Influence of Natural Organic Matter on Coagulation Efficiency

Ramóna Lugosi, Judit Gajári
lugosir@freemail.hu, gajarij@almos.vein.hu
University of Veszprém
Dept. Environmental Eng. Chemical Techn,
H-8201 Veszprém P.O.B. 158, Hungary
Phone: +3688422022/4403, Fax: +3688425049

ABSTRACT
The water of Lake Balaton contains high concentration of both organic and inorganic compounds. The determinant processes of the treatment are coagulation with metal salts, flocculation and following phase separation. The efficiency of coagulation is influenced by many parameters e.g. *type and dose of coagulant*, properties and amount of *dissolved organic matter*, *pH* of coagulation, *alkalinity* of the raw water, the *mixing intensity* of the coagulant and flocculant.
The objective of this study was the optimization of coagulation parameters for Lake Balaton water and the study of the NOM present in the water.
Three different coagulants –Ferric-sulphate, Aluminium-sulphate and Polialuminium-chloride– were tested in Jar test experiments. The measured parameters were DOC (Dissolved Organic Carbon), turbidity, pH, and the remaining coagulant concentration.
Ferric-sulphate was found to be the most effective of the tested coagulants. Efficient removal of DOC (40-60%) could be achieved with only high dosages (80-100 mg $Fe_2(SO_4)_3$/L). SPE on Oasis HLB cartridges was carried out to separate and study –by means of UV- and fluorescence- and IR- spectrophotometric methods– the characteristics of the NOM's hydrophobic fraction.

INTRODUCTION
The water of Lake Balaton has very specific properties, which makes the drinking water production complicated and inefficient. There is not enough groundwater for the drinking water supply of the residents and also the holidayers in the region of Lake Balaton, so the raw water of the lake is needed for drinking water production.
A very important aim of drinking water production is the removal of organic matter in order to prevent the generation of disinfection by-products and to prevent the multiplication of microorganisms in the distribution system.
The coagulation efficiency (elimination of natural organic matter) is impacted by many factors such as coagulation conditions (pH, temperature, stirring intensity, coagulant and flocculant characteristics and dose) characteristics, concentration of organic substances, the nature and concentration of inorganic compounds and the design of the treatment plant.[1] Unless the raw water has a low TOC concentration, coagulant dosages required are determined by the content of NOM in a water supply rather than by turbidity (particles).[2]
PH has considerable influence on coagulation efficiency. The optimum pH value for surface water coagulation is between 4,4–6,7 for ferric salts, 5,6–7,1 for alum and 6,0–6,8 for polialuminium chloride.[1] The optimum pH value for coagulation of waters with high humic matter content is typically within the range 4 to 5 with ferric salts and within the range 5 to 6 with aluminium sulphate.[3,4,5,6,7]
The achievable removal of organic matter by coagulation varies widely (generally between 10 and 90%). [8] Some researchers, testing 10 different surface water samples, found that compared to the conventional treatment practices, optimized coagulation leads to an additional removal of 32%for DOC.[1]

PROPERTIES OF LAKE BALATON
Largest lake in Hungary and Central-Europe (area: 595 km^2)
Average depth: 3-4 m ⇨ No layers of different temperature are in the water body. The water gets warm in the summer and calms down in the wintertime nearly homogenously.
Characteristics of Balaton water:
high organic and also inorganic matter content
The composition of the water varies with the weather to a great extent.

Water temperature: 1-28 °C
PH: 8.0-8.8, high alkalinity
Turbidity: 30 NTU (3-200 NTU)
Hardness: 170-190 mg CaO/L
Specific conductivity: 600-800 μS/cm

COD (Chemical Oxygen Demand): 4.5 mg O_2/L (3.5–6.0 mg O_2/L)
TOC (Total Organic Carbon): 7.5-9.5 mgC/L
Phenolic index: <2.0 µg/L

Total algae number:
100˙000/L - 15˙000˙000/L
critical period during the year: end of August, beginning of September, the algae number can even reach: 60-70 million in a litre of raw water.

DIFFICULTIES IN THE TREATMENT OF BALATON WATER
High pH and alkalinity ⇨ high coagulant doses needed to lower the pH to reach optimal organic matter removal.

Big changes in the temperature during the year:
Low raw water temperature (1-5ºC) in the winter
⇨ non-efficient and slow hydrolysis of the coagulant
High raw water temperature (20-27 ºC) in the summer
⇨ increased biological activity⇨ production of algae⇨ rise in the concentration of easily biodegradable organic substances
⇨ production of toxins

Great changes in the composition of the water during the year:
Different amount and characteristics of the organic matter.

Varying water composition with the daily weather ⇨ gales and storms increase principally the inorganic but also the organic matter content.

MATERIALS AND METHODS
Coagulation studies
Several **JAR test** experiments were performed with different coagulants, dose at different surface water treatment plants at Lake Balaton at different times of the year.
Coagulation efficiency was compared also at slow and fast mixing of the chemicals.

The tested **coagulants** were:
- Ferric sulphate
- Ferric chloride
- Aluminium sulphate
- Polyaluminium chloride

The used **flocculant** in each experiment was:
- Magnafloc LT27 (poliacrylic-amid compound)

The efficiency of coagulation was monitored by determining the:
- Organic matter (TOC (Total Organic Carbon), COD (Chemical Oxygen Demand) measurement)
- Turbidity (NTU)

Separation studies:
The hydrophobic fraction of the organic matter was extracted on Oasis HLB (Hydrophilic-Liphophilic Balance) SPE (Solid Phase Extraction) cartridges.
Fluorescence spectra of the different separated fractions were taken up and elemental analysis of the extracted organic matter was carried out.

Fig. 1: Removal of Turbidity with Different Coagulants

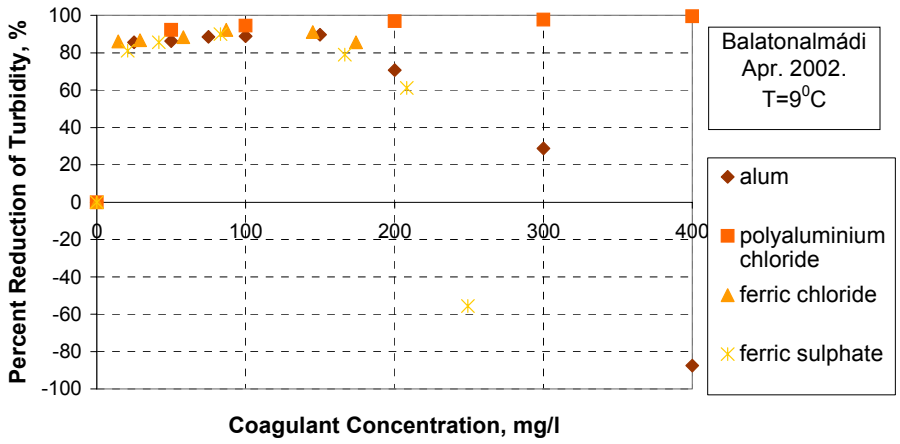


Fig. 2: TOC Removal with Different Coagulants

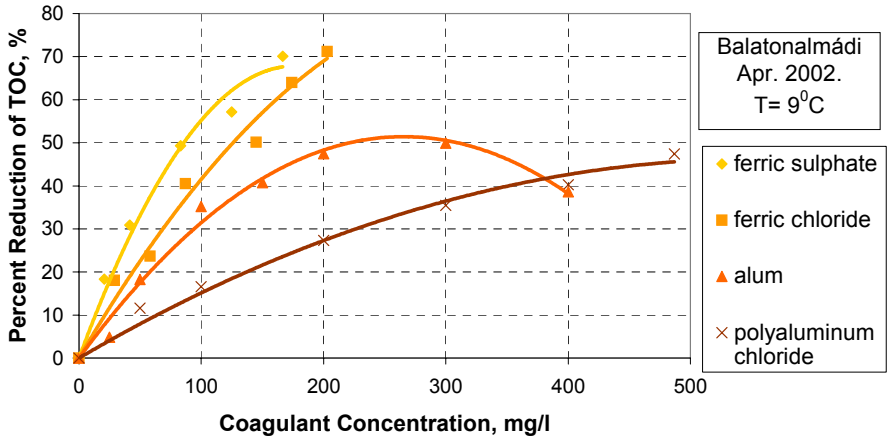
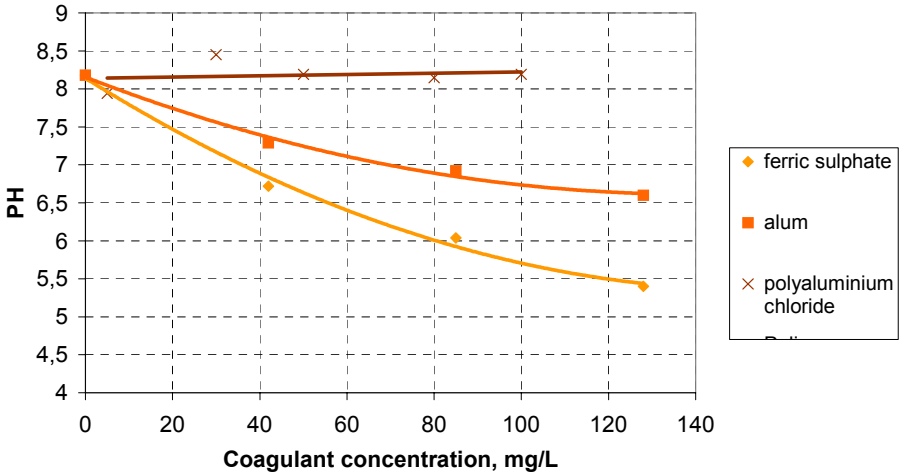


Fig.3. The relationship between the coagulant dose and the coagulation pH



DISCUSSION OF THE COAGULATION STUDIES

1. The most efficient organic matter removal during the JAR test experiments was achieved by the **ferric-salts** (Ferric-sulphate, Ferric-chloride). **70 %** maximal **organic matter removal** was reached without pH adjustment. In order to reach this efficiency the 3-4-(sometimes more)-fold of the general doses used in the treatment plants must be added.

The causes of the high dosages of coagulants needed are:

- At lower pH values the charge neutralisation mechanism (a certain mechanism of coagulation) is more effective.
- High doses generate higher adsorption surfaces. – The adsorption mechanism of the coagulation is also more effective.

2. The amount of the optimal coagulant dose was influenced by:

The **time of the measurement**: in the summer during the algal bloom higher doses were needed (different organic matter composition)

The **sampling site**: the treatment of samples from the western basin needed higher coagulant doses, but also the achieved coagulation efficiency was higher.

The quick and intensive mixing of the chemicals (200 min^{-1}) showed better efficiency than the slow stirring (40 min^{-1}).

Fig.4: Fluorescence emission spectra of raw water and treated water samples

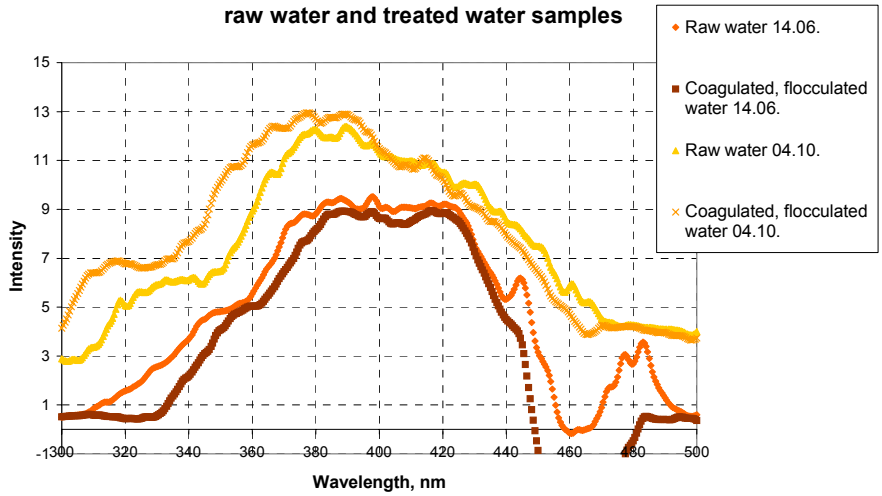
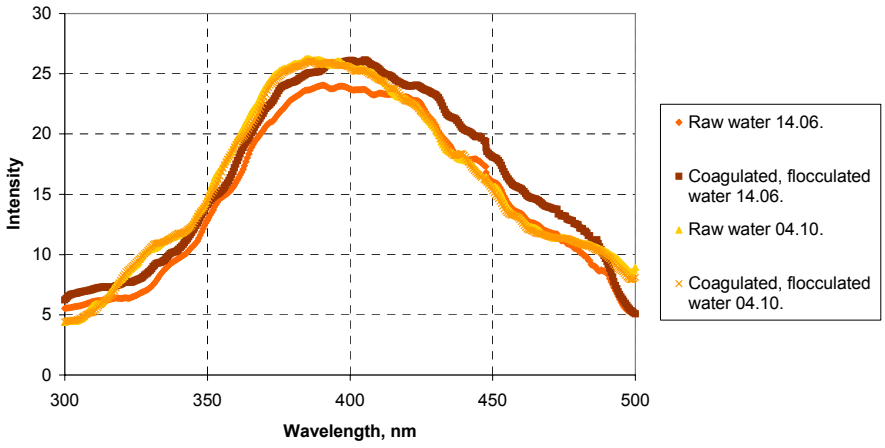


Fig.5: Fluorescence emission scpectra of the hydrophobic fractions of raw water and treated water samples



Elemental composition of the separated hydrophobic organic matter

	Raw water of Lake Balaton	Coagulated, flocculated water of the treatment plant	Literature data [Kļaviņš]
C (m%)	45,5	42,4	46-58
N (m%)	6,3	6,5	0,6-9,0
H (m%)	5,5	7,1	3,7-6,9
O (m%)	40,4	41,9	33,4-49,0
S (m%)	2,3	2,1	–
C/N	7,2	6,5	5,5-93,5
C/H	8,3	6,0	7,1-14,6

DISCUSSION OF THE SEPARATION STUDIES

While the organic matter content of the water of Lake Balaton varies with the seasons and also the daily weather changes, both the amount and the composition of the hydrophobic fraction of the organic matter is constant.

The in most cases inefficient coagulation, carried out in the surface water treatment plants, does not remove the compounds showing fluorescence, having a conjugated electron system and supposed to be trihalomethane precursors.

Approximately of the 85-90% of the organic matter content of the raw water samples is adsorbed on the SPE cartridges. This indicates that about the 10-15% of the dissolved organic matter present in the raw water has definite hydrophilic character. (The specific UV absorbance –SUVA– of the raw water is 11.)

The elemental analysis of the separated hydrophobic fraction revealed, that other components than humic substances esp. polypeptides are also present. These compounds are likely to be attached to the humic molecules with weak bounds. The results also suggest that a wide range of humic molecules from different stage of humification is present.

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