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INQUIRY OF ANIONIC DETERGENTS IN CRIŞUL REPEDE WATER

Alexandrina FODOR, Anda Ioana Grațiela PETREHELE,
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Abstract
Determination of anionic detergents in sewage is put forward based on the well known principle of the formation and extraction by chloroform of a complex of the detergent and methylen blue. All values obtained are below the maximum amount permitted by law. It can be notice an increase of anionic detergent amounth once with moving downstream. It may also notice an increase in the concentration of anionic detergents in spring and summer to respectively winter and autumn; probably due to increased consumption of detergents with theincreasing of ambient temperature. The study carried out reveale a percentage increase în anionic detergent concentration in Crişul Repede water forward movement downstream up to 45%.

Key words: *anionic surface-active materials, spectrophotometric method*

INTRODUCTION

Because of the large use of detergents this products were placed in the category of chemicals used in large quantities (HVP / high production volume), subjected to specific legislation because of environmental pressure and high volume tha may reach into the environment.

The ingredients conteined in detergents that reachease the surface waters are coming from: industrial waters of various businesses which are using synthetic detergent or are preparing detergents, use of domestic detergents and their use for cleaning the streets and from farmland treated with insecticides or fungicides containing detergents.

The volume of waste water corresponding to that annual consumption is huge and reaches a relatively important in natural waters because people does not apply everywhere wastewater treatment, some of which are discharged into surface waters without treatment. Spilled on the ground, residues from detergents and even those due to domestic consumption are washed by rains and reaches the underground.

Synthetic detergents once arrived în surface waters can affect the ecological state of the environment causing a lower settling level of suspended substances, favoring the maintenance of suspended substances finely divided, increasing the speed of settling of particles larger than 25 microns, increasing the permeability of soils and promoting the ingress of contaminants such as tar carcinogenic substances, germs and viruses, etc [1-6]. Detergents have toxicological efects (on humans and other living creatures) and ecotoxicological efects (on the environment) due to the surfactants and conditioning agents [6,7]

Synthetic detergents accumulated on the water surface, produce foam and cause aerobic bacteria destruction because is depleting the exchange at the air-water interface. Molluscs, crabs and shrimp, for example, are the most affected by the presence of detergent in water, being threatened with total disappearance [8].

Detergents are present in water sources, in amounts up to 100 mg / L in the effluent from laundries, 10 mg / L in urban waste water, 5 mg / L in surface water and 2.5 mg / L in some underground water sources [9-11]. Detergents impact on the environment is more serious as their persistence is longer. Another factor contributing to environmental degradation is their volume, increasing in sewage from year to year.

Detergent removal from wastewater and domestic sewage is caried out in wastewater treatment station typically using coagulants. It is also possible to use other methods of detergents removing such as oxidation of detergents in adsorbed at the surface molecular layer; precipitation with an cationic agent; adsorption on various substances as activated carbon, activated aluminum, sand. Some inovating methods as ion exchangers can eliminate up to 99% detergents and the foaming with aeration can remove up to 85-95% in detergents; but those methods are expensive and laborious [7].

The most effective method of detergent removal from wastewater remains their biodegradation under the influence of microbial flora and its enzymes. Anionic detergents, contrast to those nonionic present the main disadvantage of a very small extent organic-biodegradable. These detergents arrived in water or soil scarcely decompose under the action of microorganisms, so it does not lose their harmfulness. The degradation rate of "harsh detergents" is 20-30% in wastewater treatment and water courses. "soft detergents" degrades to 90% in treatment plants and watercourses [7].

The European Union is planning to do an inventory and cleaning of the contaminated soil from all 28 member states, but is unlikely to face such a challenge in the near future.

This paper has proposed to make and present a study of pollution of the river Crişul Repede with anionic detergents.

Crişul Repede is a river crossing Bihor County, Crişana, Romania and south-eastern Hungary (Körösvidek). The Crişul Repede River runs through the city of Oradea, the capital of Bihor County. It flows into the Körös River near Gyomaendrőd, in Hungary (figure 1). Crişul Repede length is 209 km from which 58.6 km is in the Hungarian.

Due to the characteristics of the Crişurilor hydrographic basin, în this area there is an increased danger of producing environmental pollution phenomena becase of cross-border effects.

For the overwhelming majority of large settlements located on the Crişul Repede course its water is the source of drinking water for public consumption therefore the savage of the water pollution is very important.

EXPERIMENTAL

Were fixed 3- sampling point along the course of Crişul Repede: în upstream from Bratca (village located în upstream largest municipalities crossed by the river), Fughiu (point out în upstream largest city-Oradea crossed by river in Romania) and Sîntion (point found in downstream of Oradea).

Water samples were taken în plastic bottles, filtered and then stored under refrigeration for transport to the laboratory where further the water samples were concentrated by evaporation under reduced pressure and stored under refrigeration.

Sampling were made throughout the four seasons in January, May, August and October.

Figure 1. The cross-border Crişurilor hydrographic basin

All reagents were analytical purity and double distilled water was used for the solutions preparation.

The spectrophotometric measurements were caried out using a UV spectrophotometer from PG Instruments type T60.

Determination of anionic surface-active materials in sewage is put forward based on the well known principle of the formation and extraction by chloroform of a complex of the detergent and methylen blue [12]. Extinction is read at the spectrophotometer at a wavelength of 600 nm. The value obtained was related to the calibration stock standard solution reached by using sodium laurisulfat (0.25g sodium laurisulfat în 250 ml bidistilled water).

RESULTS AND DISCUSSIONS

The results of spectrophotometric measurements performed on the 12 water samples are presented în Table

1.Taking as reference the water samples taken în Bratca percentage increases of detergent in Crişul Repede water are presented în Table .

2. The Bratca samples were taken as reference because is upstream of the Crişul Repede course

Table 1. The amount of anionic detergent determined in water samples

Sampling point	Anionic Detergent mg/L			
	January	May	August	October
Bratca	1,45	1,38	1,54	1,41
Fughiu	1,52	1,48	1,63	1,49
Sîntion	1,84	1,83	1,97	1,81

Table 2. The detergent percentage increase in the Crişul Repede water (the reference value is considerede the one determined in the samples taken în Bratca)

Sampling point	Creştere procentuală detergent anionic			
	January	May	August	October
Fughiu	7	10	9	8
Sîntion	39	45	43	40

All values obtained are below the maximum amount permitted by law (2.5 mg / L) [13]. It can be notice an increase of anionic detergent amounth once with moving downstream. It may also notice an increase in the concentration of anionic detergents in spring and summer to respectively winter and autumn; probably due to increased consumption of detergents with theincreasing of ambient temperature.

Downstream from Oradea (Sîntion) the increasing of the anionic detergent concentration is consistent probably because Oradea is a large city (population 206,527 196.367 / 2011) and both the population and industry discharge a large amount of wastewater.

CONCLUSIONS

The study carried out reveale a percentage increase în anionic detergent concentration in Crişul Repede water forward movement downstream up to 45% even if the amount of anionic determined were below the legal maximum permissible quantity.

The health protection measures against pollution of water sources with detergents should be a worldwide concern. They can be taken only by a control pollution of water sources with detergents by:

-establishing a regular control of the amount of detergent in effluent treatment plants in the surface waters and underground distribution networks of drinking water followed by immediate action in case of exceeding safety levels of water quality or correcting performance installations water treatment waste;

-improving the methods of measuring small quantities of synthetic anionic detergent in raw sewage;

- conducting research for introducing of new methods for wastewater treatment or improving current methods to achieve a more rapid and complete decomposition of detergents;

- research of possibilities for the manufacture of detergents based on slightly oxidized substances by existing wastewater treatment plants;

-development of legislative measures against increasing pollution of water sources with detergents and their sanitary, technical and economic consequences;

-the development of a network for all the effluents treatment.

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SEPARATION AND IDENTIFICATION OF FLAVONOIDS FROM MATRICARIA CHAMOMILLA BY TLC

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Abstract: *Matricaria chamomilla is one of the most popular herbs is the grasses, flavored commoun in all areas of the plains, meadow at the edge of the road in summy spots or on land. The main active flavonoids are: rutina,miricetina, quercetin and hyperoside . These flavonoids act as powerful antioxidants.*

Matricaria chamomilla has a leading role in promoting cardiovascular health. This includes an improvement of coronary arterial blood flow and supply of oxygen to the heart, control. He has studied the content of flavonoids in leaf extract of Matricaria chamomilla .

Key words: *Matricaria chamomilla the leaves and flowers, active flavonoids,TLC.*

INTRODUCTION

Currently, chromatographic methods have a universal diffusion, both theoretical and practical and have the highest efficacy of all methods separate used in analytical chemistry and technology.[1]

Chromatographic methods can be classified according to the following criteria: [2,3]:

- the nature of mobile and stationary phase
- nature elementary sorption process
- sorption isotherm of form basic process

Matricaria chamomilla grows as a thorny shrub with white and pink flowers and berries in Europe, Western Asia, North America and North Africa.

Parties used in the pharmaceutical industry are leaves and flowers, the fruits are used especially in traditional preparations.[4,5].

The main active flavonoids are: rutina, miricetina, quercitin and hyperoside.

These flavonoids act as powerful antioxidants. Hawthorn has a primary role in promoting cardiovascular health. This includes an improvement in coronary artery blood flow and oxygen supply to the heart such contractions of the heart muscle, stable angina, congestive heart failure.

EXPERIMENTAL

We studied the flavonoid content of leaf extract of Matricaria chamomilla . Was done by thin layer chromatography (TLC) separation and identification their off. [6,7]. The used procedure: were: 1.Extraction. 2. Separation and identification of the main flavonoids.

1) *Extraction of flavonoids.*

1,5 g the dried herb was extracted with 15 ml of 1% HCl. Both of flavonoids and extract contains proteins. To remove the protein is added a solution of 10% sodium phosphotungstic $Na_3P(W_3O_{10})_4$ when it precipitates. After centrifugation, the solution containing flavonoids passing over a column of ion exchange resin

(Amberlite R 120). Elute column with 50 ml of 10% ammonia.

The solution obtained is evaporated to dryness on a water bath. For the subsequent operations of flash residue is taken up with 1 ml 30% isopropanol.

We developed a new method for the separation and identification of flavonoids by TLC. The results were tabulated in Table 1.

Table 1.

Nr.	flavonoids	Rf
1	Miricetine	0,543
2	Rutine	0,689
3	Quercetin	0.884
4	Hyperoside	0.578

2) *Separation and identification of flavonoids.*

Separation and identification of flavonoids was done by two-dimensional thin-layer chromatography plates were used with microcrystalline cellulose.

Preparation of cellulose sheets is as follows: weigh 15 g of powdered pharmaceutical balance of microcrystalline cellulose (Merck), to which was added 30 ml of water and 5 ml of methyl alcohol.

If the cellulose suspension is prepared in water alone, after drying, the adhesive layer thereof on an inert support glass crack, which prevents the migration of the mobile phase system formed by interrupting the capillary during the stationary phase.

The formed suspension was subjected to homogenization using a magnetic stirrer for 10 minutes at warm.

Resulting homogeneous paste is spread on the machine stretched thin, the plate 20 * 20 cm, which were previously degreased for snorting stationary phase on inert support.

The plates thus obtained were allowed to dry at room temperature, for a perfectly flat surface, for 24 hours.

The thickness of the stationary phase (microcrystalline cellulose) was adjusted to 0.3 mm. At a distance of 2 cm from one end of the plate can thus be applied with a microsyringe samples analyzed plant extracts.

For hawthorn was used as the mobile phase solvent mixture butanol: acetone: acetic acid: water = 35: 35: 7: 23 (by volume).

This mixture was homogenized well by shaking, and is left at room temperature for 24 hours to separate the phases. Mixture directly into the separating funnel, and after 24 hours separates two distinct phases.

The organic phase used for the elution is evident saturated with water. Attempts to optimize the separation of flavonoids by two-dimensional TLC. For elution in the first direction to use the system butanol: acetone: acetic acid: water = 35: 35: 7: 23.

After drying the plates was done elution in the second direction using a solvent mixture: methanol: water: pyridine = 80: 20: 5. Elution was done in the direction perpendicular to the first. Both elution was done two times.

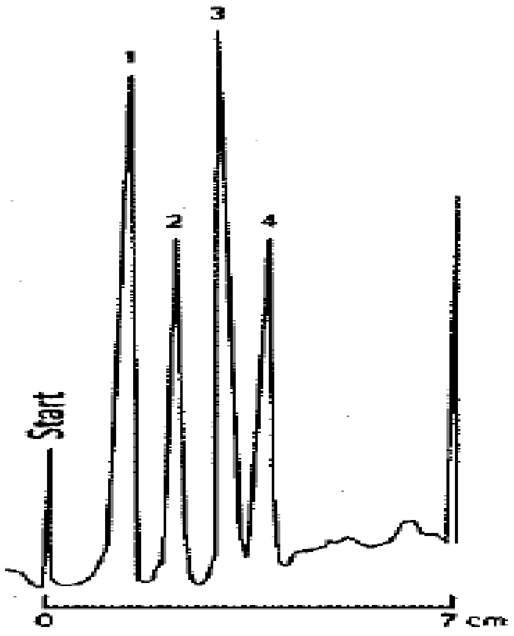

Fig.1. TLC chromatogram separation of flavonoids: quercetin, hyperoside, rutina, miricetina

For viewing using a ninhydrin solution obtained by dissolving 3.6 g of ninhydrin in 50 ml of a mixture of butanol: acetone (50: 50 v / v). Ninhydrin solution was sprayed using a spray particular, homogeneous on the whole surface of the plate.

In both cases, after elution, the plates were left at room temperature for several hours after that enter the °110 C. 15 minutes of stand on white background pink appear distinct areas - reddish of flavonoids present in the test sample.

CONCLUSIONS

- were identified and separated all the main flavonoids present in the plant, using thin layer chromatography, plant with multiple uses in pharmacology
- identify was based on retention times
- from chromatogram shows that each of flavonoid present in the extract, corresponding to this peak has increased in proportion to the contribution of the concentration of each extract
- some components appear strongly colored, others less strong component related to sensitivity reaction given reagent used

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STUDIES UPON LEAD RECOVERY FROM WASTE WATER STREAMS BY CHEMICAL PRECIPITATION. DETERMINATION OF THE OPTIMUM SEPARATION CONDITION

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Abstract: *Crystalline shape of lead oxalate was extracted from waste water streams, in specifically conditions as regarding: pH, acid oxalic dose and temperature, due to the low value of solubility product of lead oxalate. In this way it was possible a treatment method by chemical precipitation of waste water streams, recovery transitional metal Pb.and environmental protection. The optimum recovery conditions were: pH 5,5 oxalic acid 22% excess,(precipitation regent) temperature* 20^0C*, for 1000mg/*Pb^{2+}*/L concentration. White crystalline precipitate of lead oxalate was washed ,dried, and investigated through chemical methods, flame atomic absorption spectrometry, thermal analysis and FT-IR method, in order to establish chemical formula, composition and technological conditions for obtaining lead oxalate with 99% recovery degree.*

Key words: lead, oxalate, recovery, waste water, precipitation

INTRODUCTION

Lead contamination has been identified as a worldwide problem due to its long-term and widespread use. Lead enters the environment as a result of both natural process and anthropogenic activities. Natural processes include pedogenic mineral breakdown and translocation of products, as well as sedimentation, from dust storms, volcanic eruptions and forest fires. Anthropogenic activities of lead contamination include mining and smelting operations, battery recycling, combustion of leaded gasoline, salvage yards, urban and industrial wastes, continuous use of fertilizers, pesticides and use of Pb bullets[1].

Lead is a cumulative toxin in the body, like bones marrow. Lead is a powerful neurotoxin, but kidney damage also occurs as a result of exposure to Pb

In spite of these, lead is an important element with many industrial uses; however, in its ionic form in industrial wastewater is extremely toxic and strict environmental laws impose its removal from wastewater, or waste water streams.

Particularly, the electronic and galvanic industries generate **waste water streams** with Pb^{2+}, diluted nitric acid and nitrates, coming from lead deposition on steel surface. Lead concentration values are in a wide range, between 40 and 1000 mg Pb^{2+}/L.[2-5]

There are many and different possibilities for the treatment of waste waters with heavy metals like nickel, cobalt copper, led, iron and other cations from metal plating industries, electronic industries, metal processing . Waste waters streams are containing besides Ni(II), Cu(II), Co(II), Cr(VI), Zn(II) and Pb(II) various salt specifically for electroplating process like chlorides, sulfates, nitrates, fluorides and also chelating agents, surfactants, sulfuric acid, boric acid. If the process goes in alkaline pH, then, residual solutions contain carbonates, phosphates, sodium hydroxide. [6,7]

The methods used in practice, according to the specialist literature, for lead removal, depending on the concentration of its ions in the waste water streams are: ionic exchange, adsorption on zeolites, chemical precipitation, electrolysis, chemical reduction, biosorption. [8-12]

Chemical precipitation represent however an efficient way of heavy metal removal from waste water stream, with a high level of Pb^{2+} concentration. Pb^{2+} was chemically precipitated with starch xantate, sodium hydroxide, 1,3-benzenediamidoethanethiol dianion ($BDET^{2-}$), sodium di-(n-octyl) phosphinate [7, ammonium zirconyl oxalate, $(NH_4)_2ZrO(C_2O_4)_2$, respectively. [13-18].

The cations precipitation whith sodium hydroxide, carbonates, phosphates or lime stone gives amorphous compounds of Ni, Co, Cu, Cr, Pb or Zn which are difficult to separate, wash, filtered, guard and store in a stable composition because of their instability to air, humidity, CO2.

In this work we present some studies regarding lead recovery from waste water streams, by chemical precipitation as lead oxalate, also determination of the optimum lead recovery degree, using oxalic acid as precipitation reagent, taking into account the low solubility product of lead oxalate ($4,4 *10^{-10}$ mg/L) [19]

The aim of the present study is to establish the optimum precipitation conditions in terms of: pH of Pb^{2+} solution, molar ratio Pb^{2+}:reagent (quantities of oxalic acid) and temperature.

The lead recovery degree α% values are influenced by process parameters as pH, excess of oxalic acid, the temperature of precipitation process.

.

MATERIALS AND METHODS

All the reagents were chemical pure or spectral pure type (Merk, Fluka, Amex): standards solutions Merck 1000 mg Pb^{2+}/L, volumetric solution of titriplex III, 0,05M, 1N nitric acid solution, potassium permanganate 0,1N, Eriochrome Black T, lead nitrate, ammonium buffer solution (pH=10), bidistiled water, 0,05M oxalic acid solution, lead nitrate $Pb(NO_3)_2$, sulphosalycilic acid and copper 1-(2-pyrydilazo-2-naphtol (PAN) as indicator in acetate buffer solutions for Fe^{3+} and Al^{3+} for trimetric analysis. All the solutions are volumetrically with F=1.

Pb^{2+} content in the working solutions was determined by both complexonometric titration and by flame atomic absorption spectrometry (FAAS), using a spectrophotometer ThermoElectron M Serie M5 Dual, according to SR ISO 8288 [20,21]

The technical parameters and technical conditions for a good measurement of initial and finally concentrations of lead cations for ThermoElectron M Serie M5 Dual, were: λ=217,0 nm, flame air- C2H2: 15,7 mm(high's flame), acetylene flow 0,9 L/min, number of readings: 3.

The calibration curves were plotted using lead etalon standards solutions with 0,000, 0,500, 1,000 şi 3,000 mgPb^{2+}/L. The results are presented in Table 1.

It was plotting the calibration curves for lead etalon standards solutions and absorbance: ; 0,000, 0,500, 1,000 şi 3,000 mgPb^{2+}/L. The results are presented in Table 1.

Tabel . 1. Values of lead standard concentrations and absorbance

Name of standards	Conc. Pb^{2+} (mg/L)	Absorbance	RSD (%)
Pb blank	0,000	0,000	>99
Pb . St. 1	0,500	0,093	0,1
Pb . St. 2	1,000	0,175	0,4
Pb. St. 3	3,000	0,496	0,4
Pb St..check 0,4	0,422	0,076	1,2
Pb St.. check 0,2	0,20	0,041	0,7

The calibration graph, Absorbance (OY) as function of lead concentration (OX), is described by equation:

$$y= 0,2761X-0,0675$$

The working synthetic solution of $Pb(NO_3)_2$, containing 1g Pb^{2+}/L, was treated with a 0,5M solution of oxalic acid, in a well determined ratio at different working temperature and pH values, under continuous stirring. The pH was adjusted to the desired value by adding NaOH 10% solution or HNO_3 10% solution. The residual concentration of Pb^{2+} in solutions was determined by both FAAS and complexonometric titrations.

The lead oxalate precipitate has been settled, filtrated, washed and the dried powder has been characterised. For this purpose a well known quantity of oxalate was dissolved in HNO_3 1:2 vol. The cation analysis was also performed through complexonometric and FAAS methods. The oxalate anion was determinated by permanganometric titration in the presence of sulphuric acid, at 80^0C[20].

The thermal analysis of lead oxalate was made on a derivatograph Paulik,Paulik and Erdely, MOM Hungary, for a sample mass of 100 mg, a heating rate of 5°C/min, under static air atmosphere.

FT-IR analysis of the lead oxalate was performed on a JABLE-JASCO spectrometer.

RESULT AND DISCUSSIONS

The recovery purging process of lead as insoluble crystalline precipitate lead oxalate, is based on the precipitation reaction :

$$Pb^{+2} + C_2O_4^{-2} = PbC_2O_4\downarrow$$

(crystalline white precipitate)

The recovery efficiency of the cation has been calculated using the formula:

$$\alpha,\% = \frac{C_{i,Me^{2+}} - C_{f,Me^{2+}}}{C_{f,Me^{2+}}} \cdot 100$$

where: α = percentage recovery degree, %
$C_{i,Me}^{2+}$ = concentration of the cation lead, in [mgPb^{2+}/L] before the precipitation with oxalic acid
$C_{f,Me}^{2+}$ = concentration of the cation lead, in [mgPb^{2+}/L] after the precipitation as lead oxalate.

The influence of various parameter such as: reaction mass pH, excess of precipitation reagent and precipitation temperature, upon the α% parameter was studied in order to establish the optimal working conditions.

3.1 *Reaction mass pH*

The influence of the reaction mass pH on the recovery efficiency α% of lead oxalates from aqueous solutions of $Pb(NO_3)_2$, [1g Pb^{2+}/L] was studied at 20°C, using 10% excess of oxalic acid, for a time of reaction of 10 minutes, under mechanical stirring at 300 rot/min. ph values of the reaction mass were modified in the pH range 1.0 – 6.5.

The residual lead content in the remaining solution after chemical precipitation was determined by FAAS and confirmed also by complexonometry.

The obtained experimental data are shown in Table 2.

Tabelul 2. Values of recovery degree and reaction mass pH

No. Exp.	pH	Absorbance	Pb^{+2} finally [mg/lL]	RSD (%)	α (%)
1	6,5	0,185	1,090	0,3	98,88
2	5,5	0,185	1,090	0,3	98,88
3	4,5	0,185	1,090	0,3	98,88
4	3,5	0,296	1,768	0,6	98,23
5	2,5	0,296	1,768	0,6	98,23
6	1	0,3	1,790	0,6	98,21

By increasing the pH value the efficiency of the lead recovery as lead oxalate slightly increases. The recovery degree of the lead oxalate scale up with 0,67% from pH=1 to pH=4,5 where achieves the maximum value 98,88.% In the pH range 4.5 - 6.5, the recovery degree remains constant at its maximum values.

According to these results we choose the optimum pH value for the precipitation of lead as lead oxalate at 4.5

3.2 Excess *of oxalic acid (precipitation reagent)*

The experimental data obtained for the chemical precipitation of a 1g Pb^{2+}/L solution at 20°C, optimum pH value, for a reaction time of 10 min, under mechanically stirring 300 rot/min, with different excesses of oxalic acid (compared to the stoechiometric necessity) are shown in Figure 1.

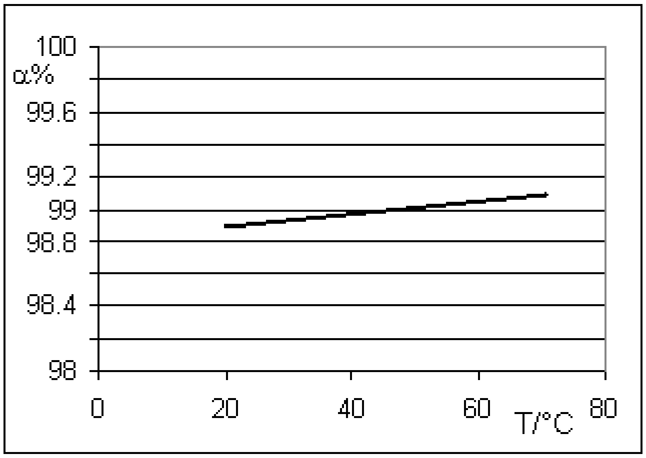

Figure 1. Dependence recovery yield of metalic oxalates on- oxalic acid excess

From the evolution of the curve presented in Figure 1**,** it results that the lead recovery degree α% is improved by the increasing in precipitation reagent excess. For a reagent excess of 100%, the lead recovery degree increases only with 0,26% and the final value was 99,2%. The value of 0,26% may be considered not significant for the process. A reagent excess of oxalic acid higher than 22% is not necessary.

From these data results that the optimum reagent excess for lead is between 10-22% of 0,5M oxalic acid solution, with a recovery degree about 99,2%.

c) The influence of precipitation temperature

The experimental data regarding the influence of temperature over the recovery degree, at optimum pH, optimum reagent excess at 20°C, respectively at 70-80°C, are shown in **Table 2**

Table 2

No	T^{o}C	α %
1	20	98,88
2	40	98,88
3	70-80	99,20

From the data shows in Table 2 results that in the case of the precipitation at 70-80°C, the influence of temperature on the recovery degree in form of lead oxalate is unimportant.

Lead recovery degree in form of crystallized oxalate becomes profitable, achieving recovery efficiency around 99,2%. Technically, it can be considered a efficient process at medium temperature, 20 ^{0}C .

d) *The chemical composition of lead oxalate*

The lead oxalate that had been obtained in optimum conditions, in form of crystalline precipitate, were filtered, washed, dried and subdued to a chemical analysis according to chapter 2, in order to obtain the chemical formula and the chemical composition of the extracted compounds [20,21]. The experimental data on the chemical composition of the oxalate obtained from complexonometric and FAAS analysis (for the cation) and from the permanganometric analysis (for the oxalate anion) are shown in **Table 3**.

Table 3
THE CHEMICAL COMPOSITION OF LEAD OXALATE

PbC_2O_4	Pb^{+2} (%)	$C_2O_4^{-2}$ (%)
Theoretically	70,18	29,82
Practically	69,41	30,02
	69,38	30,04
	69,40	30,59
Mean	69,39	30,

The experimental results confirm the anhydrous shape of lead oxalate: PbC_2O_4,

e) Thermal analysi
s

Figure 2 presents **t**he derivatogram obtained at heating in air of the separated lead oxalate until 500°C.

TG and DTA curves evolution show that the thermal decomposition of the lead oxalate occurs in a single exothermic step, around 350°C. The mass loss corresponds to the loss of CO_2 and CO according to the reaction equation:

$$PbC_2O_4=PbO+CO_2+CO$$

The thermal curves presented in Figure 3 for the isolated compound correspond qualitatively and quantitatively to PbC_2O_4, confirmed also by the chemical analysis results.

f)The FT-IR analysis

The isolated compound was characterised by FT-IR spectrometry also. Figure 4 presents the obtained FT-IR spectrum.

The FT-IR spectrum analysis is representative for a M(II) oxalate. Thus, The intense band at 1586 cm^{-1} correspond to the OCO asymmetric stretching vibrations, while the band from 1282 cm^{-1} correspond to the OCO symmetric stretching $\nu_s(OCO)$. The sharp band that appears at 772 cm^{-1} is attributed to the OCO group bending vibrations $\delta(OCO)$.

g) Technological flux lead oxalate recovery

According to experimental data and the study of improving the recovery of lead ion we offer the following technological flux to get lead oxalate.

The fully eliminate the lead after the 99,2% recovery of initial divalent lead we made a precipitation of 10% milk of lime at a pH of 10.The oxalic acid that remained falls down as calcium hydrated oxalate and lead hydroxide.

The reactions resulting by precipitating the Pb^+ ion with Ca $(OH)_2$ and by neutralizing the excess of oxalic acid are:

.

$$Pb^{2+} + Ca(OH)_2 = Pb(OH)_2 + Ca^{2+}$$

$$H_2C_2O_4 + Ca(OH)_2 \rightarrow CaC_2O_4 * 2H_2O \downarrow + H_2O$$

The slime resulted contains $Pb(OH)_2$ and Ca $(OH)_2$ and the waste discharged solution is according to the standards SR ISO 8288 concerning the accepted quantity of lead (under 1 mg Pb^{2+}/ L) see in Figure 5.

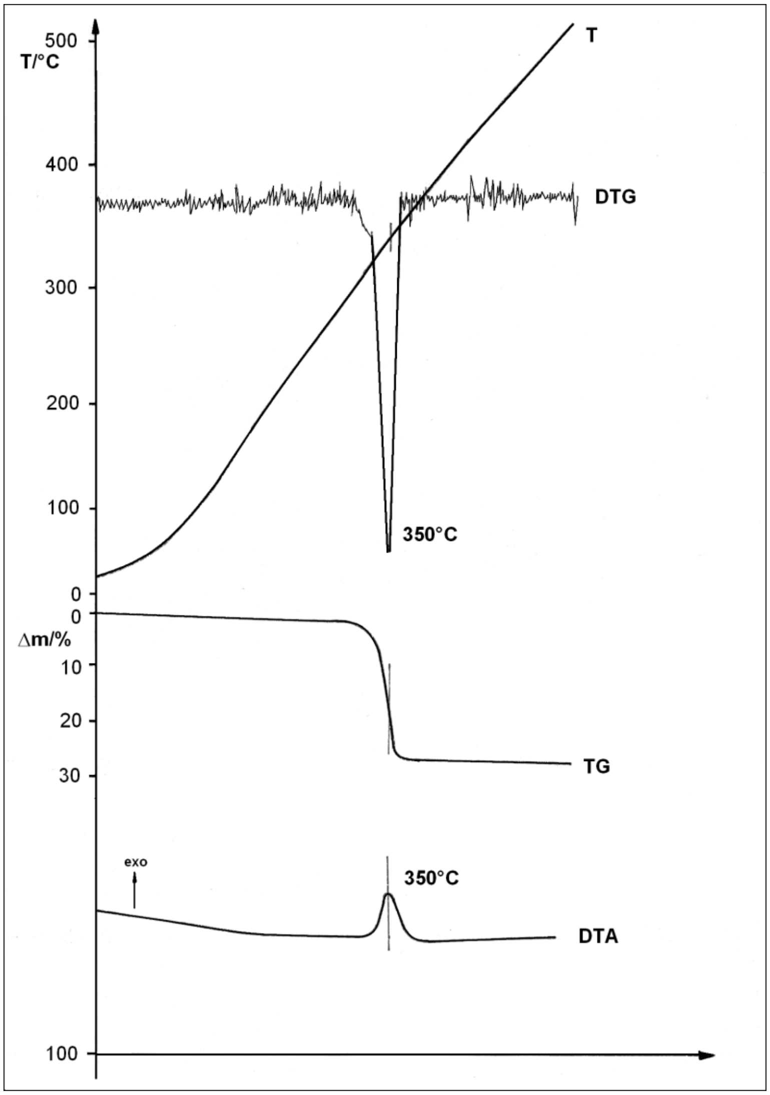

Figure 3. The derivatogram of lead oxalate

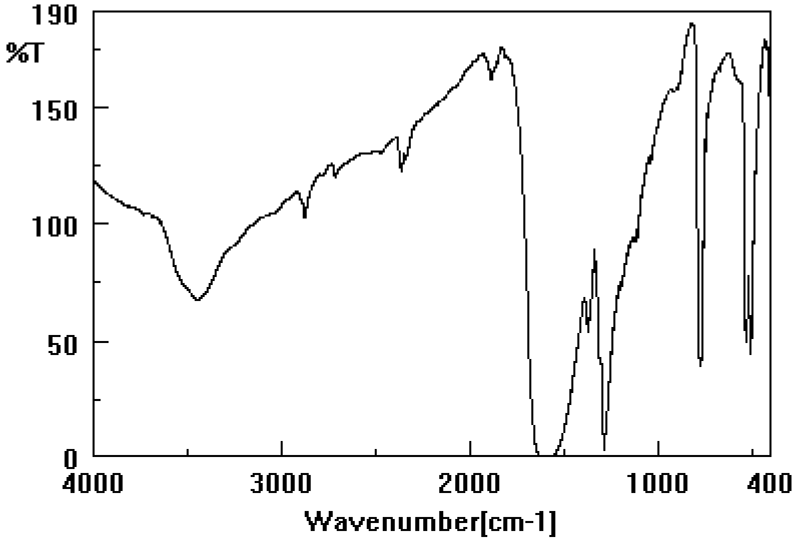

Figure 4. The FT-IR spectrum

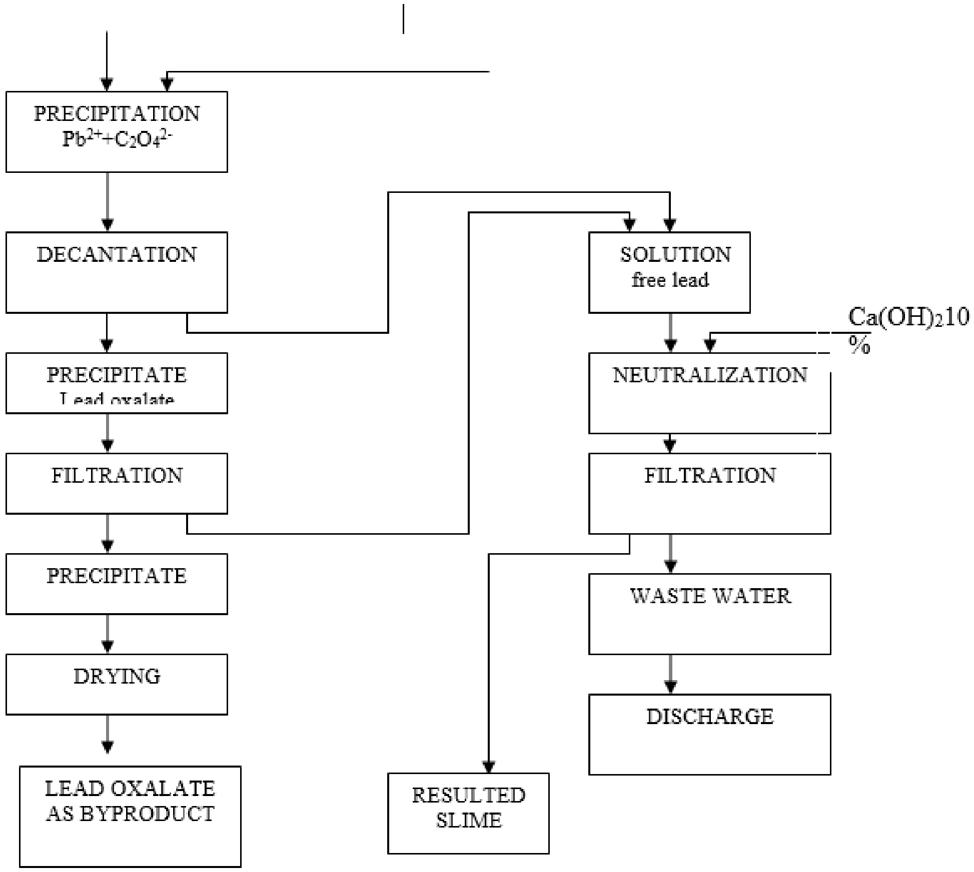

Figure 5 Technological flux of lead recovery by chemical precipitation treatment in the shape of crystalline white lead oxalate.

The discharges solution containing lead ions is treated with $H_2C_2O_2$- 0,5 M under continuous movement, 300 rotations / minute for 10 minutes time reaction, at 20^0C. The crystal – white precipitate obtained is left to fall down then it is filtered and washed. The washing waters are collected into a reaction bowl and neutralized with Ca $(OH)_2$ 10% till a pH is 8,5- 9 [2].

The slime resulted is retained, the waters are discharged according to the water standards quality.

Practically, the waste water streams were collected from Metalica S.A. Oradea citty, Bihor- Romania. It was taken 10 samples of waste water streams coming from metal acid plating with lead from $Pb(NO_3)_2$ acid baths. The mean concentration of lead in water streams was 0,9965 g Pb^{2+}/L,(around 1g Pb^{2+}/L). By chemical analysis according to chapter 2, we found small quantities of 5 -15mg Fe^{3+}/L and 2-4mg Al^{3+}/L, which have not influenced the lead recovery degree and the process is carried out on optimum conditions with 99,2% percentage lead recovery.

CONCLUSIONS

The precipitation of lead ion Pb^{2+} solutions as anhydrous lead oxalate using the method presented in the paper, can be used for treatment of waste water streams coming from acid lead coating on metal sheet**,** with 99,2% efficiency recovery degree. The purging process of lead ion as unhidrous lead oxalate, from various residual effluents has the following advantages:[22]

- speed of cleaning, filtering, washing- superior to the amorphous forms
- low and compact volume of the precipitate
- low energy costs for by-products with various usage: lead oxide
- the transformation of lead oxalate, initially obtained, into lead salts
- a precipitation reagent that is economically accessible (synthesis, price, transport, chemical stability)
- The optimum pH values are easy to obtain using suitable substances, also dose of oxalic acid and the temperature if it necessary.
- The crystalline oxalates can be easy transformed in pure oxides, at low temperature, about 350^0C, or using subsequant application.

The oxalic acid excess and the remaining cation can be eliminated by treating the filtered product and scouring waters with 10% milk of lime. Thus, the oxalate anion is precipitate as calcium oxalate and the remaining cation precipitates as a hydroxide.

The pH of the solution is corrected, the metal content being under 0.1mg Pb^{2+}/L, and the effluent can be disposed according to the environment and waters quality legislation.[23] The recovery of heavy metals as oxalates resolves the environmental problems as well as the recovery of transitional metals

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A THEORETICAL APROACH OF STEEL CORROSION

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Abstract

Corrosion and corrosion protection is a particularly important field of preventing economic losses but also of combating environmental pollution. The issue of corrosion concerns any engineering field that uses metals and alloys, but in particular those where the metal-environment interactions are very diverse, such as water and gas supply systems, power generation systems, transportation.

Key words: steel corrosion, methods, classification.

INTRODUCTION

Corrosion is defined as a complex process, influenced by factors, which depend on the wide variety of technological environments and technical metallic materials. Corrosion can be regarded as a heterogeneous redox reaction occurring at the metal / nonmetal interface [1-14].

Choosing the right material for water transport and distribution networks, modern technology currently offers a wide range of metals, alloys, plastics, ceramic or composite products. This choice is a major responsibility, and it belongs primarily to the specialists, but also to the engineers of exploitation, and it is the result of the analysis of the interaction of the material of the pipes with the environment. The negative effects of the corrosion process are the losses of about 10-15% of the world's annual output of metallic materials, plus additional costs associated with stopping repair facilities, replacing corroded parts and particularly important from the perspective of sustainable chemical contamination and / or biological, water, soil or air.

Classification of corrosion processes can be done according to the following criteria: after the mechanism of the corrosion process, after the corrosive attack and the nature of the corrosion environment [1-14].

METHODS

Using certain methods for testing the corrosion process depends on the type of corrosion evaluated, the purpose to be pursued, the place where the determination is made in the laboratory or in-situ. In most cases, for more comprehensive assessment of corrosive action, several methods are used in parallel [1,2].

The main electrochemical methods used for rapid corrosion rate measurements applied to homogeneous corrosion systems are: visual examination, microscope examination: Tafel slopes extrapolation (Stern method); polarization resistance method (Stern-Geary method); electrochemical impedance spectroscopy (EIS) [1,2].

RESULT AND DISCUSSIONS

Metal corrosion processes are carried out by an electrochemical mechanism, although some authors also use the term chemical mechanism for a particular case of electrochemical corrosion, the homogeneous one. According to the definition of corrosion as a heterogeneous redox reaction, the electrochemical mechanism of metal corrosion involves the exchange of electrical charges between metal and the environment in the form of two reactions:

- anodic oxidation reaction

$$M \rightarrow M^{z+} + ze$$

-in the cathodic reaction (the reducing an oxidant from the environment)

$$Ox + ze \rightarrow R$$

wherein: Ox, R represents the oxidized form or the reduced form of the cathodic polarizer. The two reactions occur on the surface of the metal simultaneously and at the same speed, which translates into equal speeds of the two processes during corrosion.

Depending on the location of processes on the surface of metals, three electrochemical corrosion mechanisms can be identified:

- **homogeneous corrosion** (uniform corrosion of metals in acid, alkaline and neutral solutions, etc.)

- **heterogeneous corrosion**, where the anodic or cathodic function in certain areas of the metal, a process due to the inhomogeneity of the metallic phase (polycrystalline structure, bimetallic stresses, presence of impurities, oxidation film discontinuity, uneven distribution of internal temperature or stress, etc.) as well as the inhomogeneity of the corrosion environment (different concentrations, differential aeration, etc.).

The heterogeneous corrosion is explained by the appearance and functioning of local corrosion cells, resulting in the localization of the destructive attack on the most active (anodic) areas, while the destruction of the more noble (cathodic) zones is diminished or completely stopped. In these corrosion systems there will be a macroscopic flow of electrical charges through the metal.

The consequence of corrosion by this mechanism is non-uniform and localized corrosion of metallic materials, the most common way of manifestation in practice;

-**film corrosion** characterizes the corrosion systems in which the metal surface is coated with a film of adhering reaction product and therefore the metal / reaction product interface functions as anode and the reaction / corrosion interface acts as a cathode . ("dry" corrosion);

If the anodic reaction is in any corrosion process described by the oxidation of a metal to its ion, for the cathodic reaction there are several variants related to the composition of the medium.

Below are some of the cathodic reactions possible to occur in a metal / water system that can be found in a water transport and distribution network:

-hydrogen evolution in neutral or alkaline media:

$$2H_2O + 2e \rightarrow 2OH^- + H_2\uparrow$$

-reduction of dissolved oxygen in neutral and alkaline environment:

$$2O_2 + 2H_2O + 4e \rightarrow 4OH^-$$

-reduction of metal ions:

$$M^{z_2+} + (z_2 - z_1)e \rightarrow M^{z_1+}$$

- *metal depossition*:

$$M^{z+} + ze \rightarrow M$$

Oxygen reduction is a very important cathodic reaction because oxygen is present in all natural environments, air and soil, making it one of the most common corrosion agents. Reduction of metal ions and metal deposition, although less common, causes serious corrosion problems, especially in water pipes.

According to the appearance or the distribution of the corrosive attack, corrosion can be defined as: general (fig.1.a and b) or localized (fig. 1b), depending on the appearance and distribution of the corrosive attack.

a

b

Figure 1. Corrosion of OL37 carbon steel water pipes: a) generalized external corrosion and localized-pitting; (b) interior corrosion and crust deposits [4].

The most common form of corrosion is general corrosion that affects the entire surface of the metal. The general attack, "more or less uniformly represents the greatest destruction of metal in terms of tonnage; however, from a technical point of view, this form of corrosion is not considered dangerous because the lifetime of the equipment can be estimated quite accurately based on laboratory tests. "[1]

Localized corrosion, the most dangerous form of corrosion, following the heterogeneous electrochemical corrosion process, in which the corrosive attack is made on very small but particularly intense surfaces and with a very high propagation velocity leading to the premature removal of the machine.

Localized attack forms, depending on the nature of the metallic material and the actual operating conditions; are divided into: pitting corrosion, selective corrosion, intergranular corrosion, corrosive cracking, corrosive cavitation.

Pitting or punctural corrosion occurs when the attack focuses on small areas of 0.1-2 mm, intensely destroying the metal in depth and in extreme cases, causing the perforation of the metal wall. Frequently this way, aluminum and its alloys, stainless steels and metals or alloys coated with passive protective films, acting cathodic, concentrate the destruction on weaker points. Stripping of the film may be due to a physical cause or the presence of so-called activating ions in the environment, such as halogen ions, $HCOO^-$ and others.

Selective corrosion is a form of corrosion of alloys characterized by the passage of a more active component into the solution without the appearance of a visible form of attack and without altering the size of the metal; however, the porosity of the alloys is found at the microscope, resulting in a drastic reduction of the mechanical properties. The most common examples are: delamination of brass, in which zinc is selectively shifted from the alloy and the "graphite corrosion" of the iron, in which the iron is selectively dissolved.

Intergranular corrosion (also called "intercrystalline corrosion"). The attack is located at the boundary between the crystalline grains, resulting in loss of mechanical strength and ductility, and in limited cases, causing the alloy to disaggregate. Inappropriate heat treatments lead to the intergranular corrosion of 18Cr / 10Ni austenitic stainless steels and duralumin alloys.

Crack corrosion is the type of corrosion that spreads intergranularly or transgranularly within the metal in the direction of maximum mechanical stress due to the simultaneous action of the corrosion environment and mechanical stresses (seasonal braze cracking, corrosive fatigue, corrosive friction).

Corrosive cavitation is the type of corrosion that occurs on metal surfaces in contact with liquid aggressive media in turbulent flow. The destruction of the metal is caused both by the detachment of the metal by high velocity jets (erosion) and the corrosive action of the environment.

Classification of corrosive destructions, by their degree of concentration on the metal surface or inside of the metal, is of a conventional nature. Often the same piece of metal can have various destructive types, whose rigorous delimitation is not possible

A special case is the fight against the corrosion phenomenon justified first of all by the need to ensure the safety of the transport and distribution networks of cold, hot water or district heating, as well as to limit the losses of water and materials, soil pollution, economic losses generated by stopping / repairing the plant. The corrosion behavior of a carbon steel pipe is strongly influenced by the following factors: the state of the metal surface and the possible mechanical, thermal or chemical treatments of the metallic material [4-7, 14].

CONCLUSIONS

The use of the theoretical notions regarding corrosion, in the case of anticorrosive protection of water pipes, applied to prolong the duration of operation of the transmission and distribution networks, led to the following conclusions:

- the first and most important choice is that of the pipe construction material, which means knowledge of the complex metal / medium system, ie steel material properties and potential corrosion factors both from the soil and from the transported water;

- for the avoidance of external corrosion, coverings are made with protective, insulating, non-metallic layers. Coatings are usually made of primer and one or several layers of bitumen and an outer sheath of protection. A modern design is the introduction of a carbon steel pipe into a high density polyethylene / polypropylene pipe and the filling of the intermediate space with polyurethane resin, which achieves both anticorrosive protection, but also limits the heat loss in the case of hot water and heating pipes, thus increasing the energy efficiency of the network;

- for avoiding internal corrosion, several methods have been proposed: insulation with bituminous lacquer, insulation with plastic layer or rubber, metal zinc coating, nickel-plating. Unfortunately, these variants are not very reliable: organic layers deteriorate at pipe welding, and metallic ones are expensive. Even cement or silicate coatings have been used with good results;

- the treatment of the transported water, possibly by the addition of corrosion inhibitors - the method that can be used only at the level of the buses, which should observe the closed circuit condition. The major problem would be that if the pipes break, soil and groundwater pollution or surface contamination with undesirable chemicals may occur;

- use of electrochemical protection methods: anodic protection and cathodic protection with soluble anodes or external current source;

- solving the problem of stray or dispersing electrical currents from various industrial or domestic electrical installations, as well as tramways, subways or trains, by drainage or sewerage.

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(12pt)

INSTRUCTIONS FOR AUTHORS (TIMES 14 PT BOLD, CAPITAL LETTERS, CENTRED)

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First name SURNAME[1], First name SURNAME[2] (10 pt bold)
[1]Affiliations and addresses (10 pt)Affiliations and addresses (10 pt)

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Abstract: *Abstract of 50-120 words (10 pt italic). It contains concise information about: objectives of the work, the results obtained, conclusions*

Key words: List 2-6 keywords. (l0 pt, italic).

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The paper has to be written in English. Each paper should be concise including text, figures and tables. Authors are kindly requested to submit a paper a hard copy or in electronic format in Microsoft Word file form. Acceptable versions are MS-Word 2003, 2007, 2010. The suggested structure of the main text: Introduction; Methods, techniques, materials, Study area; Results and Discussions; Conclusions; References. (10pt)

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- Use A4 format (210 x 297 mm),
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- Text: l0pt.: regular, text in tables: 10 pt, 1 line space and centred, 2 columns,
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All tables and figures follow the References or could be inserted within the text. Tables, together with figures should be placed in their order of appearance in the text. Tables should be numbered consecutively. Table captions containing the number of the tables, followed by the caption, and should be placed above the table. Tables should be clearly captioned and all symbols should be properly explained in either the table or its caption.

Figures (min. 300 dpi) can be in colour, but must also be clear enough for black and white reproduction. They should be centred and numbered consecutively and so referred to in the text. Each must be clearly captioned (after the Figure number) below the figure.

Equations will be centred and numbered consecutively (right aligned).

All references would be cited within the text as superscripts after the punctuation's marks.[1]

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All papers cited should be listed under the **REFERENCES** (1 column), in alphabetical order according to the author's last name. The list of references should follow the format given below:

(Journal Article)

[1] Abbott, M. B., Petersen, M. M., and Skovgaard, O. (1978). On the numerical modelling of short waves in shallow water, Jnl Hydraulic Res; Vol 16 (3), pp. 23-44.

(Report)

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