MONITORING OF CHLORIDE CONTAMINATION IN WASTEWATER IN THE REGION OF DEVNYA

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Abstract

The Devnya area near the town of Varna belongs to the severely industrially polluted regions in Bulgaria. Although the production of the fertilizer plants diminished in the last decade the long-lasting effects of air, soil, and groundwater contamination persisted. The authors performed a dynamic monitoring of chloride levels in the wastewater during the period from December 1990 till November 1999. Regularly, water samples were taken from 8 sites located in the industrial plants and purification installations. The chloride concentrations varied significantly between low and abnormally high values. The chloride levels in the Saya ravine increased from 32 mg/L in 1996 up to 228 mg/L in 1999. They decreased from 6750 mg/L in 1991 to 230 mg/L in 1996 in the first chloride-and-polyvinyl-chloride production plant and from 28000 mg/L in 1990 to 1711 mg/L in 1996 in the other plant of this kind. These levels lowered from 3800 mg/L in 1991 to 276 mg/L in 1997 in the main purification installation. In the sludge pumping-shaft of Padina village, the chlorides remained elevated during the whole period - between 13900 mg/L in 1994 and 30800 mg/L in 1997. Recently, complex technological measures were undertaken to normalize these concentrations in the industrial wastewater.

Introduction

The ecological safety of the area of the Northern Bulgarian Black Sea Coast is determined to a considerable extent by the neighbouring Devnya region nominated as ‘the valley of great chemistry’. There are a series of large chemical works in this region operating since 1950s onwards. Numerous investigations have proved the health risks of the chemical air and water pollution for the population in the towns of Devnya and Varna. The channel connecting the lakes in the valley and the Black Sea is a traditional source of contaminated waters. Therefore, a strict control of the concentrations of water contaminants and sufficient effectiveness of the purification processes is needed.

Recently, several publications deal with wastewater purification through removal of inorganic and organic industrial pollutants. According to estimates of WHO, the organic and chlororganic compounds take the first place in water pollution (1). The main threat of contemporary industrial activities is the usage of chlorinated organic solvents (2) An inline treatment system in which anaerobic-aerobic bioreactors perform a central role in purification processes in the pulp and paper industry has recently been proposed (3).

The purpose of the present paper is to dynamically follow-up the chloride levels in the wastewater in the valley of Devnya during the last decade and to suggest more effective water purification methods.

Methods

During the period from December 1990 till November 1999, an annual monitoring of the chloride levels in the wastewater in the valley of Devnya was performed. Water samples were collected from 3 sites located in the chloride fertilizer and soda plants, from one site at a thermoelectric power station, and from 4 initial and final purification installations. The wastewaters from the chlorine-polyvinyl chloride plant were purified in neutralization installations of different capacity.

Results

The yearly dynamics of the chloride concentrations in the wastewater was demonstrated on Table 1 and Table 2.

Our results indicate that the chloride concentrations in the wastewater differ significantly during the period of investigation. They vary between low and abnormally high. It should be outlined that no data about the concentrations of this important contaminant have been registered in some years although water samples were collected in two or three different months of other years. It is noteworthy that the levels of chlorides vary significantly in different months of one and the same year as well as in different years in one and the same site for sample collections.

Table 1: Chloride Levels In the Industrial Wastewater In the Valley of Devnya (In mg/L)

Site of sample collection	1990	1991	1994	1996	1997
Polyvinylchloride plant I	2090	2590 6750 750	934	230 244	265
Polyvinylchloride plant II	28000	14400 2720 13800 14900	3201	1711 2619	2429
Soda plant		21550	1945	389 416	404
Thermoelectric power station	706 2250 2230 679 290	135	522	690 796	723

As shown on the Table 1, the chloride levels in the first chloride-and-polyvinyl-chloride production plant have decreased from 6750 mg/L in 1991 to 230 mg/L in 1996. The reduction of the chloride levels is more outlined in the second plant of this kind - from 28000 mg/L in 1990 down to 1711 mg/L in 1996.

In the thermoelectric power station there is a reduction from a relatively higher value measured in April, 1990, of 2250 mg/L down to 135 mg/L measured in May, 1991. Two different values have been estimated in December, 1990 - of 673 mg/L and 290 mg/L.

The chloride levels in the main purification installation increased from 639 mg/L in 1990 up to 3800 mg/l in 1991. Then they reduced down to 228 mg/L in 1995 and slightly increased up to 276 mg/L in 1997. In the sludge-pumping-shaft of Padina, the concentrations of the chlorides remained strongly elevated during the whole period - between 13900 mg/L in 1994 and 30800 mg/L in 1997. The chloride levels in the Saya ravine decreased from 32 mg/L in

1996 down to 13,8 mg/L in 1998 and then sharply increased up to 228 mg/L in 1999. In the channel transporting the wastewater from the purification installations to the lake in the Devnya valley the levels of the chlorides decreased from 760 mg/L in 1990 down to 269 mg/L in 1996.

Table 2: Chloride Levels In the Wastewater In Other Sites In the Valley of Devnya (In mg/L)

Site of sample collection	1990	1991	1994	1995	1996	1997	1998	1999
Main purification installation	639 725	3800	198	228 303 264		276	260	
Padina sludge pumping-shaft		27900	27200 24950 13900	28100 20300 23700	29028 23350 28112	30800	28100	27850
Saya ravine					32 35	18,1	13,8	228
Channel to the lake	760		541		269 312		324	

Discussion

The total production of inorganic compounds in the chemical works of Devnya has reduced during the years of political and socio-economic changes in Bulgaria. This is one of the reasons for the lower values of wastewater contamination. Of course, the main reason for this favourable trend is the operation of a series of new and modern purification installations.

The extent of groundwater contamination by chlorinated hydrocarbons was examined at a spill site in Serbia (4). The effectiveness of vegetated buffer strips for removing contaminants in runoff from grassed plots after application of cattle slurry or inorganic fertilizer is investigated (5). After simulated rainfall (one, 7 and 21 days after slurry/fertilizer application) runoff and percolates are sampled and analyzed for chlorine, sodium and potassium ions as well as for faecal bacteria contents. Contaminant concentrations are markedly higher in runoff from the slurry-amended plots than in runoff from the fertilizer-amended plots. The chloride/bromide ratios have been measured in leachate derived from longhorn-cattle, quarterhorse, and pygme-goat waste at a farm in Abilene, Texas, USA (6). These ratios are below typical values for domestic wastewater and within the range commonly observed for oilfield brine. These results have important implications for identifying sources of contaminated groundwater in settings with significant livestock and/or oil production.

Residents' chronic hazard and carcinogenic risk have been estimated in a groundwater-contaminated community after on-site remediation in Taiwan (7). The U.S. Environmental Protection Agency guidelines for assessing hazardous waste sites have been followed. Empirically measured contaminant levels and exposure parameters have been used to perform health risk assessment on some chlorinated hydrocarbons such as vinyl chloride, tetrachloroethylene, trichloroethylene, etc. by gas chromatography and mass spectroscopy. It has been demonstrated that the contaminant levels, exposure duration, and time for showers are major determinants of health risk. Three years after remediation of the contaminated site by extraction and treatment, the contaminated groundwater is still unsafe for use.

Contreras-Lopez (8) proposes a methodology to a standardization procedure for complex mixtures of potentially bioaccumulating organochlorine compounds in wastewater, such as pulp mill effluents. This new procedure could be a valuable tool to complement environmental risk assessment studies of wastewater discharges. Two horizontal subsurface flow reed beds treating dairy parlor effluent and domestic sewage were used to define the efficiency of the system in reducing the polluting load in an isolated mountain rural settlement (9). Removal of suspended solids and organic load constantly remained at levels above 90 %, while those of the nutrient nitrogen are about 50 %. Chlorides, anionic and non-ionic surface-active agents and heavy metals were detected only in low concentrations. The reed beds are an appropriate treatment to reduce pollutants in wastewater from rural activities to values acceptable for discharge into surface waters.

Tannery wastewater contains large quantities of organic and inorganic compounds (10). The evaluation of wastewater quality in Chile is based on chemical specific measurements and toxicity tests. A grab sample of a final effluent based on the Phase I toxicity identification evaluation procedure is applied. Effluent from different tannery processes demonstrates high values of chemical organic demand of chloride (1813-16,500 mg/L). Toxicity is significantly reduced by the air stripping, filtration and the cationic exchange resin - by 46-76 %. The chemical parameters demonstrate that the remaining toxicity of the treated beam house effluent is associated with its chloride (11,300 mg/L Cl^-) contents.

The metallurgic wastewater generated from the processes of recovering precious metals from industrial wastes contains high concentrations of ammonia, nitric acid, sodium chloride and sodium sulfate (11). A circulating bioreactor system equipped with an anoxic packed bed and an aerobic fluidized bed is used for biological nitrogen removal. The anoxic packed bed removes effectively nitrite and nitrate from the wastewater by denitrification at a ratio of 97 %. The sludge obtained from the anoxic packed bed exhibits accumulation of nitrite at 5,0 and 8,4% NaCl concentrations, suggesting that the reduction of nitrite is the key step in the denitrification pathway under hypersaline conditions.

A sequential injection analysis system for the turbidimetric determination of chloride in different types of water is proposed based on the reaction of chloride with silver ions and the subsequent measurement of the turbidity caused by silver chloride precipitation (12). The application of toxic reagents for chloride determination is avoided. The main feature of the developed system is the use of a single configuration to carry out the determination over a wide concentration range (2-400 mg/L) by changing only the aspirated sample volume. This characteristic allows the determination of chloride in ground, surface and wastewaters using the same manifold.

Conclusions

(1) The effectiveness of the purification procedures concerning the chlorides in the industrial wastewater in the valley of Devnya remains still insufficient.

(2) The dynamic monitoring of chloride concentrations in wastewater in the valley of Devnya should be done not only regularly but also more often and at numerous sites.

(3) Introduction of more effective purification methods such as extraction, sorption, evaporation, biological filtration, reduction and chemical and biochemical oxidation along with conventional neutralization is necessary to allow a permanent successful reduction of the chloride wastewater concentrations in this region.

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