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NOM and Arsenic Removal from Natural Water by Enhanced Coagulation

ABSTRACT
Removal of NOM from the raw water is still a problem because the numerous methods used have not produced a satisfactory model for the standard drinking water quality. The registered increasing humic substances in natural water add to the purification problem. Among the many techniques of humic substances removal from water, enhanced coagulation is the most adjustable to respond efficiently to the challenge. This can be best illustrated by comparing the many techniques used, especially the coagulation by contact filtration and the alternative enhanced coagulation that efficiently remove humic substances even from the worst water compositions at the temperatures approaching zero in conventional settling units without undesirable effects of the contact filtration. The effect of humic substance removal was studied in several different types of water under laboratory and water-treatment plant conditions when conventional and enhanced coagulation methods were used.

KEY WORDS: humic substances, enhanced coagulation, sedimentation, residual Al, arsenic

INTRODUCTION
Natural organic matter (NOM), the commonest organic pollutant in natural raw water, has long been considered for its multiple degrading effects on drinking water: colour, organic load and biochemical decomposition in the water distribution systems [6], etc. Efforts to remove NOM from drinking water have increased particularly after it has been realized that during chlorination the humic load produces many cancerous and mutative halogenorganic substances [5, 14].

NOM can be removed from raw water by several processes: conventional coagulation [9] and flock separation by deposition or flotation, filtration through different media [15], membrane filtration [17], removal on ion-exchange resin [3], oxidation, absorption and biological processes [7].

There is an increasing trend of humic substances in natural water [16] and the consequently increasing problem of drinking water treatment. Many problems are considered [4], which, for the increased load, are quantified for the water purification by contact filtration.

Depending on the nature of the problem, most of the NOM removal techniques are based on coagulation as the principal process [1]. Besides the conventional technique and its variations with possible superstructure, coagulation is used to remove humic substances by membrane

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filtration. The coagulation process has long been associated with the removal of suspended matter from drinking water [1]. It was developed to deal with the removal of dissolved organic matter [19].

Coagulation depends on the ionic-composition of water [19] and the water temperature, whereas the NOM removal effect depends also on the molecular composition of the humic substances in water. US EPA established criteria for the assessment of the coagulation efficiency now termed the enhanced coagulation (Tab.1).

Table 1: Required removal of TOC by enhanced coagulation for conventional treatment [19]

SOURCE WATER	SOURCE WATER ALKALINITY (mg/L as $CaCO_3$)		
TOC (mg/L)	0 to 60	>60 to 120	>120
>2.0 - 4.0	35.0%	25.0%	15.0%
>4.0 - 8.0	45.0%	35.0%	25.0%
>8.0	50.0%	40.0%	30.0%

Arsenic has long been considered a pollutant of natural water, for which MCL in drinking water was shifted more than once. The latest MCL is 10 μg/l adopted in many countries, including the national standards of Serbia and Montenegro. Arsenic is removed from raw water satisfactorily by any of the many treatment techniques [20]. For multiple-polluted water, one must select methods that will give the best quality by all parameters taking into consideration the economic and environmental aspects.

MATERIALS AND METHODS

Humic substances are contained in many drinking water sources of Serbia. In hilly or mountainous regions, water is dominantly of low alkalinity, colour, often turbid, high in organic matter, UV-extinction, and specific UV-absorbance (SUVA) characteristic of dominantly humic substances in the total organic content. Another type of water is ground water in Vojvodina, characterized by high ionic content, Na, NH_4, ortho-P, colour, organic matter, and often As as well. Some data summarized in tab. 2.

Table 2: Some characteristics of raw water used for investigation of purification effects by models [10, 12]

No.	Drinking water supply	Type of water source	Temp.	Turb.	Colour	Alkalinity, average	Consump. $KMnO_4$	UV-abs. average	TOC average
			^oC	NTU	mgPt/l	$mgCaCO_3/l$	mg/l	1/cm	mg/l
1	Kopaonik	river	2 - 12	3 - 100	10 - 70	90	12 - 28	0.150	4.0
2	Divčibare	lake	2 - 15	3 - 12	32 - 46	160	24 - 38	0.290	6.5
3	Lebane	river	2 - 16	2 - 800	15 - 150	200	14 - 46	0.175	5.0
4	Kikinda	ground	8 - 12	1	50	500	28 - 34	0.280	8.0
5	Zrenjanin	ground	8 - 12	1	80	700	48 - 55	0.500	12.0

Water containing humic substances is only partly purified. In mountainous regions, the conventional technology is used: coagulation/sedimentation/filtration/disinfection that gives moderate effects including high residuals of Al and organic matter, colour, etc. of drinking water.

In Vojvodina, locations 4 and 5, many domestic and foreign (Degremont, Zenon, etc.) corporations searched for practical treatment models, but without satisfactory results. A likely reason for the situation is the methodological research inadequacy for the actual problem; pilot tests were conducted without a clear project assignment and a defined method of removal of many pollutants for the given case. Thus, the task in some NOM removal cases neglected the high mineral contents, Na, etc., or, in other cases, the emphasis was laid on membrane filtration that was limited by its high ionic and organic contents and the modest water source capacity.

Based on the laboratory test data, presently is given the full purification technology for water with a high concentration of humic substances and other harmful and toxic constituents such as Na, As, etc.

LABORATORY AND *IN SITU* EXAMINATION

A long research in the coagulation process and its improvement by application of Al polymers led to the development of a treatment technique for highly humic water [10]. The treatment removes humic substances and accessory natural pollutants: Fe and Al organic complexes, and later As, which is becoming a problem to be urgently addressed. The research was executed in laboratory and pilot tested, and its coagulation process slightly adjusted to obtain better effects of the water purification. The enhanced coagulation effect was accomplished using Al polymer and activated SiO_2 at the Al concentrations manifold lower than in the conventional treatment with Al sulphate, or in the standard techniques using Al polymer. The developed method best neutralizes negative charges of humic macromolecules, thus providing for optimisation of the coagulation process and the removal of humic molecules of the smallest molecular weight. Table 4. shows the implementation of the new enhanced coagulation, compared with the conventional coagulation and with the Al polymer use, on the example of the Divčibare lake humic-high water purification.

The conditions and effects of the humic substance removal from different water sources in the given area were studied in laboratory using standard methods and jar tests.

Table 3 gives laboratory data for correlation of the coagulation character with Al sulphate, the method used in location 1, and the new method [10] under the conditions equivalent to the jar test. The optimum coagulant dosage used in the water plant is the one selected for winter season, and for treatment [10] the dosage was experimental. The improvement in the purification effect by decreasing the coagulant dose is quite illustrative. At the floc deposition stage, when the new method is used, the standard water quality is obtained.

Table 3: Effects of conventional coagulation (a) and (b) new method [10], for mount Kopaonik water purification.

	Coagulant dose		Characteristics of water						
Method	Al-coag. as (mg/l Al_2O_3)	SiO_2 mg/l	Turbidity NTU	UV-abs. 1/cm	Colour mgPt/l	Consum. $KMnO_4$ mg/l	PTHM µg/l	$PCHCl_3$ µg/l	Rezid Al mg/l
a.	22.5	5.5	2.5	0.145	17	16.0	410	310	1.25
b.	4.1	1.5	0.18	0.015	2	4.0	68	34	0.040

a. Traditional method (coagulation and sedimentation) with Al sulfate and activated SiO_2.

b. New method [10] (coagulation and sedimentation) with Al polimers and activated SiO_2.

Similar effects were registered for lake-water purification on Divčibare, locality 2. An efficient humic substance removal is notable in the reduced colour, UV-extinction and $KMnO_4$ consumption within the range from 85% to 95%, or a standard water quality at the stage of coagulation and flocculation. This efficient floc-separation allows a long safe operation of sand filter without washing. Though the effects of treatment [10] were well known, a costly equipment was imported and a complicated technology of reverse osmosis introduced in the location, which could not give the standard drinking water quality, so it has been disused.

Table 4: Effects of conventional coagulation (a) and (b) new method [10] for lake water purification on Divčibare

Divčibare	Dose of Al-coag. (mg/l Al_2O_3)	Turbidity NTU	Colour mgPt/l	UV-abs. 1/cm	Cons. $KMnO_4$ mg/l	Al mg/l	TOC mg/l	PTHM, µg/l
Raw water	-	12	55	0.301	28.95	-	5.6	670
Method a.	15	9	49	0.250	24.1	0.430	5.2	580
Method b.	4	0.4	3	0.035	4.2	0.065	1.6	70

A condition for implementation of the new technology was the proof that the standard drinking water quality could be obtained in the Lebane old water plant, location 3, using the conventional treatment. Laboratory tests confirmed the highly improved treatment effects by the new technology as compared to the conventional treatment under the same operating conditions. Only the effects of the source water purification by coagulation and sedimentation (Tab. 5.) were tested. The test focused on the coagulation effects at low temperatures, which are a critical condition in the given location.

Table 5: Some results of purification of raw water from lake river Shumanka for water supply of Lebane town by traditional (a) and new method [10], (b)

	Turbidity NTU	Colour, mgPt/l	UV-abs., 1/cm	Cons. $KMnO_4$, mg/l	Rez. Al, mg/l
Raw water	35	40	0.124	22.6	-
Purification, method a.	6.5	16	0.086	11.4	0.380[1]
Purification, method b.	0.60	2	0.034	4.22	0.065[1]

[1]residual Al content in water purified by coagulation and sedimentation, without filtration

The new technology [10] tested at the Lebane water source confirmed the accuracy and representativeness of the laboratory tests for evaluation of the method and its implementation. The adjustment of rapid and slow coagulant mixing and dosage stages enabled the use of the new technology for the best water quality in a continuous system operation irrespective of the raw water load and temperature, as indicated by the control data of the competent Health Institute of Leskovac [11].

Table 6: Some relevant raw water purification data for Lebane plant by the conventional and the new method

	Conventional technology		New method [10]	
	Raw water	Purified water	Raw water	Purified water
Temp. water, °C	5 - 12	5 - 12	2 - 7	2 - 7
Turbidity, NTU	3.8 – 13.1	0.97 – 3.20	3.57 - 131	0.25 – 0.96
Colour, mg Pt /l	9 - 33	5 - 27	11 - 232	0 – 3
UV-abs., 1/cm	No data	0.076 – 0.133	0.042–0.343	0.014 – 0.042
Consumpt. $KMnO_4$, mg/l	15.5 – 23.4	9.80 – 14.86	15.6 – 38.5	4.13 – 6.95
Fe, mg/l	0.23 – 0.62	0.10 – 0.62	0.13 – 1.69	0.00 – 0.06

Method [10] is inadequate to purify ground water at Kikinda and Zrenjanin sources to the national standard level for colour (<5 mg Pt/l), $KMnO_4$ consumption (<8 mg $KMnO_4$/l) and As (<0.01 mg/l). Further coagulation enhancement, method [12], increases the coagulation effects of almost quantitative binding humic substances into flocs also separating most of As^{5+} and organic As. The innovated coagulation treatment [12] gave the best effects ($KMnO_4$

consumption and UV-extinction) of the organic matter as high as 85%, and colour and As removal up to 95% (Tab. 7.), which, plus disinfections, provided for the standard drinking water quality in the given locations.

Table 7: Purification effects for Kikinda and Zrenjanin ground water sources, coagulation and sedimentation.

	Cons. $KMnO_4$, mg/l		Colour, mgPt/l		UV-abs., 1/cm		Na, mg/l		As, mg/l	
	raw	purif.	raw	purif.	raw	purif.	raw	purif.	raw	purif.
Kikinda	26.00	5.50	46	4	0.260	0.045	220	122	0.009	0.001
Zrenjanin	52.00	7.20	80	6	0.510	0.060	250	135	0.103	0.008

Ground waters sources 4. and 5. have high organic loads and ionic contents, high Na and NH_4 concentrations, and the water of Zrenjanin source contains enormous As concentration. To remove excessive Na, some of raw water has to be passed through highly acidic cationic exchanger, as required by methods [10, 12]. With the Na removed, and water mixed, pH of water has been much reduced and made optimal for coagulation and removal of humic substances. The high acid consumption for regeneration of Na salts (NaCl or Na_2SO_4) raises a new problem of the control of these constituents. The use of electro-dialysis with membranes [13] recuperates the acid and produces NaOH, reducing the pollutant emitted into the environment, thus satisfying the technical, economic and environmental criteria of a best technology.

DISCUSSION

There are several technological models in use to remove humic substances from raw waters. Research continues in developing a model that will satisfy the ever-stricter criteria for drinking water quality. A consistent model has not yet been found even using all the available treatment techniques [2]. Consequently, the selection of the method must result from objectified criteria in the techno-economic and environmental spheres.

Strong oxidants that are effective purifiers of raw water, particularly that containing artificial, organic micropollutants, are not recommendable for purification of water with high humic contents [13, 14, 18], because they generate molecules of small molecular weight and increase PTHM that are difficult to remove in the following stages of the treatment. The use of bioactive AC in many case examples [7] was not quite satisfactory.

Membrane processes are increasingly used where source water is stable in composition. Problems are faced in places where high coagulation level is required, especially when RO was used, as was found out at the plant on Divčibare (location 3) where the improved equipment could not be made operative for years and was left virtually unused.

Most treatment models include coagulation, either as the basic purification stage followed by more complex treatments, or combined with an accessory treatment as an integral process.

Ionic exchange is also used in small water plants the treatment [3] but the treatment had a limited effect. A combined use of ion-exchange resin MIEX® and conventional coagulation [8] increases NOM removal for about 35 % to 60 %.

Contact filtration, coagulation in a filtering medium, has long been used, particularly in the areas of low water temperature. This technique is applicable only for raw water of stable composition and low turbidity. The technique can be economic only where the water load and the amount of coagulant are low, though the specific filter-washing demand is high. The frequency of filter washing, water loss, treatment costs are increasing with the NOM concentration, at the simultaneous degrading drinking water quality [4]. Because many water plants in Nordic countries use contact filtration as the basic purification process, and because NOM concentrations in raw water have been increasing through the last few decades, this problem is considered even more seriously where the drinking water standard is tried to be upgraded.

No wonder the standards should be raised, because they are at present <20 mg Pt/l for colour, <5 mg/l for TOC, and as low as possible for THM [9]. Because these waters have low ionic strength and high SUVA - waters that easily coagulate - the demand for higher standards is based on the available implementation techniques. The case examples of efficient coagulation of waters with high concentrations of humic substances, from the experiences in Serbia, are a reliable indicator of the possible drinking water quality standard upgrading in a large area.

Relating the present technical level, the available technology for removal of humic substances and arsenic from natural water [12] to the state-of-the-art, or the required enhanced coagulation defined by US EPA [19, 20], a qualitative change in all aspects of enhanced coagulation has obviously been provided. First of all, the purification effects, removal of humic substances, for any type of water, have been increased two to three times in relation to the standard [19]. The best effects are achieved for waters of high ionic strength, e.g. purification of ground water for Zrenjanin. Improvements have been attained also in the reduced consumption of Al polymer, reduction of residual Al in drinking water and Al emission into the environment. The coagulation process evolves equally fast and efficient even under extremely low temperatures overcoming thus the problem of contact filtration both in the purification efficiency and the water purification cost.

Very small intervention in the existing plant (coagulation-sedimentation-sand filtration-disinfection) of Lebane and implementation of method [10] gave the standard drinking water quality for any raw water load and extremely low temperature over many years of the drinking water quality control. It also initiated a massive use of the technology in water treatment plants over Serbia, and wherever the removal of humic substances from natural water was the problem.

CONCLUSIONS

The enhanced coagulation technique, models [10 and 12], gave two to three times better effects of the humic substance removal than required by US EPA [19]. The method has many advantages for purification of highly humic waters. It simply and efficiently neutralizes the negative charge of humic molecules allowing, without destruction, the humic molecules even of the smallest molecular weight to separate from the aquatic phase by coagulation and flock separation. The coagulation evolves at a high specific reduction of the coagulant, which makes the method suitable from the techno-economic and environmental aspects. Stable flocs form even under the most unfavourable climatic conditions, thus excluding the contact filtration, and allow purification of water with a high concentration of humic substances. The enhanced coagulation technique [12] is highly effective in removing humic substances and other harmful or toxic matters, Na, As, etc. purifying raw water of high ionic strength to the drinking water standards.

REFERENCES

[1] Amirtharajah A., O'Melia C. O., (1990) Coagulation Processes: Destabilization, Mixing and Flocculation, Water Quality and Treatment, A Handbook of Community Water Supplies, AWWA, Fourth Edition, New York, pp. 269-367.

[2] Drikas M., Morran C., Pelekani C., Hepplewhite C. & Bursill D. B. (2002) Removal of natural organic matter - a fresh approach, Water Science & Technology: Water Supply, Vol. 02, No 01, pp. 71 - 79.

[3] Hongve D., Baann J., Becher O. and Beckmann O. (1999) Experiences from operation and regeneration of an anionic exchanger for natural organic matter (NOM) removal, Water Science & Technology: Water Supply, Vol. 40, No 9, pp. 215 – 221.

[4] Eikebrokk, B., Vogt R. D. and Liltved H. (2004), NOM increase in Northen European source waters: discusion of possible causes and impacts on coagulation/contact filtration processes, Water Science & Technology: Water Supply Vol 4, No. 4, pp. 47-54.

[5] Kronberg L, (1999) Water treatment practice and the formation of genotoxic hlorohydroxyfuranones, Water Science & Technology, Vol. 40, No 9, pp. 31-36.

[6] Langmark J., Storey M. V., Ashbolt N. J. And Stenstrom T. A. (2005) Biofilms in an urban water distribution system: measurement of biofilm biomass, pathogens and pathogen persistance within the Greater Stockholm area, Sweden, Water Science & Technology: Water Supply Vol 52, No. 8, pp. 181-189.

[7] Melin E., Eikebrokk B., Brugger M., & Odegard H., (2002) Treatment of humic surface water at cold temperature by ozonation and biofiltration, Water Science & Technology: Water Supply, Vol. 02, No 05-06, pp. 451 - 457.

[8] Morran, J.Y. Drikas, M. Cook D. and Bursill D.B. (2004) Comparison of MIEX® treatment and coagulation on NOM Character, Water Science and Technology: Water Supply Vol 4, No. 4, pp. 129-137.

[9] Odegard H., Eikebrokk B., Storhang R., (1999) Processes for the removal of humic substances from water - an overview based on Norwegian experiences, Water Science & Technology, Vol. 40, No 9, pp. 37-46.

[10] Perišić, M., (2000) Method for treatment of water containing humic matter for the production of drinking water with enhanced coagulation stage using inorganic polymers of Al and SiO_2, European patent application 01939966.6-2104/1294642.

[11] Perišić, M., Cibulić Violeta, (2003) Some aspects of enhanced coagulation application at drinking water treatment plant of the Lebane town, II Regional Symposium 'Chemistry and environment', pp. 311-312, Kruševac

[12] Perišić, M., (2005), Removal of humic substances and arsenic from raw water by enhanced coagulation using inorganic polymer of Al and SiO_2®, SCG. Application No. 2005/0606.

[13] Perišić, M., (2005), A new method of drinking water purification for Zrenjanin conforming to the techno-economic and environmental quality standards, Tehnika, No. 5, pp. 9 - 17.

[14] Rook, J. J. (1974) Formation of haloforms during chlorination of natural waters, Water Treatment Examination 23 (2): pp. 234 -243.

[15] Saltnes T., Eikebrokk B, & Odegaard H, (2002) Contact filtration of humic waters - performance of an expanded clay aggregate filter (Filtralite) compared to a dual anthracite/sand filter, Water Science & Technology: Water Supply, Vol. 02, No 05-06, pp. 17–23.

[16] Skjelkvaale, B. I. (2003) The 15-year report: Assessment and monitoring of surface waters in Europe and North America: acidification and recovery, dynamic modelling and heavy metals. ICP-Waters report 73/2003. Norwegian Institute for Water Research, 113 p.

[17] Thorsen T., (1999) Membrane filtration of humic substances-state of the art, Water Science & Technology: Water Supply, Vol. 40, No 9, pp. 105-112.

[18] USEPA, (1998) National Primary Drinking Regulation: Disinfectants and Disinfections Byproducts, Federal Register, 63(241), 69390-69476.

[19] USEPA, (1998) Enhanced Coagulation and Enhanced Precipitative Softening Guidance Manual, US EPA, 815-R-99-012.

[20] USEPA, (2000) Technology and Costs for Removal of Arsenic from Drinking Water, EPA 815-R-00-028, pp. 284.