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EDITORIAL PREFACE

In addition to food and energy, access to water is a strategic issue influencing everyday life of over 7 billion people worldwide. Although water is available in vast quantities on Earth, the amount of fresh water is only approximately 3% of the total. About 68% of fresh water is captured in polar ice caps and glaciers, and 30% is present in the soil as ground water. The amount of surface water in lakes, rivers, and swamps is only 0.3%.

Currently humans consume 54% of the renewable fresh water. This figure is predicted to increase to 70% by 2025. It is anticipated that by 2050 the fresh water demand will increase by an additional 70%. Thus, the shortage of water will be very soon a critical issue leading to local and even global geopolitical conflicts unless effective measures are taken. The inefficient use of or simply wasting water in the developed countries makes this delicate issue even more complicated. In a modern household, 60% of good quality water is used to flush toilets and for washing, while only 20% is utilised in the kitchen, and another 20% in the bathroom.

The desired “green growth with blue sustainability” requires immediate actions for handling the consequences of climate change (floods, droughts) and environmental pollution. Wastewater should be considered as “water wasted”. Thus, a good water management must find balance between economy, society, and environment *via* a series of actions, such as analysis, monitoring, and implementation. Since approximately 80% of water discharged worldwide is polluted, there is a need for resource-oriented science and technology that encourages green innovation. This must be done by simultaneously keeping in mind development in engineering, financial resources, and social acceptance. The growing demand of industry for water can only be handled with the introduction of closed loop technologies, where water is reused and recycled. The water issue is more and more in the mainstream of politics as exemplified by the Budapest Water Summit in 2013 and international conferences since then. There is a chance now for making radical and innovative actions with the proper combination of governance, technology, and finance for eliminating imbalance in water use.

The University of Pannonia in Veszprém, Hungary was the first to introduce environmental engineering education in Hungary. It took the leading role in environmental monitoring and in the development of expert systems for wastewater treatment. In June 2014 the „*First National Conference on Water Chemistry and Technology*” was held in Veszprém in the frame of the TÁMOP-4.1.1.C-12/1/KONV-2012-0015 project supported by the European Union and co-financed by the European Social Fund. In this Thematic Issue of the Hungarian Journal of Industry and Chemistry, selected papers are presented from the Conference program that represent some of the important topics of the water sector: e.g. heavy metal removal from waste water and monitoring the bioavailability of heavy metals in river catchment areas; nitrogen removal from municipal waste water; mineralisation of herbicides in water; equilibrium calculations to solve complex aqueous speciation problems; photocatalytic remediation of pesticide-contaminated ground water; purification of dairy-food waste water via biofilms, and novel plasma spectroscopic methods in the analysis of aqueous solution.

We do hope that these topics will be of interest to the broad scientific community.

Veszprém, June 2015

Prof. Dr. JÁNOS KRISTÓF, D.Sc.
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HEAVY METAL BALANCE IN A COMMUNAL WASTEWATER TREATMENT PLANT

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Heavy metal removal from a municipal wastewater treatment plant was evaluated in the given study. The aim of the work was to find water or sludge streams in the technology that could be treated separately for heavy metal removal to maximise the efficiency of the entire treatment. The results proved that in the plant studied 70–80% of the metal content was discharged. Only 5–20% was retained in the digested sludge. A small percentage of the metal content of the influent could only be measured in the primary and secondary sludges. Otherwise, there were very similar metal concentrations in these sludge streams. The reject water exhibited an inconsiderable level of metal recycling in the technology, no more than 2–3% of the influent load. Some 2–10% of the heavy metal content of the inlet was removed from the sand trap. We did not find the separate heavy metal removal from the sludge streams efficient as most of the heavy metal load finally was discharged from the treatment plant with the treated effluent into the recipient.

Keywords: activated sludge, heavy metals, mass balance, municipal wastewater

1. Introduction

Industrial discharges into municipal wastewaters from metal refining and other industrial sources are hazardous with regard to purification process due to their heavy metal contents. That is why nowadays heavy metal removal from these discharges at the site of the waste production is strictly regulated. The next possibility for removing heavy metals from wastewater is the activated sludge process of the Publicly Owned Treatment Works (POTWs) [1]. The mechanism of heavy metal removal in the activated sludge process is not completely understood yet [2]. Even the inhibition effects of some metals for specific microorganisms are not properly known. That is why our study tried to summarise the heavy metal removal of an activated sludge plant on the basis of its detailed mass balance. We excluded from this study the influence of any technological parameters like oxygen supply, pH, sludge age, complexing agents, etc. or the microbial composition of the working biomass [2–3].

An overview of the possibility of the removal of metals from sludges of sewage treatment plants has already been presented [2, 4]. Rather different removal efficiencies were published from many measurements all over the world. These studies concluded that around 70% of the Mn and Cu load can be accumulated in the activated sludge, while 50–60% of the Cr, Cd, Pb, Fe, Ni, and Zn will leave the plant as it is discharged into the recipient with the treated

effluent. It is well known, that some special forms of these heavy metals in the sludge or activated sludge process are more critical than their total concentrations [5].

In our study, we measured the heavy metal concentrations in the different liquid and sludge streams of a Hungarian wastewater treatment unit in Veszprém treating municipal effluent relatively free of industrial metal discharges. We calculated a total mass balance for the plant and evaluated the feasibility of the separate removal of some metal contaminants from the sludge residue to produce more valuable agricultural soil amendment.

2. Materials and Method

The studied activated sludge process treats daily 13,000 m³ of sewage, while its nominal daily capacity of 21,000 m³ shows considerable underutilisation. It has a proper digestion capacity for the primary and secondary sludge of the main stream. We considered that it is important to measure the heavy metal concentrations at the inflow and in purified effluent in some mixed liquid streams and the final dried sludge as well. From the material balance established from these data, it seemed possible to decide about the reality of the use of some separate heavy metal removal steps in the treatment line.

To establish a heavy metal mass balance, we took samples several times from the liquid, mixed sludge and dried sludge as well. The sampling points in the technology can be seen in *Fig.1*.

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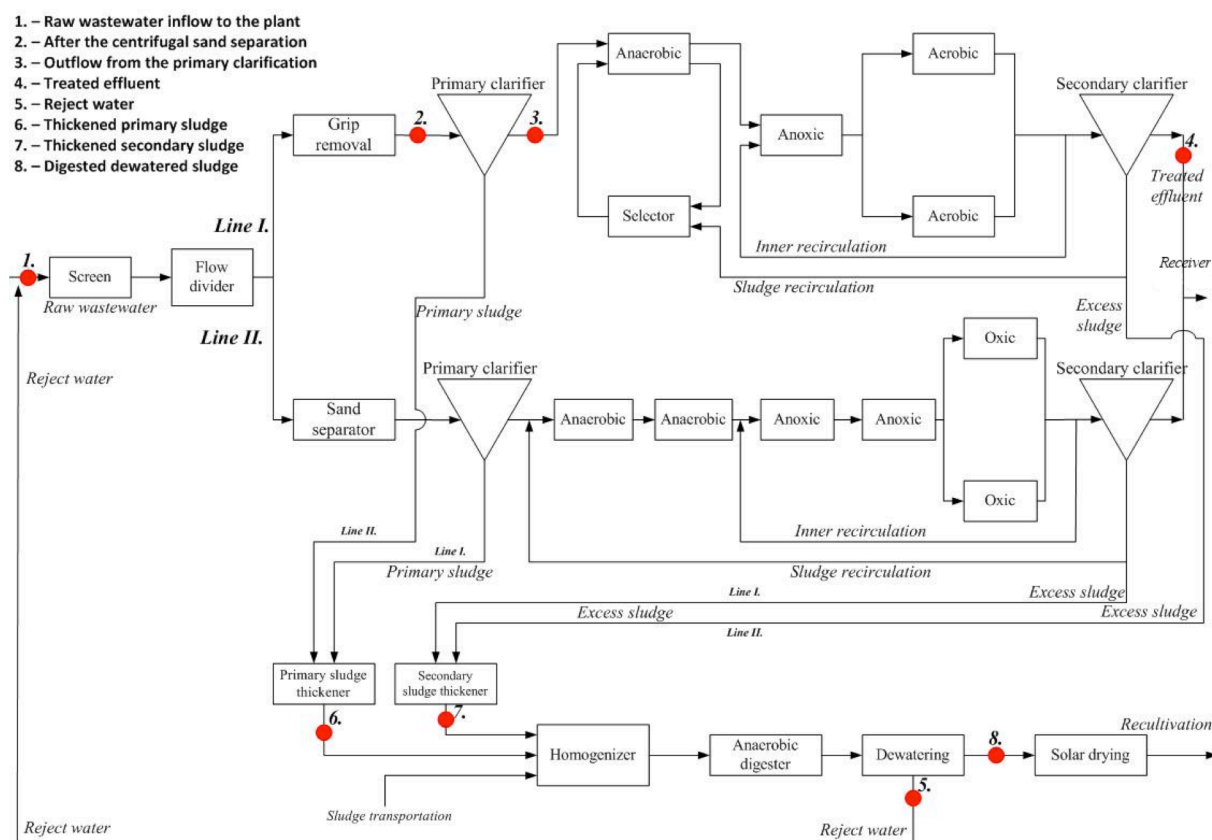


Figure 1. The technology and sampling points for checking heavy metal concentrations.

Samples 1 to 4 were collected during the day every other hour. Samples 5–8 were collected when sludge pumping or drying was in operation. These were homogenised, cooled, and stored as prescribed by Hungarian Standard MSZ 318-2:1985 protocol.

The dissolution of the metal content was followed by the atomic absorption spectrophotometric measurement for eight (Cd, Co, Mn, Ni, Cr, Cu, Fe, and Pb) metal contaminants. From these data, the metal content of the sludge phases was determined for the suspended (SS) and total solid (TS) contents for Samples 5–8. It was assumed that the dissolved heavy metal content of the liquid phase equals to that of the treated effluent in Samples 6 and 7 and with that of the reject water in Sample 8.

For measuring SS and TS contents of the sludge containing samples (No. 6–8), we used the Hungarian Standard MSZ 260/3-73 standardised method. The average daily amount of the reject water had to be calculated for the calculation of the material balance from these measured values, as the flow was not measured in the plant.

Dissolution of the metals from the different samples was carried out by a Mars 6 microwave digester. The temperature program of the digester was optimised in a preliminary study [6]. For the addition of chemicals for digestion, we followed the recommendation of Hungarian Standard MSZ 1484-3 protocol (Chapter 4.2.2.3). Before digestion, 3 ml of 68% HNO₃ and 9 cm³ of concentrated HCl was given to every 0.5 cm³ sample. The microwave digestion of the sludge samples was carried out according to the same

heating program for all samples. After 20 min of heating, digestion was completed in 10 min at 180 °C. After digestion and dilution, the heavy metal concentrations were measured by a Thermo Scientific ICE 3000 Atomic Adsorption Spectrophotometer.

3. Results and Discussion

During the control study, the samples were taken over three one week-long periods. We measured the weekly homogenised samples stored in a refrigerator a week later than sampling in triplicates. The average metal contents for the entire measurement period are shown in Table 1.

As shown in Table 1, there was no Pb detected in the influents of the wastewater treatment plant. The Cd concentration was low (0.03 mg dm⁻³). Mn and Ni levels were a bit higher within the range of 0.08–0.15 mg dm⁻³. Co exhibited a slightly higher concentration (0.1–0.3 mg dm⁻³) than Mn and Ni. The Cu content was constant at around 0.2 mg dm⁻³. These values are as expected from our earlier measurements at this plant. The Fe had the highest concentration in the inflow (up to 356 mg dm⁻³) and it remained similarly high relative to the other metal contaminants in the outflow from the plant.

To calculate the heavy metal mass balance in the process, the flow rates and sludge production had to be taken into account. As the hydraulic retention time (HRT) in the plant was more than one day and the sludge age was nearly 20 days, we used average

Table 1. The total heavy metal concentrations (mg dm⁻³) of the liquid and sludge-containing streams of the activated sludge process (variation in concentrations is in the order of $\pm 31\%$).

samples	Cd	Co	Mn	Ni	Cr	Cu	Fe	Pb
raw wastewater	0.023	0.169	0.123	0.123	0.185	0.231	7.938	<0.001
after grit removal	0.023	0.166	0.105	0.120	0.174	0.223	7.819	<0.001
primary clarified wastewater	0.022	0.161	0.094	0.109	0.168	0.214	7.168	<0.001
treated effluent	0.021	0.152	0.062	0.107	0.161	0.202	0.079	<0.001
reject water	0.005	0.128	0.093	0.048	0.160	0.095	10.147	<0.001
thickened primary sludge	0.021	0.462	1.973	0.414	0.565	0.750	58.509	<0.001
thickened secondary sludge	0.019	0.673	2.709	0.633	0.696	1.030	355.813	<0.001

Table 2. The main technological parameters (volumes are in m³, solid content in mass percent) used to calculate heavy metal mass-balances (variation in flow rates is in the order of $\pm 22\%$).

I. stream	Volume of wastewater		Thickened sludge streams		Sludge drying			
	influent	effluent	primary	secondary	volume	dry solid content before	after	
7250	6500	13750	13190	112	134	243	2.4	23

Table 3. Daily heavy metal mass (in grams per day) in the streams shown in Figure 1.

samples	Cd	Co	Mn	Ni	Cr	Cu	Fe
raw wastewater	150	1,100	800	800	1,200	1,500	51,600
after grip removal	149	1,080	682	778	1,132	1,448	50,826
primary clarified wastewater	144	1,048	614	706	1,093	1,388	46,595
treated effluent	139	991	400	697	1,049	1,310	516
reject water	1.6	38.5	28	14.4	48	28.5	3,044
thickened primary sludge	2.4	51.7	221	46.4	63.3	84	6,553
thickened secondary sludge	1.5	42.9	170	52.8	78	82.5	44,170
digested dried sludge	2.5	90.2	363	84.8	93.3	138	47,679

Table 4. Relative quantity of the heavy metals in streams measured as mass percentage of the influent concentrations in raw wastewater (100%).

samples	Cd	Co	Mn	Ni	Cr	Cu	Fe
after grit removal	99	98.1	85.2	97.2	94.3	96.5	98.5
primary clarified wastewater	96.2	95.2	76.7	88.3	91.1	92.5	90.3
treated effluent	92.5	90.1	50	87.1	87.4	87.3	1
reject water	1.3	3.5	3.5	1.8	4	1.9	5.9
thickened primary sludge	1.6	4.7	37.6	5.8	5.3	5.6	12.7
thickened secondary sludge	1	3.9	31.3	6.6	6.5	5.5	85.6

numbers for the calculation of the balance. The same was used for the primary and secondary sludge streams, as their removal was not continuous, but the material we examined had been properly homogenised. The average daily values for the streams are summarised in Table 2.

Some parameters required for the calculation were not measured at the plant. The average daily quantity of the reject water was calculated from the SS concentration of the digested sludge stream entering the drying centrifuge and that of the dried digested sludge. The quantity of the dried digested sludge was calculated from the volume of the sludge transported from the centrifuges to the solar drying part of the plant and its average dry solid content determined. This resulted in negligible errors (less than 0.1 g/g) since the dissolved material content of the sludge water or reject water was low enough.

Flows were calculated (Table 3) using the concentrations and daily flows of heavy metals in these sewage and mixed liquids (Tables 1 and 2). In the sewage entering the plant, the concentration of the different heavy metals did not change considerably. As

a result, their mass stream had to change according to the volumetric load of the plant. This was not true for the sludge streams, as the plant had a great equalisation for the total sludge mass.

From Tables 1 and 3, it can be seen that the concentrations of the measured heavy metals did not change or decrease significantly in the sewage streams or even in the treated effluent. At the same time, the sludge containing streams containing around 1 and 3–4% dry material showed much higher heavy metal levels. Heavy metals removed from the influent (dissolved and solid) were expected to concentrate in the sludge phase of these streams and in the dried sludge as well. This means that the removal of heavy metals in this treatment facility was very poor. We hypothesise that the low specific organic material load (estimated daily value of 0.2 g KOI per g MLSS) and the high sludge age (more than 20 days) may result in the dissolution of the heavy metals into the liquid phase.

From data in Table 1, the leftover heavy metal content of the different streams can be calculated. The results are shown in Table 4. According to the results, Cd was not removed from the sewage by the activated

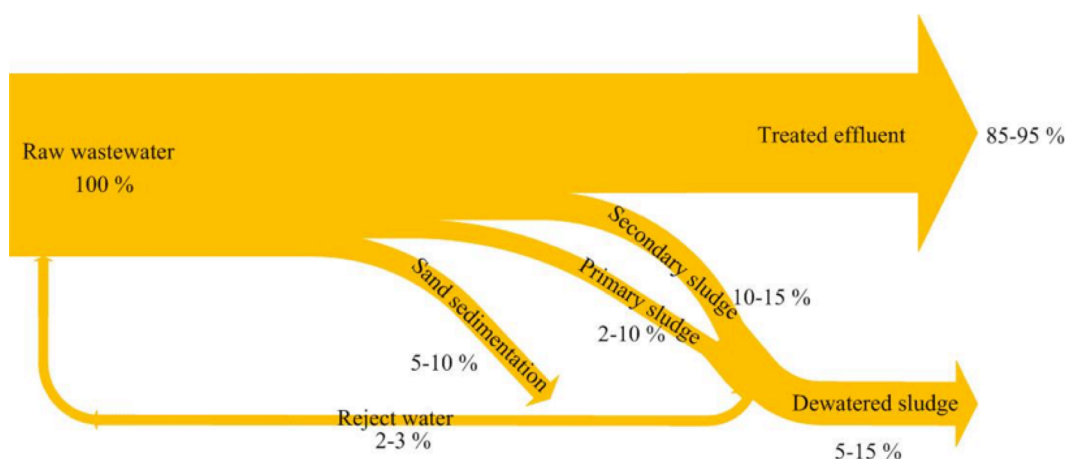


Figure 2. Removal of the heavy metals in the activated sludge of a Publicly Owned Treatment Works (percentages indicate the average daily quantities relative to the inflow values for the studied metal except Fe).

sludge process. It was absent in the reject water of the plant and only 1.0+1.6% of the Cd load was adsorbed in the final sludge produced. The load of Co, Mn, Ni and Cu was one order of magnitude bigger within a narrow daily load range (800–1,600 g per day). A significant portion of all these metals left the plant with the treated effluent. No more than 4–5% of the Co remained in the dried sludge according to our measurements and only 1–3% of the total load was recycled to the inlet point with the reject water. Approximately less than half of the Mn remained in the purified water and the rest was concentrated in the dried sludge. Around 1.5% of the Mn content of this sludge was recycled at the inlet with the centrifuge water. The metal adsorption of the primary and secondary sludge seemed to be similar, which also suggested that about three quarters of the inlet Mn load remained in the sewage stream after primary purification. In the case of Ni, only 15–20% remained in the solid residue and one tenth of that was recycled at the inlet with the reject water. The Ni seemed to be adsorbed and present in the two types of sludge in a similar ratio. Cr seemed to be bound to the primary sludge while only a small portion was removed by the biological step. These two stages of the sludge processes could not remove more than 5% of the initial level. However, this removal efficiency seems to be enough, since the inlet concentration is low enough ($< 0.5 \text{ mg dm}^{-3}$). The removal efficiency of the treatment for Cu seemed better than for other metals, but it was no more than 15–20%. Most of the removed Cu was captured in the secondary sludge. It has been observed before that some municipal sewage sludge contains high concentrations of Cu due to the high Cu content of the raw sewage. According to the given study, Fe exhibits the highest concentration in the sewage, around 500 times greater than the other metals studied here. The Fe is oxidised in the activated sludge process and is present in the biomass as hydroxide. The removal efficiency was 99% according to the measurements.

Table 3 indicates that sand removal has practically no influence on the metal content of the sewage. In the primary purifier, metal removal is poor except for the cases of Mn and Fe. Removal of metals within the secondary sludge was a bit more efficient than within

the primary one. Only Mn was better adsorbed onto the biomass (around 50%). However, Fe was almost totally removed within the sludge phase (99% removal). Concentrations of the other metals studied decreased by only a modest 5–15%.

Depending on the sludge removal from the digesters to centrifuges the average daily reject water quantity is around 200 m^3 . With this flow only 2–3% of the heavy metal load is recycled into the sewage stream entering the plant. This is such a small percentage that separate metal removal from that stream is not needed. However, the biggest problem of this sewage treatment facility is the poor removal of the heavy metals within the sludge. A similar average removal of heavy metal pollutants from the sewage can be seen from the inflow and treated effluent concentrations in Table 1 and the removal percentages of the metals in different processing steps in Table 4. From other investigations, we learnt that around half or a slightly greater proportion of these metals can be removed within the sludge residue. In our studies, we could not measure such high levels of removal neither in the primary nor secondary sludges. Moreover, only a small ratio of the metal content of the raw sludge can be dissolved during anaerobic digestion. According to our measurements, most of the heavy metals left the plant within the effluent.

Changes to the total heavy metal content of the different streams in the plant tested are graphically illustrated in Fig.2 for most of the metals studied here. Fe is an exception, as it is efficiently removed within the different sludge fractions. It cannot be dissolved even in the digester, its hydroxides and sulphides of limited solubility are strongly adsorbed by the bioproduct of the treatment. Fig.2 clearly indicates that heavy metals are recycled within the reject water in a small ratio. The dried digested sludge also removed a very small ratio of the sewage load.

4. Conclusions

According to our measurements in an activated sludge at a publicly owned municipal sewage treatment plant,

the removal of heavy metals can be moderate, which is far from the removal efficiencies published by previously. A large proportion of the heavy metal content of the inflow sewage remains in the aqueous phase and leaves within the treated effluent. Only a minor ratio of approximately 5-15% is adsorbed in the sludge or taken up by the biomass produced in the treatment. The primary and secondary sludges exhibited similar heavy metal removal efficiencies except for iron, which is mainly removed by the secondary sludge. The heavy metal content of the mixed primary and secondary sludges decreased by a small extent (5-15%) during digestion. The reject water containing the dissolved metals exhibited such low metal concentrations that treatment of it separately does not seem to be economical. It contains only 2–3% of the total heavy metal load of the plant. At the same time 80–90% of that leaves the plant within the treated effluent.

Consequently, we could not find high heavy metal concentrations in the dried digested sludge of this plant. The sludge reprocessing and reuse pose no problems in the plant with respect to heavy metal content. The low influent concentrations of the heavy metals at the same time can be correlated with the merely pure municipal effluent from the small town and its surrounding villages.

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MULTI-ELEMENTAL INDUCTIVELY COUPLED PLASMA-OPTICAL EMISSION SPECTROSCOPIC CALIBRATION PROBLEMS OF THE SEQUENTIAL EXTRACTION PROCEDURE FOR THE FRACTIONATION OF THE HEAVY METAL CONTENT FROM AQUATIC SEDIMENTS

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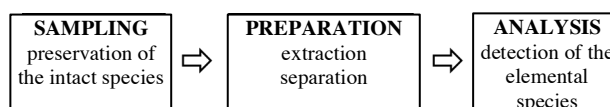
For the characterisation of the environmental mobility of heavy metal contamination in aquatic sediments, the EU Bureau of Reference has proposed a fractionation by sequential extraction procedure. For its validation, the CRM-701 sample is available containing Cd, Cr, Cu, Ni, Pb, and Zn. In this paper, the matrix-matched calibration problems are presented. A multi-elemental inductively coupled plasma-optical emission technique is employed for the detection of heavy metals in the extracts. It was established that the sensitivities are strongly influenced by the extractants, which causes significant matrix effects: the sensitivities are strongly influenced by the solvents applied in extraction steps; the summarised recoveries show an acceptable agreement with the certified values; however, in the individual extraction steps for certain elements significant differences may occur due to the neglected interferences. Therefore, further optimisation is required utilising the flexible line selection possibility offered by the HORIBA Jobin Yvon ACTIVA-M instrument.

Keywords: fractionation, sequential extraction, multi-elemental ICP-OES, matrix-matched calibration, heavy metal contamination, sediments

1. Introduction

Environmentally toxic elements, such as heavy metals, are the most significant inorganic pollutants. The role of different chemical elements in food production has been an important question of agrochemical research since the middle of the nineteenth century. Numerous extraction methods have been developed for determining biologically available fractions of nutritionally relevant elements in soils. Environmental researchers have confronted similar problems over the last few decades of the twentieth century in characterising the human- and eco-toxicological impacts of increasing heavy metal pollution. This challenge has created new requirements for analytical methodology and contributed to the development of speciation analytical chemistry. This scientific discipline provides the foundation for the evaluation of toxicological impacts of chemical elemental species detectable in environmental systems [1,2]. In such procedures, the original physico-chemical structural forms of chemical elements present in the system must be preserved during sampling and sample preparation. Then, appropriate separation methods must be applied before element specific analytical detection (*Fig.1*).

The European Union established the European Virtual Institute for Speciation Analysis in 2002 for promoting cooperation, collection, reviewing, and discussion of information and knowledge related to chemical speciation analysis (www.speciation.net). Attention was drawn to the mobility and biological impact of heavy metals in environmental systems influenced by their chemical speciation. Biological risk assessment of contaminated areas therefore requires the total speciation of all chemical elements present in the system. However, due to the complex structure of solid environmental samples (e.g. soils, sediments, gravitation dust, mining waste, etc.), these analytical tasks in practice cannot be fully completed. As a compromise, the fractionation of the heavy metal content according to environmental mobility and estimation of biological availability by sequential extraction procedures have become the main research approaches. Papers published in this area and their citations exponentially increased in the period of 1995



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Figure 1. Scheme of the speciation analysis procedure.

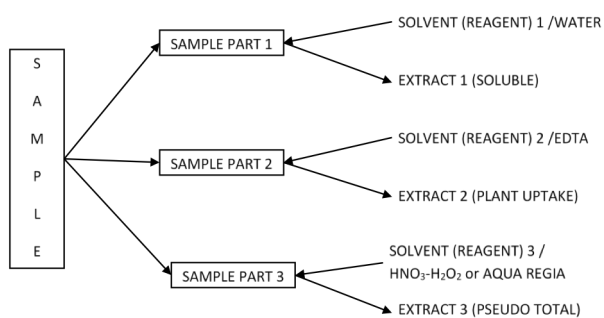


Figure 2. Strategy of serial single-step extractions.

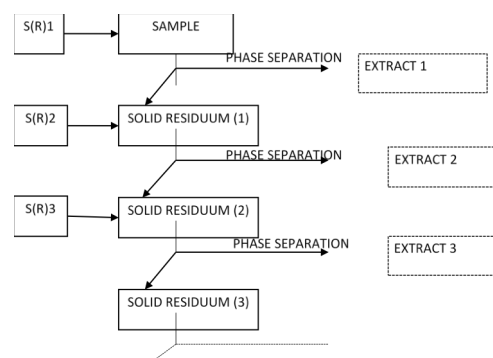
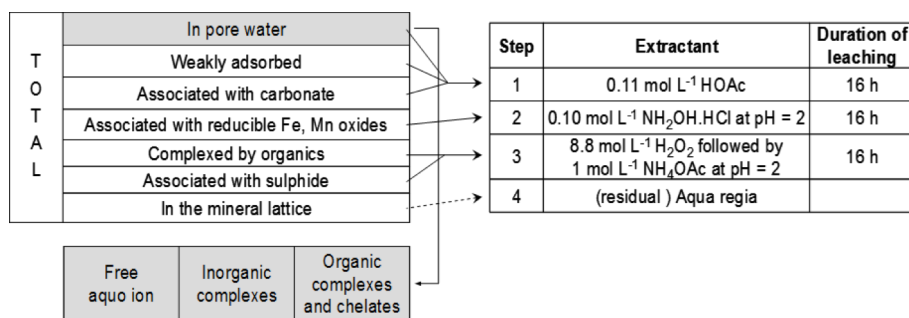


Figure 3. Strategy of sequential extractions (S(R) stands for SOLVENT(REAGENT)).



Scheme 1. Element fractions in aquatic sediment as classified by Kersten and Förstner [4], Caroli [3], and Tessier [5] (left-hand side) and the original BCR sequential extraction steps [6-8] (right-hand side)

and 2013: from 200/year to 700/year; according to related citations from 1000/year to 19,000/year based on Thomson Reuters, Web of Science database. A primary risk assessment of heavy metal contamination in the soil/water/atmosphere system was based on the fractionation of metallic element content of environmental samples according to their environmental mobility. The term “fractionation” was recommended by the IUPAC in 2000 [2]. The mobility of an element according to the different solubilities of different binding classes can be estimated by solvents sequentially applied containing physico-chemically increasingly aggressive reagents [3,4]. In agricultural chemistry, the serial single step strategy (Fig.2), in environmental chemistry the strategy of sequential extraction has become dominant (Fig.3).

The first sequential extraction procedure for the characterisation of the mobility of heavy metals in aquatic sediments was developed by Tessier *et al.* [5], who classified the metal content of sediments according to the solubility and binding forms of metallic species as presented in Scheme 1.

Based on this essential work [5], numerous 5-8-step sequential extraction schemes have been developed by which the original chemical structures (binding forms) are gradually dissolved and/or decomposed [9]. The complete duration of these procedures is 5–6 days, while the duration of the batch leaching steps is determined by a long setup time of solubility and heterogeneous chemical equilibria. The proposal for a 3(+1)-step sequential extraction procedure issued by BCR in 1993 is a simplified version of the above-mentioned schemes [6], but it is still time-consuming and labour-intensive.

As shown in Scheme 1, the water soluble, weakly adsorbed, and carbonate-associated metal fractions are extracted simultaneously by acetic acid in the first leaching step. In the second step, the metal fractions associated with reducible Fe and Mn oxides are produced after reduction by hydroxylamine. A fraction of metals coordinated to organic molecules and associated with sulphides is extracted after oxidation by H₂O₂ in the third step. In the extra step, the residual fraction can be obtained by means of digestion with *aqua regia* or HNO₃/H₂O₂.

Re-adsorption of extracted metals during phase separation can lead to analyte losses. In the extracts, the high concentration of the reagent may cause strong matrix effects during spectrochemical element detection. The CRM 601 sediment reference material issued in 1997 has been certified for this procedure only for Cd, Cr, Ni, Pb, and Zn [7,8]. During the analysis of the BCR 701 sediment materials, the original BCR procedure was modified to avoid analyte loss during the second leaching step due to pH instability [10–13]. However, this modification in BCR procedure may cause significant differences relative to previously obtained data. The BCR procedures in their original and modified versions were successfully applied to aquatic sediments and soils; however, soil CRM has not been issued for this procedure up to now [14–21].

It can be concluded that the Tessier-based fractionation procedures [5] are widely used for heavy metal contamination assessments in soils and aquatic sediments, but the realistic interpretation of these data requires standardisation. However, this has been hindered due to methodological problems of measurements and analysis [22–23]. These problems limiting the application of the BCR sequential

Table 1. Overview of the cooperative research projects between Szent István University Gödöllő and the Technical University Košice

Limitations of the BCR scheme	Achievements by SZIE and TU Košice research groups
Does not match the natural mobilisation pathways	→ Better modelling of environmental mobility by the application of H ₂ O and H ₂ O/CO ₂ solvents [24].
Does not preserve the intact species of the sample	→ Application of aqueous extractions for the elaboration of biological tests [25].
Time consuming (4-5 days)	→ Acceleration of batch leaching by means of sonification [26]. → Development of continuous flow operation in the supercritical fluid extractor for CO ₂ , H ₂ O and H ₂ O/CO ₂ solvents [24]
Cross-contamination during operation and applied reagent	→ Reduction of operations and reagents
Limited applicability and validation:	
Validation and available CRM only for sediments	→ Extension of the application to other matrices: soils, gravitation dusts, biofilms, red mud, and composts [26-30].
Validation of the procedure for Cd, Cr, Cu, Ni, Pb, Zn	→ Multi-elemental calibration and validation for different matrices and extracts [27].
High reagent and organic content of the extracts	

extraction procedure have initiated a cooperative research project between Szent István University Gödöllő and the Technical University Košice as summarised in *Table 1*.

The aim of the given study was the evaluation of changes in the environmental mobility of heavy metals at two polluted areas (Upper Tisza/2000–2001 and Gödöllő-Isaszeg lake system/1995–1998) by means of the repeated BCR fractionation of heavy metals in the sediments and soils [31–34]. A flexible, multi-elemental Inductively Coupled Plasma-Optical Emission (ICP-OES) technique with a Charge-Coupled Device (CCD)-detection system was employed instead of the formerly applied flame atomic absorption spectroscopy (FAAS). The latter had to be optimised for each analyte element individually. Hereby, the problems of the matrix-matched multi-elemental calibration of the ICP-OES method are described using different solvent applied from the BCR procedure. The validation of the calibration was controlled by the fractionation of the CRM 701 sample.

2. Experimental

2.1. Elemental Analysis and Instrumentation

For element detection in different extractant matrices, the HORIBA Jobin Yvon ACTIVA-M ICP-OES spectrometer was employed, which is able to record the entire UV-vis spectrum range by rapid scanning CCD-detection. It also makes possible the flexible analytical line selection for 75 elements. The wavelength scale calibration of recorded spectra is based on a reference line position set by the user. The C 193.026 nm line is proposed by the manufacturer in routine analytical applications. The instrument's scheme and technical

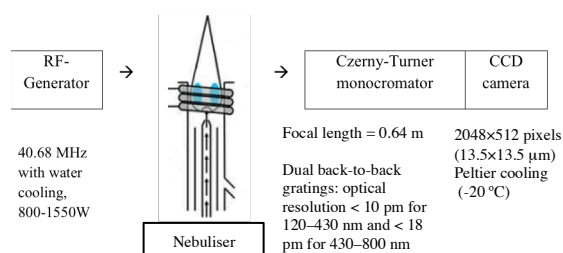


Figure 4. Scheme of the HORIBA Jobin Yvon ACTIVA-M ICP-OES spectrometer and relevant technical parameters

parameters are presented in *Fig.4*. Introduction of the sample can be performed by a concentric glass nebuliser and glass cyclone spray chamber fed by a 3-channel peristaltic pump.

2.2. ICP-OES Operation Parameters

The operation parameters of ICP-OES were selected on the basis of the manufacturer's manual proposed for multi-elemental analysis as follows:

- Incident power: 1000 W,
- Plasma gas flow: 13.14 dm³ min⁻¹,
- Sheath gas flow: 0.32 dm³ min⁻¹,
- Nebuliser gas flow: 0.28 dm³ min⁻¹,
- Nebuliser gas pressure: 2.86 bar, and
- Nebuliser sample flow uptake: 0.85 cm³ min⁻¹.

2.3. Matrix Matched Calibration Solutions

Amounts of 1 mg dm⁻³ (in cc HNO₃) mono-elemental Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, and Zn (Précis Certified Standards for ICP Spectroscopy, HORIBA Scientific, France) standard solutions corresponding to 0, 5, and 20 mg dm⁻³ concentrations were pipetted into a 50 cm³ volumetric flask and then diluted by solvents applied in the BCR sequential extraction procedure:

- 1st step: 0.11 M acetic acid.
- 2nd step: 0.1 M hydroxylamine-hydrochloride.
- 3rd step: 1 M ammonium acetate.
- extra step: 13 g/g nitric acid.

2.4. Analytical Lines

The following analytical lines were selected according to the manufacturer's proposal for multi-elemental analysis:

- Cd 214.441 nm
- Co 230.785 nm
- Cr 205.571 nm
- Cu 324.754 nm
- Fe 259.940 nm and 240.489 nm
- Mn 257.610 nm
- Ni 222.296 nm (instead of 221.650 nm!)
- Pb 220.353 nm
- V 309.311 nm
- Zn 213.857 nm

In the first, second, and extra step, the wavelength readout started from the C 193.026 nm reference line. In the third step, the correct wavelength readout was only

Table 2. The calibration lines ($y = mx+b$, at wave length λ in nm), correlation R^2 values, residual standard deviations (RSD), background equivalent concentrations (BEC in $\mu\text{g dm}^{-3}$), and detection limits ($C_{L(3\sigma)}$ in $\mu\text{g dm}^{-3}$) obtained by a 0.11 M acetic acid matrix.

	λ	$C_{L(3\sigma)}$	BEC	m	b	R^2	RSD
Cd	214.441	0.5	65	43778	2867	0.9999	1.1%
Co	230.785	0.8	145	41860	6064.7	0.9997	2.5%
Cr	205.571	1.5	174	18298	3184.2	0.9996	2.9%
Cu	324.754	0.2	121	159951	19374	0.9998	2.0%
Fe	259.940	0.5	72	205720	14716	0.9999	1.2%
Mn	257.610	0.2	105	902188	94673	0.9999	1.8%
Ni	222.296	2.0	115	7154	823.38	0.9998	2.0%
Pb	220.353	3.5	17	4087.4	68.946	1.0000	0.3%
V	309.311	0.6	34	259817	8897	1.0000	0.5%
Zn	213.857	0.6	148	60540	8951	0.9998	2.2%

Table 4. The calibration lines ($y = mx+b$, at wave length λ in nm), correlation R^2 values, residual standard deviations (RSD), background equivalent concentrations (BEC in $\mu\text{g dm}^{-3}$), and detection limits ($C_{L(3\sigma)}$ in $\mu\text{g dm}^{-3}$) obtained by a 1.00 M ammonium-acetate matrix.

	λ	$C_{L(3\sigma)}$	BEC	m	b	R^2	RSD
Cd	214.441	0.6	57	70051	-4008.3	1.0000	1.0%
Co	230.785	1.4	2	54840	-119.26	1.0000	0.03%
Cr	205.571	1.2	21	25579	546.52	1.0000	0.3%
Cu	324.754	2.5	213	151053	32156	0.9994	3.5%
Fe	259.940	15.8	160	258243	41379	1.0000	0.6%
Mn	257.610	0.4	2	1291505	2013	1.0000	0.02%
Ni	222.296	2.3	17	9902	-170.25	1.0000	0.3%
Pb	220.353	3.5	148	5905.2	-874.08	0.9997	2.6%
V	309.311	1.4	85	312207	26636	0.9999	1.4%
Zn	213.857	14.5	33	79775	2643.2	0.9968	1.9%

Table 5. The calibration lines ($y = mx+b$, at wave length λ in nm), correlation R^2 values, residual standard deviations (RSD), background equivalent concentrations (BEC in $\mu\text{g dm}^{-3}$), and detection limits ($C_{L(3\sigma)}$ in $\mu\text{g dm}^{-3}$) obtained by a 13 g/g nitric acid and hydrogen peroxide matrix.

	λ	$C_{L(3\sigma)}$	BEC	m	b	R^2	RSD
Cd	214.441	0.4	392	74770	29293	0.9980	6.6%
Co	230.785	3.5	319	50151	16009	0.9986	5.4%
Cr	205.571	1.7	328	23088	7580.7	0.9986	5.5%
Cu	324.754	0.9	343	104399	35859	0.9985	5.6%
Fe	259.940	0.7	219	216961	47594	0.9995	3.2%
Mn	257.610	0.5	211	1056725	222941	1.0000	3.6%
Ni	222.296	0.5	320	9282.3	2974.7	0.9987	5.4%
Pb	220.353	8.7	265	6483.7	1717.4	0.9991	4.4%
V	309.311	0.7	54	256488	13775	1.0000	0.9%
Zn	213.857	17.3	517	87624	45308	0.9968	8.3%

possible when the readout started from the Ar 404.442 nm reference line due to the use of 1 M ammonium acetate solution.

2.5. Validation

For validation of the CRM 701 sediment, the reference sample was applied. The fractionation of its element content was performed according to the modified BCR proposal [10–13] in triplicates. For the extraction of the

Table 3. The calibration lines ($y = mx+b$, at wave length λ in nm), correlation R^2 values, residual standard deviations (RSD), background equivalent concentrations (BEC in $\mu\text{g dm}^{-3}$), and detection limits ($C_{L(3\sigma)}$ in $\mu\text{g dm}^{-3}$) obtained by a 0.10 M hydroxylamine-hydrochloride matrix.

	λ	$C_{L(3\sigma)}$	BEC	m	b	R^2	RSD
Cd	214.441	0.9	87	47809	-4145.2	0.9999	1.5%
Co	230.785	1.4	19	44538	-856.49	1.0000	0.3%
Cr	205.571	1.4	14	18911	-258.4	1.0000	0.2%
Cu	324.754	0.9	72	163871	11765	1.0000	1.0%
Fe	259.940	0.3	1	204879	236.82	1.0000	0.2%
Mn	257.610	0.2	63	911472	57160	0.9999	1.1%
Ni	222.296	3.7	63	7505.8	471.04	1.0000	1.0%
Pb	220.353	3.9	4	4375.2	-17.636	1.0000	0.2%
V	309.311	0.2	58	260057	-15164	1.0000	1.0%
Zn	213.857	1.5	45	63846	2845.5	1.0000	0.5%

Table 6. Results for the BCR-fractionation of element content (in $\mu\text{g dm}^{-3}$) of the CRM 701 sample.

steps		measured	certified	recovery
1 st	Cd	6.45±0.07	7.34±0.35	88%
	Co	1.68±0.06		
	Cr	1.88±0.08	2.26±0.16	83%
	Cu	44.93±0.25	49.3±1.7	91%
	Fe	57.74±2.53		
	Mn	133.17±6.52		
	Ni	12.52±0.34	15.4±0.9	81%
	Pb	1.92±0.19	3.18±0.21	60%
	V	0.06±0.23		
	Zn	160.07±4.22	205±6	78%
2 nd	Cd	3.96±0.08	3.77±0.28	105%
	Co	2.71±0.03		
	Cr	26.53±0.78	45.7±2	58%
	Cu	87.61±0.81	124±3	71%
	Fe	5648±50		
	Mn	106.99±2.90		
	Ni	19.55±0.35	26.6±1.3	73%
	Pb	92.17±2.24	126±3	73%
	V	8.50±0.09		
	Zn	98.77±2.27	114±5	87%
3 rd	Cd	1.17±0.01	0.27±0.06	435%
	Co	1.80±0.08		
	Cr	196.4±8.24	143±7	137%
	Cu	63.59±2.92	55.2±4	115%
	Fe	4652±133		
	Mn	43.65±1.25		
	Ni	24.49±0.35	15.3±0.9	160%
	Pb	60.14±0.82	9.3±2	647%
	V	5.86±0.21		
	Zn	66.44±0.62	45.7±4	145%
extra	Cd	1.38±0.01		
	Co	7.63±0.18		
	Cr	101.12±4.79		
	Cu	49.48±1.92		
	Fe	24988±805		
	Mn	302.9±3.7		
	Ni	44.50±1.36		
	Pb	12.77±0.30		
V	40.30±0.67			
Zn	127.12±1.36			

residual fraction in the extra step and for the determination of the pseudo total element content microwave supported cc $\text{HNO}_3/\text{H}_2\text{O}_2$ digestion was applied.

Table 7. Comparison of the summarised element content (in mg kg⁻¹) extracted in BCR steps 1-3 using certified values for the CRM 701 sample.

	steps 1-3	certified	recovery
Cd	11.58	11.38	102%
Co	6.19		
Cr	224.8	191.0	118%
Cu	196.1	228.5	86%
Fe	10358		
Mn	283.8		
Ni	56.6	57.3	99%
Pb	154.2	138.5	111%
V	14.42		
Zn	325.3	364.7	89%

Table 8. Comparison of the summarised element content (in mg kg⁻¹) extracted in BCR steps 1-3 using pseudo-total values.

	steps 1-3+extra	pseudo-total	recovery
Cd	12.96	9.63	135%
Co	13.81	10.68	129%
Cr	325.9	290.5	112%
Cu	245.6	257.7	95%
Fe	35323	31285	113%
Mn	586.4	567.7	103%
Ni	101.0	77.2	131%
Pb	167.0	158.2	106%
V	54.68	39.20	140%
Zn	452.3	417.7	108%

3. Results and Analysis

The parameters of analytical calibration lines, background equivalent concentrations (BEC) and detection limits ($C_{L(3\sigma)}$) obtained by different extraction matrices are summarised in *Tables 2–5*. It can be established that the extraction matrix solvents significantly influence the sensitivity (B) values for all elements in the order of $B(3^{\text{rd}}) > B(\text{extra}) > B(2^{\text{nd}}) > B(1^{\text{st}})$ as a function of steps taken. With the exception of some outliers, the residual standard deviation values are in the range of 1–2% and the detection limits are in the range of 0.5–2 $\mu\text{g dm}^{-3}$. The outliers for Pb, Zn and Fe in certain matrices refer to neglected spectral interferences.

The results of the fractionation of the element content of the CRM 701 sample by applying the matrix matched calibration for determining the element contents in the extracts are summarised and compared with the certified and pseudo-total values in *Tables 6–8*. It can be seen that the metal content in BCR Steps 1–3 shows an acceptable agreement ($< \text{mg dm}^{-3}$) with certified values. In the individual steps, there are larger differences for elements than are acceptable: 1st step: Pb; 2nd step: Cr, Cu, and Pb; 3rd step: Cd, Ni, Pb, and Zn.

4. Conclusion

Based on the results presented here, it can be concluded that the extractants applied in the BCR sequential extraction procedure cause significant matrix effects even in the case of matrix-matched multi-elemental calibration of the ICP-OES determination of element content. The sensitivities were strongly influenced by the extractant media, therefore, a much higher incident power was required to eliminate these differences to ensure conditions that are more robust. The recoveries of certified values of the CRM 701 sample were within the acceptable range when the summary of extracted amounts in the BCR Steps 1–3 was compared. Significant differences occurring in individual extraction steps between the measured and certified values refer to neglected spectral interferences. This requires a detailed study utilising the flexible line

selection possibility offered by the HORIBA Jobin Yvon ACTIVA-M instrument.

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NITROGEN REMOVAL CONTROLLED BY AN AMMONIUM-ANALYSER AT THE NORTH PEST WASTEWATER TREATMENT PLANT

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At the North Pest Wastewater Treatment Plant, a nutrient removal process has been in operation since 2011. New tanks have been built, which can receive approximately half of the pre-settled wastewater. A pre-denitrification system has been planned and built both to the old and new lines. Due to the relatively small anoxic zones, periodic aeration was initiated first in the new line to achieve the lowest possible effluent total nitrogen concentration. Because of its positive impact, the operation of periodic aeration was initiated in the old line as well. Ammonium-analysers are used to control the aeration periods. Due to this process, the plant can provide a very low total nitrogen effluent value (below 10 mg dm^{-3} on average) as well as save energy and operational costs.

Keywords: wastewater treatment, nitrogen removal, nitrification, denitrification, ammonium-analyser, operation control, periodic aeration

1. Introduction

In the North Pest Wastewater Treatment Plant, the nutrient removal phase has been in operation since 2011. The pre-settled wastewater is divided into two parts: one part is led to the “A” biological line and the other to the “B” line. Both biological lines were constructed for pre-denitrification with anoxic selectors. Since the volume of these selectors is relatively small, the operation of periodic aeration is carried out in order to provide more time for the denitrifying bacteria to use the slowly biodegradable particulate chemical oxygen demand (COD) as well.

The aim of its operation is to keep the effluent total nitrogen (TN) concentration under an annual average value of 10 mg dm^{-3} . Therefore, the precise control of periodic aeration is important to fulfil this aim and save energy and costs as well.

1.1. Nitrification and Denitrification

In the case of municipal wastewaters, the hydrolysis of nitrogen containing compounds takes place mainly in the sewage system. Therefore, ammonium is the main form of nitrogen present in the influent wastewater. The nitrogen content of the filtration originates from the sludge treatment technology, which could also be significant for wastewater treatment plants.

The first step of the biological nitrogen removal process is nitrification, which is the biological oxidation of ammonia or ammonium to nitrite followed by the oxidation of the nitrite to nitrate. The process is performed by autotrophic bacteria as follows:



where (MO_A) and $(\text{MO}_A)'$ stand for autotrophic bacteria.

The growth rate and specific sludge production of the nitrifying bacteria are lower than for heterotrophic bacteria, thus the growth of the autotrophic bacteria has to be in the appropriate ratio of wastewater quality to amount of sludge production [1, 2]. Therefore, appropriate sludge loading can balance out the conditions for the growth of the two groups of bacteria. Increasing the sludge retention time and decreasing the organic loading rate of the activated sludge could balance out the disadvantage posed by the nitrifying bacteria [3, 4].

The second step of nitrogen removal is denitrification, when special heterotrophic facultative anaerobic bacteria produce molecular nitrogen (N_2) from nitrate as follows:



where BOD_5 , (MO_H) , and $(\text{MO}_H)'$ stand for biological oxygen demand, and heterotrophic bacteria, respectively.

2. Experimental Setup

During the construction of the nutrient removal phase a pre-denitrification system was built both in the “A” and “B” lines with 2–2 ganged, rectangular, mixed anoxic reactors for each section. Both “A” and “B” lines have four parallel sections. In the case of the “A” line, the anoxic selectors were separated from the beginning of

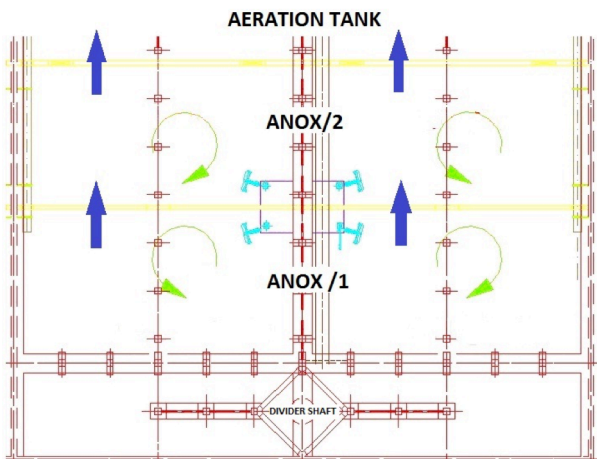


Figure 1. Schematic overview of anoxic selectors in the "A" line.

Table 1: Planned and real daily loads in kg.

Load	planned	actual		deviation in %	
	annual	2013 annual	2014 1 st quarter	2013 annual	2014 1 st quarter
COD	133 406	73 103	74 692	55	56
BOD ₅	72 800	41 390	42 043	57	58
TSS	63 336	41 408	37 316	65	59
NH ₄ -N	7 553	6 298	6 357	83	84
TN	11 575	9 137	9 487	79	82
TP	1 984	1164	1279	59	65

Loads: COD = chemical oxygen demand, BOD₅ = biological oxygen demand, TSS = total suspended solids, NH₄-N = ammonium nitrogen, TN = total nitrogen, TP = total phosphorous

the existing rectangular aeration tanks (Fig.1). As for the "B" line, the new anoxic reactors were built before the new Caroussel type aeration tanks (Fig.2). The volume of the anoxic tanks is relatively small, since only 18 vol.% of the total activated sludge can be held in both lines.

The best available effluent total nitrogen value was chosen for the design of the control system of the nitrogen removal program instead of the smallest ammonium nitrogen value. The standard value for total nitrogen is 35 mg dm⁻³, but the aim of the plant was to keep the effluent total nitrogen under 10 mg dm⁻³ as an annual average. The problem was that for the small anoxic volumes there was not enough time for the denitrification to take place completely. The other challenge was that the quality of the incoming wastewater had changed, since the original design of the nutrient removal phase was made. The incoming wastewater was diluted, but the rate of dilution was not the same for each parameter (Table 1).

3. Results and Analysis

The organic matter content (COD, BOD₅) and the total suspended solids (TSS) decreased the most, while the decrease in nutrients, especially in the nitrogen forms was only modest. The difference was caused by the filtration water of the sludge dewatering system (Table 2). At the wastewater treatment plant, there are two

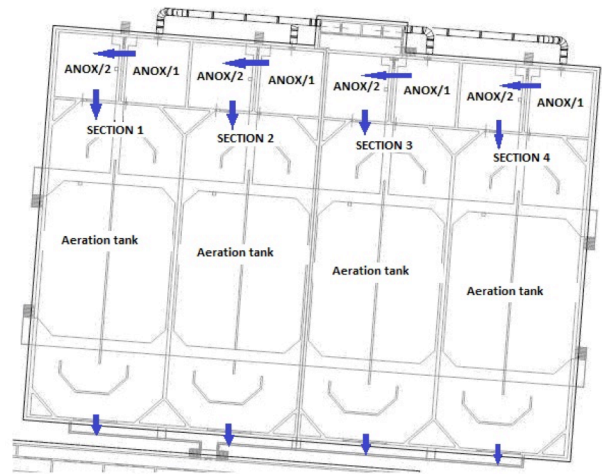


Figure 2. Schematic layout of the "B" line.

Table 2. Average COD and nitrogen content of the filtration water in mg dm⁻³.

	COD	N (NH ₃ -NH ₄)	TN	COD:TN ratio
2013	847	1,163	1,326	~1:1.6
2014 1st quarter	815	1,091	1,262	~1:1.5

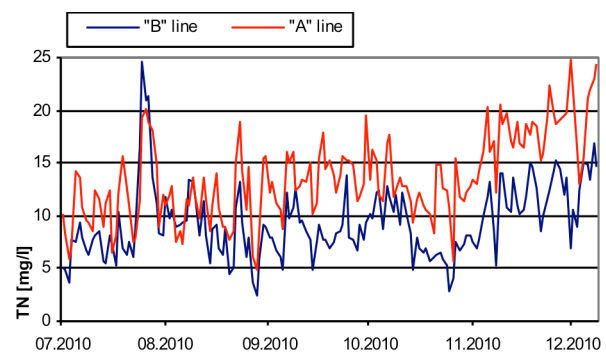


Figure 3. Effluent total nitrogen values between July and December 2010.

operating mesophilic digesters with a volume of 12,000 m³ each. These digesters receive not only the thickened sludge from the plant, but other wastes containing high quantities of organic matter, such as dried sludge, industrial wastewater, and animal protein. In Table 2, it can be seen that the nitrogen content of the filtration is very high so the ratio of the nitrogen in the influent wastewater is higher, too.

Considering the planned values from Table 1, the COD:TN ratio is 11.5:1 while the actual ratio is only 7–8:1. Previous experiments showed that the readily biodegradable soluble COD (S_s) content of the wastewater is only about 20% [5], thus the total amount of organic matter isn't available for the denitrifying bacteria in the anoxic zones. The average hydraulic retention time in the anoxic zones is about 3.5 hours. With periodic aeration (Fig.3), the denitrifying bacteria can consume not only the S_s, but the slowly biodegradable particulate COD, which becomes available as a result of hydrolysis.

Table 3. Control parameters for aeration in the “B” line.

NH ₄ -N level (mg dm ⁻³)	Sections with aeration on [pcs]	Sections with aeration off [pcs]
< 5.0	1	3
5.0 - 7.0	2	2
7.0 - 10.0	3	1
> 10.0	4	0

Table 4. Average effluent values in mg dm⁻³ between January and August 2014

Load	Effluent	Standard
COD	30	125
BOD ₅	< 10	25
TSS	5	35
NH ₄ -N	2.54	10
TN	9.63	35
TP	1.39	5

Loads: COD = chemical oxygen demand, BOD₅ = biological oxygen demand, TSS = total suspended solids, NH₄-N = ammonium nitrogen, TN = total nitrogen, TP = total phosphorous

First, the periodic aeration system was evaluated in the “B” line as shown in Fig.3. The blue diagram shows the effluent total nitrogen values from the “B” line, the red from the “A” line. It can be seen that with periodic aeration the effluent values from the “B” line are much lower compared to the “A” line. Due to this positive effect, the periodic aeration process has been used in the “A” line since 2011 as well.

3.1. Controlling Periodic Aeration

In the case of the “B” line, controlling the system is quite simple, because the treated wastewater coming from four parallel, activated sludge tanks is mixed before the final settling tanks. There is a short channel before the wastewater is divided and led to the eight rectangular secondary sedimentation tanks, where a ‘Hach Lange AMTAX sc.’-type ammonium-analyser is set up. Aeration is controlled by the measured ammonium-nitrogen value (Table 3). Due to the Carousel race-track type activated sludge tanks, aeration can be switched off even for 3 hours, because the four agitators in each section do not let the sludge settle.

Controlling the “A” line was much more difficult partly because there are no agitators in the rectangular activated sludge tanks. On the other hand, the wastewater coming from four sections is only mixed after the final settling. Thus, the ammonium-nitrogen level has to be measured separately for each section.

There are two ‘AMTAX sc.’-type ammonium-analysers in dual channel mode for the “A” line for Sections 1–2 and separately for Sections 3–4. Because of the lack of agitators, there is a time limit in order to prevent the sludge from settling. After 60 minutes, the aeration has to be switched on even if the measured ammonium is not over the set value.

In the “A” line, all the sections are controlled separately. The hours when aeration is switched on and

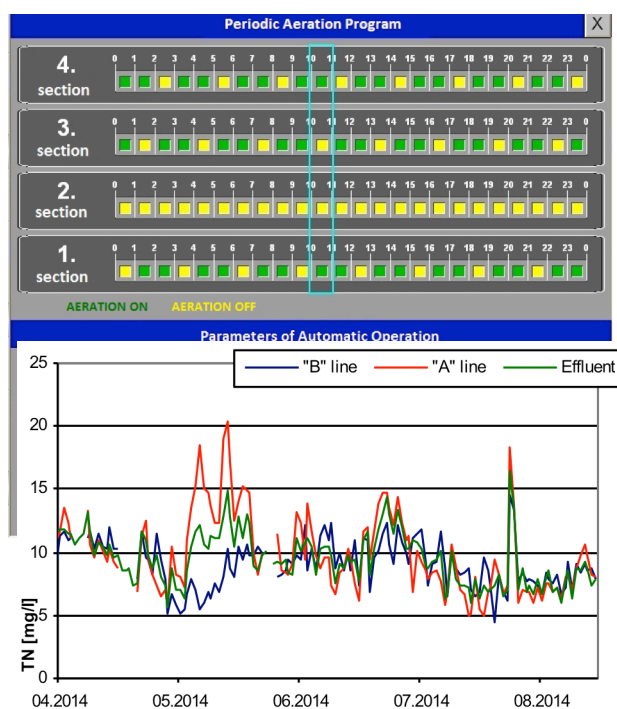


Figure 5: Effluent total nitrogen levels between April and August 2014.

off can be chosen. There are “manual”, “time control”, and “automatic” modes as shown in Fig.4. In “time control” mode the operator can fill in a timetable with aeration periods (green). Yellow areas show the hours when the aeration is turned off.

In “automatic” mode, the program calculates an average NH₄-N for each section from the past hour and compares it to the set values. If the average value is under the minimum in a section then there will be two hours with aeration on and one hour off (Fig.4). If the value is between the limits, there will be three aeration hours and one without. If the average value is over the maximum limit, aeration remains on until the value decreases below the limit. The operation of the blowers is also an important parameter. Aeration must not be switched off in every section at once.

Fig.5 shows the effluent total nitrogen levels for the controlled periodic aeration of both lines. In May, the “A” line operated under “time control”, thus the effluent results were much better in the “B” line. Automatic control of the “A” line was turned on in the summer of 2014 as shown in Fig.5. Sometimes the effluent values in the “A” line are better according to the TN than in the “B” line as can be seen from data point 06.2014. Due to periodic aeration, the effluent total nitrogen level was under the annual average of 10 mg dm⁻³ (Table 4).

4. Conclusion

Our study indicates that with periodic aeration external carbon sources are not needed at the North Pest Wastewater Treatment Plant in order to ensure the requested total nitrogen value. For optimal operation, control by ammonium analysers is essential, while the time-controlled system did not prove to be sufficient.

Acknowledgement

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EVALUATION OF THE HEAVY METAL CONTENT OF THE UPPER TISZA RIVER FLOODPLAIN SOILS OVER THE LAST DECADE

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In early 2000, two contamination events at Baia Mare first and Baia Borsa second involving large amounts of toxic elements impacted the Hungarian section of the River Tisza with disastrous ecological and economical impacts. We evaluated the short- and long-term effects of this pollution by determining the total and bioavailable concentrations of potentially toxic metals from soil samples collected along the Tisza (Tivadar, Vásárosnamény, Rakamaz, and Tiszacsege) in 2000 and between 2011 and 2013. The current and previous results were compared in respect of copper and lead contents.

Keywords: River Tisza, floodplain soils, heavy metal pollution, Lakanen-Erviö extraction, nitric acid/peroxide extraction

1. Introduction

There were intensive Cu, Zn, Pb, Au, and Ag mining activities during early 2000 in the catchment area of the River Tisza [1]. In the last two decades of the previous century, the processing of tailings pond using cyanide was popular as a recovery technology. The resulting wastewaters contain fine-grained sediments with heavy metal contents [2].

In early 2000, two contamination events (at Baia Mare first and Baia Borsa second) involved the release of large amounts of toxic elements that impacted the Hungarian section of the River Tisza with disastrous ecological and economical consequences. The first one released 100,000 m³ wastewater that contaminated with cyanide and heavy metals the river Tisza via its tributary Lápos-Szamos. The second disaster sent about 20,000 tons of mud containing heavy metals into the river Lápos-Tisza along with a simultaneous flood settling, forming a layer of approximately 5–10 cm in depth on the pre-existing soil [3–8]. Metals were primarily bound to floating material and deposited in floodplain areas.

The metal pollution of the floodplains was also observable [9, 10]. The environmental risk of this type of soil contamination is that the buffer capacity of new layer is smaller than the previously and the potential

decreases in pH enhance metal bioavailability and toxicity. The mobility and phytoavailability of metals depend on their chemical forms [11]. The speciation justifies the use of sequential extraction method (SEP) for analyzing these soil samples.

Considering the above information, it is likely that the residual heavy metal load may entail economic effects that cannot be envisaged at the moment as the valley of River Tisza is under agricultural use (pastures, meadows, orchards, and arable land). This is the reason why intensive research has aimed at testing and monitoring the ecological systems of both water and floodplains. This paper presents only the vertical distribution and forms of heavy metals in polluted areas, although plant relations were also examined [6]. The aim of this study was to evaluate the effects of these sources of pollution on the total and bioavailable metal contents of soil samples collected in 2000 and between 2011 and 2013 from floodplains and pastures along the Tisza (Tivadar, Vásárosnamény, Rakamaz, and Tiszacsege) and compare these results to earlier ones.

2. Materials and Methods

Soil samples were collected in 2000 after the flood and in April 2011 and September 2013 by deep drilling using a Nordmeyer drill (Nordmeyer Holland, Overveen, The Netherlands). We sampled the 3 m-deep soil layer in triplicates. Sampling sites are represented in *Table 1*.

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Table 1. Summary of sampling sites.

Sampling sites	Geographical coordinates	River km	Types of samples	Additional information
Tivadar	N 48° 04' 00.6" E 22° 31' 04.8"	709	active floodplain	affected by the second pollution event
Vásárosnamény	N 48° 07' 46.5" E 22° 19' 39.5"	683	pasture	affected by the first and second pollution events
Rakamaz	N 48° 07' 43.8" E 21° 26' 28.7"	543	pasture	affected by the first and second pollution events
Tiszacsege	N 47° 42' 59.9" E 20° 57' 08.7"	455	active floodplain	affected by the first and second pollution events 8 years ago the area was refilled with soil

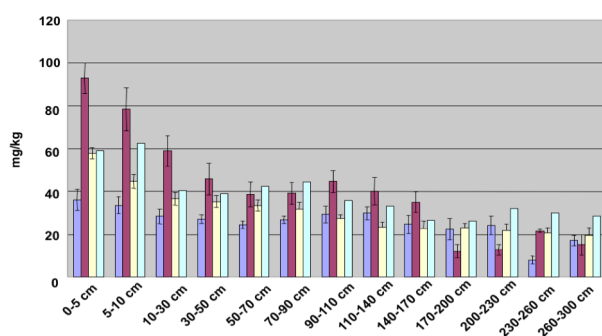


Figure 1. $\text{HNO}_3\text{-H}_2\text{O}_2$ -extractable copper concentration of different layers of soils (blue: Tivadar; burgundy: Vásárosnamény; yellow: Rakamaz; and light green: Tiszacsege).

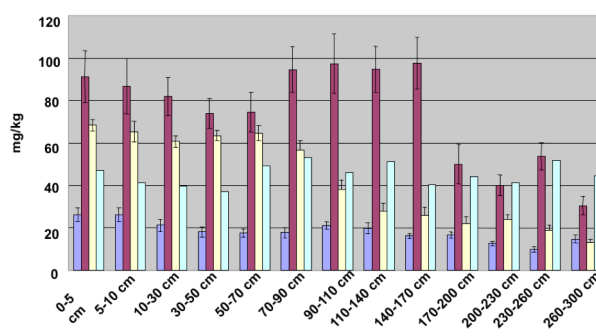


Figure 2. $\text{HNO}_3\text{-H}_2\text{O}_2$ -extractable lead concentration of different layers of soils (blue: Tivadar; burgundy: Vásárosnamény; and yellow: Rakamaz; light green: Tiszacsege).

Soil samples were air dried and sieved (< 2 mm) for further analysis. The chemical analysis was carried out in accordance with a Hungarian Standard [12], using $\text{HNO}_3\text{-H}_2\text{O}_2$ digestion, which yields total elemental contents. The extraction of the easily available metal contents was conducted according to Lakanen and Erviö [13].

Sequential extractions were performed to determine the concentration of metals associated with different operationally defined soil fractions, in the course of which, stronger and stronger extractants are used to remove metals from the sample. In this case the McGrath method [14] was used, which uses 0.1 M CaCl_2 to determine water soluble and exchangeable metal fractions, 0.5 M NaOH to determine the fraction of metals bound to organic matter; 0.05 M Na_2EDTA to determine metals bound to carbon and finally, destruction using *aqua regia* determines the residual fraction. In order to obtain the standard data we used a Merck-made (E. Merck, Darmstadt, Germany) analytical grade HNO_3 (65%) solution. Merck and BDH standard solutions were used to prepare the stock solutions, and REANAL (Budapest, Hungary) solid chemicals were used. Ultrapure water was used to prepare the solutions (Millipore, Paris, France).

Samples were analysed using an Inductively Coupled Plasma - Optical Emission Spectrometer (ICP-OES) to determine Cu content (Perkin-Elmer Optima 3300 DV; Perkin-Elmer Ltd., Shelton, USA). The Pb content was measured by a QZ 939 GF-AAS (Unicam) in 2000 and by an X7 ICP-MS (Thermo Fischer Scientific) between 2011 and 2013.

Target analytics were Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, and Zn. In this study, we focused on Cu and Pb, because these

elements were connected to the contamination on the floodplain. Certified standard materials used in QA/QC were BCR CRM 141R: calcareous loam soil [15]; BCR CRM 142R: light sandy soil [16], and BCR CRM 143R: sewage sludge amended soil [17]. We assumed that the investigation of the upper 30 cm soil layer every five years using sequential extraction could give accurate information about the changes in the bioavailability of heavy metals and the rearrangement among fractions. All statistical analyses were performed using SPSS (version 22.0).

3. Results and Discussion

Figs. 1 and 2 show the total elemental composition for the four sampling sites. Although replicate cores and sampling locations differ, they show an overall trend. The Cu content of the topsoil was higher than that of the lower layers formed earlier. Data indicates that the Cu and Pb contents of the topsoil are greater in Vásárosnamény compared to in Tivadar, possibly due to the combined effects of the two contamination incidents convening at the confluence of the rivers Tisza and Szamos. The 70 to 170 cm soil layers at Vásárosnamény show high lead content.

The Lakanen-Erviö soluble element content is shown in Figs. 3 and 4. Data indicate that the heavy metal content of the floodplain soils is greater in Vásárosnamény compared to in Tivadar. From this point downstream, the level of contamination appears to decrease with distance, with the lowest value (data not shown) in the topsoil of the arboretum at Tiszakürt (275 river km) where atmospheric deposition may be the

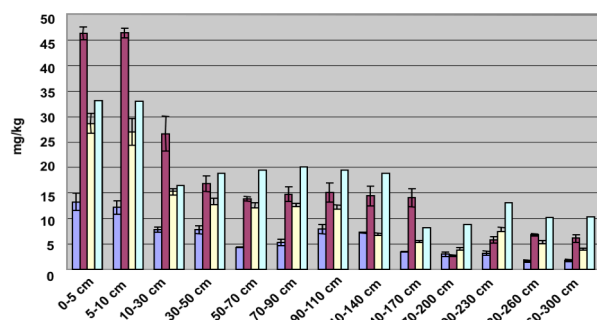


Figure 3. Ammonium-acetate-EDTA (Lakanen-Erviö)-extractable Cu concentration of different layers of soils (blue: Tivadar; burgundy: Vásárosnamény; yellow: Rakamaz; and light green: Tiszacsege).

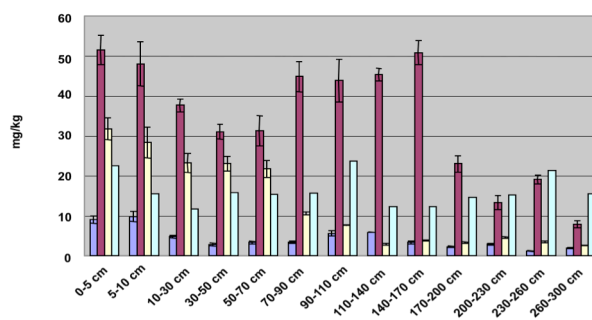


Figure 4. Ammonium-acetate-EDTA (Lakanen-Erviö)-extractable Pb concentration of different layers of soils (blue: Tivadar; burgundy: Vásárosnamény; yellow: Rakamaz; and light green: Tiszacsege).

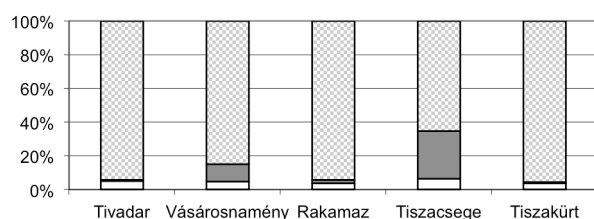


Figure 5. Proportions of the different Cu fractions in the topsoil (solid: CaCl_2 soluble, hollow: NaOH soluble, small dotted: Na_2EDTA soluble, checked: aqua regia soluble).

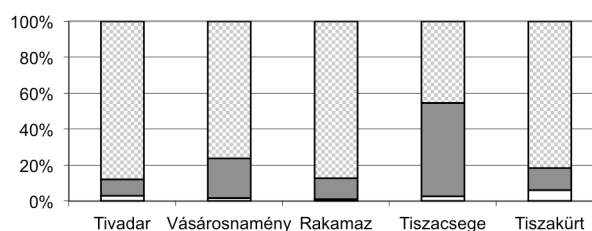


Figure 6. Proportions of the different Pb fractions in the topsoil (solid: CaCl_2 soluble, hollow: NaOH soluble, small dotted: Na_2EDTA soluble, checked: aqua regia soluble).

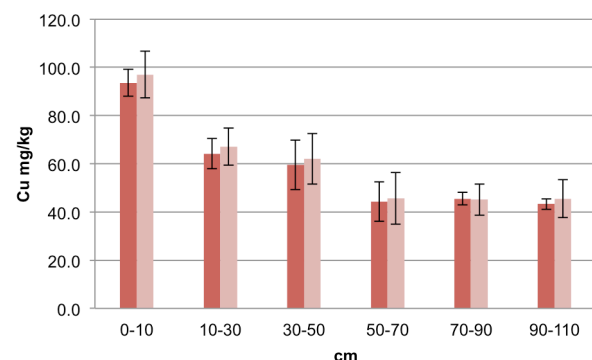


Figure 7. Total Cu concentration ($\text{HNO}_3/\text{H}_2\text{O}_2$ soluble) at Vásárosnamény (dark: 2002, light: 2013).

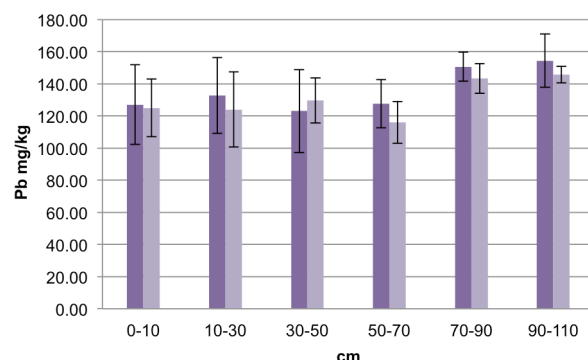


Figure 8. Total Pb concentration ($\text{HNO}_3/\text{H}_2\text{O}_2$ soluble) at Vásárosnamény (dark: 2002, light: 2013).

source of pollution. The Cu content of the upper 10 cm soil layer is nearly twice as high as levels measured in the other layers. The bioavailable Cu and Pb contents at Vásárosnamény exceeded the temporary limit values of Lakanen-Erviö extractable metal contents for soil contamination [18], while the upper soil layer of the Tivadar floodplain appeared to be uncontaminated.

The McGrath method of sequential extraction can be used for assessing the contents of toxic and potentially toxic elements in soil, and their biological effects, i.e. for the determination of the amounts bound to various forms of compounds in soils. The proportion of the water soluble and exchangeable fractions (CaCl_2 extraction fraction) is negligible as regards Cu and Pb. The ratio of metals bound to organic matter (NaOH extraction) is low, according to the expectations, as metals bound to carbonates (Na_2EDTA extraction) is higher in the Vásárosnamény and Tiszacsege soils, but lower at the

other sites. The residual fraction of metals (*aqua regia* extraction) is the largest amongst the samples (Figs.5 and 6).

We determined the Cu and Pd content of the floodplain soils after ten years of the previous waves of contamination. Figs.7 and 8 illustrate the vertical distribution of $\text{HNO}_3/\text{H}_2\text{O}_2$ extractable Cu and Pb contents. There is no statistically proven difference between the results of the samples taken at two different times.

Figs.9–12 show the Lakanen-Erviö soluble element contents of the same core. There is no statistically significant difference between the results of the samples taken at the two different times. The effect of the second source of pollution (Baia Borsa, March 2000) on the available metal contents of the Tivadar floodplain was not detectable, which is in accordance with the results of Szabó et al. [19].

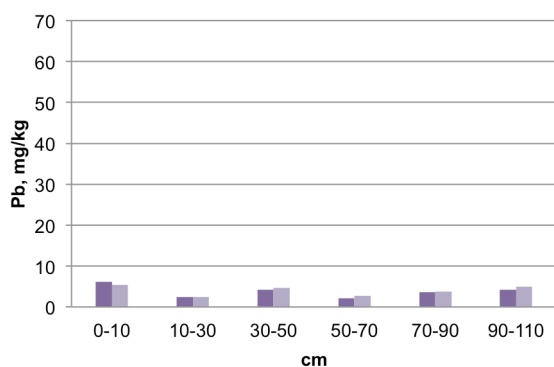


Figure 9. Soluble Pb contents of the 110 cm deep soil profile at Tivadar (dark: 2002, light: 2013).

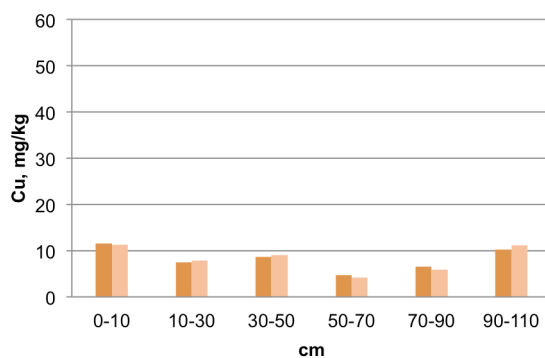


Figure 10. Soluble Cu contents of the 110 cm deep soil profile at Tivadar (dark: 2002, light: 2013).

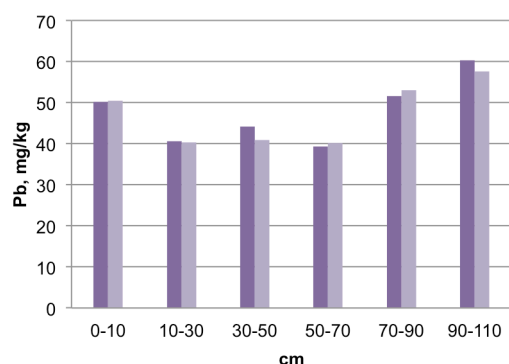


Figure 11. Soluble Pb contents of the 110 cm deep soil profile at Vásárosnamény (dark: 2002, light: 2013).

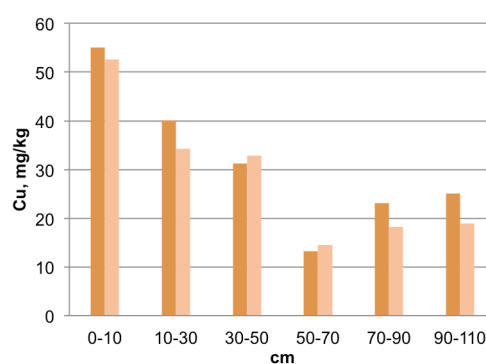


Figure 12. Soluble Cu contents of the 110 cm deep soil profile at Vásárosnamény (dark: 2002, light: 2013).

4. Conclusion

The Cu and Pb contents of the topsoil were found to be the highest in the upper 10 cm layer as a result of the latest sources of contamination. The degree of this effect varies according to the sampling sites. The lowest element content was measured at Tivadar, while samples from Vásárosnamény showed a maximum for many elements because of the first coincidence of the two pollution waves. According to the core samples, higher element contents could be found in some of the deeper layers as marks of former sources of pollution. The investigation of the upper 30 cm soil layer in the coming years using sequential extraction could give accurate information about the changes in the bioavailability of heavy metals and the rearrangement among fractions in addition to laboratory experiments of the effects on soil acidity.

Acknowledgement

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Soós Ernő Water Technology Research and Development Centre was established in 2014 by the Faculty of Engineering at the University of Pannonia, Nagykanizsa Municipality of County Rank and Hidrofit Water Treatment Ltd. The activities at the Research Centre are built on decades of experience and expertise gained in Nagykanizsa in the field of water treatment and water purification. The goal of the Centre is to perform international-level research activities in different areas of water purification and treatment. Nagykanizsa aims to become a centre of knowledge in national and international relations as well. Besides the fundamental research, the Research Centre plays an active role in industrial development activities, putting a great emphasis on drinking water treatment, power plants, the water management of cooling towers, horticulture and irrigation water treatment, seawater desalination, pharmaceutical and infusion solutions, water supply technologies and related control procedures, and areas of measurement technology.

The areas utilising the development results include:

- Treatment methods for drinking and process water,
- Purified water, ultra pure water, and the pre-treatment of water for the injection of pharmaceuticals,
- Water treatment for horticulture and irrigation,
- Wastewater treatment in the oil and gas industries,
- Grey-water recycling,
- Seawater and brackish desalination,
- Water treatment for swimming pools,
- Monitoring and the control of water treatment, and development of instrumentation.

The Soós Ernő Research Centre is named after a pioneer in the water treatment field who was a chemical and environmental engineer. He made great contributions to the field with his innovative thinking. Several patents in water treatment are tied to his name. The desire of the research team is to advance his work by drawing on his leadership and scientific work as new frontiers in water treatment are pursued.

As an initiative of this decision, the Research Centre organised its first scientific conference in December 2014, entitled **Water and Wastewater Treatment in Industry**. Nearly 50 presenters attended the conference from both industry and academia with about 170 participants. Based on unanimous support, this conference has become international. In addition to industry and academia, companies from the service sector are also invited. The conference will be held on **28th October 2015**, and will be preceded by a project partner meeting.

At the conference, the winners of the **Soós Ernő Young Researchers Award** will also be announced. This award is a scientific grant for MSc and PhD candidates. The candidates are invited to submit their theses for nomination from the field of water and wastewater treatment and related disciplines.

The University of Pannonia has a long tradition of academic excellence based on the training of engineering specialists for industry and the economy. The Faculty of Engineering and the Nagykanizsa Campus of the University of Pannonia are committed to forging close and productive partnerships with industry. The **water and wastewater treatment system operation programme** is designed for engineering and non-engineering graduates who are interested in pursuing a career within companies and organisations involved in water and wastewater treatment.

High-quality academic education is offered together with hands-on training. By participating in the study programme, state-of-the-art knowledge compatible with the current needs of industries and the most advanced water purification technologies applied are acquired.

TOXICOLOGY ASPECTS OF THE DECOMPOSITION OF DIURON BY ADVANCED OXIDATION PROCESSES

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Diuron is a phenylurea-based residual herbicide with toxic and endocrine disrupting effects. The aims of the present work were the comparison of the efficiency of various advanced oxidation processes, such as direct ultraviolet photolysis, ozonation, their combination, and heterogeneous photocatalysis from the point of view of the transformation rate of diuron, rate of mineralisation and dehalogenation, formation of aromatic intermediates, and ecotoxicological effects of the formed multicomponent solutions during the treatments. The initial rates of transformation of diuron are in the order of ozonation < heterogeneous photocatalysis < UV photolysis < combination of UV photolysis and ozonation. Each method provided similar tendencies in the decrease of the concentration of organically bound chlorines (AOX) since, until the diuron was completely degraded, the concentration of AOX decreased almost to zero in each case. However, only heterogeneous photocatalysis was found to be effective in terms of mineralisation. Ecotoxicological results showed that in each case, except for ozonation, the toxicity of the treated solutions changed through a maximum during the transformation of diuron. The maximum value was found to be lower in the case of heterogeneous photocatalysis. Thus, the formation and decomposition of by-products of relatively higher toxicity than diuron can be supposed. Our results confirmed that the amount of the formed (aromatic) intermediates, their quality and specific toxicity strongly depend on the applied processes.

Keywords: phenylurea, ozonation, ultraviolet photolysis, heterogeneous photocatalysis, *Daphnia magna*, *Vibrio fischeri*

1. Introduction

Diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea, *Fig. 1*) is a phenylurea-type residual herbicide that is widely used throughout the world. It is registered in the European Union's pesticide database, in the U.S. EPA, and the Australian APVMA. Its use is strictly controlled due to its known toxic and presumed endocrine disrupting effects.

It has a broad spectrum of uses, mainly as a total herbicide in non-agricultural areas (roads and railways) for the pre- and post-emergence control of weed-type plants, but it also has plant protection purposes in the case of certain species (e.g. sugar cane and corn) [1]. Another application is as an antifouling agent, either in aquariums or in paint, to prevent algal growth on hulls of boats for example [2]. Diuron has a relatively low water solubility of 42 mg dm⁻³ at 25 °C. It is quite

persistent in soil with a typical half-life of 75.5 days and in water-sediment of 48 days [3]. Based on these data and other investigations [4], it can be concluded that this compound and its metabolites pollute the environment over an extended period of time, by leaching and run-off into ground and surface waters. This causes concerns regarding the ecosystem, mainly for aquatic plants (as the main method of action of the compound is to block photosynthesis), but also lower aquatic animals, and later presumably even more advanced organisms in the wild as well as the human body. Therefore, contaminated soils and waters have to be treated in an efficient and environmentally friendly

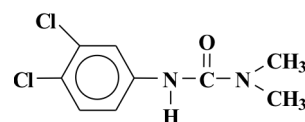


Figure 1. Schematic chemical structure of diuron (N-(3,4-dichlorophenyl)-N,N-dimethylurea).

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manner. For water treatment purposes advanced oxidation processes (AOPs) seem to be sensible choices as secondary treatments, as they are effective, environmentally friendly and economical methods for the elimination of pollutants such as pesticides. These treatments are based mainly on the generation of highly reactive hydroxyl radicals that can induce the degradation of organic matter. The transformation of the target substance can be induced by direct photolysis given that the target molecule is able to absorb irradiating light. It can also be induced by ozonation, which is used as an industrial scale supplementary water treatment method. Alternatively, heterogeneous photocatalysis, the Fenton-reaction or a combination of all the above can also be used [5–9]. Benítez et al. [10] investigated the transformation of phenylurea herbicides during the ozonation of natural waters and determined the reaction rate constants of diuron with both ozone ($16.5 \pm 0.6 \text{ mol dm}^{-3} \text{ s}^{-1}$) and the hydroxyl radical ($6.6 \pm 0.1 \times 10^5 \text{ mol dm}^{-3} \text{ s}^{-1}$).

During the oxidative transformation of diuron several aromatic by-products form. The main attack sites for hydroxyl radicals are the aromatic ring and the methyl group, leading to de-chlorinated or demethylated derivatives. In some cases, the reaction with the hydroxyl radical can lead to ring opening by-products. The most important intermediates are 1-(3,4-dichlorophenyl)-3-methylurea, N'-(3-chlorophenyl)-N,N-dimethylurea, 1-(3,4-dichlorophenyl)urea and 3,4-dichloroaniline [4].

Toxicological studies regarding diuron and its metabolites showed that the parent compound is usually less toxic than a multicomponent solution containing its metabolites; however, total toxicity decays with treatment time [4]. The mode of action of diuron is to block the Hill reaction during photosynthesis. Two of its metabolites, 1-(3,4-dichlorophenyl)-3-methyl-urea and N'-(3-chlorophenyl)-N,N-dimethylurea, retain this specific effect; however, the demethylation of diuron decreases its ability to bind to photosystem II [11].

The aim of the present work was the comparison of the efficiencies of various advanced oxidative processes, such as direct ultraviolet (UV) photolysis, ozonation, the combination of these and heterogeneous photocatalysis. This comparison was made regarding the rate of transformation of diuron, the rate of mineralisation and dehalogenation, the formation of aromatic intermediates and the ecotoxicological effects of the multicomponent solutions formed as a result of the treatments.

2. Experimental

2.1. The Light Sources and Experimental Apparatus

For ozonation and its combination treatment, the light source was a low-pressure mercury vapour lamp, which emits 254 nm ultraviolet (UV) and 185 nm vacuum ultraviolet (VUV) light (UV/VUV lamp). This lamp

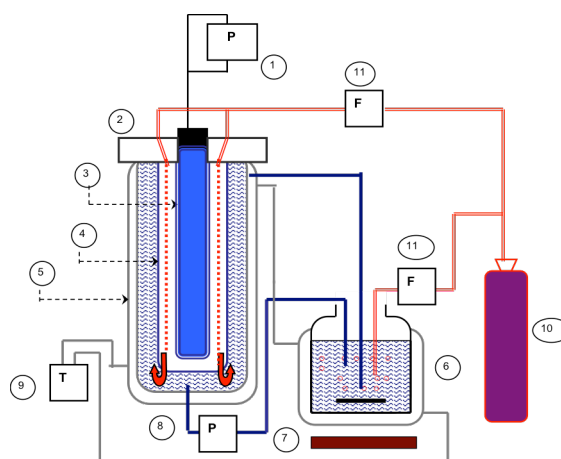


Figure 2. The experimental apparatus. 1: power supply; 2: teflon packing ring; 3: light source with sleeve; 4: envelope; 5: reactor; 6: reservoir; 7: magnetic stirrer; 8: pump; 9: thermostat; 10: air bottle; 11: flow meter from Ref. [13].

(GCL307T5VH/CELL, LightTech, Hungary) was covered with a high purity quartz sleeve, which transmits both 185 nm VUV and 254 nm UV light. Ozone was generated by the VUV photolysis of pure molecular oxygen in the gas phase. For direct UV photolysis, the sleeve of the same low-pressure mercury vapour lamp made of commercial quartz (GCL307T5/CELL, LightTech, Hungary), which transmits 254 nm UV light and absorbs 185 nm VUV light (UV lamp). Another light source, a specific fluorescent UV lamp (LighTech, Hungary) emitting between 300 and 400 nm (maximum intensity at 365 nm) was applied during heterogeneous photocatalysis.

The electric (15 W electric input) and geometric parameters (227 mm arc length, 307 mm length and 20.5 mm external diameter of the sleeves) of the different light sources corresponded to each other. The emitted photon fluxes were determined by ferrioxalate actinometry [12] and were found to be $8.10 \pm 0.65 \times 10^{-6} \text{ mol photon}(254\text{nm})\text{s}^{-1}$ for low-pressure mercury vapour lamps (UV/VUV and UV) and $1.20 (\pm 0.06) \times 10^{-5} \text{ mol photon}(300\text{--}400\text{nm})\text{s}^{-1}$ for the specific fluorescent lamp.

All experiments were performed in the same photoreactor (Fig.2). The light source, surrounded by an envelope was centred in a water-cooled, tubular glass reactor (340 mm length, 46 mm inner diameter). In the course of the measurements, envelopes (320 mm length and 28 mm internal diameter) made of various materials were used. The thermostat controlled ($25 \pm 0.5 \text{ }^\circ\text{C}$) solution of pesticide (500 cm^3 , $c_0 = 1.7 \times 10^{-4} \text{ mol dm}^{-3}$) was circulated ($375 \text{ cm}^3 \text{ min}^{-1}$) continuously and stirred with a magnetic stirrer bar in the reservoir. Before each experiment, air was bubbled through the solution at least for 10 min. The injection of the air was continued throughout the experiment. The kinetic measurements were initiated by switching on the light source.

Ozonation, UV photolysis or the combination of these methods could be applied by the careful selection of the light source and apparatus envelope. Ozonation

was performed using a UV/VUV lamp and perforated glass envelope. Oxygen flowed through the Teflon packing ring between the wall of the lamp and envelope, which separates the gas phase and aqueous solution, as shown in Fig.2. The ozone was generated by the direct VUV photolysis of molecular oxygen and bubbled through the perforated envelope into the solution.

Using a UV lamp and non-perforated quartz envelope, UV photolysis at 254 nm could be investigated. In the case of the combination of UV photolysis with ozonation, a perforated quartz envelope was used. When heterogeneous photocatalysis was applied, the specific fluorescent lamp and non-perforated glass envelope were used. Thus, the efficiency of these processes could be compared using the same energy consumption.

2.2. Analytical Methods and Materials

The concentration of diuron was determined using an HPLC system (Merck Hitachi L-7100 with L-4250 UV-Vis detector). The separation of aromatic compounds was achieved with an RP-18 column (Licrospher 100), using 60 % methanol and 40 % water as eluents, with a flow rate of $0.8 \text{ cm}^3 \text{ min}^{-1}$. The quantification wavelength for UV detection was 210 nm.

Spectra (200 to 400 nm) of the samples during each degradation measurement were acquired on an Agilent 8453 spectrophotometer using 2 mm cuvettes. The concentration of ozone in the gas phase was measured using the same spectrophotometer in a flow cell at 254 nm ($\epsilon(254 \text{ nm}) = 2,952 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ [14]), and was found to be $1.37 \times 10^{-5} \text{ M}$, using oxygen gas.

The adsorbable organic halogen (AOX) content was recorded using an AOX analyser, which consisted of an Analytik Jena multiX 2500 AOX sample unit and an APU2 sample preparation unit. Samples were adsorbed on active carbon, transferred into the AOX furnace and burned at $950 \text{ }^\circ\text{C}$ under an oxygen flow. Chlorine was quantified using a micro-coulometric method. The total organic carbon (TOC) content was determined using a multi N/C 3100 analyser (Analytik Jena).

The toxicity towards *Daphnia magna* was determined using Daphtoxkit FTM magna (MicroBioTests Inc.) tests according to the ISO Standard 6341. The ephippia were used after 72–90 h of hatching time at $21 \text{ }^\circ\text{C}$, applying 6000 lx bottom illumination and after 2 h of pre-nourishment. The zooplankton containing samples were incubated under the same conditions for 48 h, and 8–10 neonates were added to each sample. The number of the neonates was counted using a $3 \times 8 \times$ table-gooseneck magnifier (VWR). Mortality values were given as the percentage of the dead and/or immobilised neonates compared to their initial number.

The toxicity towards *Vibrio fischeri* luminescent bacteria was determined by measuring the natural light emission of these microorganisms using a HACH-LANGE LUMISTox 3000 luminometer. The inhibition of the light emission in the presence of the sample was determined against a non-toxic control. NaCl was added to each sample to obtain a 2 % solution. The samples

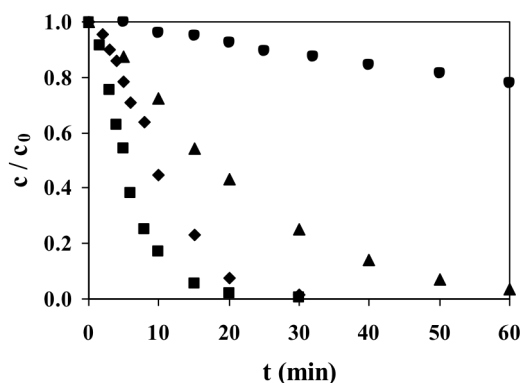


Figure 3. Kinetic curves of the transformation of diuron using ozonation (●), heterogeneous photocatalysis (□), direct UV photolysis (◆) and the combination of UV photolysis with ozonation (■).

were diluted by half with 1.0 mol dm^{-3} NaOH and 1.0 mol dm^{-3} HCl solutions to achieve a pH value of 7 ± 0.2 . Samples containing bacteria were incubated at $15 \text{ }^\circ\text{C}$ for 15 min before the toxicity measurements. Samples for the toxicity tests were taken at the same degradation degrees (0, 12, 25, 50, 75, 100, and above 100 %) of diuron for the treatments.

The decomposition of diuron, as characterised by the initial rate of transformation, which was obtained from linear regression fits to the actual concentration of pesticide versus the time of irradiation, up to 30 % of the concentration of the transformed target compound.

Diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea, purity 98 %) was purchased from Sigma-Aldrich and used without further purification. Ultrapure water obtained from a Millipore Milli-Q System was utilised for the preparation of all stock solutions and HPLC eluents. HPLC-grade methanol was purchased from Hipersolv Chromanorm. The Degussa P25 photocatalyst ($49 \text{ m}^2 \text{ g}^{-1}$ surface area, 90:10 anatase/rutile ratio with 25.4 and 40 nm primary particle size, respectively) with 0.5 g dm^{-3} loading was used during the heterogeneous photocatalytic experiments.

3. Results and Discussion

3.1. The Rate of Transformation of Diuron

In the present work, the initial rate (r_0) of transformation of diuron was determined using various advanced oxidation processes. These can be ranked as ozonation ($r_0 = 1.0 \pm 0.05 \times 10^{-8} \text{ mol dm}^{-3} \text{ s}^{-1}$) < heterogeneous photocatalysis ($r_0 = 7.9 \pm 0.3 \times 10^{-8} \text{ mol dm}^{-3} \text{ s}^{-1}$) < UV photolysis ($r_0 = 13.6 \pm 1.2 \times 10^{-8} \text{ mol dm}^{-3} \text{ s}^{-1}$) < combination of UV photolysis and ozonation ($r_0 = 27.3 \pm 1.2 \times 10^{-8} \text{ mol dm}^{-3} \text{ s}^{-1}$) (Fig.3).

The rate of direct photolytic transformation is determined by the molar absorbance of the target compound and quantum yield of the photolytic process. The absorption coefficient of diuron at the irradiation wavelength of the lamp (254 nm) was determined by using the Beer-Lambert law, and was found to be $\epsilon = 15,000 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$. Djebbar et al. [15] determined

the quantum yield of the photolysis of diuron at 254 nm to be 0.0125, insensitive to pH within the range 2–8.5. The apparent quantum yield of the photoinitiated transformation of diuron was calculated on the basis of the absorbed photon flow and initial transformation rate of the target molecule. In the present work, this value was found to be 0.008. At the applied initial concentration ($c_0 = 1.70 \times 10^{-4}$ M), the solution of diuron fully absorbed the emitted photons.

Ozonation was found to be the least effective method (Fig.3). In aqueous solutions, the decomposition of ozone yields reactive oxygen containing species such as hydroxyl radicals, which are generally a stronger oxidising agent than molecular ozone. The decomposition of ozone in an aqueous solution is initiated by hydroxide ions. At a neutral pH and/or under acidic conditions, molecular ozone should be the dominant oxidant species. During the ozonation of diuron the pH strongly decreased from 8.3 to 4.1, consequently, ozone reacts with diuron mainly as molecular ozone and the formation of hydroxyl radicals is irrelevant. Referring to the reaction mechanisms, molecular ozone can react with organic substrates either through cycloaddition to unsaturated bonds or in electrophilic and nucleophilic reactions [16]. Nucleophilic reactions occur at molecular sites exhibiting an electron deficit and, more frequently, on carbons carrying electron-withdrawing groups, such as chlorine.

Based on the values of the initial rate of decomposition, it can be concluded that, by applying the combination of UV photolysis and ozonation, the synergistic effect occurred. The addition of ozone, although in a relatively low concentration, caused the rate of decomposition to double ($r_0(254 \text{ nm} / \text{O}_3) / r_0(254 \text{ nm}) = 2.0$) (Fig.3). Both UV photolysis and ozonation are quite selective methods in the oxidative transformation of organic substances. Their combination via UV photolysis of ozone itself can produce reactive species, mainly hydroxyl radicals. Consequently, the combination of UV photolysis with ozonation generally results in a less selective and more effective method for the oxidative transformation of organic substances. It has to be mentioned, that the relative contribution of direct photolysis to the transformation probably remains high, because of the high molar absorbance of diuron and the relatively low concentration of ozone. Under the employed experimental conditions, light absorption of ozone was negligible compared to that of diuron.

In the present work, the light emitted by the fluorescent lamp was suitable for the excitation of TiO_2 . The direct photolysis of the compound was excluded by the chosen experimental conditions. This was controlled during the measurements. Upon irradiation in the near UV range, electron hole pairs are formed in the TiO_2 nanoparticles. These charges may reach the surface of the catalyst particle, and undergo redox reactions with substrates or dissolved molecular oxygen, producing highly reactive species such as hydroxyl radicals and hydroperoxyl or superoxide radicals, which can efficiently oxidise the organic pollutants. Besides, contaminants adsorbed on the surface of the catalyst

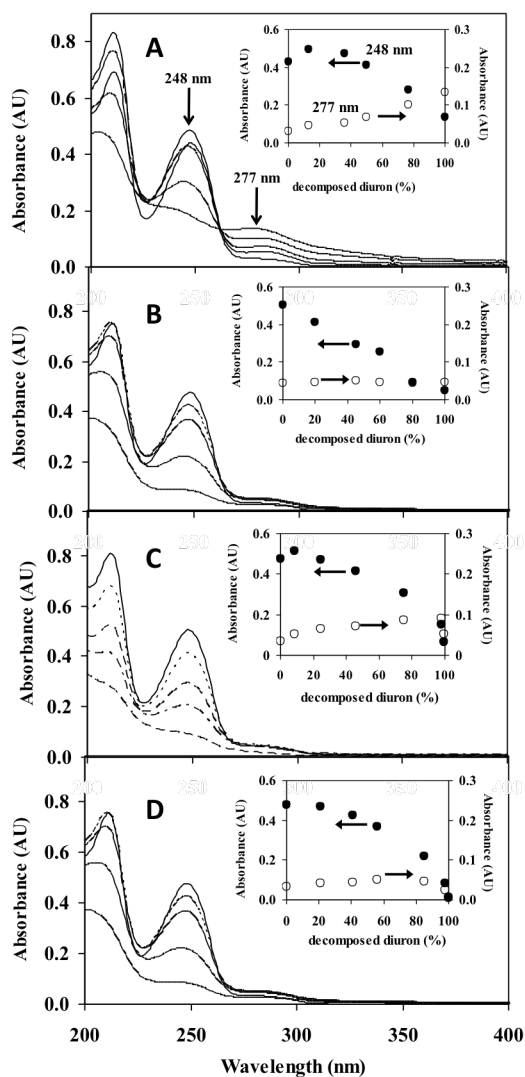


Figure 4. Spectra of the samples treated with UV photolysis (a), ozonation (b), combination of UV photolysis with ozonation (c) and heterogeneous photocatalysis (d) at 0, 25, 50, 75 and 100 % decomposition of diuron (inserted figures show the absorbances at 248 nm (●) and 277 nm (○) versus the decomposed diuron).

particles can directly react with the photochemically formed holes and electrons, promoting the processes of mineralisation. Comparing the efficiency of heterogeneous photocatalysis to direct photolysis, this method is less efficient, but much more efficient than ozonation in the case of the transformation of diuron (Fig.3).

3.2. Spectrophotometric Measurements

Spectrophotometric measurements were carried out on each treatment experiment. The spectra of solutions show that the absorbance at 277 nm increased during the decomposition of diuron while the absorbance at 248 nm changed according to the maximum curves in UV irradiated solutions (Fig.4a). It has to be mentioned, that the absorbance at 277 nm decreased slowly after the decomposition of diuron. This suggests that aromatic

intermediates accumulated and probably decomposed during the UV initiated transformation.

The maximum value of the absorbance at 277 nm was found to be much higher in UV irradiated solutions (0.145) (Fig.4a) than in the case of the combination of ozonation with UV photolysis (0.09) (Fig.4c). This suggests that the addition of ozone strongly enhanced the rate of formation and decomposition of these intermediates and consequently, hindered their accumulation, most likely due to radical based reactions. The time dependence of the relative absorption at 277 nm suggests that not only the formation, but also the decomposition of these aromatic intermediates took place. This latter process was partly completed in parallel with the transformation of the parent compound, and partly after its transformation. The colour of the aqueous solution of diuron changed from colourless to intensive yellow-pink when UV photolysis was applied. At the same time, when the combination of UV photolysis with ozonation was applied, the change in colour was less intensive. Each solution became colourless after the decomposition of diuron. Using ozonation (Fig.4b) or heterogeneous photocatalysis (Fig.4d) neither the change in colour of the solution, nor increase in absorbance at 277 nm was observed. This suggests that the coloured aromatic intermediates were most probably formed mainly during the direct UV photolysis of diuron. These results and observations also suggest that the amount and quality of the aromatic intermediates strongly depend on the applied process.

3.3. Dehalogenation and Mineralisation

UV photolysis, ozonation, the combination of these and heterogeneous photocatalysis provided similar tendencies with respect to the decrease in concentration of adsorbable organically bound chlorines (AOX), since in each case, until the 100 % transformation of diuron was achieved, the concentration of AOX decreased by almost 100 % (Fig.5a). This means that not only the pesticide itself, but the formed halogenated by-products were also de-chlorinated simultaneously within the timeframe of transformation of the parent substance. It has to be mentioned, that the rate of dechlorination was higher in the case of UV photolysis than heterogeneous photocatalysis, mainly at the beginning of the treatment. Direct UV photolysis is a quite selective method for the transformation of organic substances and can be effective for the transformation of compounds, which highly absorb at 254 nm (such as diuron and probably its aromatic intermediates), mainly by the dissociation of the carbon-halogen bond. On the other hand, in the case of heterogeneous photocatalysis, adsorption has an important role. Competitive adsorption can occur between the aromatic compounds containing chlorine atom(s) and the formed intermediates, which do not contain chlorine atom, and exhibit better adsorptivity (mainly carboxylic acids). Consequently, the formation of these intermediates and their adsorption on the

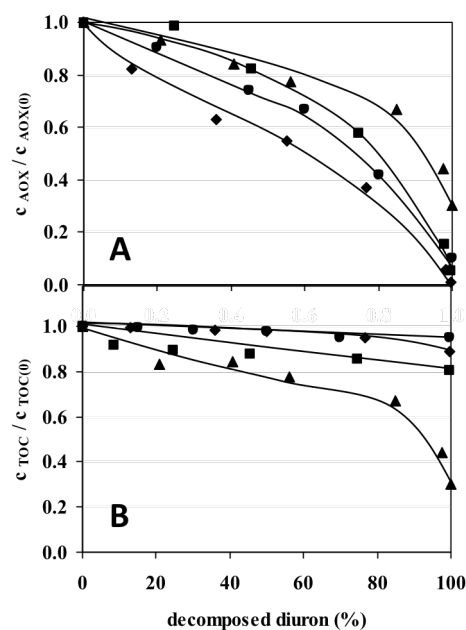


Figure 5. Kinetic curves of the transformation of diuron using ozonation (●), heterogeneous photocatalysis (□), direct UV photolysis (◆) and the combination of UV photolysis with ozonation (■).

surface of the photocatalyst can cause a relatively slow decrease in the rate of dechlorination (Fig.5a).

Ozonation is a quite selective method for the transformation of organic substances, similar to direct UV photolysis. These methods are generally not effective in terms of mineralisation, as also observed in this work (Fig.5b). In the case of the combination of these methods the TOC content slightly decreased, most likely because of the hydroxyl radical based reactions. In the case of heterogeneous photocatalysis, the rate of mineralisation was very low at the beginning, but the TOC decreased rapidly in the final stage of decomposition of diuron (Fig.5b). Compared to UV photolysis and ozonation, heterogeneous photocatalysis is a less selective method and generally results in the transformation and, in most cases, the mineralisation of a large variety of organic substances.

However, the transformation of compounds takes place on the surface of TiO_2 particles, thus adsorption has a crucial role in this case, as mentioned previously. It is probable that the superior adsorptivity of aliphatic intermediates (mainly carboxylic acids) is the reason why mineralisation takes place in parallel with the transformation of parent compounds. This explanation is in agreement with the observation that the rate of the change in concentration of AOX increased when mineralisation became dominant (Fig.5).

3.4. Ecotoxicological Measurements

The results obtained from both Daphtoxkit FTM and *Vibrio fischeri* luminescence inhibitory tests showed that the toxicity of the treated solutions changed through a maximum value within the time frame of transformation of diuron in solutions irradiated with 254 nm UV light (Figs.6a and 7a). Consequently, the

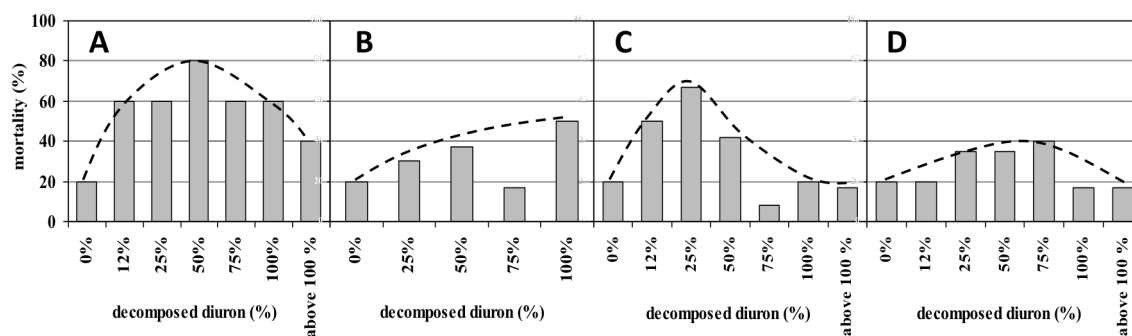


Figure 6. Mortality of *Daphnia magna* after UV photolysis (a), ozonation (b), the combination of UV photolysis with ozonation (c) and heterogeneous photocatalysis (d) at 0, 12, 25, 50, 75, 100 % and above 100 % (samples taken 10 minutes after total decomposition) decomposition of diuron.

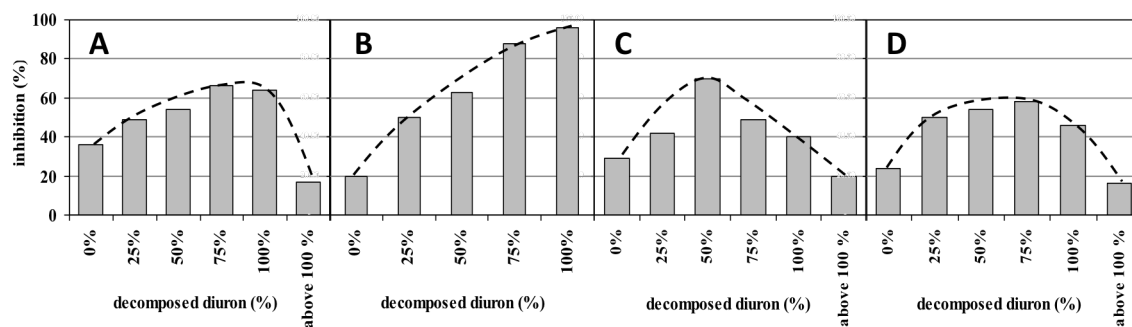


Figure 7. Inhibition values for *Vibrio fischeri* after UV photolysis (a), ozonation (b), the combination of UV photolysis with ozonation (c) and heterogeneous photocatalysis (d) at 0, 12, 25, 50, 75, 100 % and above 100 % (samples taken 10 minutes after total decomposition) decomposition of diuron.

formation and decomposition of by-products exhibiting relatively higher toxicities than expected from diuron.

During ozonation, both the mortality and inhibitory effect increased, which can be explained by the formation and accumulation of intermediates more toxic than the parent compound (Figs.6b and 7b). The tendencies of mortality and the inhibitory effect were similar, although mortality increased slightly, and the inhibitory effect increased strongly during the transformation of diuron. It can be supposed, that *Vibrio fischeri* is more sensitive to the presence of the intermediates formed due to the reaction of molecular ozone with diuron, which can be the reason for this observation.

In the case of the combination of UV photolysis with ozonation, the mortality and inhibitory effect changed through maxima (Figs.6c and 7c), in a similar way to direct UV photolysis. However, in this case the maxima were reached at 25 % and 50 % decomposition of diuron (Figs.6c and 7c), while during UV photolysis the maxima were reached at 50 % and 75 % decomposition of diuron (Figs.6a and 7a).

Using heterogeneous photocatalysis, the mortality and inhibitory effect changed also through maxima (Figs.6d and 7d). At the same time, it has to be mentioned, that in this case, the values of the maxima were found to be lower than those determined in the case of UV photolysis and its combination with ozonation, mainly in the case of results obtained using the Daphtoxkit FTM test. The mortality using heterogeneous photocatalysis did not reach 40 %, while in the case of UV photolysis and its combination with UV photolysis it exceeded 60 %. This confirms that the amount of the aromatic intermediates was less, and/or

their specific toxicity was lower than in the case of UV photolysis and its combination with ozonation.

At this point, a correlation can be established between the results of spectrophotometric measurements and ecotoxicological tests. In the case of UV photolysis, the formation and accumulation of aromatic intermediates were supposed, while in the case of the combined method, their amount was likely to be lower. At the same time, in the case of heterogeneous photocatalysis, their formation was less favourable than in the presence of 254 nm UV light. These observations, together with the results of the ecotoxicological tests, suggest that the toxic intermediates are most likely aromatic by-products.

4. Conclusion

In this work, various advanced oxidation processes, such as UV photolysis at 254 nm, ozonation, their combination and heterogeneous photocatalysis were investigated and compared regarding the oxidative transformation of diuron. The initial rates of transformation were determined at the same electric energy input and exhibited the following order: ozonation < heterogeneous photocatalysis < UV photolysis < combination of UV photolysis and ozonation.

The results obtained from spectrophotometric measurements suggested that aromatic intermediates accumulated during the UV initiated transformation of diuron. The addition of ozone of relatively low concentration strongly enhanced the rate of formation and/or decomposition of these intermediates. Using ozonation or heterogeneous photocatalysis, the amount

of the formed aromatic intermediates was likely to be lower.

UV photolysis, ozonation, their combination and heterogeneous photocatalysis provided similar tendencies in the decrease of the concentration of adsorbable organically bound chlorines (AOX) since, in each case, until the 100% degradation of diuron was achieved, the concentration of AOX decreased by almost 100%. On the other hand, only heterogeneous photocatalysis was found to be effective in terms of mineralisation during the decomposition of diuron. In this case, the rate of mineralisation was low at the beginning, but the total organic carbon content decreased rapidly in the final stage of the decomposition of diuron.

Ecotoxicological measurements were carried out with both Daphtoxkit FTM and *Vibrio fischeri* luminescence inhibitory tests. The results showed that the toxicity of the treated solutions changed through a maximum curve within the time of transformation of diuron in each case, except for with ozonation. Thus, the formation and decomposition of by-products, having relatively higher toxicity than diuron, can be supposed. Using heterogeneous photocatalysis, the mortality and inhibitory effect also changed through maxima, but the values of the maxima were found to be lower than that determined in the case of UV photolysis and its combination with ozonation. Our observations and results confirmed that the aromatic intermediates formed, their quantity, and specific toxicity strongly depend on the applied process.

Acknowledgement

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ORGANISATION OF THE ANALYTICAL, STOICHIOMETRIC, AND THERMODYNAMIC INFORMATION FOR WATER CHEMISTRY CALCULATIONS

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A common feature of the chemical processes of the hydrosphere and water treatment plants is that essentially the same types of chemical equilibrium reactions occur in both fields. These equilibria could be acid/base, complexation, redox, precipitation, and interfacial processes. Since these reactions may also occur in combination, the aqueous environments are unavoidably multispecies systems. Due to multiple equilibria, the state of aggregation, the state of oxidation, as well as the electric charge of the species may change dramatically. Calculation of the equilibrium concentration of the species is facilitated by the availability of analytical, stoichiometric, and thermodynamic information that are consistently organised into an ASTI matrix. The matrix makes it possible to apply a uniform algebraic treatment for all occurring equilibria even, if later on, further reactions have to be included in the chemical model. The use of the ASTI matrix enables us to set up the necessary mass balance equations and equilibrium relationships, which together form a non-linear system of equations (NLSE). The goal of our paper is to show that the use of the ASTI matrix approach in cooperation with the powerful engineering calculation software, MATHCAD14, results in fast and easy handling of the NLSE-s and, consequently, the calculations of speciation in aqueous systems. The paper demonstrates the method of application in three examples: the calculation of the pH dependence of the solubility of calcite in closed and open systems, the calculation of the pH and p_e in a system where acid/base reactions, complexation equilibria, and redox equilibria occur, and a study of adsorption of lead ions on aluminium oxide.

Keywords: multiple solution equilibria, ASTI matrix method, solubility of calcite, redox calculation, adsorption of lead

1. Introduction

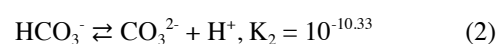
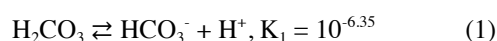
Information on the speciation profile of aqueous systems is of primary importance in many fields of chemistry. The usual acid/base, complexation, redox, precipitation, and interfacial reactions may occur simultaneously leading to the formation of a large number of species in both natural and artificial aquatic systems. Contemporary numerical and graphical treatments of aqueous equilibria were presented in seminal publications in the fields of environmental engineering [1], natural aquatic systems [2–7] and geochemistry [8, 9]. An important aspect of the recent approaches is the systematic organisation of the analytical, stoichiometric, and thermodynamic information relevant to the studied system. The input of structured information became particularly indispensable in the use of the modern computer programs dedicated to chemical equilibrium modelling: MINEQL [10], MINEQL+ [11], MINTEQA [12], PHREEQC [13], and WHAM [14], to name a few.

2. Methods

2.1. Organisation of Information into the ASTI Matrix

In order to collect and organise data for the equilibrium calculations a strict distinction has to be made between the terms: reagent, reactions, species and components. Under laboratory conditions, reagents (denoted hereafter by A) are simply those chemicals that are present at the beginning of reactions. Each reagent is characterised by its analytical molar concentration (c in mol dm^{-3} or M). Under environmental conditions, we have to assume the presence of a ‘contaminating’ compound of reagents: e.g. acid rain forms as a result of due to the presence of nitric acid in rainwater.

When reagents are mixed, several reactions may take place (the total number of reactions is denoted by R). For each reaction, the relevant equilibrium constant (K) refers to the correct stoichiometry of the reaction, such as



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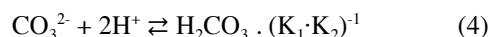
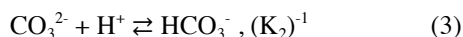
where the K values are given for a specified temperature (25 °C), pressure (101.3 kPa), and ionic strength (0.1 M).

The considered reactions or chemical models generate a large number of chemical particles with appreciable stabilities. This set of entities is called species (the number of species is denoted by S). The smallest subset of selected species that enable us to describe the formation of all the other species of the system are called components (their number is denoted by C). In order to meet the requirements of the Gibbs phase rule [15], the needed number of components has to be calculated from the relationship $C = S - R$. If there are 6 reactions and 10 species then from the list of species four species have to be selected as component $C = 4$. The concept of this component is the “key and door” to the organisation of the database and, consequently, to equilibrium calculations.

In principle, any subset of the species can be selected (promoted) as a component, but chemical considerations dictate some rules that have to be kept in mind:

1. H_2O and H^+ have to always be selected as components,
2. Species with fixed activities whose concentrations do not change during the reactions have to be selected as components too; such species are the solvent (H_2O), solid phases (e.g. $CaCO_3$), and gases of known pressure (e.g. atmospheric CO_2 , $p = 10^{-3.5}$ atm), and
3. Species that are presumably present in dominant concentrations will also be selected as components.

After selecting the components, the formation reactions for the rest of the species have to be written up in terms of these components. The equilibrium (formation) constant of the species is calculated by Hess's law using algebraic manipulation of the reactions, in such a way, to obtain the target reaction. The left-hand side of the target reaction only contains components and the right-hand side only displays the species e.g.: if in the studied system CO_3^{2-} is selected as a component (besides H_2O and H^+) then by using *Eqs.(1)* and (2), the formation of the HCO_3^- and H_2CO_3 species should be given as:



When the formation of all the ($S - C$) species is expressed in this way then the stoichiometric relationship between the components and species is revealed. In addition to this, the stoichiometric connection between the components and reagents has to be established too. This can be done by synthesising the reagents through the reaction of the components, just like in the case of species, but now only the stoichiometric coefficients are relevant.

The above procedure highlights the central role of the component and allows us to arrange the available analytical, stoichiometric and thermodynamic

information into a coherent matrix abbreviated hereafter as the ASTI matrix. The columns and rows of the matrix list the C number of components and all the S number of species, respectively. The elements of the matrix are filled with the respective stoichiometric coefficients (including zeros too). Analytical concentrations (c) and the equilibrium constants (K) are introduced into this matrix as shown in the examples discussed below.

For the calculation of the unknown concentration of S species, we need the S stoichiometrically independent equation. The main purpose of our effort to develop the ASTI matrix is to draw up the required S equations. Based on the columns and rows matrix two types of equations can be drawn up. The mass balance equations (MB) are based on the columns of the ASTI matrix and are drawn up usually for all the C components (in exceptional cases, not all the MB equations are needed, see Example 1. below). The MB equation is, in fact, an additive relationship showing the weighed concentration sum of all species containing the particular component. The weighing factors are the respective stoichiometric coefficients. The other type of equations, based on the ASTI matrix, are the equilibrium relationships (ER). This multiplicative type of equations are drawn up on the basis of the rows of the species. The ER gives the equilibrium concentration of the ($S - C$) species expressed as a product of the concentration of all the C components raised to the power of the stoichiometric coefficients (which could be zeros too). Consequently, the ER-s expresses the concentration of the species in terms of the concentration of the components. It is worth noting, that a different choice of components yields different MB equations and ER (a further indication of the importance of the choice of component in the equilibrium calculation). The application of these principles will be shown in the examples below. The mass balance equations together with the equilibrium relationships form a (usually) non-linear system of equations (NLSE) for calculating the concentration of all the S species.

2.2. Solving the Non-Linear System of Equations (NLSE) using MATHCAD

MATHCAD 14 (PTC. Inc.) is a versatile and powerful engineering calculation software. It works seamlessly with numbers, units, equations, texts, and graphs. After giving the required K , analytical concentration data, and assigning initial values for the unknown variables, the S number of NLSE is introduced on the screen between the Given and Find commands. MATHCAD then rapidly solves the NLSE by using the iterative Levenberg - Marquardt algorithm [16]. For example, the solution of the NLSE with ten unknowns takes only a couple of seconds.

To assign a good guess for ten variables is rather cumbersome; therefore, the algebraic reduction of the number of unknowns is desirable. This can be done by substituting the equilibrium relationships into the mass balance equations, which reduces the number of variables against the number of components ($C < S$). In

Table 1. Comparison of speciation in the $\text{CaCO}_3(\text{s})$ - $\text{H}_2\text{O}(\text{l})$ (closed) and $\text{CaCO}_3(\text{s})$ - $\text{H}_2\text{O}(\text{l})$ - $\text{CO}_2(\text{g})$ (open with $p\text{CO}_2 = 10^{-3.5}$ atm) systems both at 25 °C.

-log C	Closed system	Open system
pH	9.9	8.3
-logCa	3.9	3.3
-log CO_3^{2-}	4.4	5.0
-log HCO_3^-	4.1	3.0
-log H_2CO_3	7.8	5.0

this case, the solution of the C number of NLSE (instead of the S) returns the equilibrium concentration of the components, which are then substituted into the applicable ER to obtain the concentration of the $(S - C)$ species. In addition to this algebraic method of the reduction of variables, chemical considerations may also be applied to reduce the number of species. Chemical background information often suggests that certain species of the system are present in minor concentrations only. These terms may then be safely omitted from the additive type of MB equations and neglected from the set of ER-s. This principle works for the opposite case too. Sometimes it is desirable to improve the original chemical model by including further equilibria. This can be done seamlessly if the new equilibria are expressed also in terms of the components and the ASTI matrix is augmented by the required new data.

The above considerations clearly highlight the appreciable advantage of using the ASTI matrices in association with MATHCAD. The ASTI matrix can be decomposed and treated by the well known methods of matrix algebra. Here; however, we like to keep chemistry in focus, so the matrix algebraic solution is not treated here explicitly, because its elegant and concise formalism conceals chemical insights.

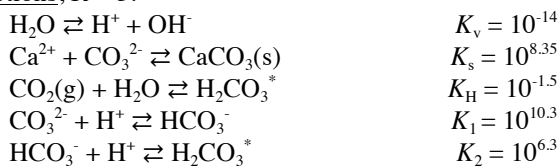
3. Simulation Results

3.1. Calculation of the pH Dependence of the Solubility of Calcite in Open and Closed Systems (Example 1)

The solubility of $\text{CaCO}_3(\text{s})$ in water is calculated as a function of pH for an open and a closed system. The open system is exposed to the atmosphere where $p\text{CO}_2$ is $10^{-3.5}$ atm, where the exchange of CO_2 molecules between the solution and gas phases is allowed. Considering the similarities between the two systems, and for brevity, the process leading to the ASTI matrix and the NLSE is shown only for the open system, while the results are presented for both systems. In the open system, we have three species whose equilibrium concentrations (activity, a) are known ($\text{H}_2\text{O}(\text{l})$ with $a = 1$, $\text{CaCO}_3(\text{s})$ with $a = 1$, $p\text{CO}_2 = 10^{-3.5}$ atm) so, according to rules of selection from above, they have to be selected as components. The details of the procedure are shown below:

Reagents, $A=3$: $\text{H}_2\text{O}(\text{l})$, $a = 1$, $\text{CaCO}_3(\text{s})$, $a = 1$, $p\text{CO}_2 = 10^{-3.5}$

Reactions, $R = 5$:



Species, $S = 9$: H_2O , H^+ , OH^- , CO_3^{2-} , HCO_3^- , H_2CO_3^* , $\text{CO}_2(\text{g})$, $\text{CaCO}_3(\text{s})$, Ca^{2+}

Components, $C = S - R = 4$

H_2O , H^+ , $\text{CaCO}_3(\text{s})$, $\text{CO}_2(\text{g})$

ASTI matrix

S/C	H_2O	H^+	$\text{CO}_2(\text{g})$	$\text{CaCO}_3(\text{s})$	K	(logK)
H_2O	1					
H^+		1				
$\text{CO}_2(\text{g})$			1			
$\text{CaCO}_3(\text{s})$				1		
OH^-	1	-1			K_w	(-14)
Ca^{2+}		2	-1	1	$K_s^{-1} \cdot K_H^{-1} \cdot K_1 \cdot K_2$	(9.8)
H_2CO_3^*	1		1		K_H	(-1.5)
HCO_3^-	1	-1	1		$K_H \cdot K_2^{-1}$	(-7.8)
CO_3^{2-}	1	-2	1		$K_H \cdot (K_1 \cdot K_2)^{-1}$	(-18.1)
A/TOT						M
$a(\text{H}_2\text{O})$	1				1	
$a(\text{CaCO}_3(\text{s}))$				1	1	
$p\text{CO}_2(\text{g})$			1		$10^{-3.5}$	

Mass balance equations, MB

$$\text{TOT} = [\text{H}^+] - [\text{OH}^-] + 2[\text{Ca}^{2+}] - [\text{HCO}_3^-] - 2[\text{CO}_3^{2-}] = 0$$

Equilibrium relationships, ER

$$\begin{aligned} [\text{OH}^-] &= K_v \cdot [\text{H}^+]^{-1} \\ [\text{Ca}^{2+}] &= K_s^{-1} \cdot K_H^{-1} \cdot K_1 \cdot K_2 \cdot (p\text{CO}_2)^{-1} \cdot [\text{H}^+]^2 \\ [\text{H}_2\text{CO}_3^*] &= K_H \cdot p\text{CO}_2 \\ [\text{HCO}_3^-] &= K_H \cdot K_2^{-1} \cdot p\text{CO}_2 \cdot [\text{H}^+]^{-1} \\ [\text{CO}_3^{2-}] &= K_H \cdot (K_1 \cdot K_2)^{-1} \cdot p\text{CO}_2 \cdot [\text{H}^+]^{-2} \end{aligned}$$

The required six equations (MB + ER) are therefore available for the calculation of the six unknown concentrations (H^+ , OH^- , CO_3^{2-} , HCO_3^- , H_2CO_3^* , and Ca^{2+}). The NLSE was solved by MATHCAD and the results are shown in Table 1.

For the closed system, the ASTI matrix can be obtained by omitting the CO_2 from the list of reagents, species and components as well as the K_H equilibria from the list of reactions. As shown in Table 1, the dissimilarity between the pH values is the most remarkable difference between the equilibrium systems. The solubility of the $\text{CaCO}_3(\text{s})$ was also calculated for both systems as a function of pH. Fig.1 shows that in a closed system the solubility tends to be a limiting value as pH increases. The solubility vs. pH function changes dramatically, if the system is open to the atmosphere, $p\text{CO}_2 = 10^{-3.5}$ atm, as shown in Fig.2. As opposed to the closed system, when the calcium-carbonate-water system is open to the atmosphere ($p\text{CO}_2 = 10^{-3.5}$ atm), the solubility continuously decreases as pH increases (compare Figs.1 and 2).

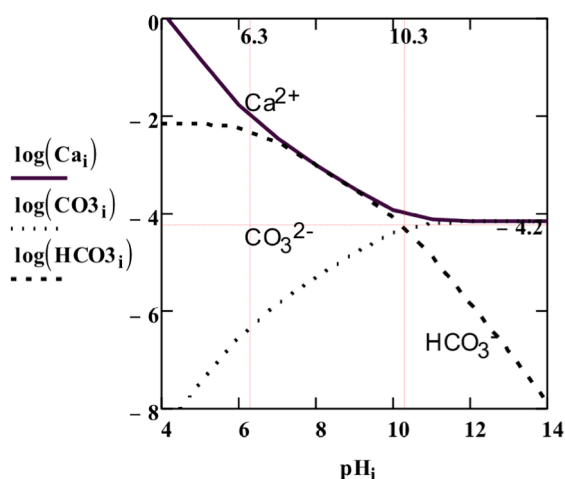


Figure 1. Change in the $-\log(\text{solubility}) = -\log[\text{Ca}^{2+}]$ of the $\text{CaCO}_3(\text{s})$ in a closed system as a function of pH (graphs for $-\log[\text{CO}_3^{2-}]$ and $-\log[\text{HCO}_3^-]$ are also presented).

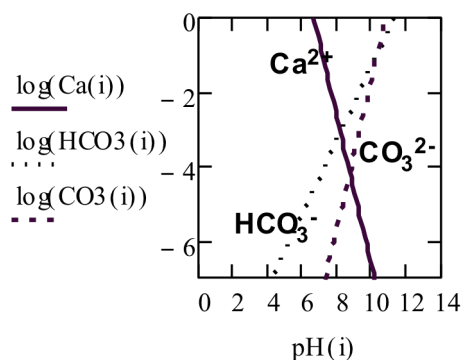


Figure 2. Change in the $-\log(\text{solubility}) = -\log[\text{Ca}^{2+}]$ of the $\text{CaCO}_3(\text{s})$ in an open system as a function of pH (graphs for $-\log[\text{CO}_3^{2-}]$ and $-\log[\text{HCO}_3^-]$ are also presented).

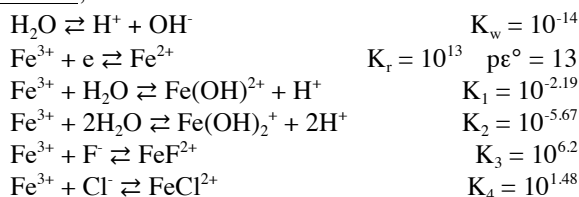
3.2. Calculation of Speciation in the Iron(II)/Iron(III) System Involving Complexation (Example 2)

The pH and $p\epsilon$ values are calculated for the ferrous/ferric ion redox system involving the complexation of the metal ion with the OH^- , Cl^- and F^- ions starting from a hypothetical solution of FeCl_2 , FeCl_3 , NaCl , and NaF . Two additional questions were also addressed, such as what is the measurable redox potential of the system, and if a trace quantity of arsenic gets into this system, what will be the dominant redox form of the arsenic. The organisation of information follows the same flow as outlined above.

Reagents, A

$c(\text{Fe}^{2+}) = 10^{-4} \text{ M}$, $c(\text{Fe}^{3+}) = 10^{-4} \text{ M}$, $c(\text{Cl}^-) = 105 \cdot 10^{-4} \text{ M}$,
 $c(\text{Na}^+) = 105 \cdot 10^{-4} \text{ M}$, $c(\text{F}^-) = 5 \cdot 10^{-4} \text{ M}$

Reactions, R = 6



Species, S = 13: H_2O , H^+ , OH^- , Fe^{3+} , Fe^{2+} , $\text{Fe}(\text{OH})^{2+}$,
 $\text{Fe}(\text{OH})_2^+$, F^- , FeF^{2+} , Cl^- , FeCl^{2+} , Na^+ , e^-

Components, C = S - R = 7: H_2 , H^+ , Fe^{3+} , F^- , Cl^- , Na^+ , e^-

ASTI matrix

S/C	H^+	Fe^{3+}	F^-	Cl^-	Na^+	e^-	K
H^+	1						
Fe^{2+}		1					
F^-			1				
Cl^-				1			
Na^+					1		
e^-						1	
OH^-	-1						K_w
$\text{Fe}(\text{OH})^{2+}$	-1	1					K_1
$\text{Fe}(\text{OH})_2^+$	-2	1					K_2
FeF^{2+}		1	1				K_3
FeCl^{2+}		1		1			K_4
Fe^{2+}		1				1	K_r
TOT							M
cFeCl_2		1		2		1	10^{-4}
cFeCl_3				3			10^{-4}
cNaCl				1	1		10^{-2}
cNaF			1				$5 \cdot 10^{-4}$

Mass balance equations, MB

$$\begin{aligned} \text{TOT H} &= [\text{H}^+] - [\text{OH}^-] - [\text{Fe}(\text{OH})^{2+}] - [2\text{Fe}(\text{OH})_2^+] = 0 \\ \text{TOT Fe} &= [\text{Fe}^{3+}] + [\text{Fe}(\text{OH})^{2+}] + [\text{Fe}(\text{OH})_2^+] + [\text{FeF}^{2+}] + \\ &\quad + [\text{FeCl}^{2+}] + [\text{Fe}^{2+}] = 2 \cdot 10^{-4} \end{aligned}$$

$$\text{TOT F} = [\text{F}^-] + [\text{FeF}^{2+}] = 5 \cdot 10^{-4}$$

$$\text{TOT Cl} = [\text{Cl}^-] + [\text{FeCl}^{2+}] = 3 \cdot 10^{-4} + 2 \cdot 10^{-4} + 10^{-2}$$

$$\text{TOT Na} = [\text{Na}^+] = 10^{-2} + 5 \cdot 10^{-4}$$

$$\text{TOT e} = [e^-] + [\text{Fe}^{2+}] = 10^{-4}$$

Equilibrium relationships, ER

$$[\text{OH}^-] = K_w \cdot [\text{H}^+]^{-1}$$

$$[\text{Fe}(\text{OH})^{2+}] = K_1 \cdot [\text{H}^+]^{-1} \cdot [\text{Fe}^{3+}]$$

$$[\text{Fe}(\text{OH})_2^+] = K_2 \cdot [\text{H}^+]^{-2} \cdot [\text{Fe}^{3+}]$$

$$[\text{Fe}(\text{F})^{2+}] = K_3 \cdot [\text{Fe}^{3+}] \cdot [\text{F}^-]$$

$$[\text{Fe}(\text{Cl})^{2+}] = K_4 \cdot [\text{Fe}^{3+}] \cdot [\text{Cl}^-]$$

$$[\text{Fe}^{2+}] = K_r \cdot [\text{Fe}^{3+}] \cdot [e^-]$$

The system of NLSE generated by seven MB and six ER equations was solved by MATHCAD and the results are summarised in Table 2.

Since the charge and oxidation state of the introduced arsenic species are controlled by the pH and $p\epsilon$ values of the environment, the calculated pH and $p\epsilon$ data make it possible to visualise, which oxidation state would dominate the studied redox-complex system. The relevant predominance area ($p\epsilon$ vs. pH) diagram is shown in Fig.3. According to Fig.3, the calculated pH = 4 and $p\epsilon = 10$ values corroborate the existence of the H_2AsO_4^- anionic arsenic species in this hypothetical system.

Table 2. Calculated pH and pε values and the concentration of the species occurring in the Fe²⁺/Fe³⁺ redox system containing the OH⁻, Cl⁻ and F⁻ coordinating ligands. The measurable electromotive force (EMF) with respect to a calomel reference is also shown (ε_{ref} = 0.244 V).

pH = 4.13	pε = 9.93
[Fe ²⁺] = 1.0 · 10 ⁻⁴	[Fe ³⁺] = 8.5 · 10 ⁻⁸
[Fe(OH) ²⁺] = 7.4 · 10 ⁻⁶	[Fe(OH) ₂ ⁺] = 3.3 · 10 ⁻⁵
[FeCl ²⁺] = 2.7 · 10 ⁻⁸	[FeF ²⁺] = 5.9 · 10 ⁻⁵
[F] = 4.4 · 10 ⁻⁴	[Cl] = 1.0 · 10 ⁻²

ε_{ind} = 0.059 · pε = 0.59 V; EMF = ε_{ind} - ε_{ref} = 0.35 V

Table 3. Speciation of Pb(II) in the presence of adsorbent (γ-Al₂O₃), in 0.1 M NaCl solution at pH = 6.

Species	Molarity
≡XOH	6.3 · 10 ⁻⁵
≡XOH ₂ ⁺	6.3 · 10 ⁻⁵
≡XOPb ⁺	2.4 · 10 ⁻⁶
≡XO ⁻	1.3 · 10 ⁻⁶
Pb ²⁺	1.5 · 10 ⁻⁶
PbCl ⁺	6.0 · 10 ⁻⁶
PbOH ⁺	3.0 · 10 ⁻⁸

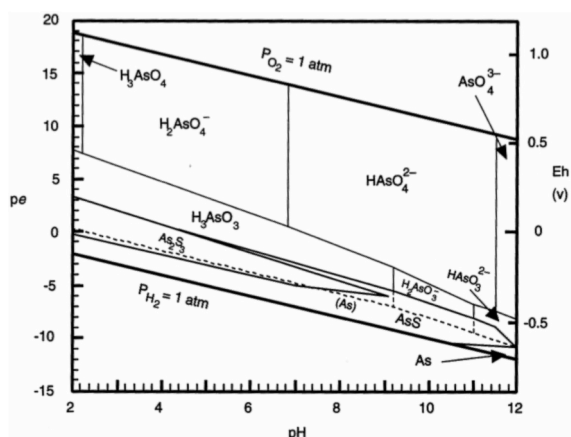


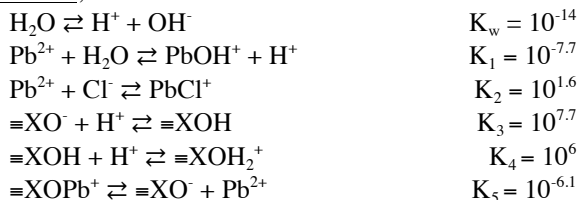
Figure 3. Predominance area (Pourbaix) diagram of the arsenic showing the existence of the species of various oxidation states (from p.193 of Ref [8]).

3.3. Adsorption of Lead(II) Ions on the Surface of γ-Al₂O₃ Adsorbent (Example 3)

The ASTI matrix based approach of the equilibrium calculation makes it possible to include heterogeneous reactions in the calculation like *e.g.* adsorption and ion exchange. Here the adsorption of the Pb(II) ions from PbCl₂ on γ-Al₂O₃ is studied as a function of pH and the concentration of chloride ions from excess NaCl. The active surface group, -OH of the adsorbent is denoted here by ≡XOH. The mechanism of lead adsorption is interpreted using the surface complexation model [5] leading to the formation of the surface complex defined by the symbol ≡XOPb⁺.

Reagents: m(γ-Al₂O₃) = 0.3846 g
 Volume of the solution, V = 500 cm³
 Adsorption capacity, Q = 1.3 · 10⁻⁴ mol g⁻¹
 Concentration of surface sites, c≡X = m · Q/V = 10⁻⁴ M
 c(Pb²⁺) = 10⁻⁵ M; c(Cl⁻) = 0.1002 M; c(Na⁺) = 0.1 M;
 pH = 6

Reactions, R = 6:



Species, S = 11: H₂O, H⁺, OH⁻, Pb²⁺, PbOH⁺, Cl⁻, PbCl⁺, ≡XO⁻, ≡XOH, ≡XOH₂⁺, ≡XOPb⁺

Components, C = S - R = 5: H₂O, H⁺, Pb²⁺, Cl⁻, ≡XOH₂⁺

ASTI matrix:

S/C	H ⁺	Pb ²⁺	≡XOH ₂ ⁺	Cl ⁻	K
H ⁺	1				
OH ⁻	-1				K _w
Pb ²⁺		1			
PbOH ⁺	-1	1		1	K ₁
Cl ⁻				1	
PbCl ⁺		1		1	K ₂
≡XOH ₂ ⁺			1		
≡XOH	-1		1		(K ₄) ⁻¹
≡XO ⁻	-2		1		(K ₃ · K ₄) ⁻¹
≡XOPb ⁺		1	1		(K ₃ · K ₄ · K ₅) ⁻¹
TOT					M
cPb		1			10 ⁻⁵
c≡X			1		1.3 · 10 ⁻⁴
cNaCl				1	0; 0.1; 0.5

Mass balance equations, MB:

(MB for water is usually omitted, if the pH is fixed then TOT_H is not needed and Cl⁻ is known):

$$\text{TOTPb} = [\text{Pb}^{2+}] + [\text{PbOH}^+] + [\equiv\text{XOPb}^+] + [\text{PbCl}^+] = c\text{Pb}$$

$$\text{TOTXOH}_2 = [\equiv\text{XOH}_2^+] + [\equiv\text{XOH}] + [\equiv\text{XO}^-] + [\equiv\text{XOPb}^+] = c\equiv\text{X}$$

Equilibrium relationships, ER:

$$[\text{PbOH}^+] = K_1 \cdot [\text{Pb}^{2+}] \cdot [\text{H}^+]^{-1}$$

$$[\text{PbCl}^+] = K_2 \cdot [\text{Pb}^{2+}] \cdot [\text{Cl}^-]$$

$$[\equiv\text{XOH}] = (K_4)^{-1} \cdot [\equiv\text{XOH}_2^+] \cdot [\text{H}^+]^{-1}$$

$$[\equiv\text{XO}^-] = (K_3 \cdot K_4)^{-1} \cdot [\equiv\text{XOH}_2^+] \cdot [\text{H}^+]^{-2}$$

$$[\equiv\text{XOPb}^+] = (K_3 \cdot K_4 \cdot K_5)^{-1} \cdot [\equiv\text{XOH}_2^+] \cdot [\text{Pb}^{2+}] \cdot [\text{H}^+]^{-2}$$

The two MB-s and five ER-s define the unique value of the concentration of the seven dissolved and surface species. The MATHCAD solution of the NLSE yields the data summarised in Table 3.

Considering that the ER equations are valid at all pH values and chloride concentrations, arbitrary useful functions can be defined by using these concentration functions. Let this function now be the distribution coefficient widely used in liquid chromatography and defined as the ratio of the total concentrations of the lead (TOTPb) in the two phases:

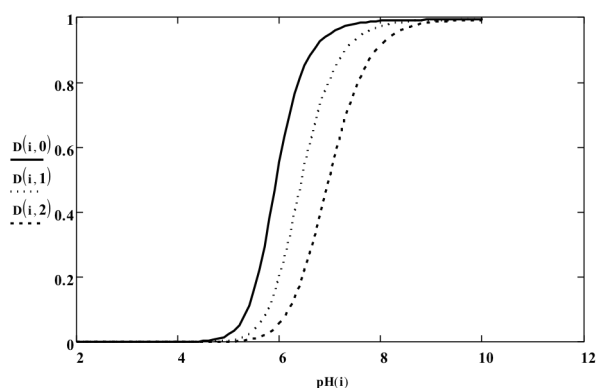


Figure 4. Change in the distribution of the Pb(II) ions as a function of pH at different chloride ion concentrations. The second index of D refers to the chloride ion concentration (Eq.(5)): 0 = no chloride, 1 = 0.1 M, 2 = 0.5 M.

$$D = \frac{\text{TOTPb on the ads.}}{\text{TOTPb in the solutn.}} = \frac{[\text{XOPb}^+]}{[\text{Pb}^{2+}] + [\text{PbOH}^+] + [\text{PbCl}^+]} \quad (5)$$

After substituting the appropriate ER relationship into the above equation the distribution coefficient can be calculated as a function of pH and the chloride ion concentration. The result is shown in Fig.4.

As shown in Fig.4, the adsorption of lead increases sharply with the increase of pH, since the formation of surface complexes is preferred at higher pH values. It is interesting to observe that at pH 6 the adsorption of the positive Pb(II) species is significant despite the fact that the surface species, $\equiv\text{XOH}_2^+$, is also positively charged at this pH.

4. Conclusion

In order to solve complex aqueous speciation problems a logical scheme for arranging the available data is needed. This convenience scheme is provided by the tabulated form of the arrangement of analytical, stoichiometric, and thermodynamic information. This matrix of data allows us to set up the necessary mass balance and equilibrium equations of the calculation. This paper presented typical examples of the use of these principles in the field of water chemistry.

SYMBOLS

A	number of reagents
ASTI	analytical stoichiometric and thermodynamic information
C	number of components
ER	equilibrium relationship
H_2CO_3^*	$\text{H}_2\text{CO}_3 + \text{CO}_{2(\text{aq})}$
K	equilibrium constant
MB	mass balance
NLSE	non-linear system of equations

R	number of reactions
S	number of species
TOTX	total concentration of species 'X'

Acknowledgement

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GROUNDWATER REMEDIATION USING BIOLOGICAL AND PHOTOCATALYTIC METHODS

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The degradability of two commercially available pesticides was studied using heterogeneous photocatalytic and activated sludge treatment methods. The first pesticide contained 5% quizalofop-P-ethyl as an active ingredient and petroleum naphtha as a solvent, the latter causing difficulties both in photocatalytic and biological treatment methods. The active ingredient of the second compound was acetamiprid. The photocatalysis proved to be effective both under laboratory conditions (using UV light) and when exposed to sunlight, but the pesticides remained stable during the employed biological treatment. Preliminary information on its behaviour in soil was obtained from transport modelling.

Keywords: heterogeneous photocatalysis, groundwater remediation, quizalofop-P-ethyl, acetamiprid, biological treatment

1. Introduction

The drinking water supply of Hungary largely relies on underground water resources. The water quality has been endangered by both industry over the last century and the still significant pesticide-intensive agriculture. Excessive amounts of pesticides contaminating soil may be fully or partially degraded by natural chemical and biochemical reactions. The latter may lead to bioaccumulation. The transport into groundwater and/or surface water bodies is affected by several factors, such as precipitation, evapotranspiration, infiltration, and runoff besides the physicochemical characteristics of soil and the attributes of the substance.

The application of pesticides is an inefficient procedure, since only a small amount is utilised for the desired purpose. Most of the compound is released unused into the soil and if it degrades partially or at a slower pace, the pesticide might accumulate and enter the food chain. In order to avoid the release of pesticides that are persistent and harmful to the environment and humans, it is necessary to have licencing procedures and strict controls on the use of such materials [1]. In Hungary, authorisation is regulated by the Decree 89/2004 of the Ministry of Agriculture and Rural Development in agreement with the Council Directive 91/414/EEC [2].

A common method to treat contaminated aquifers is groundwater pump-and-treat technology [3], where extraction wells are used to remove the contaminated water that is treated with adequate techniques after which it is re-injected into the aquifer or released into a surface water body. The treatment method is dependent on the degradability and toxicity of the pollutant.

Bioremediation cannot be used in cases when the compound is not biodegradable or even toxic to microorganisms. Oxidative methods, such as heterogeneous photocatalysis may be adequate in such cases [4]. In this process, the radicals formed due to the photogenerated charge-carriers on the surface of the semiconductor. They react with the pollutant molecule initiating its degradation. The catalyst is often reusable and recycled. The semiconductor catalyst has to be chemically and biologically inert, but photocatalytically active. It should be easily produced and economical. Since TiO_2 fits these requirements, it is the best among the semiconductors for extensive use [5]. Research over the past years has proved that on a laboratory scale different organic compounds (aliphatic and aromatic hydrocarbons [6], alcohols and organic acids [7], phenols [8] and chlorinated compounds [9]) could be effectively degraded to inorganic end products using heterogeneous photocatalysis [10].

The aim of this paper is to report on the degradability of organic contaminants in the soil and groundwater with biological and photocatalytic methods using model compounds. Their behaviour in the soil

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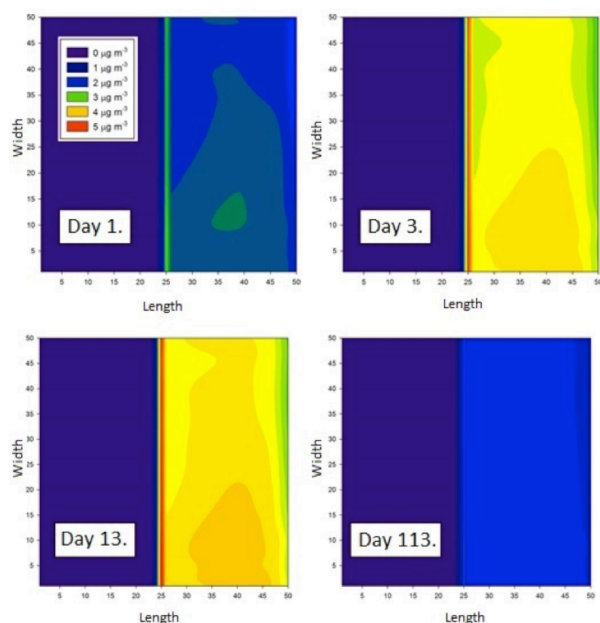


Figure 1. The concentration of quizalofop-P-ethyl in the second layer in the case of normal use (a unit equals 2 m).

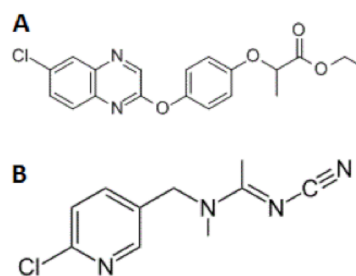
was determined by hydraulic and transport models. The model compounds were a herbicide (Leopard 5 EC) and an insecticide (Mospilan 20 SG). Both fall into category III meaning that they are available without a special licence. Their metabolites remain stable in soil for a long period.

2. Methods and Materials

The substance with the brand name Leopard 5 EC contains 5% quizalofop-P-ethyl (Scheme 1A) as an active ingredient, 77-83% petroleum naphtha as a solvent and other emulsifying excipients. The active substance is especially dangerous to mammals, aquatic organisms, and birds and moderately toxic to bees. It is insoluble in water; it emulsifies due to the additives. Its metabolites are more soluble in water, but do not hydrolyse. Their half-lives are between 35 and 39 days.

The active ingredient of the insecticide called Mospilan 20 SG is 20% acetamiprid (Scheme 1B), which is highly toxic to mammals and birds and moderately toxic to aquatic organisms. The substance is very soluble in water, hence its high mobility upon infiltration. Its metabolite is not easily degraded under natural conditions in soil and water (its half-life is 133 days), and it is moderately toxic to aquatic life.

Heterogeneous photocatalytic irradiation experiments were performed in a photoreactor with an effective volume of 2.5 dm³. Internal recirculation was provided in the tube reactor. TiO₂ was used as a catalyst with a concentration of 1 g dm⁻³, while the air flow was 40 dm³ h⁻¹. The radiation source placed in the axis of the reactor was a 40 W fluorescent lamp specially manufactured for such purposes. The vast majority of light emitted is of a longer wavelength than 300 nm.



Scheme 1. Schematic structures of pesticides studied in this work (A: quizalofop-p-ethyl, Ref: DPX 79376, <http://sitem.herts.ac.uk/aeru/ppdb/en/Reports/583.htm> (11.05.2015); B: acetamiprid, Ref: NI 35, <http://sitem.herts.ac.uk/aeru/ppdb/en/Reports/11.htm> (11.05.2015)).

Biological treatment was carried out in an activated sludge, aerated sequenced batch reactor. An operating cycle lasted for a day. The effective volume of the reactor was 5 dm³ and the sludge concentration was kept at 4 g dm⁻³. The rate of aeration was kept constant throughout the process. A non-adapted municipal sludge was used for the experiments.

Modelling was carried out using Processing MODFLOW for Windows (PMWIN) 5.3. This version is freely available, while later versions can be obtained commercially. The test area was chosen to be the size of 1 acre divided vertically into three homogenous layers with average Hungarian properties. Simulations were run for 1–3–13–113 day intervals. The environmental factors taken into consideration were the following: groundwater flow and porosity, infiltration due to precipitation (1.9 mm day⁻¹), and evapotranspiration (1.2 m day⁻¹) [11]. The hydraulic conductivity was 129.6 mm day⁻¹ for all three layers [12].

3. Results and Analysis

3.1. Leopard 5 EC

The degradability of the substance with heterogeneous photocatalysis was examined under laboratory (UV-light) and natural (sunlight) conditions. The initial concentration of the active ingredient was 3.26 g dm⁻³. The solution was heavily foaming whilst the reactor was being filled. During irradiation, the majority of the catalyst deposited onto the bottom or adhered to the walls of the reactor and buffer tank after an hour despite being stirred. The organic carbon content of the mixture did not change, which indicates that no degradation took place.

In the biological treatment, the components of the solution entering the cycle were: 100 cm³ of herbicide with a concentration of 3.26 g dm⁻³, 100 cm³ of acetic acid (0.93 g dm⁻³), 10 cm³ of ammonium chloride solution (30 mg N dm⁻³), and 10 cm³ of sodium phosphate (30 mg P dm⁻³). After turning the stirrer and aeration on the liquid started to foam heavily and smelled strongly of oil. At the end of the cycle in the settling phase the effluent was turbid. Colloids and a part of the activated sludge deposited on the wall of the

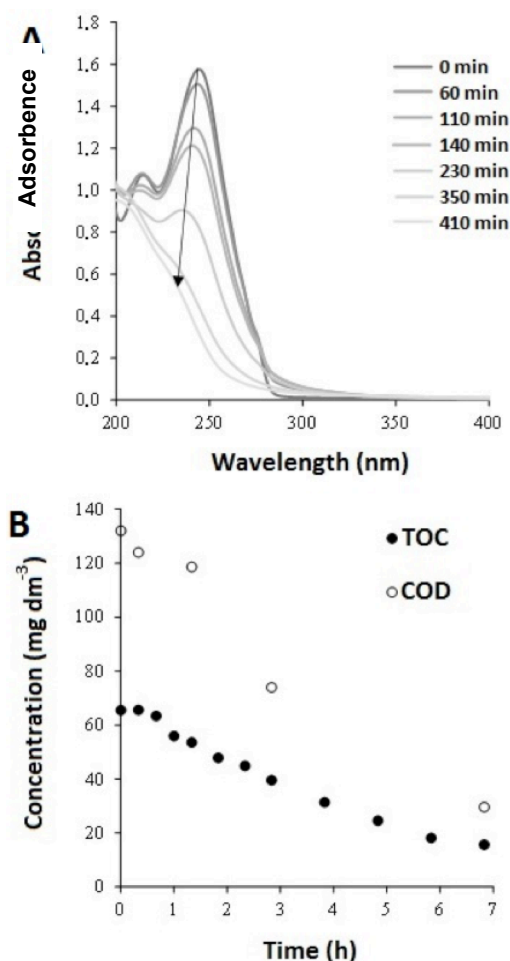


Figure 2. Spectra of Mospilan suspension treated with catalyst (optical path length: 0.5 cm) (A); chemical oxygen demand and total organic carbon concentrations as function of time (B).

sequenced batch reactor and surface of the sensors and dried there. The following cycle ended with the same results. The treatment using activated sludge turned out to be ineffective due to the experienced foaming and cumulated active ingredient. Inspections revealed that the degradation of the solvent did not start either.

The transport models created with the software (Fig.1) showed that pesticide under normal conditions of use did not threaten drinking water resources and due to hydrolysis the concentration decreased by half in the second stratum over 113 days. In the case of accidental spillages (the same amount of compound was hypothetically released over a 2 m² area) the effect was significant, the concentration was a thousand times greater compared to normal use scenarios.

3.2. Mospilan 20 SG

In the experiments the concentration of Mospilan used was 170 mg dm⁻³ in agreement with the suggested concentration of application. A 20% active ingredient content was achieved by an acetamiprid solution with a concentration of 34 mg dm⁻³. Photodegradation was monitored by recording the UV-VIS spectra of the mixture and measuring the organic carbon content (TOC).

The solution was first irradiated with UV-light without a catalyst under atmospheric pressure for three hours. During this time neither the TOC concentration nor the pH of the mixture changed; the variation of the results stayed within the measurement error, which suggested that the insecticide was not degradable by UV-light in itself.

The second experiment was carried out with TiO₂ as a catalyst and the process was not stopped for seven hours. During this time the rate of light absorption between 200 and 300 nm gradually decreased and the maximum of the band shifted from 245 nm to 230 nm (Fig.2). These spectral changes indicate clearly that the compound degraded in the heterogeneous photocatalytic experiments.

The suspension was circulated in the reactor for 20 minutes before irradiation. From changes in TOC concentration, it can be concluded that during this period a proportion of the organic material had adsorbed onto the catalyst particles. The rate of adsorption in terms of TOC was 10%. By the end of the process, the TOC concentration of the suspension reduced by 76% while the COD amount became 78% less. According to the data, the initial rate of decay was calculated to be 13.59 mg dm⁻³ h⁻¹ based on the curve fitted to the TOC.

A major advantage of the heterogeneous photocatalyst is that the reaction may be carried out with solar radiation; thus, costs and also environmentally harmful emissions can be reduced. Photons are on the one hand 'pure' reagents and on the other hand 'pure' energy. The changes in the spectrum, such as the decrease in absorbance and the shift in location of band peaks were the same under laboratory conditions, while the reaction rate was lower. The initial rate of decay due to solar radiation was 6.07 mg dm⁻³ h⁻¹. During measurements the UV-B radiation was "strong" (UV index 6.5, Hungarian Meteorological Service).

The results show that the heterogeneous photocatalytic degradation of the insecticide may be efficiently achieved by using sunlight. This can be utilised when disposing of different chemical residues. The organic contaminants may be mineralised using solar radiation on site in a carefully designed "reactor".

The biodegradability of the pesticide was studied with a prepared solution based on an average concentration of application. In the first case, an additional substrate (acetic acid) was added to the sequenced batch reactor while in the second case only the insecticide was supposed to serve as a substrate. Based on the results (Fig.3), it can be stated that the biodegradation of Mospilan cannot be achieved with municipal activated sludge under the employed conditions.

The results of the transport model (Fig.4) show that acetamiprid acts in a similar way to quizalofop-P-ethyl. Since it does not hydrolyse the active ingredient, it would remain for longer in soil and accumulation might appear therefore the compound may more easily enter the food chain. In the case of accidental spillages of the substance over a small area, the effect would be more significant just as was the case with quizalofop-P-ethyl.

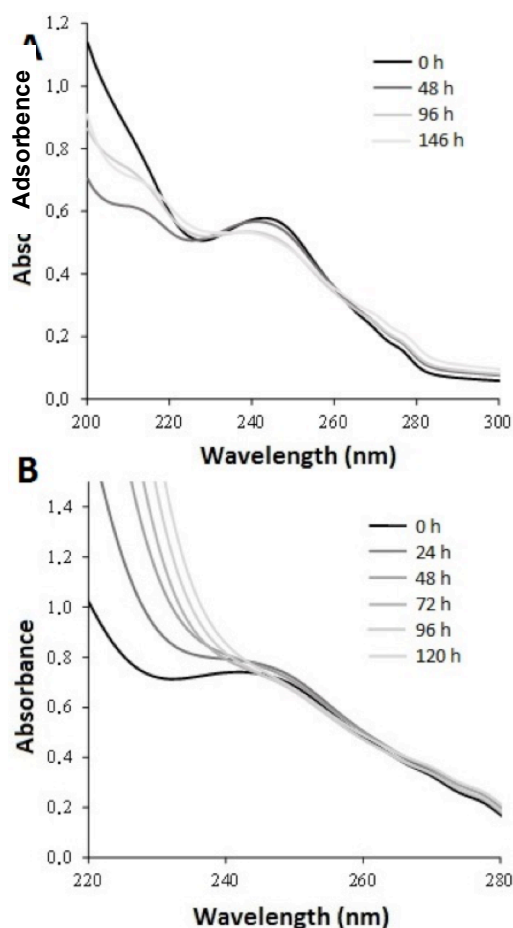


Figure 3. Changes in absorbance spectra during biological treatment with (A) and without additional substrate (B) (optical length: 0.5 cm).

The concentration in soil would be a thousand fold greater. Besides it would not decrease significantly over time, since the compound is stable in aqueous media.

4. Conclusion

The studied Leopard 5 EC and Mospilan 20 SG pesticides are available to purchase without any permit, although they are toxic to different extents to mammals, birds and aquatic organisms. Their improper application might cause serious environmental damage. The degradability of the two substances was studied by means of heterogeneous photocatalysis and biological treatment.

In the case of Leopard 5 EC neither of the methods was successful. The petroleum naphta solvent and/or the emulsifiers poisoned the TiO_2 catalyst. The dollops formed settled and the surface of the catalyst particles was reduced greatly due to the adhesion effect of the organic material. The photocatalytic degradation reaction could not take place. A similar process was observed in the biological reactor. The mixture together with the biomass adhered to the surface of the sequenced batch reactor and sensors. In both cases the conditions made the treatment processes impossible. In order to be able to study the degradation of the

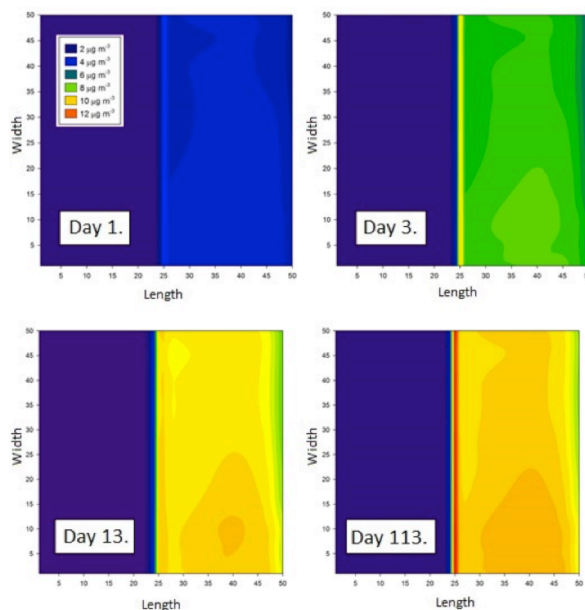


Figure 4. The concentration of acetamiprid in the second layer in the case of normal use (a unit equals 2 m).

compound, pre-treatment, possibly the destabilisation of the emulsion is needed.

Mospilan 20 SG could be treated using heterogeneous photocatalysis both under laboratory conditions (with a UV lamp) and utilising solar radiation. However, it can be stated that the insecticide cannot be treated with municipal activated sludge under the applied conditions based on the results of sequenced batch reactor experiments.

According to the simulation results, neither of the pesticides poses a threat to drinking water resources in the case of normal use in compliance with the specifications provided by the manufacturer. Nonetheless, Mospilan 20 SG is likely to accumulate if used multiple times or for extended periods. Should there be an emergency the impact on the environment might multiply.

The results of the present study show that unlicensed use does not necessarily mean easily degradable substances. The biological method was unsuccessful in both cases, photocatalysis is not applicable for water-immiscible chemicals but in the case of hydrophilic organic materials, the treatment may be efficient.

Acknowledgement

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BIOLOGICAL PURIFICATION OF CHEMICALLY PRE-TREATED DAIRY WASTEWATER BEFORE DISCHARGE INTO A MUNICIPAL SEWAGE SYSTEMS

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Dairy production is one of the most inefficient processes with respect to water usage in the food industry. It was estimated that the production of a litre of milk creates three to four litres of wastewater. Dairy wastewater contains a high amount of dissolved and suspended solids. Moreover, it contains high concentrations of fat, protein, and carbohydrate. Consequently, the dairy wastewater content of organic compounds is high and so is its chemical oxygen demand. The majority of organic compounds are biodegradable with a high biological and chemical oxygen demand ratio. In this work, we examined the biological purification of physico-chemically pre-treated wastewater from a Hungarian milk-processing factory before it was discharged into the public sewage system. The chemical oxygen demand of the pre-treated wastewater ranged from 500 to 2500 mg dm⁻³. We found that it was possible to achieve efficient organic material removal from nutrient-poor wastewater without nutrient dosage contrary to the literature. The activated sludge system manifested efficient organic material removal that required a smaller biological volume. Experiments with biofilms have shown that a thicker biofilm needs more dissolved oxygen, which dictates oxygen input levels to be sufficient for creating an aerobic environment.

Keywords: activated sludge, biofilm, dairy wastewater, chemical oxygen demand, nutrient-poor wastewater

1. Introduction

Milk processing requires high specific water consumption and considerable raw material waste effluents [1]. Wastewater composition depends mainly on the produced material, production process, actual operations of the production process, and the water usage [2]. Clean water is practically used in all the process operations, like cleaning, sterilisation, heating and cooling. Wastewaters produced in these plants are usually polluted with chemicals, used for cleaning the containers, pipes, and some other equipment [2–4]. On average processing a cubic metre of milk produces 3–4 m³ of wastewater [5].

Milk processing effluents (dairy wastewaters - DWW) contain high concentrations of dissolved and suspended solids. They contain high concentrations of fat, protein mainly as fine colloids, and carbohydrate (lactose and lactic acid) [6–9]. Among the carbohydrates, lactose can be found in a high ratio [5]. However, the lactic acid content can also be very considerable in the case of the discharge of whey. Suspended solids of dairy wastewater originate from cheese and cottage cheese as well, but their final concentration highly depends on the processing methods at a given plant.

As a result of these ingredients of an approximate total concentration of around 2 g/g of the effluent, dairy wastewaters can exhibit high chemical oxygen demand (COD). The majority of the organic contaminants are biodegradable. The ratio of biological and chemical oxygen demand (BOD/COD) of the DWW-s is high [10]. All organic contaminants are in principle nutrients for microorganisms of the active sludge (AS) biological treatment. However, preliminary physico-chemical removal of particular components of the DWW, such as fats, most of the proteins, and casein considerably decreases the cost of biological purification required for permitting the discharge of this industrial effluent into municipal sewage systems.

2. Material and Method

We studied the biological purification of physico-chemically pre-treated wastewater from a Hungarian milk processing and dairy factory located in Székesfehérvár. Polyaluminium chloride, hydrochloric acid, and polyelectrolyte were used before flotation. Presently, the mixed wastewater after this treatment is discharged into the public sewage collection system. Intermittently, its COD concentration is higher than the prescribed limit, which results in an extra fee being charged for the discharge and municipal purification.

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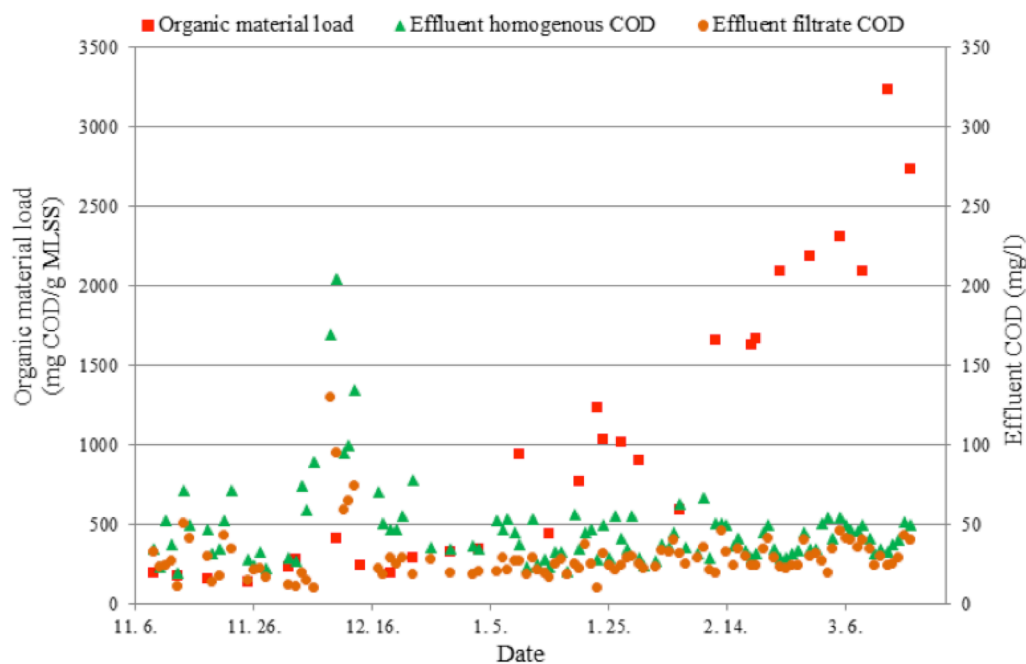


Figure 1. The chemical oxygen demand of the studied activated sludge sequencing batch reactor system.

COD of the pre-treated wastewater normally changed between 0.5 and 2.5 g dm⁻³ during the measurements, while the limit value was 1 g dm⁻³. The total organic material content was commensurable with the suspended solid concentration at the same time the magnitude of dissolved organic compounds was constant. The ammonium concentration in the pre-treated wastewater was low (3–10 mg dm⁻³), while the phosphorous content was negligible. Thus, the wastewater we purified biologically was lacking in N- and P-nutrients. We intentionally did not add any N- or P-nutrients.

We carried out parallel studies in an activated sludge sequencing batch reactor (AS-SBR) and a biofilm system, moving bed biofilm sequencing batch reactor (MBBR-SBR). The activated sludge reactor was inoculated with municipal activated sludge. The growth of biofilm was initiated by the addition of municipal wastewater during the first and second weeks. There were aerobic and anoxic periods in the SBR cycles (approximately in a 3 to 1 ratio) to cater for the needs of different microorganisms. Anoxic periods were used to improve the sludge settling. During the aerobic periods, the maximum dissolved oxygen concentration was set to 2 mg dm⁻³. Mechanical mixing was used during the anoxic phases. The activated sludge concentration in the AS-SBR reactor was between 3 and 5 g dm⁻³, on the contrary in the MBBR reactor it was at most 1 g dm⁻³ in the first part of the experiment.

The volume of biofilm carrier in the reactor was 0.5 dm³ and the total volume of the MBBR-SBR reactor was 2 dm³ giving a filling ratio of 25%. The biofilm reactor was continuously aerated and the dissolved oxygen level had to be increased, when the specific biofilm load considerably increased.

3. Results and Analysis

The sludge-loading rate in both systems was increased continuously throughout the experiment. At the beginning, it was approximately 0.2–0.3 g COD/g MLSS and was slowly raised to over 2 g COD/g MLSS by the end.

On the contrary, the COD of the purified wastewater did not change considerably (*Fig.1*). It was between 20 and 50 mg dm⁻³. The COD was simultaneously measured from the filtered effluents to observe the influence of the suspended sludge content of these effluents.

The treated wastewater was nutrient-poor. According to the demands of microorganisms in biological wastewater treatment, a C : N : P ratio of around 100 : 5 : 1 is optimal. This ratio is typical for communal wastewater. The average relative sludge yield rate is 0.7 g MLSS/g COD if the nutrient ratio is optimal. In our study, we could only measure a low specific sludge yield of approximately 0.1 g MLSS/g COD, which we rationalise by the lack of nitrogen- and phosphorous-nutrients. The COD removal was very effective even at very high sludge loads and with a lack of nutrients.

In the MBBR system (*Fig.2*), the variability of organic material removal was observable. COD of the purified wastewater varied between 50 and 200 mg dm⁻³. The main reason for lower COD removal values was probably due to the inefficient settling of the fine biofilm particles. They could not aggregate as much as the AS sludge flocs can. During the course of settling, the biofilm carriers float up to the surface of the water. This can also limit the proper settling of the sludge if the treated wastewater contained so much suspended sludge.

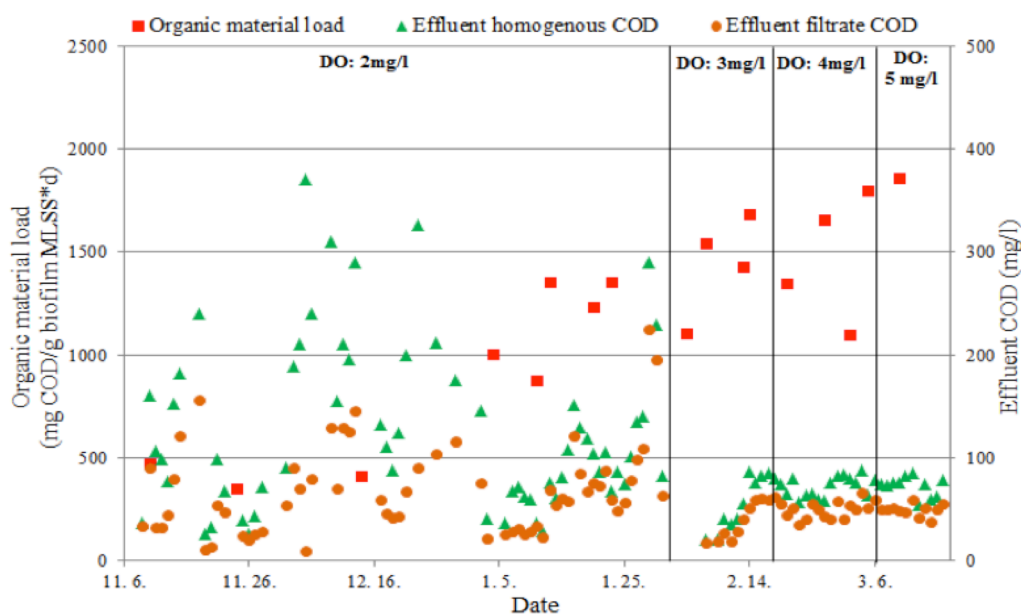


Figure 2. The chemical oxygen demand of the moving bed biofilm sequencing batch reactor (MBBR-SBR) system.

The biofilm loading rate was between 0.2 and 2.0 mg COD/g biofilm MLSS. The biofilm concentration in the MBBR-SBR system was 0.5–1.5 g biofilm dm⁻³ in contrast to the AS-SBR reactor where the activated sludge concentration was 3–5 g MLSS dm⁻³. The MBBR-SBR reactor was operated by a lower hydraulic load.

When the dissolved oxygen concentration was set to 2 mg dm⁻³ over 1 g COD/g biofilm MLSS loading rate, the biofilm could not survive due to limited oxygen diffusion from the liquid phase to inside the biofilm. This corresponds to anoxic conditions at the carrier surface. We had to increase the dissolved oxygen concentration to 3 mg dm⁻³. When the biofilm loading rate increased to 2 g COD/g biofilm MLSS, the dissolved oxygen concentration should be increased further to 5 mg dm⁻³ in order to achieve efficient organic material removal.

4. Conclusion

We observed that it was possible to achieve efficient organic material removal as expressed by the chemical oxygen demand values from pre-treated dairy wastewater both in AS and biofilm treatments without a dose of N- and P-nutrients. This is contrary to what has been proposed in the literature. In the similar active sludge treatment of apple juice effluents even with a proper dosage of urea and phosphate, sometimes we could measure serious sludge bulking because of a lack of micronutrients.

Our results showed that the activated sludge system ensured efficient organic material removal even around 2 g COD/g MLSS loading rate in the case of the pre-treated dairy wastewater. At the same time, the specific sludge load of the municipal sewage treatment plants without nitrification and denitrification is at most 1 g COD/g MLSS. When we have to nitrify and

denitrify the organic carbon load has to be around a third of this value. High loaded systems require a smaller biological volume. Iron ions, which remained in pre-treated wastewater, facilitated the settling of activated sludge, therefore in the AS-SBR system this gives an opportunity for increasing the sludge concentration. Because of an extended sludge concentration the biological volume demand would be reduced. Our experiments with the biofilm system show that the thicker biofilm requires a much greater dissolved oxygen concentration. This fact is mentioned also in some other studies. The oxygen input needs to be balanced against the level for creating an aerobic environment for the biofilm.

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STUDY OF THE INTERFERENCE EFFECTS OF ALUMINIUM ON THE ATOM- AND ION-LINES OF ALKALINE EARTH METALS IN AQUEOUS SOLUTIONS USING AN ICP SPECTROMETER WITH AXIALLY VIEWED PLASMA

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The main advantage of inductively coupled plasma spectrometers with axially viewed plasma relative to the radially viewed plasma is the better detection power. The detection limits of the former are about 5–10 times lower than the latter. On the other hand, the axially viewed plasma has disadvantages. The most notable is the increased number of interference effects. In this paper, the study of the interference effects of aluminium on the atom- and ion-lines of alkaline earth metals are presented by examining different types of sample-introduction devices, such as a simple Meinhart-type concentric nebuliser, a V-groove nebuliser using a Sturman-Masters spray chamber, and an ultrasonic nebuliser.

Keywords: aluminium interference effects, ICP atom- and ion-lines, alkaline earth metals, sample-introduction device, axially viewed plasma

1. Introduction

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) is a widely used method for the elementary analysis of different types of material due to its advantageous features. The axial plasma view offers an increased detection power, which is important when the element of interest is present in trace levels. On the other hand, the emitted light is subjected to strong interferences as it reaches the entrance slit of the optical system of the spectrometer. Therefore, it is an important task to understand the origin and nature of the interference effects [1–3].

The interference may affect both the sample-introduction and excitation processes taking place in the plasma. In the first case, they may have different effects on the different types of sample-introduction devices, while they might affect the atom- and ion-lines of a given element in different ways [4].

ICP is commonly used for the analysis of liquid samples, where different types of nebulisers are the most frequently applied devices for sample-introduction. During nebulisation, the liquids to be analysed are dispersed into small droplets. The difference regarding the different nebulisers lies partially in different processes resulting in small liquid droplets and the nebulisation efficiency. These kinds of effects may be different when different nebulisers are applied, while they appear in the case of both radially and axially viewed plasma.

The spectral interferences are stronger and more frequent when an axially viewed ICP source is used. This is due to the light being emitted from the hot internal part of the plasma that has to travel a long way to reach the entrance slit of the optical system. On its way, the emitted light goes through layers of plasma at a lower temperature. This process may be subjected to strong self-absorption effects. Consequently, the intensity of the ion- and atom-lines of a given element may change. This change affects the relationship between the emitted line intensity and analyte concentration in the sample, and thus the calibration procedure.

The alkaline earth metals may be present from trace up to high concentration levels in different materials, such as surface and groundwater, different types of rocks and minerals, metal alloys, etc. In many cases, these materials may contain aluminium in high concentrations that contributes to the observation of interferences [2,3]. In the present work, we studied the effect of aluminium on the spectral lines of alkaline earth metals present in low-concentrations in aqueous solutions, as well as the influence of different sample-introduction devices.

2. Experimental

2.1. ICP Spectrometer

For the presented experiments, a Varian 720 ES spectrometer was used, which is an axially viewed, instrument with key parameters summarised in *Table 1*.

Table 1. Characteristics of the ICP spectrometer used in the given study.

Plasma-view:	axial
The frequency and power of the RF generator:	40 MHz, 900–1500 W adjustable via software
The optical system employed:	Echelle build-up with a double monochromator
Detector used:	Two-dimension CCD
Wavelength range:	160 – 780 nm
Available sample-introduction systems:	Concentric (K-type) nebuliser, V-groove nebuliser, Ultrasonic nebuliser
Controlling software:	ICP Expert II (Microsoft Win XP OS)

Due to the layout of the optical system, many (even several hundred) spectral lines can be measured simultaneously, which makes the study of the interferences on several atom- and ion-lines of a given element possible. In the course of line selection, care was taken in choosing both more and less sensitive lines, where enough lines were available. The spectral lines examined in this study are summarised in *Table 2*.

2.2. The Sample-Introduction Devices

Three types of sample-introduction device were used in the given set of experiments: a concentric nebuliser, a V-groove nebuliser, and an ultrasonic nebuliser. The concentric nebuliser is the one that is used most commonly for the ICP-AES analysis of liquid samples. Its nebulisation efficiency is rather low, but it can be operated easily, and its maintenance demand is low. Generally, it is used in combination with a cyclone-type glass spray chamber.

The V-groove nebuliser eventually becomes a modified Babington-type nebuliser. It is used with a Sturman-Masters type spray chamber, which has a special plastic surface and is resistant to almost all chemicals including hydrogen fluoride. Its detection power is slightly less than that of the concentric nebuliser, but it has an excellent salt-enduring ability.

The CETAC 5000 type ultrasonic nebuliser boasts a detection power 10 times better than the former two devices. On the other hand, its operation is more difficult and it may be sensitive to higher matrix concentration levels.

2.3. Samples Used

The solution samples contained some acid, the alkaline earth analyte elements and aluminium as a matrix component. The matrix element was diluted from a Spectrascan (Teknolab) stock solution containing aluminium at a concentration of 10 g dm⁻³. The aluminium concentration in the sample solutions was 0, 200, 500, 1000, and 5000 mg dm⁻³. The analyte elements were diluted from a multi-element Spectrascan solution of 0.1 g dm⁻³. The concentrations of the elements studied were in the range of 0.1 and 10 mg dm⁻³. The solutions contained hydrochloric acid in a concentration of 0.5 mol dm⁻³.

Table 2. The spectral lines (wavelength λ in nm and excitation energy E in eV) studied.

Element	Type of the line	λ	E
Be	Be I	234.861	5.30
Be	Be I	249.473	5.01
Be	Be II	313.042	3.99
Be	Be II	313.107	3.99
Mg	Mg I	285.213	4.38
Mg	Mg I	383.829	3.23
Mg	Mg II	279.553	4.47
Mg	Mg II	280.270	4.59
Ca	Ca I	422.673	2.96
Ca	Ca II	317.933	3.93
Ca	Ca II	393.366	3.18
Ca	Ca II	396.847	3.15
Sr	Sr I	460.780	2.71
Sr	Sr II	216.596	5.76
Sr	Sr II	407.771	3.07
Sr	Sr II	421.552	2.96
Ba	Ba I	705.994	1.77
Ba	Ba II	233.527	5.36
Ba	Ba II	455.403	2.75
Ba	Ba II	493.408	2.53

2.4. Measurements

Each of the solutions was measured at a 1050 W output of high frequency power. The recorded signal intensity was averaged from 3–10 s long replicates. The raw intensities were corrected applying the so-called two-side off-peak background correction method.

In order to easily evaluate the effects, the net intensities measured using sample solutions containing no aluminium were used as reference values, and the net intensity values measured in the presence of aluminium were divided by these reference values. In other words, the evaluation presented here is based upon the relative intensities.

3. Results

In the experiments, we studied the intensity changes of several atom- and ion-lines of the alkaline earth metals as a function of aluminium concentration, analyte concentration and that of the device used for sample-introduction. The results measured using a concentric nebuliser are presented in *Figs.1–10*. The net intensities obtained using a V-groove nebuliser (*Figs.11 and 12*) and an ultrasonic nebuliser (*Figs.13 and 14*) are also presented for the case of calcium ions.

4. Discussion

Figs.1–10 show that by using the concentric nebuliser both atomic- and ionic-lines of all alkaline earth metals are affected by aluminium. Nevertheless, substantial differences can be seen depending on the element, type

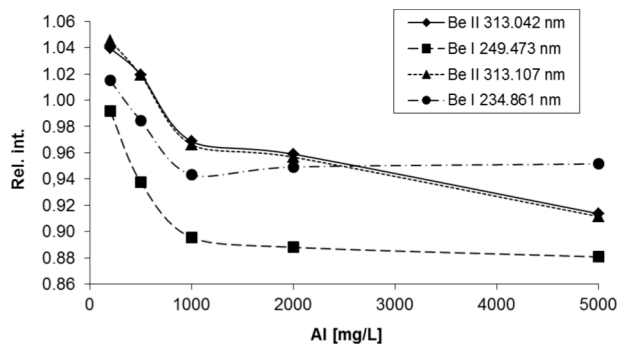


Figure 1. The relative intensities of 0.1 mg dm^{-3} Be as a function of Al concentration, using a concentric nebuliser.

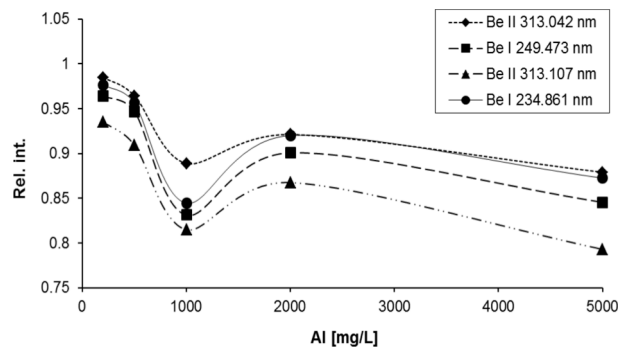


Figure 2. The relative intensities of 10 mg dm^{-3} Be as a function of Al concentration, using a concentric nebuliser.

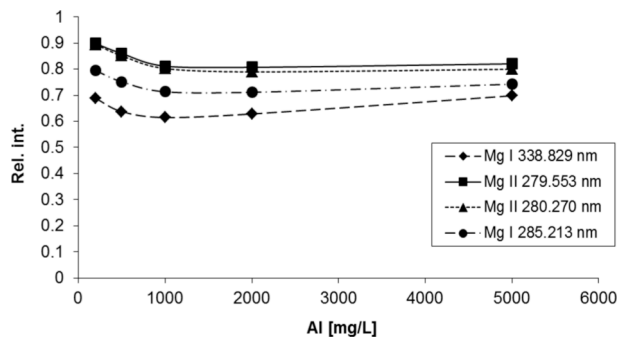


Figure 3. The relative intensities of 0.1 mg dm^{-3} Mg as a function of Al concentration, using a concentric nebuliser.

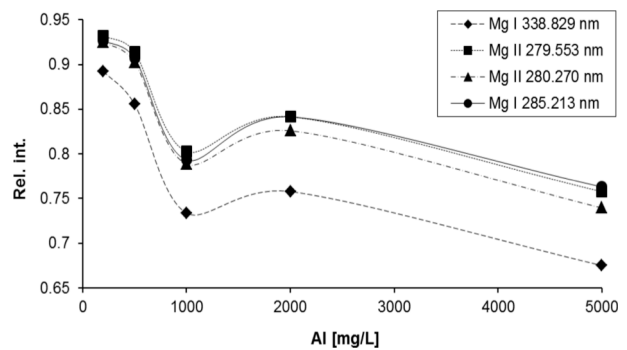


Figure 4. The relative intensities of 10 mg dm^{-3} Mg as a function of Al concentration, using a concentric nebuliser.

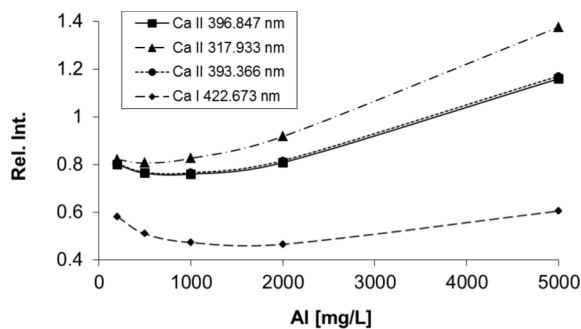


Figure 5. The relative intensities of 0.1 mg dm^{-3} Ca as a function of Al concentration, using a concentric nebuliser.

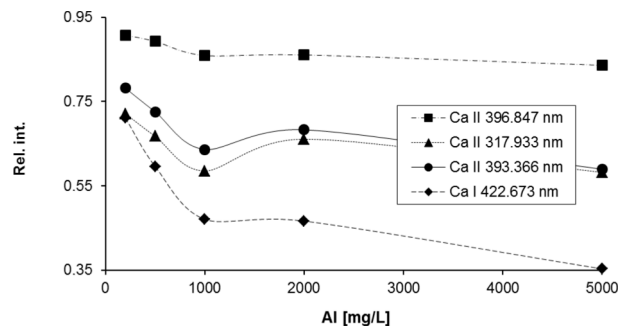


Figure 6. The relative intensities of 10 mg dm^{-3} Ca as a function of Al concentration, using a concentric nebuliser.

of spectral line studied, concentration of aluminium, and that of the analyte. At low beryllium concentrations (0.1 mg dm^{-3}) the intensities on all lines are heavily affected even at relatively low aluminium concentration (1 g dm^{-3}) levels. Higher aluminium concentrations cause only a moderate reduction in the signal. Similar behaviour can be observed in the case of magnesium, strontium, and barium. As for calcium, the greatest decrease was observed also at an aluminium concentration of 1 g dm^{-3} , but higher aluminium concentrations cause a smaller decrease, even some increase can be observed in the ion-lines. It can also be observed that atom-lines are usually more strongly affected than ion-lines.

At higher analyte concentrations, the effect of aluminium is greater on all the lines examined and

increases with increasing aluminium concentration. The only exception is the intensities measured at an aluminium concentration of 1 g dm^{-3} , where in the case of each analyte the relative intensities are significantly lower than both the values gained at aluminium concentrations of 0.5 and 2 g dm^{-3} concentration, though the extent of the effect is different. This effect is larger or even larger in the case of beryllium, magnesium, and barium, and it is less profound for calcium and strontium.

With respect to the different types of lines, in the case of beryllium, where all the lines studied are sensitive, one of the atom-lines (234.861 nm) is less, while the other (249.473 nm) is more affected than the ion-lines. One of the atom-lines (388.829 nm) of magnesium is a weak line, while the other one (285.213

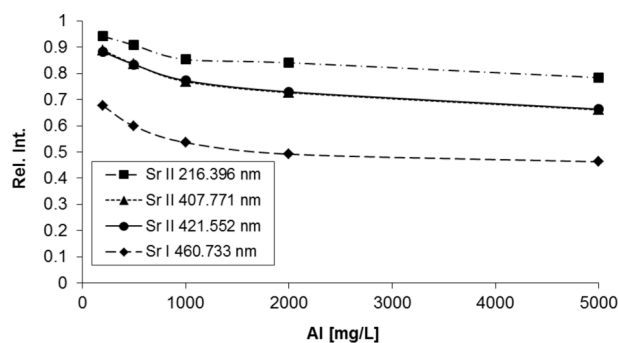


Figure 7. The relative intensities of 0.1 mg dm^{-3} Sr as a function of Al concentration, using a concentric nebuliser.

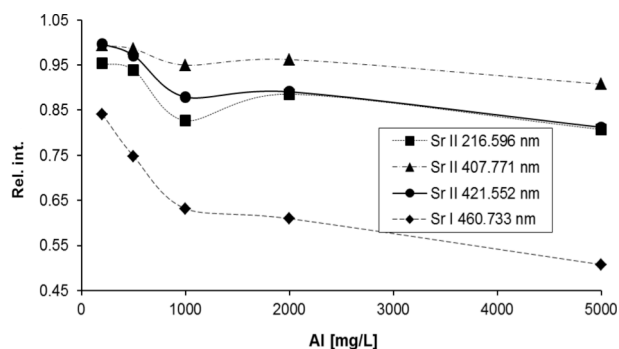


Figure 8. The relative intensities of 10 mg dm^{-3} Sr as a function of Al concentration, using a concentric nebuliser.

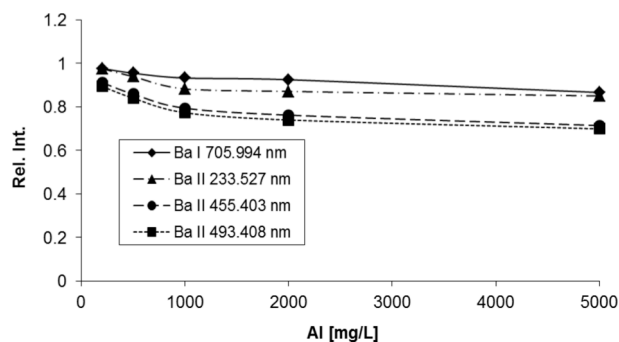


Figure 9. The relative intensities of 0.1 mg dm^{-3} Ba as a function of Al concentration, using a concentric nebuliser.

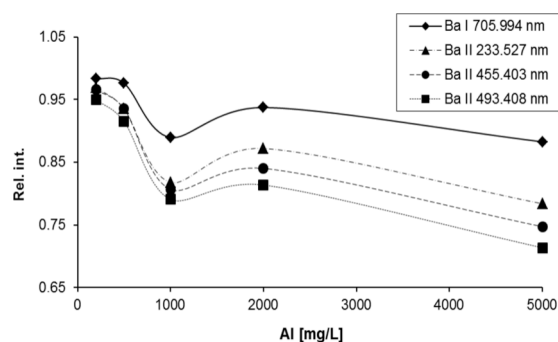


Figure 10. The relative intensities of 10 mg dm^{-3} Ba as a function of Al concentration, using a concentric nebuliser.

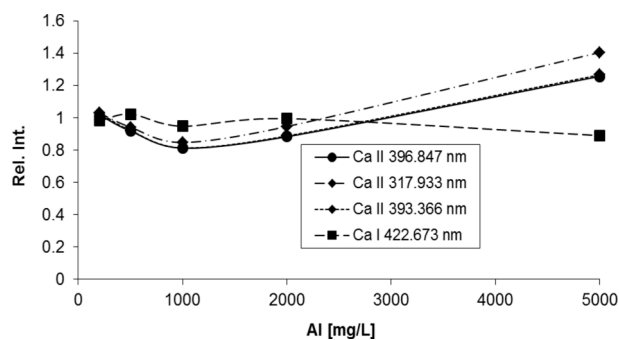


Figure 11. The relative intensities of 0.1 mg dm^{-3} Ca as a function of Al concentration, using a V-groove nebuliser.

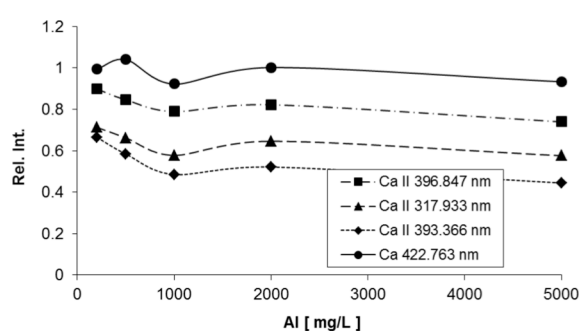


Figure 12. The relative intensities of 10 mg dm^{-3} Ca as a function of Al concentration, using a V-groove nebuliser.

nm) is sensitive. The first is heavily affected by aluminium, while the other lines manifest smaller effects. In the case of calcium and strontium, the atom-line is much more affected than the ion-lines, while the reverse can be observed for barium. Its atom-line is much less affected than its sensitive ion-lines.

The effect of the sample-introduction devices in Figs. 11–14 in the case of calcium manifests that at low analyte concentrations (0.1 mg dm^{-3}) almost the same type of curve is observed with the help of an ultrasonic nebuliser. Using a V-groove type device, only slight effects were detected. At higher analyte concentrations, all the lines are affected using the V-groove nebuliser; while in the case of the ultrasonic device the sensitive ion-lines (393.366 nm and 396.847 nm) are only slightly affected.

5. Conclusion

Using the axially viewed plasma, the light emitted from the high-temperature inner part of the plasma has to pass through the flame to reach the entrance slit of the optical system. As the photons travel, they pass through plasma layers of lower and lower temperatures. In the cooler environment, self-absorption, secondary excitation, and scattering processes can take place. These processes depend on the local temperature, which is also influenced by the high/higher concentration of elements in the sample than the analyte. All these processes make the relationship between line-intensities emitted and analyte concentration rather complicated.

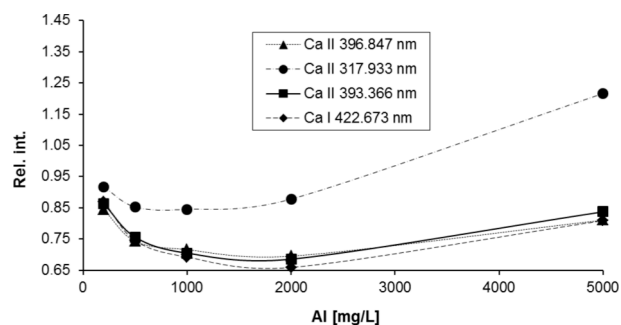


Figure 13. The relative intensities of 0.1 mg dm^{-3} Ca as a function of Al concentration, using an ultrasonic nebuliser.

It can be concluded that aluminium exhibits a strong interference effect on the emitted spectral line intensities of all alkaline earth elements studied. It can also be seen that atom-lines are usually more affected than ion-lines.

Although the relationship between the interferences and line intensities is complicated, in practice it can be eliminated by careful matrix-matching, i.e. the calibration solutions must contain the interfering element (Al) possibly at the same concentration level as the analyte in the samples. In addition, calibration curves can be extended, only with care in the presence of Al, as it could be observed that the extent of the interference is different at low and high analyte concentrations.

Acknowledgement

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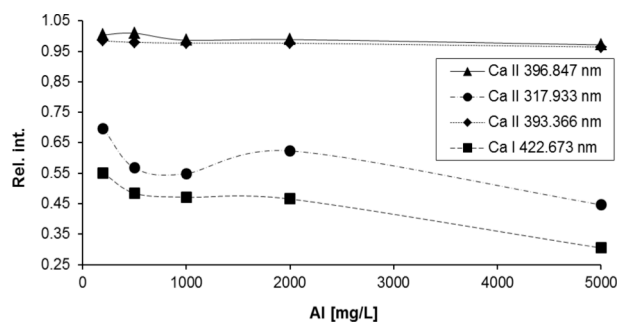


Figure 14. The relative intensities of 10 mg dm^{-3} calcium as a function of Al concentration, using an ultrasonic nebuliser.

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Soós Ernő Water Technology Research and Development Centre was established in 2014 by the Faculty of Engineering at the University of Pannonia, Nagykanizsa Municipality of County Rank and Hidrofit Water Treatment Ltd. The activities at the Research Centre are built on decades of experience and expertise gained in Nagykanizsa in the field of water treatment and water purification. The goal of the Centre is to perform international-level research activities in different areas of water purification and treatment. Nagykanizsa aims to become a centre of knowledge in national and international relations as well. Besides the fundamental research, the Research Centre plays an active role in industrial development activities, putting a great emphasis on drinking water treatment, power plants, the water management of cooling towers, horticulture and irrigation water treatment, seawater desalination, pharmaceutical and infusion solutions, water supply technologies and related control procedures, and areas of measurement technology.

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- Water treatment for horticulture and irrigation,
- Wastewater treatment in the oil and gas industries,
- Grey-water recycling,
- Seawater and brackish desalination,
- Water treatment for swimming pools,
- Monitoring and the control of water treatment, and development of instrumentation.

The Soós Ernő Research Centre is named after a pioneer in the water treatment field who was a chemical and environmental engineer. He made great contributions to the field with his innovative thinking. Several patents in water treatment are tied to his name. The desire of the research team is to advance his work by drawing on his leadership and scientific work as new frontiers in water treatment are pursued.

As an initiative of this decision, the Research Centre organised its first scientific conference in December 2014, entitled **Water and Wastewater Treatment in Industry**. Nearly 50 presenters attended the conference from both industry and academia with about 170 participants. Based on unanimous support, this conference has become international. In addition to industry and academia, companies from the service sector are also invited. The conference will be held on **28th October 2015**, and will be preceded by a project partner meeting.

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