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Pollution in Keban Dam Lake: Trace Metals from Classical Activated Sludge System

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Determination of trace elements below µg/L levels in water matrices is of increasing importance in the control of environment pollution. The heavy metals such as cadmium, nickel, lead, and chromium are among the toxic elements that can be harmful to plants and animals, and through their introduction into the food chain, to human health. Toxic metals may enter the food chain from a number of different sources such as soil, sewage sludge, effluent and fertilizers (Coutate 1992).

The potentials link between Cd and carcinogenicity (IPCS 1992), the highly toxic cumulative poison of Pb in humans and animals (Berman 1980), the allergenic and in some of its compounds even a carcinogenic effect of Ni (Nriagu 1980) and the classification of Cr as carcinogenic to humans by the International Agency for Research on Cancer (Aitio 1991) have drawn attention to these metal concentrations in environmental samples.

In the present time, the domestic wastewater and its sludge, sewage sludge, is a critical problem in regard to our life, and has different concentration of toxic metals. Thus, the wastewater is treated in several treatment facilities, generally in the conventional activated sludge facility (Figure 1). Since the effluent has very low concentration of heavy metals it cannot be directly determined by Flame Atomic Absorption Spectrometry (FAAS). However, their determinations are still important because they will accumulate in the receiving environment with time. For this purpose, trace elements are pre-concentrated by using various enrichment methods. A separation and/or pre-concentration step are usually used owing to the extremely low concentrations of trace metals in various matrices (Yaman and Gucer 1994, 1995a, 1995b, 1998; Yaman 1997, 1998, 1999; Gucer and Yaman 1992).

The chemical composition of waste sludge can vary greatly from one treatment facility to another, depending on the raw waste composition, treatment processes employed, and a host of other variables (Eckenfelder and Santhanam 1981). The toxic metals described above in sewage sludge, which are very likely in organic chelated forms, are readily available to plants and therefore may be highly phytotoxic (Pendias and Pendias 1986). We will consider sewage sludge used as

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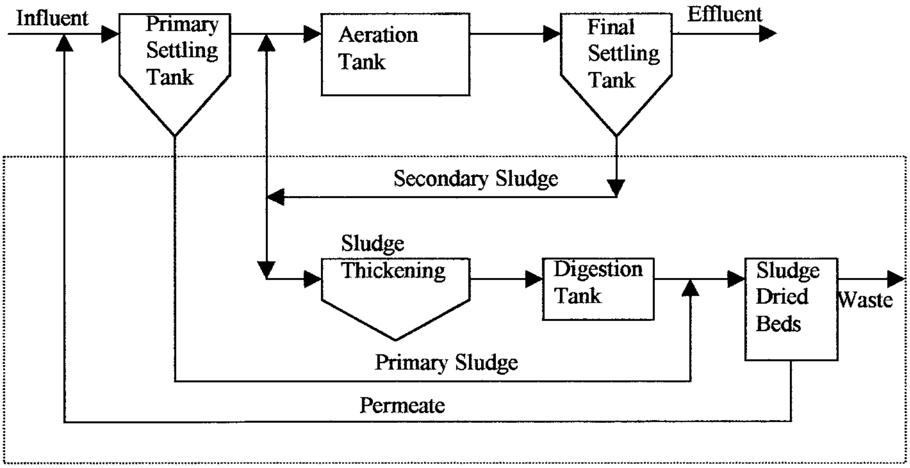

Figure 1. Conventional activated sludge treatment facility

fertilizer, and ultimate disposal on land. When sludge is used for these purposes, it is possible for heavy metals in the sludge to reenter the ecosystem by leaching and migration into groundwater and plants, followed by uptake and accumulation in living organisms, potentially culminating in man.

The effluent from the Elazig-City treatment facility is discharged to Keban Dam Lake. Sewage sludge is also used as fertilizer and/or ultimate disposal on land. In this study, the metals lead, chromium, nickel, and cadmium were determined in both effluent and sludge of Elazig-City Wastewater Treatment Units.

MATERIALS AND METHODS

The determinations of Pb, Cr, Ni and Cd were carried out by means of FAAS after the treatment with activated carbon enrichment procedure for water samples. The Slotted Tube Atom Trap (STAT) was used for increasing in the sensitivity of heavy metals. An ATI UNICAM 929 Model flame atomic absorption spectrophotometer (FAAS) equipped with ATI UNICAM Hollow cathode lamps were used for the determinations. The optimum conditions for FAAS are given in Table 1.

Table 1. Operating parameters for FAAS.

Parameter	Pb	Cr	Ni	Cd
Wavelength, nm	217.0	357.9	232.0	228.8
HCL current, mA	10.0	11.5	14.5	7.5
N_2O flow rate, L/min	-	4.7	-	-
Acetylene flow rate, L/min	0.5	4.2	0.5	0.5
Air flow rate, L/min	4.0	-	4.0	4.0
Slit, nm	0.5	0.5	0.2	0.5

Unless stated otherwise, all chemicals used were of reagent grade. Throughout all analytical work, double distilled water was used. All glass apparatus were kept permanently full of 1 M nitric acid when not in use. In the digestion procedures, concentrated nitric acid (65%, Merck) and hydrogen peroxide (35%, Merck) were used. Stock solution of Ni, Pb, Cr and Cd (1000 mg L^{-1}) were prepared by dissolving their nitrate compounds (Merck) in 1.0 mol L^{-1} nitric acid. A method was used to prepare activated carbon suspension (Yaman and Gucer 1995 a).

1.0 g sample dried at 90 °C was placed into evaporating dishes and digested in 2 mL of mixtures of nitric acid/hydrogen peroxide (2/1) by occasionally stirring on a hot plate with low heat. Thereafter, the residue was dissolved with 1.5 mol.L^{-1} nitric acid and diluted to 2.0 ml. After centrifugation, the clear digests were analyzed for Pb, Cr, Ni and Cd. A blank digest was prepared in the same way.

Chelation and adsorption on activated carbon were chosen as enrichment method because high separation efficiency was obtained when the metal ions were encapsulated in organic structures prior to the adsorption step. Particularly, if the complexing agent has an aromatic structure, -orbital overlap interaction between the aromatic structures of the molecule and the activated carbon surface may occur resulting in larger adsorption energy. Therefore, cupferron, which has an aromatic structure, was used as a chelating reagent. For the chelation and adsorption conditions on activated carbon, the optimized enrichment steps in the previous work (Yaman and Gucer 1995 a, 1998) were followed with slight modification.

The pH of standard solutions and water samples (100-300 ml according to metal concentrations) was adjusted to 5.0±0.2 by adding HNO_3 and NaOH at the necessary concentrations. 40 mL of buffer solution, 40 mL of cupferron solution and 5 mL of activated carbon suspension were added and the pH of the solution was re-adjusted. The mixture was stirred mechanically for 45 minutes and filtered through a filter paper (Advantec Toyo 5B white ribbon). The residue was dried at 105 °C for 1 h. The concentrated nitric acid (5 mL) was added to the residue in a glass beaker and evaporated until it dried. 2.0 mL of 1.5 mol.L^{-1} HNO_3 was then added and, after centrifuging twice, the clear solution was separated for measurements. The studied metal solutions prepared as above were determined by means of the FAAS and STAT-FAAS.

RESULTS AND DISCUSSION

Calibration curves for sludge samples were obtained by using lead (0.25-1.5), chromium (0.2-1.0), nickel (0.25-2.0), and cadmium (0.03-0.3) solutions at mgL^{-1} levels. Calibration curves for water samples were obtained by using 100-300 ml of solutions in concentration range of 2.0-30 μg.L^{-1} for Pb,, 2.0-20.0 μg.L^{-1} for Cr, 4-30 μg.L^{-1} for Ni, and 1-30.0 μg.L^{-1} for Cd. The described enrichment procedure was applied to these solutions (pH 5.0±0.2). The clear solutions were analyzed by means of FAAS and STAT-FAAS. The graphs obtained for both samples were in a rectilinear form in the concentration ranges described above.

Pollutants in a wastewater treatment facility are either removed in the physical and biological treatment processes or pass through the treatment facility into the effluent. The distribution of heavy metals in the wastewater treatment facility is a result of physical, chemical, and biological phenomena (Lue-Hing et. al. 1992). The observed concentrations of Pb, Cr, Ni, and Cd in the facility units are presented in Table 2.

While the chromium concentration of domestic wastewater was measured at 20 µg/L (ppb) level, this value in the effluent of primary settling tank decreased to 17 µg/L. It was found that the removal of Cr in this unit was about 15%. A partial removal of the metals occurs in the primary settling tank but the principal removal mechanisms of the metals from wastewater are by adsorption on biological flocs and subsequently by settling. The water of activated sludge taken from aeration tank was separated from biomass by filtration. The concentration of Cr was at 3.6 µg/L level for filtrate, and 15 mg/kg (ppm) for sludge. It was shown that the chromium entering the aeration tank was removed with biomass at 79% level. The effluent was discharged into the receiving environment, Keban Dam Lake and/or agricultural lands, at 2.4 µg/L Cr level. The sludge settled in the secondary settling tank is generally transported into the sludge thickening tank to reduce the sludge volume. The sludge samples taken at the end of thickening tank were filtered, and the concentration of Cr was found to be 9 µg/L for filtrate and 22.5 mg/kg for sludge. These values for the sludge digestion were also found to be 3.5 µg/L and 41 mg/kg, respectively. The calculations revealed that the overall removal of Cr was 88% level.

Table 2. Distribution of metals in the activated sludge units.

	Water samples				Sludge samples			
	Cr	Cd	Pb	Ni	Cr	Cd	Pb	Ni
	µg/L				mg/kg			
Influent	20	30	25	23	-	-	-	-
End of primary settling	17	22	22.5	16	-	-	-	-
In aeration tank	3.6	15	4	3.6	15	0.55	8.6	27
End of Secondary settling	2.4	15	2.4	7.5	18	0.4	9.2	14
Sludge thickening	9	40	2.4	9	22.5	0.47	9.4	20
Sludge digestion	3.5	9	2.4	3.5	41	0.70	11.6	30

The Pb content of influent was measured as 6 µg/L. It was found that the Pb in the aeration tank was removed with activated sludge, biomass, at 82.2% level. The concentration of Pb in the activated sludge was however at 8.6 mg/kg level. It was shown that an important amount of Pb was absorbed and/or adsorbed by biomass. The concentration of Pb in the secondary settling sludge reached to 9.2 mg/kg level. The concentration of Pb in the effluent was found to be 2.4 µg/L. The concentration of Pb in the sludge digestion was also found to be 2.4 µg/L for filtrate, and 11.6 mg/kg for sludge. The overall removal of Pb was calculated as 90.4% level.

The concentrations of Ni in the influent and effluent of primary settling tank were measured as 23 μg/L and 16 μg/L, respectively. The removal in the primary settling tank was calculated at 30% level. While the concentration of Ni in the water of the activated sludge was found to be 3.6 μg/L, this value in the sludge was found at 27 mg/kg level. It was shown that 77 % of Ni entering the aeration tank was removed with biomass. The effluent of treatment facility was determined at the concentration level of 7.5 μg/L. In the secondary settling tank, the concentration of Ni in the effluent increased because released from sludge with N_2 gas after the denitrification process occurred to dominance anoxic conditions. In the sludge thickening tank, the entering of Ni from the sludge to filtrate taken place, too. The concentration of Ni in the digestion tank was found to be 3.5 μg/L for filtrate, which was higher than the effluent, and 30 mg/kg for the sludge. The overall removal of Ni was at 89 % level.

It was observed that the removal of Cd was at 27 % level in the primary settling tank. The concentration of Cd was at 15 μg/L level in the water of the activated sludge, and 0.55 mg/kg for the sludge. However, the effluent discharged into the receiving environment was determined at 15 μg/L of concentration. In the sludge thickening, it was shown that the concentration of filtrate increased related to the volume reduction. In the sludge digestion, the concentration of Cd in the filtrate and sludge was 9 μg/L, and 0.70 mg/kg, respectively. The overall removal of Cd was at 50 % level.

The effluent having the metal concentrations below the limits of dedection will cause metal accumulation in Keban Dam Lake and the agricultural lands if used in the irrigation fields, and cause groundwater pollution. Because of these reasons, the determinations of the heavy metals below μg/L levels are very important. A method was developed for the determination of trace amounts of Cr, Cd, Pb, and Ni in the activated sludge facility by using the activated-carbon enrichment with FAAS. It was shown that the sorption of trace elements with biomass varied as Pb>Cr>Ni>Cd.

The effluent is completely discharged into Keban Dam Lake , which has a surface area of 179.12 km^2. It was measured that the flow rate of discharged effluent was 800 L/s on an average. The lake has been polluted with respect heavy metals due to the high mass of effluent. Our calculations suggest that the amounts of Cr, Cd, Pb and Ni entering into the lake are 62 kg/year, 387.9 kg/year, 62 kg/year, and 193.8 kg/year, respectively. The surface area loading was calculated to be 0.346 kg/km^2.year for Cr and Pb, to be 2.17 kg/km^2.year for Cd, and to be 1.08 kg/km^2.year for Ni. This is an important situation according to pollution of the lake a long time period.

An other point is that mirror carp (*Cyprinus carpio*) now are present in high numbers due to high organic matter. On the conclusion that since these fish contact trace metals directly, toxic metals accumulated in their body which can be harmful to human health with introduction into the food chain.

Sewage sludge containing high amounts of Cr, Ni and Pb metals, is also used as fertilizer and/or ultimate disposal on land, and is an important problem involving the pollution of groundwater and soil. Toxic metals accumulated on soil are filtered together with rainwater, and may be introduced into groundwater in a short time.

Sludge from digestion tank are dried in the sludge dried beds. The digestion sludge utilized as fertilizer and/or ultimate disposal on land contains high amounts of Cr, Ni and Pb metals, which is 41 mg/kg, 30 mg/kg and 11.6 mg/kg, respectively, and is important problem involving the polluttion of groundwater and soil. Toxic metals accumulated on soil are filtered together with rainwater, and may be introduced into graundwater in a short time.

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