



Occurrence and removal of metals in urban wastewater treatment plants

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ARTICLE INFO

Article history:

Received 16 December 2008

Received in revised form 25 May 2009

Accepted 18 July 2009

Available online 25 July 2009

Keywords:

Urban wastewater

Metals

Wastewater stabilization pond

Activated sludge process

Water quality

ABSTRACT

In this study, nine metals (Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) found in urban wastewater treatment plants (WTPs) in Bursa (Turkey) were monitored for 23 months in 2002 and 2007. Metal influent and effluent concentrations of wastewater stabilization ponds (WSPs) and the activated sludge process (ASP) measured via 24-h composite samples were used to determine removal efficiencies. Average influent concentrations ranged between 2 µg/L (Cd) and 1975 µg/L (Fe). In the stabilization ponds, the removal efficiency was 58% for Cr, while for Cd, Mn, and Pb, it was less than 20%. The activated sludge process yielded high removal efficiencies, ranging from 47% for Ni to 95% for Cr. The use of treated wastewaters for agricultural purposes was investigated, and it was determined that all metal concentrations met application limits, with the exception of Cr in wastewater stabilization pond effluent. Results showed that wastewater stabilization pond effluent reduced the receiving water quality with respect to Cr, Cu, Ni, and Pb. In addition, it was shown that effluent from the activated sludge process temporarily improved the receiving water quality with regard to the Cd, Cu, Mn, and Zn parameters. However, considering the periodic variations of the metals in both processes, water quality, and agricultural practices, it was determined that they should be monitored continuously.

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1. Introduction

Wastewater treatment plants (WTPs), serving both municipal and industrial districts, receive complex mixtures of nutrients and organic and inorganic micropollutants, which are treated to reduce their concentrations so that they do not impact the environment [1]. Most WTPs throughout the world are designed and regulated to remove nutrients from wastewaters, but it is also known that large amounts of potentially toxic elements, such as metals, enter the wastewater [2]. The presence of metals in industrial and urban wastewater is one of the main causes of water and soil pollution. Accumulation of these elements in wastewater depends on a number of local factors, including the industry type, peoples' way of life, and their awareness of the impacts to the environment by careless disposal of wastes [3,4]. Metals in urban wastewater originate mainly from domestic activities [5,6], industrial activities, and storm water runoff [7]. Metal discharges to the environment not only cause acute toxicity to aquatic organisms, microorganisms, and plants, but also strongly reduce microbial activity, which adversely affects biological WTPs [8]. Wastewater stabilization ponds (WSPs) [9,10] and the activated sludge process

(ASP) [11,12] are among the biological processes used in wastewater metal removal. In addition to biological and physicochemical conditions, process operating conditions and design determine metal removal in biological wastewater treatment. However, in spite of the complexity of these factors, various metals can be removed in biological wastewater treatment processes [13,14]. WSPs are particularly efficient in removing metals. The anaerobic WSP has a higher resistance to toxic materials and shock loading [15]. Most removal occurs in the primary ponds (anaerobic or facultative) as a result of the sedimentation of solids to which the metals are adsorbed [16,17]. In biological WTPs, metal removal efficiency depends on the metal species and concentration, the reactivity of the available biopolymers or biomass, and the composition of other wastewater components [18,19]. ASP provides good removal of metals such as Cd, Cr, Cu, Zn, Ni, and Pb. Metal removal by ASP is due to sorption of the flocs [20].

In this study, weekly samples taken from wastewater entering urban WTPs in east Bursa (Turkey) were analyzed in 2002 and 2007 to determine influent/effluent metal characteristics. Removal efficiencies for metals in these WTPs were monitored for 1-year using monthly average values, and the WTP effluent suitability for agricultural irrigation was assessed. Additionally, metal variation was monitored in samples taken from the Nilüfer Stream during two periods to determine the effect of the treated wastewater on the receiving environment.

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Nomenclature

WSP	waste stabilization pond
ASP	activated sludge process
WTP	wastewater treatment plant
BEWTPs	Bursa east urban wastewater treatment plants
U	upstream
D	downstream

2. Material and methods

2.1. Description of the Bursa city eastern urban wastewater treatment plants (BEWTPs)

The BEWTPs (40° 13'N, 29° 04'E) were established to control pollution into the Nilüfer Stream, which is the receiving water body. The plants were gradually installed over several years. The anaerobic WSPs were put into operation in 1998 and then replaced with an extended aeration ASP in 2006 [21]. Seven WSP units were built, having a total volume of 314.443 m³ and pond depth of 4 m [22]. The ASP, which has been in operation since 2006, has the capacity able to treat wastewater for a population of approximately 1,550,000 [23]. The plant consists of pre-treatment units containing screens, grit removal, screw pumps, a selector tank, anaerobic bio-phosphorus tanks, aeration tanks, a secondary sedimentation tank, and sludge dewatering units, and it treats approximately 160 ML/d.

2.2. Sample preparation

The 24-h composite samples were analyzed once per week from wastewater entering the plants to determine metal content. Samples from the WSPs between January and December of 2002, and those from the ASP between January and November of 2007 were collected as weekly 24-h composite samples using an ISCO 3700 portable sampling kit. The 2-h composite samples were collected from upstream and downstream sections of the Nilüfer Stream on dry days in 2002 (06/20/2002 and 09/19/2002) and 2007 (06/22/2007 and 09/27/2007), and the water quality of the receiving environment with respect to metals (except Al, Fe, and Mn) was analyzed. All samples were collected in polyethylene flasks and pre-cleaned with 30% HNO₃ (Merck) and deionized water according to standard methods [24]. pH and temperature were measured with a Mettler Toledo pH meter.

Metal samples were prepared with a preliminary digesting process via the CEM MARS-5 model microwave instrument. The sample preparation procedure was as follows: a 40-mL sample was placed into the cell, and then 6 mL of HNO₃ (65% analytical grade) and 4 mL of HCl (37% analytical grade) were added to the cell. The cells were covered and a maximum pressure of 180 psi and a temperature of 160 °C were applied for 20 min. In the second step, the samples were allowed to cool for 10 min. After 30 min, the samples were cooled to room temperature and transferred into a 100-mL flask. The digested samples were filled with distilled water to the 100-mL mark, and used in ICP-AES (Vista MPX, Varian) analysis.

2.3. Analysis

The metal concentrations in the digested samples were analyzed using ICP-AES. Nine metals were targeted: Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn. The blanks, standard calibration solutions, and digested samples were put into tubes in an automatic sampler and the analysis was started. The standard calibration solutions employed in the analyses were prepared at concentrations of 0.05, 0.1, 0.25, 0.5,

and 1 mg/L. For sample concentrations higher than 1 mg/L, calibration solution concentrations were prepared at 1, 2, 5 and 10 mg/L. The blanks were prepared by adding concentrated 5% HNO₃ into ultra pure water that was produced from the Milli-Q (Millipore Co.).

Quality controls were performed with certified liquid samples (multi-elements standard, catalogue number 900-Q30-002, lot number SC0019251, SCP Science, Lasalle, Quebec) to ensure the accuracy of the measurements. Quantification limits were: 2 µg/L for Cd, 3 µg/L for Pb, 5 µg/L for Cr and Cu, 10 µg/L for Mn and Zn, 20 µg/L for Ni, 100 µg/L for Fe, and 200 µg/L for Al. Certified liquid samples were used to check analytical accuracy, which ranged between 1% and 10%.

2.4. Statistical analysis

All reagents used were of analytical grade or better. Multivariate analyses (element coefficient correlations) were used to determine the metal levels of the influent samples, which were performed using the SPSS statistical package program. A probability of 0.05 or less was considered as statistically significant.

3. Results and discussion

3.1. Untreated wastewater characterization

Variations in the metals analyzed from untreated wastewater in 2002 and 2007 are given in Table 1. The results illustrate that the wastewater metal composition is complex and quite variable. Similar results were obtained in other studies of untreated wastewaters [25–27]. The annual average values of 2007 show that the Al, Cd, Fe, Pb, and Zn metal concentrations increased by more than 20% compared with 2002. The variation in wastewater metal content was caused by the diversity in economic activities throughout the region. There are 80 textile, 90 leather, 26 metal plating and processing, 160 car maintenance, 6 auxiliary, 16 plastic rubber, 8 food, 13 laundry, 7 concrete, and 31 catering industries that are not included in the organized industrial district [28]. The textile industry is likely to produce Cr and Zn and the leather industry has Cr in its effluent, while Cr, Cu, Fe, Ni, and Zn are attributed to the metal industry [29]. Al, Cr, Fe, and Zn generally entered the treatment plants at high concentrations. The reason these metals had higher concentrations than the others is that the textile and leather sectors were intensified in the region. In addition, groundwater used by these industrial companies increases the Fe and Mn values. The BEWTP influent includes household and industrial wastewaters. Industrial wastewater from the factories operating outside of the organized industrial zones and household wastewaters are treated by the BEWTP in the east side of the city and discharged into the Nilüfer Stream [30].

Table 1
Range and mean values of metals in untreated wastewater (µg/L).

Metal	2002		2007	
	Range	Mean ± SD	Range	Mean ± SD
Al	849–1916	1302 ± 338	603–3753	1891 ± 872
Cd	0–10	2 ± 3	0–137	19 ± 40
Cr	742–1171	1009 ± 339	174–2120	1086 ± 509
Cu	9–400	64 ± 108	12–179	60 ± 43
Fe	994–2259	1499 ± 406	1038–3580	1975 ± 712
Mn	42–139	104 ± 28	97–217	126 ± 33
Ni	0–202	84 ± 57	59–202	100 ± 41
Pb	1–47	16 ± 14	6–358	84 ± 100
Zn	204–1036	387 ± 240	303–982	533 ± 209

SD: standard deviation.

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