PURIFICATION OF NITROGEN COMPOUNDS FROM WASTE WATER IN AN ECOLOGICALLY POLLUTED REGION

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Abstract

The Devnya valley in the proximity of the town of Varna, an internationally recognized sea resort at the Bulgarian Black Sea Coast, occupies a leading position in the chemical industry for years. The channel connecting the lakes in the valley and the Black Sea represents traditional source of contaminated waters that necessitates a strict control and sufficient effectiveness of the purification processes. A monitoring of the levels of nitrate nitrogen, nitrite nitrogen and ammonia nitrogen in the wastewater during the period from 1990 till 2000 was carried out. Samples were taken from 9 sites in the industrial enterprises and in the purification installations. The concentrations of these contaminants differed considerably ranging from low and moderate to abnormally elevated values. Ammonia nitrogen levels in the outflow of the neutralization station of a fertilizer plant increased from 41,30 mg/L in 1990 up to 172,8 mg/L in 1996 and sharply decreased in the central purification installation down to 0,39 mg/L in 1998 and 0,369 mg/L in 2000. Nitrate nitrogen values in this installation ranged between 2,9 mg/l in 1990 and 10,23 mg/l in 1998. Several more effective neutralization methods were suggested to maintain a successful elimination of the nitrogen compounds from wastewater in this region.

Introduction

In the recent decades, there is an intensive development of international summer tourism at the Bulgarian Black Sea Coast. The town of Varna is an industrial, cultural, educational, transport and tourism center of North Eastern Bulgaria. The ecological safety of this area is determined mainly by the neighbour Devnya region called ‘the valley of great chemistry’ because of the numerous chemical works operating there since 1950s onwards. Many investigations have proved the unfavourable effect of the chemical air pollution on human health of the population in the towns of Devnya and Varna as well. The channel connecting the lakes in the valley and the Black Sea represents traditional source of contaminated waters. This situation, obviously, necessitates a strict control of the concentrations of water contaminants and sufficient effectiveness of the purification processes.

The issues of wastewater purification through removal of organic and inorganic industrial pollutants occupy a key position in contemporary environmental research and practice. In Poland, nitrogen originates mainly from underground run-off but also through the emission of nitric oxides from the industrial plants and car traffic (1). The most problematic pollution in the aquifers of Slovenia is nitrate. Nitrates are found in all fields (2). Elevated contents of ammonia, nitrates and nitrites are consequence of the high concentration of organic matter (3). Chlorinated hydrocarbons are sources of groundwater contamination (4). In Denmark, in the ‘nitrate belt’, the groundwater quality is useless for drinking water purposes, due to high contents of nitrates (5). It has been pointed out that in 1992 the principal agricultural concerns are the potential nitrate contamination in rural areas of Bulgaria, Czechoslovakia, Hungary and Romania (6). An inline treatment system in which anaerobic-aerobic bioreactors perform a central role in purification processes in the pulp and paper industry is described (7). An effective chemical removal and biological elimination of nitrate from drinking and industrial wastewater has been suggested (8).

The purpose of the present paper is to study the dynamic changes of nitrogen compounds' levels in the wastewater in the valley of Devnya during the recent years and to suggest more effective water purification methods.

Methods

During the period from 1990 till 2000 an annual monitoring of the levels of nitrate nitrogen, nitrite nitrogen and ammonia nitrogen in the wastewater in the valley of Devnya was carried out. Nitrite nitrogen samples were taken between 1990 and 2000 from 7 sites - in 4 industrial enterprises and in 3 outer purification installations. Nitrate nitrogen and ammonia nitrogen samples were collected between 1990 and 1999/2000 from 6 sites each - in 4 chemical plants and in 2 external purification installations. The main purification method consisted in neutralization of the contaminants in the wastewater.

Results

The levels of the nitrite nitrogen, nitrate nitrogen and ammonia nitrogen are presented on Tables 1 through 3. Our results indicate that these concentrations in the wastewater differ considerably during the period of observation. They vary between low and moderate and abnormally high.

Table 1: Nitrite Nitrogen Concentrations In the Valley Of Devnya (In mg/L)

Site of sample collection	1990	1991	1993	1994	1995	1996	1997	1998	1999	2000
Polyvinylchloride plant I		0,67 0,24			0,31	0,22				
Polyvinylchloride plant II		0,057			0,05	0,06				
Collecting channel		1,3			1,2	1,35 2,06				
Fertilizer plant								0,027	0,019 0,151	0,019
Main purification station	0,25 0,32	0,3	0,3 0,2	0,4	0,48 0,012 0,5	0,1	0,014	0,09		
Padina village	0,7	0,63		0,7 0,36 0,2	0,381 0,88 0,55	0,87 0,79 0,98	0,838	0,581		
Saya ravine	1,3	1,1		1,05		1,0 0,98				

It is noteworthy that, while in certain years the samples were collected in two or three different months, in other years no data about the concentrations of the contaminants were registered at all.

Table 2: Nitrate Nitrogen Concentrations In the Valley Of Devnya (In mg/L)

Site of sample collection	1990	1991	1993	1995	1996	1997	1998	1999
Polyvinylchloride plant I		12,9		14,2	19,6 11,8			
Agropolychim		146		137	125 134			
Collecting channel		35		37	40 38,8			
Fertilizer plant II							6,036	3,88
Main purification station	0,0 2,9	0,86	2,0 5,7	15,5 8,6 6,75	7,1	3,5	10,23	
Padina village	0,3	0,4	0,2	1,2 5,75 6,05	198 218,1			

Nitrite nitrogen levels in the main purification station vary between 0,32 mg/L in 1990 and 0,012 mg/L in 1995. Nitrate nitrogen values in this installation vary between 2,9 mg/L in 1990 and 10,23 mg/L in 1998. Ammonia nitrogen levels in the outflow of the neutralization station of the Agropolychim fertilizer plant increase from 41,30 mg/l in 1990 up to 172,8 mg/l in 1996. After that they decrease sharply in the central purification installation of the plant down to 0,39 mg/l in 1998 and 0,369 mg/l in 2000.

Table 3: Ammonia Nitrogen Concentrations In the Valley Of Devnya (In mg/L)

Site of sample collection	1990	1991	1993	1995	1996	1997	1998	1999	2000
Polyvinylchloride plant I		1,42		5,2	6,2 6				
Agropolychim		41,30		145,1	172,8		0,39	0,214 0,358	0,369
Collecting channel	23,1	35		33,2	37,1 40,3				
Soda plant		0,93	2,71	3,14	15,8 38,4				
Main purification station	0,4 0,2	1,02	1,86 4,9	2,38 0,03 0,2	0,81	1,703	0,33		
Padina village	0,3	19,66	5,2 3,33 2,4	33,15 5,18 40,42	115,2 6,42 76,4	23,01	10,9		

Discussion

It is noteworthy that the total production of fertilizers in the chemical works of Devnya has diminished during the years of political and socio-economic changes in Bulgaria. This is one of the reasons for the reduced 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 experience of other countries gained with the methods of effective removal of the nitrogen compounds from groundwater and industrial wastewater deserves a special attention.

Submerged biofilters were applied for nitrite removal (9). Nowadays these filters seem to be the preferred technology for denitrification purposes. Optimization of biological nitrogen is based on the nitrate shunt in order to save two of the involved steps. A built-up of nitrite can be achieved by an appropriate control of the nitrification process in suspended or in fixed cultures. The effect of different types of carbon sources (acetate, ethanol and urban wastewater) on the performance of a submerged down biofilter, as well as the influence of the hydraulic loading is studied. Maximum nitrogen removal rates are similar for both acetate and ethanol. At the same time, they are significantly higher than for urban wastewater. Nitrogen mass loading is the limiting factor for efficiency rather than the hydraulic loading.

The simultaneous biological phosphorus and nitrogen removal with enhanced anoxic phosphate uptake in an anaerobic-aerobic-anoxic-aerobic sequencing batch reactor was examined (10). Significant amounts of phosphorus-accumulation organisms capable of denitrification can be accumulated in a single sludge system coexisting with nitrifiers. The ratio of the anoxic phosphate uptake to the aerobic phosphate uptake capacity increases by six times by introducing an anoxic phase in an anaerobic aerobic sequencing batch reactor. This system shows stable phosphorus and nitrogen removal performance. The average removal efficiency of nitrogen was 88 %. Nitrite (up to 10 mg $N0_2$-N/l) is not detrimental to the anoxic phosphate uptake and can serve as an electron acceptor like nitrate. The phosphorus uptake rate is even faster in the presence of nitrite as an electron acceptor compared to the presence of nitrate. The real-time controlled sequencing batch reactor exhibits better performance in the removal of nitrogen and phosphorus than that with fixed-time operation. The removals of ammonium and nitrate compounds using activated carbon from palm shells as adsorbent and support media have been investigated (11). Experiments have been carried out at several loadings and hydraulic residence times of 24, 12, and 8 hours. The process of agrarian industry wastewater treatment achieves removal of 62 % for the total nitrogen. The removals of contaminants from river water have been carried out in sequencing batch reactor and activated carbon biofilm reactor. The removals achieved by the combination of sequencing batch reactor adsorption and biodegradation are of 58,8 % for NH_3-N and 25,5 % for $N0_3$-N. By adsorption alone, however, the removals are of 35.2 % for NH_3-N and 13,8 % for $N0_3$-N. In the activated carbon biofilm reactor, at hydraulic residence times between 1,5 and 6 hours, removals vary from 16,7 to 100 % for $N0_3$-N and from 13,5 % to 100 % for NH_3-N. The removals are significantly decreased at lower hydraulic residence times. Therefore, the processes of adsorption-biodegradation by biofilm on activated carbon ensure a substantial removal of nitrate compounds from wastewater and river water as well.

The numerical modeling of scavenging processes was compared with data for rainwater and aerosol chemistry in the Brazilian Amazon region (12). Nitrate and ammonium concentrations have been determined in rainwater and in aerosol samples. The scavenging processes have been evaluated on a rainfall event basis, via numerical modeling, in order to stimulate the rainwater concentrations and compare them with the observed data. A regional atmospheric modeling system is used to simulate cloud structures. It has been established that modeled sulfate in rainwater is a better fit to the observed data values than ammonium and nitrate.

The removal of nitrogen and phosphate through crystallization of struvite ($MgNH_4PO_4.6H_2O$) has gained increasing interest (13). Since wastewaters tend to be low in magnesium relative to ammonia and phosphates, addition of this mineral is usually required to effect the struvite crystallization process. Nitrogen removals with bittern were somewhat lower than with the alternate Mg^{2+} sources. Application of bittern to biologically treated wastewater from a swine farm achieved high phosphate removal, but ammonia removals were limited by imbalance in the N:P ratio. Two horizontal subsurface flow reed beds treating dairy parlor effluent and domestic sewage were used to determine the efficiency of the system in reducing the polluting load in an isolated mountain rural settlement (14). Removal of suspended solids and organic load constantly remained at levels above 90 %, while those of the nutrient nitrogen are about 50 %. Nitrates, 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 (15). 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. Toxicity is significantly (by 46-76 %) reduced by the air stripping, filtration and the cationic exchange resin. The chemical parameters demonstrate that the remaining toxicity of the treated beam house effluent is associated with its ammonia (120 mg/L N-NH_3) 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 (16). 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.

An effective electrochemical treatment of domestic wastewater using 0,8 % (w/v) sodium chloride as electrolyte has been described (17). Domestic wastewater is passed through an electrolytic cell using Ti/Pt as anode and Stainless Steel 304 as cathode. The organic nitrogen is wet oxidized to carbon dioxide and precipitated as calcium phosphate. Ammonia nitrogen is reduced by 82 % The application of electrolytic oxidation of domestic wastewater is more advantageous compared to conventional biological treatment especially for small works.

Conclusions

(1) The dynamic monitoring of wastewater concentrations of the nitrate nitrogen, nitrite nitrogen and ammonia nitrogen in the valley of Devnya should be done more regularly and more often - in case of abnormally elevated pollutant concentrations.

(2) Based on our own data and on the results reported in the literature available a series of more effective neutralization methods can be suggested. In this way one can permanently maintain a successful elimination of the nitrogen compounds from wastewater in this region.

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