ANNALS of Faculty Engineering Hunedoara
International Journal of Engineering
ISSN: 1584 - 2665

COMPARE INFLUENCE OF CHEMICAL AND CHEMICAL COMPONENT OF ROAD SALTS ON NITRIFICATION IN THE WASTEWATER TREATMENT

[1]Eliška HORNIAKOVÁ, [2]Lucia MARCINOVÁ, [2]Milan BÚGEL

[1.] Faculty of Mining Ecology Process Controll and Geotechnology, Technical University in Košice, Košice, SLOVAKIA
[2.] Institute of Montaneous Sciences and Environmental Protection, Faculty of Mining Ecology Process Controll and Geotechnology, Technical University in Košice, Košice, SLOVAKIA

Abstract
The research deals with the influence of chemical component in road salts that flow in the biological stage of wastewater treatment plant during the snow-melt, on the nitrification process in the activation tank. The influence of road salts on nitrification was simulated in laboratory conditions and than compared with the influence of chemical substances (NaCl and $MgCl_2$). The influent containing chemical component of road salts increases the values of conductivity, sludge index and ammonia nitrogen in the activated tank.
Keywords: road salt, activated tank, conductivity, sludge index, COD, ammonia nitrogen

1. INTRODUCTION

During snow-melt road salts flow from roads to the sludge, to underground water and receiving water. Snow, cold wind and the influent cold water cool the suspension in the biological stage of the wastewater treatment plant. This stage of the wastewater treatment is used to remove dissolved and colloidal organic matter in the wastewater.

Chemical composition of the suspension in the activation tank is changing following metabolisms of organisms and chemical composition of influent wastewater. The chemical composition of wastewater is changing during the day, according to the day schedule of inhabitants people releasing wastewater to the wastewater treatment plant, according to the season and according to immediate atmospheric conditions. In sewage there is a lot of fat and detergents from households and cafeteries. When snow-melt flows into the sewage, road salt used for winter road maintenance also flows into the sewage. In Slovak Republic mixture of inert mass with chemical component of road salt is used for winter road maintenance salting (Pietriková, A., et al.,2005)

Microorganisms are adapted to the conditions of variable chemical composition during the day but they are not adapted to floods and the season of snow-melt. Consequently undercoolling and poisoning of nitrifying microorganisms cause their dying out in the activation tank due to lysii of cell (Zekeová-Nanáčková, Z., 1976; Strom, P.F., 1976). This is a seasonal effect which is periodically occurring in winter.

2. ROAD SALT

For winter road maintenance salts and sand mixtures with chemical matter or moisture innert matter – sand are used. As chemical sprinkle the following material is used:

- sodium chloride NaCl,
- calcium chloride $CaCl_2$,
- mixture of sodium chloride and calcium chloride,
- solmag (industrial name) $MgCl_2$,
- tonacal (industrial name),
- urea (carbanit).

The total amount of chemical sprinkle matter used in all winter season must not exceed 2 kg m^{-2} by number of maintenance days up to 100. Approximate sprincle batch in a town is 100 g m^{-2} (Bouldin, D., R., 2005), maximum sprinkle amount is 500 g m^{-2} (www.ssc.sk/user/view_page.php?page_id=448 - , 2007) and it depends on the actual local climatic condition.

Sand sprayer is equipped with moistener with batching control of spreaded solid mixture that garantees balanced deicing in all sprinkle width. Moisture solids are prepared from NaCl, in protected water areas from $CaCl_2$, or diferent matter that unloads the environment(Windey, et al 1999; Okabe, S. et al, 1999; Šilhánková, Ľ., 1995).

Solmag is an industrial deicing on the basis of $MgCl_2$ (Windey, et al 1999).

Automobile wheels splash the deicing mixture from roads and contaminate the area in the distance of 3 to 5 m from roadway. This inert matter collected by scavenger cars is than cleaned up and used again in another winter maintenance period.

During spring snow-melt, soluble deicing from roads flows into the sewages of towns and villages, underground water and water body where it changes their chemical composition (Šilhánková, Ľ., 1995).

3. INFLUENCE OF CHLORIDE ON BIOLOGICAL REMOVAL OF NITROGEN

NaCl raises intracelular tension and people with hypertension have to reduce salt in food. This process also works in bacterial cells, where NaCl causes continual cytolysis. In the time of snow-melt run off, low temperature and chemical composition change the chemical composition of water in sewage in the activated tank of wastewater treatment. These changes cause chemical and temperature shock in the microorganisms (Zekeová-Nanáčková, Z., 1976; Wilderer, P. A., 2001) and then lysis of bacterial cells occures. The bacterial cell membrane can not withstand the osmotic pressure of the water inside and collapses, bursting out full content of the cells. Then it takes specific time to recondition general biocenoses of microorganisms in the tank.

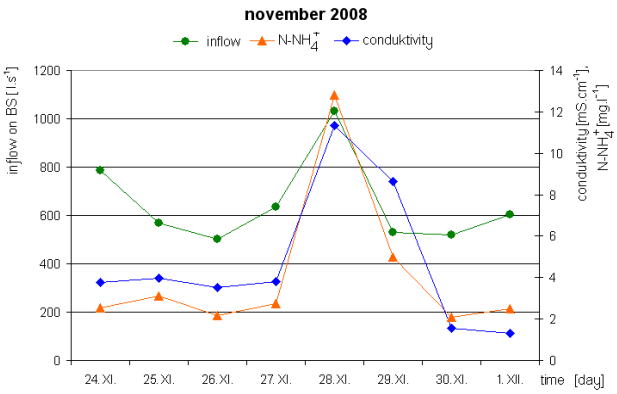

Figure 1. Connection between conductivity, continuous increase of concentration of $N\text{-}NH_4$ and inflow in the biological stage

Road salt in sewage and in the activated tank indicates increase of conductivity in the tank that is measured in the outflow from wastewater treatment and its values are authentic for the whole plant. The increased amount of ammonia-nitrogen $N\text{-}NH_4$ causes consequent increase of conductivity and therefore influence of deicing and undercooling are retrograde conditions for metabolism of nitrifying bacteria.

The consequence of atmospheric conditions, external air temperature, runoff road salt during snow-melt is cooling of the suspension in the activated tank (Figure. 1). Increased inflow of cold wastewater causes increase of conductivity, hence total salinity of water in the tanks of the plant and ammonia-nitrogen $N\text{-}NH_4$ in activated tank follow the values of $N\text{-}NH_4$ in the secondary tank.

Values of pH are strictly kept in needed range and they do not influence the nitrification.

4. EXPERIMENTAL

Winter road maintenance with chemical sprinkle in the town of Košice is carried out on the street with local public transportation and on the main street. According to the map of local public transportation (http://www.cassovia.sk/dpmk/trace/, 2008) the main street covers 1/49 part of this map. On the main street there is winter road maintenance with chemical sprinkle $MgCl_2$. Other streets are salted with rock salt (RS) and industrial salt (TIS) (http://www.euromarsro.sk/cert2_.jpg, 2008) . Amount of mixture under examination was

$$0{,}5\ g.l^{-1} = 0{,}0102\ g.l^{-1}\ MgCl_2 + 0{,}2449\ g.l^{-1}\ RS + 0{,}2449\ g.l^{-1}\ TIS.$$

The simulation of the influence of deicer on the suspension in the activation tank was performed in static discontinual reactor. The reactor used with continual aeration and it was without inflow and outflow.

In four single reactors there were 10 l of water and sludge from the activated tank of municipal plant with:

a. chemicals NaCl and $MgCl_2$:

1. without salt,
2. with 5 $g.l^{-1}$ of NaCl,
3. with 7 $g.l^{-1}$ of NaCl,
4. with 5 $g.l^{-1}$ of $MgCl_2$.

b. real road salt:

1. without salt,
2. with 0,5 g.l^{-1} of mixture,
3. with 1 g.l^{-1} of mixture,
4. with 0,5 g.l^{-1} of Solmag.

In the single reactor conductivity, temperature, COD, BOD, BOD_5, contents of Na^+, Mg^+, Cl^- ions were observed (Horáková, M., et al. 1986). The first and last day sludge index SI was evaluated (Table 1). In individual calculations, suspension sampling, monitoring and transpiration were included. COD was estimated by dichromate method from filtrate sample of 20 ml. BOD was performed with an oximeter Oxi 538 and BOD_5 provided biological oxygen demand of nitrification.

Content of Na^+ ions was acquired from filtered sample by AAS (atomic absorbent spectrophotometry). Content of Mg^{2+} ions was determined by chelatometric titration, and content of Cl^- ions was determined by argentometric titration.

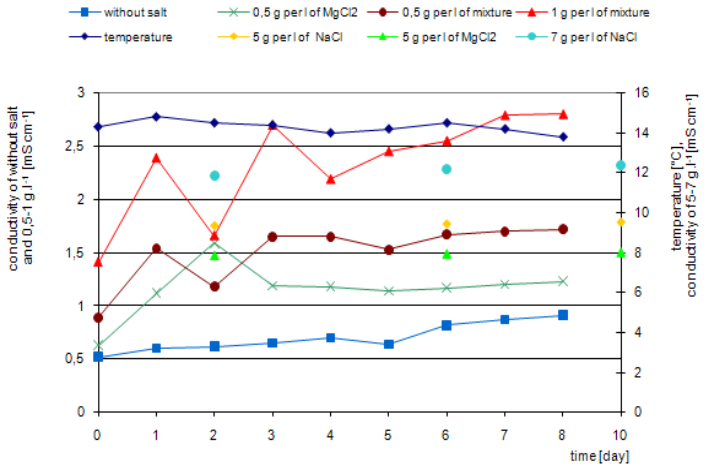

Figure 2. Dependence of conductivity on time with connection to temperature

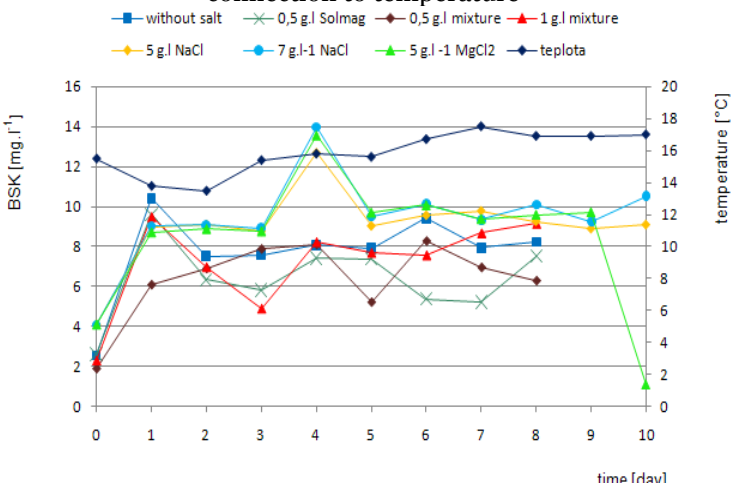

Figure 3. Biochemical oxygen demand

5. DISCUSSION

The values of sodium and magnesium concentration in reactors increased only minimally and lineary with the evaporated water.

The conductivity in reactors with 5 g.l^{-1} NaCl and $MgCl_2$ and 7 g.l^{-1} NaCl was measured only 3 times, because conductivity in reactors with salt was measured only 3 times per 10 days and the values of conductivity increased with evaporation (Figure 2). The values of suspension conductivity from activated tank increased pro portionally with concentration of salt (Figure 2).

Concentration of chlorides increases with input concentration of added mixture and with evaporation.

The values of BOD were influenced by actual temperature of the measurement (13-17 °C), exhaustion of the substrate in reactor without salt and by 5 g.l^{-1} $MgCl_2$ (Figure 3).

COD is chemical oxygen demand for oxidation of all organic matter in solution. In wastewater treatment, dichromate method for its determination is used. In Figure 4, high values of COD are presented. In this method was not used higher amount of catalyser $HgSO_4$ according to the amount of chlorine concentration in the samples with chemicals.

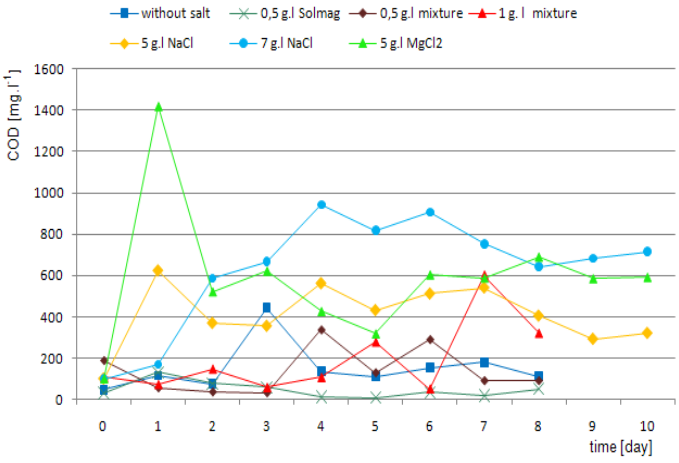

Figure 4. Chemical oxygen demand

Chlorine concentrations were up to 1 g.l^{-1} and a higher amount of catalyser was not necessary. Since the sample containing real road salt as a chemical component also contains ferrocyanidepotassium and cyanide, an atypical behaviour of COD is obsarved.

From volume of sludge in 30 min sedimentation in 1 l measuring cylinder we can assume temporary defloculation. The values of sludge index of salt suspension refer to a decrease setleable

solids of sludge with NaCl and real road salt. Volume of sludge in 1 l measuring cylinder show the influence real road salt on defloculation. Influence of $MgCl_2$ was insignificant (Table 1).

Table 1. Sedimentation and sludge index of samples with and without salt and chemicals

Sample	Volume of sludge [ml]	SI [ml.g^{-1}]	Sample	Volume of sludge [ml]	SI [ml.g^{-1}]
without salt, 0 day	140	148,97	without salt, 0 day	500	144,1
without salt, 9 day	240	73,846	without salt, 9 day	465	128,8
5 g.l^{-1} NaCl 9 day	350	135,66	0,5 g.l^{-1} of mixture, 9 day	675	126,17
7 g.l^{-1} NaCl 9 day	310	133,66	1 g.l^{-1} of mixture, 9 day	950	115,15
5 g.l^{-1} $MgCl_2$ 9 day	400	82,82	0,5 g.l^{-1} of Solmag, 9 day	920	149,35

6. CONCLUSION

Values of conductivity in the activated tank in wastewater treatment under real conditions are from 40 to 170 mS.cm^{-1}. These values are provided by influence of real road salt.

Increased values of conductivity of the mixture of about 0,5 g.l^{-1} are identical to the real values from wastewater treatment. The other values of NaCl concentration and real road salt are higher and insignificant. To compare NaCl and real road salt it is better to use a mixture of real road salt because rock salt and industrial salt, althought they have the same basis – NaCl, show different results. This is caused by the anticlinker additive – ferrocyanidepotassium that is present in the real road salt. The rock salt contains no ferrocyanidepotassium.

Acknowledgement

The authors wish to thank Mrs. Blažena Palaščáková for providing the high value conductance measurements. This work was supported by the Scientific Grant Agency of the Ministry of Education of Slovak Republic under the grant No. 1/4184/07 and by the Slovak Research and Development Agency under the contract No. APVV-0068-07.

REFERENCES

[1] *Zekeová-Nanáčková, Z.: Vplyv solnatosti na čistenie odpadových vôd aktivovaným kalom, Výskumný ústav vodného hospodárstva, Veda, Bratislava 1976.*

[2] *Pietriková, A., Búgel, M., Neubauer, M.: Environmentálny spôsob zimnej údržby komunikácii na báze $MgCl_2$, Silniční obzor, roč. 66, 10/2005, str. 263-269.*

[3] *Wilderer, P. A.: Effects of low temperature on nitrogen removal processes, Baltic sea environment proceedings, No. 30, 2nd. Seminar on wastewater tratment in urban areas Tampere Finland, 2001.*

[4] *Strom, P.F., Matulewich, V. A., Finstein, M. S.: Concentration of nitrifzing bacteria in sewages, effluents, and a receiving stream and resistance of these organism to chlorination, Applied and environmental microbiology, may.1976, p. 731-737.*

[5] *[16. 6. 2007], www.ssc.sk/user/view_page.php?page_id=448 - 20k*

[6] *Bouldin, D., R.: Chloride in Fall Creek as influenced by road salt, Crop and soil science, CALS 23. 5.2005, Cornell University in Ithaca New York.*

[7] *Hamoda, M. F., Al-Attar, I. M. S.: Effects of high sodium chloride concentrations on activated sludge treatment, Water Science and Technology 39/9, pp. 61-72.*

[8] *Okabe, S., Hisashi, S., Watanabe, Y.: In situ analysis of nitrifying biofilms as determined by in situ hybridization and the use of microelectrodes, Applied and Environmental Microbiology, july 1999, pp. 3182-3191.*

[9] *Šilhánková, L.: Mikrobiologie pro potravináře a biotechnology, Victoria publishing, a.s. Praha 1995.*

[10] *[18. 12. 2008], http://www.euromarsro.sk/cert2_.jpg*

[11] *Horáková, M., Lischke, P., Grünwald, A.: Chemické a fyzikální metody analýzy vod, SNTL Praha, 1986, str. 104-208.*

[12] *[18. 12. 2008], http://www.cassovia.sk/dpmk/trace/*