contents in the feed. Biomass concentration in the aeration tank increased and the sludge volume index (SVI) decreased with increasing PWS loading rate due to elimination of Cu(II) from the feed wastewater by PWS addition. PWS addition to the Cu(II) containing wastewater was proven to be effective for removal of Cu(II) by biosorption before biological treatment. Approximately, 1 g PWS h⁻¹ should be added for 28 mg Cu h⁻¹ loading rate for complete removal of Cu(II) from the feed wastewater to obtain high COD removals in the activated sludge unit.

© 2007 Published by Elsevier B.V.

Keywords: Activated sludge; Biosorption; Copper(II); Powdered waste sludge; Toxicity

1. Introduction

Heavy metals present in many industrial wastewaters such as automobile, metal finishing, leather tanning, electroplating, petroleum and textile dyeing are known to have toxic effects to the receiving environment. 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 [1–4].

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 ions at ppm (mg l⁻¹) level are known to be toxic to most of the organ-

isms because of irreversible enzyme inhibitions by 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 (SRT) and hydraulic residence time [5]. A number of studies were reported in literature on toxic effects of heavy metal ions on activated sludge organisms [5–21].

One effective method of removing heavy metals ions from wastewater is by biosorption onto microorganisms. Metal ions present in wastewater 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

* Corresponding author. Tel.: +90 232 4127109; fax: +90 232 4531143.
E-mail address: fikret.kargi@deu.edu.tr (F. Kargi).

irreversible inhibition of extracellular or intracellular enzymes upon binding of metal ions [22]. Removal of heavy metals from wastewater by biosorption has been studied extensively by many investigators [23–29]. However, integration of biosorption processes into biological treatment systems for heavy metal ion removal before treatment has not been reported in literature.

Therefore, the major objective of this study is to investigate the utilization of pre-treated powdered waste sludge (PWS) for removal of Cu(II) ions from wastewater by biosorption before biological treatment in order to improve the performance of an activated sludge unit. The activated sludge unit operated at a hydraulic residence time (HRT) of 10 h and sludge age (SRT) of 10 days was fed with the low Cu(II) content wastewater after biosorption of Cu(II) onto PWS and sedimentation of PWS containing Cu(II) ions. The system was operated at different PWS loading rates ($0.1\text{--}1\text{ g PWS h}^{-1}$) while the Cu(II) loading rate was constant ($12\text{ or }19\text{ mg Cu h}^{-1}$) throughout the operations to investigate Cu(II), COD and toxicity removal performance of the activated sludge unit at different PWS loadings.

2. Materials and methods

2.1. Experimental set-up

A schematic diagram of the experimental set-up is depicted in Fig. 1 which consisted of a feed reservoir, a mixing tank placed on a magnetic stirrer, a primary sedimentation tank and an activated sludge unit. The feed reservoir (50 l) was placed in a deep refrigerator at 4°C to avoid any decomposition in the feed. The mixing tank placed on a magnetic stirrer was made of plexi-glass (3 l). The primary sedimentation tank was (1.5 l) was made of stainless steel. The activated sludge 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. The aeration tank was vigorously aerated (approx. 5 min^{-1} , v/v) 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 mixing tank with a desired flow rate (0.85 l h^{-1}) by a peristaltic pump (Watson–Marlow 505 D_i/L). Powdered waste sludge (PWS) was added automatically to the mixing tank with the aid of a feeder and timer with a desired loading rate ($0.1\text{--}1\text{ g PWS h}^{-1}$). Hydraulic residence time (HRT) in the mixing tank was 3.5 h to allow adsorption of Cu(II) ions in the feed onto PWS. The effluent of the mixing tank was fed to the sedimentation tank where the PWS with adsorbed Cu(II) was separated from the feed wastewater by sedimentation ($\text{HRT}_{\text{ST}} = 1.8\text{ h}$). Solids (PWS containing adsorbed Cu(II)) were removed from the bottom of the sedimentation tank everyday to avoid desorption of Cu(II) ions. The activated sludge unit was fed with the effluent from the top of the sedimentation tank (0.85 l h^{-1}) by gravitational flow. Temperature, pH and dissolved oxygen (DO) concentrations in the aeration tank were $T = 25 \pm 2^\circ\text{C}$, $\text{pH} = 7.0 \pm 0.2$ and $\text{DO} = 2 \pm 0.5\text{ mg l}^{-1}$.

2.2. 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 $\text{COD}_0 = 2000 \pm 100\text{ mg l}^{-1}$, total nitrogen (N_T) = $160 \pm 10\text{ mg l}^{-1}$, phosphate-phosphorous ($\text{PO}_4\text{-P}$) = $30 \pm 1\text{ mg l}^{-1}$, $\text{MgSO}_4 = 50\text{ mg l}^{-1}$, $\text{Cu(II)} = 14\text{ or }22\text{ mg l}^{-1}$. Concentrated molasses was diluted by a factor of 500 to obtain dilute molasses with a COD content of nearly 2000 mg l^{-1} . pH was nearly 6.9 in the feed wastewater which increased to $\text{pH} > 7.5$ in the aeration tank because of ammonia released from biodegradation of urea. pH of the aeration tank

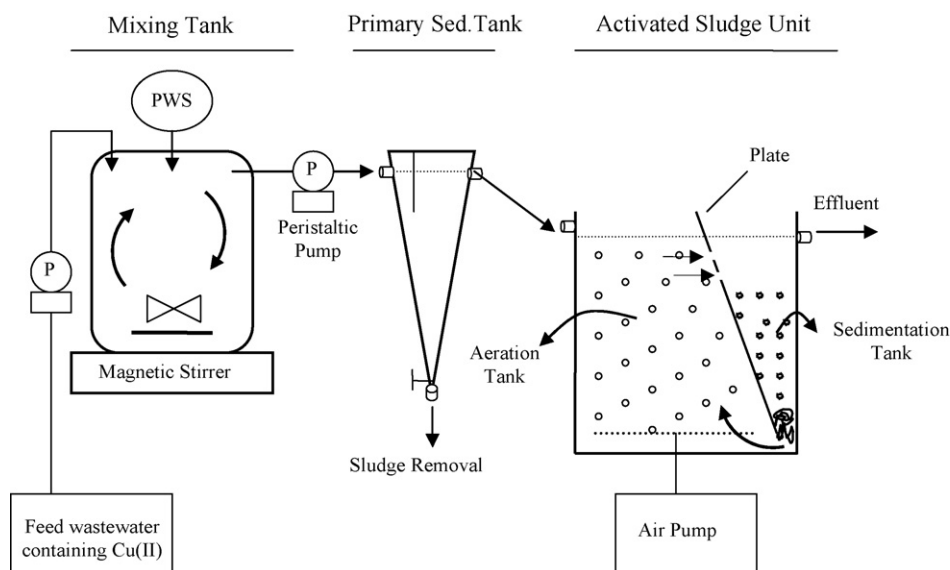


Fig. 1. Schematic diagram of experimental system.

content was adjusted manually to pH 7 by addition of dilute sulfuric acid (0.1 M) several times a day.

2.3. Microorganisms

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.

2.4. Powdered waste sludge (PWS)

The raw sludge was obtained from the DYO paint industry (Izmir, Turkey) activated sludge unit contained $16 \mu\text{g l}^{-1}$ Cr, $58 \mu\text{g l}^{-1}$ Zn, $2 \mu\text{g l}^{-1}$ Cu, $1 \mu\text{g l}^{-1}$ Pb, $80 \mu\text{g l}^{-1}$ Fe, $20 \mu\text{g l}^{-1}$ Mn, and no detectable Ni and Cd with a density of 1.2 g cm^{-3} . The sludge was dried at 80°C , ground and sieved to $64 \mu\text{m}$ particle size before use in experiments. Due to low biosorption capacity of the untreated powdered waste sludge (PWS), the PWS samples were pre-treated using 1% H_2O_2 solution. Hydrogen peroxide solution of 200 ml was mixed with 2 g of PWS in a 500 ml erlenmeyer flask and placed on a gyratory shaker (Gallenkamp) at 150 rpm and 25°C for 6 h. Pre-treated PWS was washed with deionized water on a blue-ribbon filter paper until the filtrate pH was neutral. Pre-treated and washed PWS samples were dried at 80°C , reground and sieved to different mesh sizes. Biosorption capacity of pre-treated PWS was considerably higher than that of the untreated PWS. Only the size fraction between 200 and 270 mesh with an average particle size of $64 \mu\text{m}$ was used in the experimental studies. The BET surface area of dried sludge with a particle size of $64 \mu\text{m}$ was $69 \text{ m}^2 \text{ g}^{-1}$ after pre-treatment with 1% H_2O_2 .

2.5. Experimental procedure

Experiments were started batch wise. About 7 l of the synthetic wastewater was placed in the aeration tank and was inoculated with 1 l of the activated sludge culture. The system was operated in batch mode for several days to obtain a dense activated sludge culture before starting the continuous operation. Feed wastewater was fed to the system with a desired flow rate and removed with the same rate. Temperature, pH and DO were approximately $T = 25 \pm 2^\circ\text{C}$, $\text{pH} = 7.0 \pm 0.2$, $\text{DO} = 2 \pm 0.5 \text{ mg l}^{-1}$ throughout the experiments. Two sets of experiments were performed with the feed Cu(II) of 14 and 22 mg l^{-1} . The loading rate of PWS was varied between 0.1 and 0.6 g h^{-1} with the feed Cu(II) of 14 mg l^{-1} and between 0.2 and 1 g h^{-1} when the feed Cu(II) was 22 mg l^{-1} . The sludge age (SRT) and HRT was kept constant at 10 days and 10 h, respectively, throughout the experiments. Sludge age was adjusted to 10 days by removing 10% of the sludge from the aeration tank everyday. Hydraulic residence time (HRT) in the aeration tank was kept at 10 h by adjusting the feed flow rate to 0.85 h^{-1} . Experiments were performed in the order of increasing PWS loading rate. Every experiment was continued until the system reached the steady-state yielding the same COD, Cu(II) and toxicity levels in the effluent

for the last 3 days. Average time elapsed for each experiment was 2–3 weeks. Two experiments (the lowest and the highest PWS loadings) from each set were repeated twice to test the reproducibility of the results. Due to good reproducibility of the repeated experiments (standard deviations of less than 5%), the other experiments were not repeated. The samples collected from the feed and effluent of the mixing and sedimentation tanks and also from the activated sludge unit at the steady-state were analyzed for COD, Cu(II), biomass concentrations and also for toxicity by the resazurin method after centrifugation.

2.6. Analytical methods

Samples were withdrawn from the effluent of each unit everyday for analysis and centrifuged at 8000 rpm ($7000 \times g$) for 20 min to remove solids from the liquid phase. Clear supernatants were analyzed for COD and Cu(II) ion contents and also for toxicity. Chemical oxygen demand (COD) was determined using the closed reflux method according to the Standard Methods [30]. Clear supernatants were analyzed for total Cu(II) ion concentrations using an Atomic Absorption Spectrometer (ATI Unicam 929 AA Spectrometer) at 324.8 nm wavelength. Biomass concentration in the aeration tank was determined by filtering the samples through $0.45 \mu\text{m}$ milipore 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. Sludge volume index (SVI) was determined by settling 1 l sludge in an Imhoff cone for 1/2 h and determining the settled biomass concentration (X_r) by filtering and drying. The SVI was calculated by using the relationship of $\text{SVI} = 10^6/X_r$, where X_r is in mg l^{-1} and SVI is ml g^{-1} .

Resazurin reduction method was used to determine the toxicity of the feed and effluent wastewater [31–34]. The test organisms (washed activated sludge) to be subjected to the toxic feed and effluent wastewater were cultivated on nutrient broth before using for determination of the toxicity of wastewater samples. The test cultures were transferred to new medium everyday to keep the sludge age constant during the course of toxicity measurements. In the presence of active bacterial culture with dehydrogenase enzyme activity, resazurin changes color from blue to pink forming the reduced compound resorufin. Inactive bacteria does not cause any change in the color of resazurin and the color remains blue. Therefore, the color of the resazurin solution is an indicator of bacterial activity. A spectrometer (Aqualytic Inc.) was used to determine the color at 610 nm.

3. Results and discussion

3.1. Experiments with 14 mg l^{-1} Cu(II) in the feed

The results of the continuous experiments with PWS addition to the feed wastewater are depicted in Figs. 2–5 where the feed PWS loading was varied between 0.1 and 0.6 g h^{-1} while the Cu(II) loading was constant at 12 mg Cu h^{-1} . Fig. 2 depicts variation of percent Cu(II) removals with PWS loading rate in the effluents of the mixing tank and activated sludge unit. Cu(II) concentrations in the effluents of the mixing and

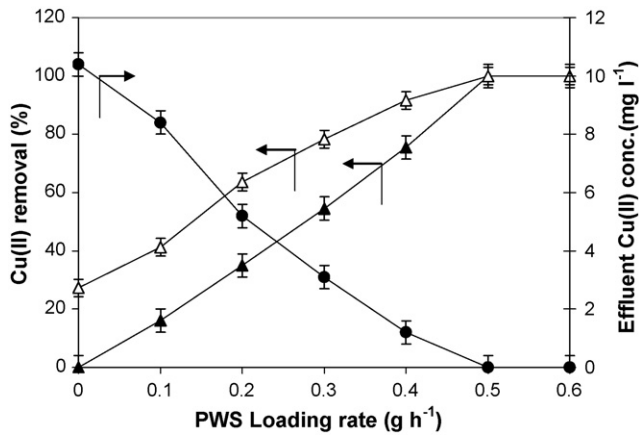


Fig. 2. Variations of effluent Cu(II) and percent Cu(II) removals with the PWS loading rate. (▲) Mixing tank effluent and (△ and ●) activated sludge effluent. $Cu_0 = 14 \text{ mg l}^{-1}$.

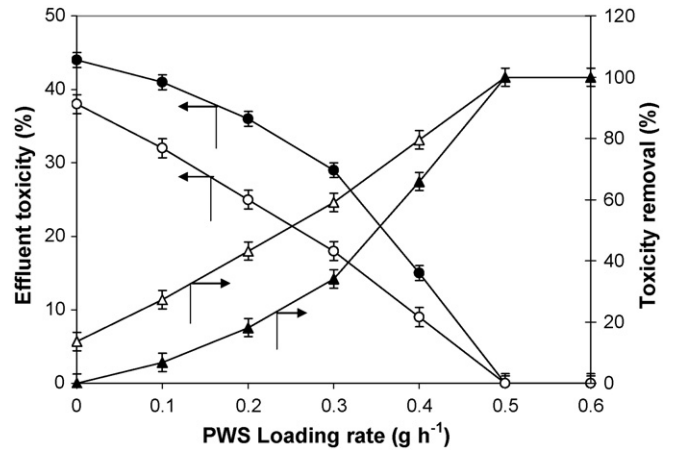


Fig. 5. Variation of effluent toxicities and percent toxicity removals with the PWS loading rate. (● and ▲) Mixing tank effluent and (○ and △) activated sludge effluent. $Cu_0 = 14 \text{ mg l}^{-1}$.

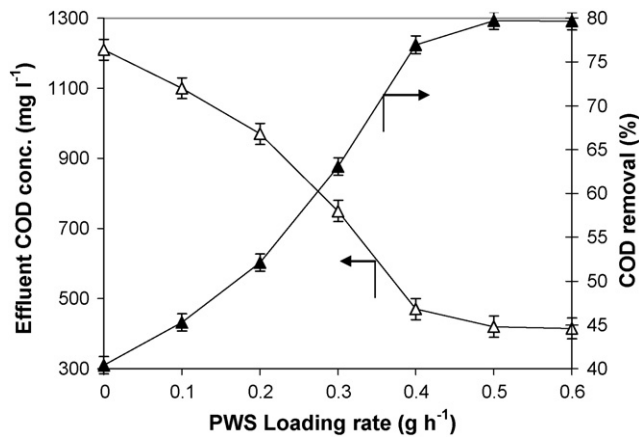


Fig. 3. Variations of effluent COD and percent COD removals with the PWS loading rate. (△) Effluent COD and (▲) percent COD removal. $Cu_0 = 14 \text{ mg l}^{-1}$.

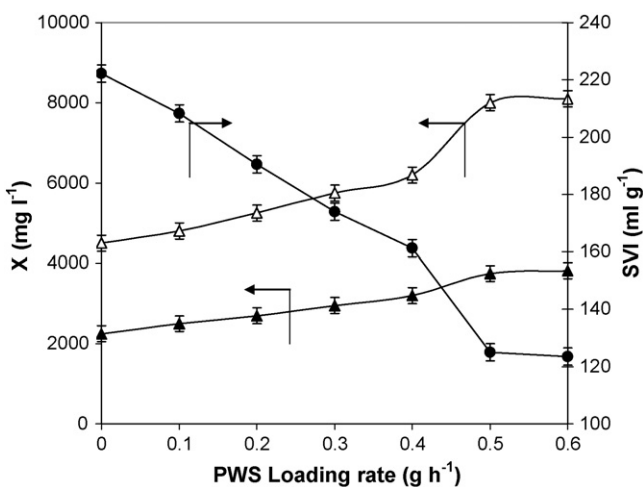


Fig. 4. Variations of biomass concentrations and the sludge volume index (SVI) with the PWS loading rate. (▲) Biomass in the aeration tank (X), (△) settled biomass concentration (X_r) and (●) sludge volume index (SVI). $Cu_0 = 14 \text{ mg l}^{-1}$.

the sedimentation tanks were approximately the same since adsorption of Cu(II) ions onto PWS took place in the mixing tank. Cu(II) ions in the effluent of the mixing tank decreased from 12 to 3.5 mg l^{-1} and further to 0 with 16%, 76% and 100% Cu(II) removals when the PWS loading rate was increased from 0.1 to 0.4 and further to 0.5 g h^{-1} due to increased adsorption of Cu(II) ions onto PWS. Cu(II) concentrations in the effluent of the activated sludge unit were considerably lower than those of the mixing and sedimentation tank effluents due to further adsorption of Cu(II) ions onto activated sludge organisms in the activated sludge unit. Cu(II) concentrations in the effluent of the activated sludge unit decreased from 8.4 mg l^{-1} (41% removal) to zero (100% removal) when PWS loading rate was increased from 0.1 to 0.5 g h^{-1} due to increased adsorption of Cu(II) onto biomass in the activated sludge unit. Approximately 1 g h^{-1} PWS addition was required for 28 mg h^{-1} Cu(II) loading for complete removal of Cu(II) ions in the mixing tank in order to obtain Cu-free feed for the activated sludge unit.

Fig. 3 depicts variation of COD removal in the activated sludge unit with PWS loading rate when $COD_0 = 2000 \text{ mg l}^{-1}$ and $Cu_0 = 14 \text{ mg l}^{-1}$. Effluent COD concentration decreased and percent COD removal increased with increasing PWS loading rate due to increased removal of Cu(II) ions by adsorption onto PWS. Percent COD removal was 45% and 77% with effluent COD's of 1100 and 470 mg l^{-1} at PWS loadings rates of 0.1 and 0.4 g h^{-1} which increased to 80% with an effluent COD of 420 mg l^{-1} at a PWS loading of 0.5 g h^{-1} . Further increases in PWS loading rates did not improve COD removal performance since complete removal of Cu(II) was achieved with a PWS loading of 0.5 g h^{-1} corresponding nearly 1 g PWS requirement for 28 mg Cu removal.

The extent and the rate of COD removal in the activated sludge unit is closely related with the biomass concentration in the aeration tank. Biomass concentration in the aeration tank increased with increasing PWS loading rate as shown in Fig. 4 due to elimination of Cu(II) toxicity on activated sludge bacteria with PWS addition. Biomass concentration in the aeration tank increased from 2500 to 3200 mg l^{-1} and further to 3820 mg l^{-1}

when PWS loading rate was increased from 0.1 to 0.4 g h⁻¹ and further to 0.6 g h⁻¹, respectively, yielding higher rates and extent of COD removal. Settled biomass concentration in the sedimentation tank (X_r) also increased with increasing PWS loadings yielding better settling sludge with lower sludge volume index (SVI) at high PWS loadings. SVI decreased from 208 to 125 ml g⁻¹ with increases in X_r values from 4800 to 8000 mg l⁻¹ when PWS loading was increased from 0.1 to 0.5 g h⁻¹. PWS loading rate of 0.5 g h⁻¹ eliminated Cu(II) ions from the feed wastewater yielding high biomass concentration and better settling sludge with low SVI values.

Removal of Cu(II) toxicity is another important parameter investigated and depicted in Fig. 5. Toxicities of the mixing tank and the activated sludge effluents decreased and percent toxicity removals increased with increasing PWS loading rate due to removal of Cu(II) from the feed by PWS addition. Percent toxicity of the feed with Cu(II) = 14 mg l⁻¹ was 44% with respect to Cu(II)-free water which decreased to 41% in the mixing tank effluent and further to 32% in the effluent of the activated sludge unit when PWS loading rate was 0.1 g h⁻¹. Percent toxicity removal in the activated sludge effluent as compared to the feed increased from 27% to 80% and further to 100% when PWS loading was increased from 0.1 to 0.4 g h⁻¹ and further to 0.5 g h⁻¹. Further increases in PWS loading rates did not result in any improvement in toxicity removal since Cu(II) was completely removed with the addition of 0.5 g PWS h⁻¹ corresponding 1 g h⁻¹ PWS addition per 28 mg h⁻¹ Cu(II) loading.

3.2. Experiments with 22 mg l⁻¹ Cu(II) in the feed

Similar experiments were performed with the feed Cu(II) concentration of 22 mg l⁻¹ where the PWS loading rates were varied between 0.2 and 1.0 g h⁻¹ while HRT and SRT were constant at 10 h and 10 days, respectively. Fig. 6 depicts variation of percent Cu(II) removal with PWS loading rate in the effluents of the mixing tank and activated sludge unit. Cu(II) concentrations in the effluents of the mixing and the sedimentation tanks were approximately the same since adsorption of Cu(II) ions by PWS took place in the mixing tank. Cu(II) ions in the effluent of the mixing tank decreased from 17 to 7.7 mg l⁻¹

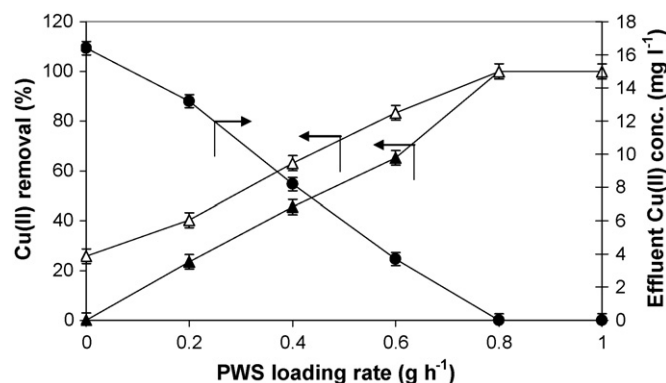


Fig. 6. Variations of effluent Cu(II) and percent Cu(II) removals with the PWS loading rate. (▲) Mixing tank effluent and (Δ and ●) activated sludge effluent. $Cu_0 = 22 \text{ mg l}^{-1}$.

and further to zero with 24%, 65% and 100% Cu(II) removals when the PWS loading rate was increased from 0.2 to 0.6 g h⁻¹ and further to 0.8 g h⁻¹ due to increased adsorption of Cu(II) ions onto PWS. Further adsorption of Cu(II) ions onto activated sludge organisms reduced Cu(II) concentrations in the effluent of the activated sludge unit as compared to the mixing and sedimentation tank effluents. Cu(II) concentrations in the effluent of the activated sludge unit decreased from 13.2 mg l⁻¹ (40% removal) to zero (100% removal) when PWS loading rate was increased from 0.2 to 0.8 g h⁻¹ due to increased adsorption of Cu(II) onto biomass in the activated sludge unit. Again, approximately 1 g h⁻¹ PWS addition was required for 28 mg h⁻¹ Cu(II) loading for complete removal of Cu(II) ions in the mixing tank in order to obtain Cu-free feed for the activated sludge unit.

Variations of effluent COD and percent COD removal in the activated sludge unit with PWS loading rate are depicted in Fig. 7 when $COD_0 = 2000 \text{ mg l}^{-1}$ and $Cu_0 = 22 \text{ mg l}^{-1}$. Effluent COD concentration decreased and percent COD removal increased with increasing PWS loading rate due to increased removal of Cu(II) ions by adsorption onto PWS. Percent COD removal was 33% and 58% with effluent COD's of 1340 and 860 mg l⁻¹ at PWS loadings of 0.2 and 0.6 g h⁻¹ which increased to 79% with an effluent COD of 420 mg l⁻¹ at a PWS loading of 0.8 g h⁻¹. Further increases in PWS loading rates did not improve COD removal performance since complete removal of Cu(II) was achieved with a PWS loading of 0.8 g h⁻¹ corresponding nearly 1 g PWS requirement for 28 mg Cu removal.

Biomass concentration in the aeration tank of the activated sludge unit is an important parameter affecting the rate and extent of COD removal which increased with increasing PWS loading rate as shown in Fig. 8 due to elimination of Cu(II) toxicity on the activated sludge bacteria with PWS addition. Biomass concentration in the aeration tank increased from 2030 to 3040 mg l⁻¹ and further to 3900 mg l⁻¹ when PWS loading rate was increased from 0.2 to 0.6 g h⁻¹ and further to 1.0 g h⁻¹, respectively, yielding higher rates and extent of COD removal. Settled biomass concentration in the sedimentation tank (X_r) also increased with increasing PWS loadings yielding better settling sludge with lower sludge volume index (SVI) at high PWS loadings. SVI

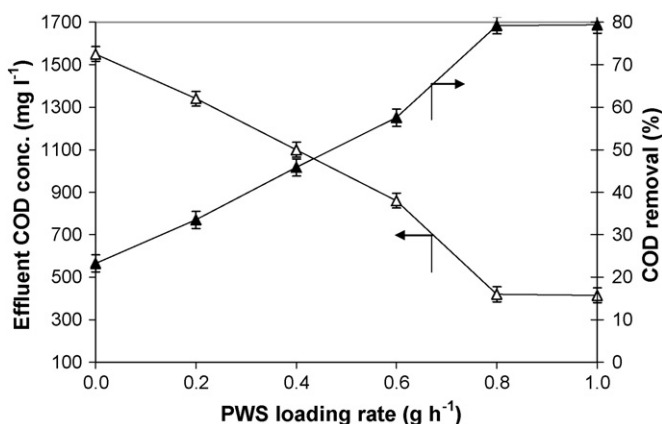


Fig. 7. Variations of effluent COD and percent COD removals with the PWS loading rate. (Δ) Effluent COD and (▲) percent COD removal. $Cu_0 = 22 \text{ mg l}^{-1}$.

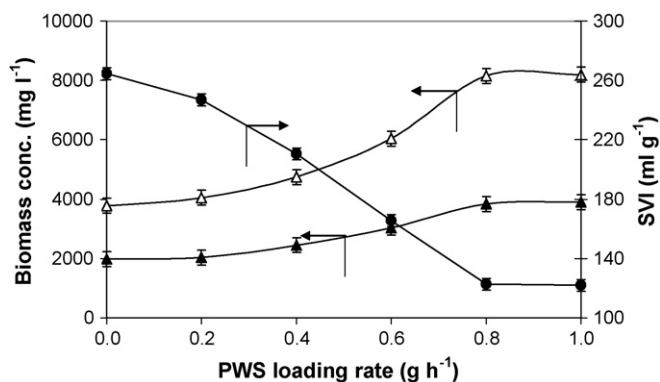


Fig. 8. Variations of biomass concentrations and the sludge volume index (SVI) with the PWS loading rate. (▲) Biomass in the aeration tank (X_r), (△) settled biomass concentration (X_r) and (●) sludge volume index (SVI). $C_{u0} = 22 \text{ mg l}^{-1}$.

decreased from 247 to 122 ml g^{-1} with increases in X_r values from 4050 to 8200 mg l^{-1} when PWS loading was increased from 0.2 to 1.0 g h^{-1} . PWS loading rate of 0.8 g h^{-1} completely eliminated Cu(II) ions from the feed wastewater yielding high biomass concentration and better settling sludge with low SVI values.

Variations of effluent toxicity and percent toxicity removals with PWS loading rate are depicted in Fig. 9. Toxicities of the mixing tank and the activated sludge effluents decreased and percent toxicity removals increased with increasing PWS loading rate due to removal of Cu(II) from the feed by adsorption onto added PWS. Percent toxicity of the feed with $C_{u0} = 22 \text{ mg l}^{-1}$ was 69% with respect to Cu-free water which decreased to 47% in the effluent of the mixing tank and further to 37% in the effluent of the activated sludge unit when PWS loading rate was 0.2 g h^{-1} . Percent toxicity removal in the activated sludge effluent as compared to the feed increased from 46% to 80% and further to 100% when PWS loading was increased from 0.2 to 0.6 g h^{-1} and further to 0.8 g h^{-1} . Further increases in PWS loading rates did not result in improvement in toxicity removal since Cu(II) was completely removed with the addition of 0.8 g h^{-1}

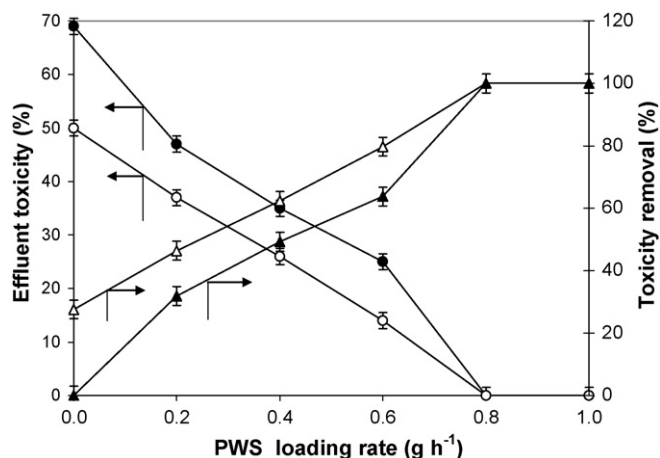


Fig. 9. Variation of effluent toxicities and percent toxicity removals with the PWS loading rate. (● and ▲) Mixing tank effluent and (○ and △) activated sludge effluent. $C_{u0} = 22 \text{ mg l}^{-1}$.

PWS corresponding 1 g h^{-1} PWS requirement for 28 mg h^{-1} Cu(II) loading rate.

There are no reported studies on removal of metal ions from wastewater by biosorption before biological treatment in order to eliminate metal ion toxicity. Most of the literature studies are on the adverse effects of metal ions on activated sludge performance [5–21] or biosorption of metal ions on different biosorbents including PWS in batch systems with no biological treatment [22–29]. Since the toxic effects of metal ions on activated sludge bacteria are well documented in literature, this study provides a good option to eliminate metal ion toxicity in activated sludge systems. Although the biosorption capacity of PWS for Cu(II) were reported to be higher in some batch biosorption studies [28,29], the difference in experimental conditions and longer duration of biosorption in batch studies could be responsible for this difference.

4. Conclusions

Powdered waste sludge (PWS) was added to synthetic wastewater containing 14 or 22 mg l^{-1} Cu(II) for removal of Cu(II) ions by adsorption before biological treatment in an activated sludge unit in order to eliminate Cu(II) toxicity on microorganisms. Feed wastewater containing Cu(II) and PWS were mixed in a mixed tank and the mixture was settled in a sedimentation tank to separate PWS from the wastewater. The effluent of the sedimentation tank with low Cu(II) content was fed to the activated sludge unit for COD removal. The system was operated with different PWS loading rates while the HRT and SRT were constant at 10 h and 10 days, respectively. Cu(II) was effectively removed from the wastewater by adsorption onto PWS before biological treatment reducing the toxicity of the feed wastewater and hence improving the performance of the activated sludge unit. Cu(II) removal from the feed wastewater increased with increasing PWS loading rates yielding high biomass concentrations in the activated sludge unit and therefore high COD removals. Cu(II) removal by PWS addition also improved the settling characteristics of the activated sludge bacteria resulting in SVI values as low as 122 ml g^{-1} . The minimum PWS loading rate was found to be 1 g h^{-1} per 28 mg h^{-1} Cu(II) loading rate to achieve complete Cu(II) removal from the feed wastewater to eliminate Cu(II) toxicity.

Acknowledgement

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

References

- [1] J.E. Fergusson, *The Heavy Metal Elements: Chemistry, Environmental Impact and Health Effects*, Pergamon Press, Oxford, UK, 1990.
- [2] B. Volesky (Ed.), *Biosorption of Heavy Metals*, CRC press, Boca Raton, FL, USA, 1990.
- [3] D. Kratochvil, B. Volesky, *Advances in the biosorption of heavy metals*, *Tibtech* 16 (1998) 291–299.
- [4] Z. Aksu, *Application of biosorption for the removal of organic pollutants: a review*, *Process Biochem.* 40 (2005) 997–1026.

- [5] F.B. Dilek, C.F. Gokcay, U. Yetis, Combined effects of Ni(II) and Cr(IV) on activated sludge, *Water Res.* 32 (1998) 303–312.
- [6] U. Yetis, C.F. Gokcay, Effect of nickel(II) on activated sludge, *Water Res.* 23 (1989) 1003–1007.
- [7] C.F. Gokcay, U. Yetis, Effect of chromium(VI) on activated sludge, *Water Res.* 25 (1991) 65–73.
- [8] J.I. Lombrana, F. Varona, F. Mijanos, Biokinetics behaviour and settling characteristics in an activated sludge under the effect of toxic Ni(II) influents., *Water Air Soil Pollut.* 69 (1993) 57–68.
- [9] A. Cabrero, S. Fernandez, F. Mirda, C. Garcia, Effects of copper and zinc on the activated sludge bacteria growth kinetics, *Water Res.* 32 (1989) 1355–1362.
- [10] P. Madoni, D. Davoli, L. Guglielmi, Response of SOUR and AUR to heavy metal contamination in activated sludge, *Water Res.* 33 (1999) 2459–2469.
- [11] U. Yetis, G.N. Demirer, C.F. Gokcay, Effect of chromium(VI) on the biomass yield of activated sludge, *Enzyme Microb. Technol.* 25 (1999) 48–54.
- [12] A.S. Stasinakis, D. Mamais, N.S. Thomaidis, T.D. Lekkas, Effect of chromium(VI) on bacterial kinetics of heterotrophic biomass of activated sludge, *Water Res.* 36 (2002) 3341–3349.
- [13] S. Ong, P. Lim, C. Seng, M. Hirata, T. Hano, Effects of Cu(II) and Cd(II) on the performance of sequencing batch reactor treatment system, *Process Biochem.* 40 (2005) 453–460.
- [14] F. Dilek, C.F. Gokcay, U. Yetis, Effects of Cu(II) on a chemostat containing activated sludge, *Environ. Technol.* 12 (1991) 1007–1016.
- [15] C.F. Gokcay, U. Yetis, Effect of nickel(II) on the biomass yield of the activated sludge, *Water Sci. Technol.* 34 (1996) 163–171.
- [16] J. Mazierski, Effect of chromium (Cr^{IV}) on the growth of activated sludge bacteria, *Water Res.* 29 (1995) 1479–1482.
- [17] S. Vankova, J. Kupec, J. Hoffmann, Toxicity of chromium to activated sludge, *Ecotoxicol. Environ. Safety* 42 (1999) 16–21.
- [18] S.A. Ong, P.E. Lim, C.E. Seng, Effects of adsorbents and Cu(II) on activated sludge microorganisms and sequencing batch reactor treatment process, *J. Hazard. Mater. B* 103 (2003) 263–277.
- [19] A. Nicolau, M.J. Martins, M. Mota, N. Lima, Effect of copper in the protistan community of activated sludge, *Chemosphere* 58 (2005) 605–614.
- [20] M.Y. Pamukoglu, F. Kargi, Copper(II) ion toxicity in activated sludge processes as function of operating parameters, *Enzyme Microb. Technol.* 40 (2007) 1229–1234.
- [21] M.Y. Pamukoglu, F. Kargi, Mathematical modeling of copper(II) ion inhibition on COD removal in an activated sludge unit, *J. Hazard. Mater. B* 146 (2007) 372–377.
- [22] B. Arican, C.F. Gokcay, Y. Yetis, Mechanistic models of nickel sorption by activated sludge, *Process Biochem.* 37 (2002) 1307–1315.
- [23] U. Strotmann, S. Zaremba, W.R. Bias, Rapid toxicity tests for the determination of substance toxicity to activated sludge, *Acta Hydrochim. Hydrobiol.* 20 (1992) 136–142.
- [24] Z. Aksu, U. Açikel, E. Kabasakal, S. Tezer, Equilibrium modelling of individual and simultaneous biosorption of chromium(VI) and nickel(II) onto dried activated sludge, *Water Res.* 36 (2002) 3063–3073.
- [25] Y. Liu, S.F. Yang, H. Xu, K.H. Woon, Y.M. Lin, J.H. Tay, Biosorption kinetics of cadmium(II) on aerobic granular sludge, *Process Biochem.* 38 (2003) 997–1001.
- [26] Y. Sag, B. Tatar, T. Kutsal, Biosorption of Pb(II) and Cu(II) by activated sludge in batch and continuous-flow stirred reactors, *Bioresour. Technol.* 87 (2003) 27–33.
- [27] F. Kargi, S. Cikla, Biosorption of zinc(II) ions onto powdered waste sludge (PWS): kinetics and isotherms, *Enzyme Microb. Technol.* 38 (2006) 705–710.
- [28] M.Y. Pamukoglu, F. Kargi, Removal of copper(II) ions from aqueous medium by biosorption onto powdered waste sludge, *Process Biochem.* 41 (2006) 1047–1054.
- [29] M.Y. Pamukoglu, F. Kargi, Batch kinetics and isotherms for biosorption of copper(II) ions onto pre-treated powdered waste sludge (PWS), *J. Hazard. Mater. B* 138 (2006) 479–486.
- [30] A.D. Eaton, L.S. Clesceri, E.W. Rice, A.E. Greenberg (Eds.), *Standard Methods for the Examination of Water and Wastewater*, 21st ed., American Public Health Association (APHA), Washington, DC, 2005.
- [31] M. Farre, D. Barcelo, Toxicity testing of wastewater and sewage sludge by biosensors, bioassays and chemical analysis, *Trends Anal. Chem.* 22 (2003) 299–310.
- [32] H. Brouwer, Testing for chemical toxicity using bacteria, *J. Chem. Educ.* 68 (1991) 695–697.
- [33] D. Liu, Resazurin reduction method for toxicity assessment of water soluble and insoluble chemicals, *Toxic. Asses.* 1 (1986) 253–258.
- [34] U.J. Strotmann, B. Butz, W.R. Bias, The dehydrogenase assay with resazurin: practical performance as a monitoring system and pH dependent toxicity of phenolic compounds, *Ecotoxicol. Environ. Safety* 25 (1993) 79–89.