Article

Application of sodium aluminate from alumina Bayer process to the treatment of surface water, wastewater and sludge from tannery industry

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Abstract
This paper presents the application of sodium aluminate, directly or after small adjustments in concentration and purity, in some other valuable intermediary products. Sodium aluminate is an intermediary product in Bayer technology applied by Alum SA Tulcea production of alumina and alumina products. Mainly, sodium aluminate is a carrier of aluminum hydroxide between important manufacturing stages in the Bayer process, bauxite processing, and aluminum hydroxide crystallization. After a short investigation of the uses of sodium aluminate, it was decided to choose and study the possibility of converting this secondary product into ecological material for the treatment of natural or industrial wastewater. Actually, on the market, products similar to sodium aluminate from Alum SA Tulcea provide treated waters with high purity and reasonable quality, excellent coagulation rates, rapid flotation, and sedimentation, and in addition, significant side effects, such as excellent removal of phosphorus and silica from treated water. Treatments do not require lime or hydroxide to control alkalinity, and chemical sludge remains at a minimum volume and mass. The test performed with sodium aluminate from Alum SA Tulcea was comparable with other tests with $Al_2(SO_4)_3$ and $FeCl_3$. The maximum removal yields of global organic load expressed by chemical oxygen demand (COD) and biochemical oxygen demand (BOD_5), chromium (Cr VI), and total suspended solids (TSS) were: 83% COD, 71% BOD_5, 99.7% Cr VI and 93% TSS.

Keywords: sodium aluminate, water, wastewater, hardness, silica

INTRODUCTION

Aluminum hydroxide is an essential material for manufacture of many industrial products like low temperature industrial aluminas (desiccants, absorbents, catalysts, rubbers, fillers for paper and plastics flame retardants, and various construction materials), as well as, for the high ceramic materials (especially insulators and refractories). Alum SA Tulcea is the biggest unit in Eastern Europe, producing wet and dried alumina hydrate and metallurgical alumina for aluminum production. Recently, this factory started production of a new product from the special alumina grades called dried, milled and classified aluminum hydroxide. This product manufacture is requiring a more purity of the sodium aluminate used in the aluminum hydroxide process. In turn, more available purified and relatively diluted aluminate has to be recycled or to be used as secondary product in the new or old applications.

Some choices of using sodium aluminate in different products are presented below.

Sodium aluminate product
Pure sodium aluminate ($NaAlO_2$) is an anhydrous compound. The anhydrous sodium aluminate structure contains a 3D framework with four AlO_4 tetrahedra linked to each other by their corners

[1÷3]. Anhydrous sodium aluminate is hygroscopic. When sufficient water was adsorbed by the anhydrous material, a new compound was born, the hydrated sodium aluminate, which is a meta-aluminate with four hydroxyl ions in its structure - $NaAl(OH)_4$.

Sodium aluminate for water and waste water treatments

Sodium aluminate is a product with undoubted qualities, mainly when it comes to the process of making natural waters potable and waste water parameters brought to the safe resonable values. This readily available product combines the most advantageous properties for clean drinking water, providing treated water with high purity and reasonable quality, excellent coagulation rates, rapid flotation and sedimentation and, in addition, significant secondary effects such as excellent phosphorus removal and silica in the treated water. All treatments do not require lime or sodium hydroxide to control alkalinity, and chemical sludge remains at a minimum volume and mass. In addition to all these features, the product transport is cheep, and also, the product costs themself is resonable.

Treatment of natural water as a source of raw water for water intended for human consumption

Sodium aluminate in combination with other coagulants eliminates the hardness of processed water, precipitates iron, manganese and removes phosphates and organic matter from raw water. The advantages of using sodium aluminate in the first of processing of raw natural water compared to other substances used for softening obvious and profitable, because the entire process is easy and provides efficient safe storage [4, 5].

Treatment of wastewater before discharge into natural collectors

Sodium aluminate is used to treat water heavily contaminated with organic and inorganic substances and to treat sludge resulting from the biological treatment of wastewater. With the growing of global economy and increasing the water pollution, the need for effective water treatment solutions was rising, thereby driving the market to more demands for sodium aluminate and safty additional chemicals. The same above assumptions are valid also, for the waste industrial waters treatments, requering elaborated technologies for cleaning, neutralization and disinfection [6, 7]. One of the main drivers for the market is the increasing demand for sodium aluminate in the wastewater treatment industry. Sodium aluminate is widely used as a coagulant in wastewater treatment plants to remove impurities and to improve the quality of the send back in the collector lines [4÷7].

Sodium aluminate for cement production

Construction industry growth is sustaining the demand for more cement, increasing the demand for more sodium aluminate. Sodium aluminate is used as a main component in cements [8] or, as an accelerator in special cement formulations [9], enabling faster setting times and improved strength of concrete. The booming construction activities in emerging economies and infrastructure development projects provide financially rewarding opportunities for production growth.

Composite cement is a group of materials in which are added recycling materials [10, 11], or other materials to improve quality or to change properties of the composite cements [12÷16]. A mixture of sodium aluminate, together with other cementitious materials increased the rate of cement hardening, waterproof, stiffen the fresh mortar and increase the hardening capacity of cement at low temperature [17]. Sometimes, very poor materials, but with low reactivity, are added to drop the prices [18].

Sodium aluminate for zeolite production

Zeolites belong to a large class of alumino-silicates, with various aluminum/silicon ratios and variable properties depending largely on the mineral composition and many details in manufacturing technology. Zeolites are builders in the manufacture of detergents, catalysts or supports for catalytic materials and serve for the manufacture of the ion exchangers. adsorbents, catalysis, detergents and various advanced materials, including medicine, horticulture, odour control chemistry, medium for hydroponics growing, for pure materials fabrication, etc. [19÷25].

Sodium aluminate for manufacture of driling fluid

Mixed with sodium silicates, sodium aluminate forms the drilling fluids intended for the water proofing of wells and for increasing the mechanical resistance of soils, as well as, for stiffening and reducing soil compressibility [26÷29].

Sodium aluminate for paper making industry

In the paper manufacture, sodium aluminate control the opacity retentions for fibers and filling material, and also, control the paper strength. Sodium aluminate is a good stabilizer of the pH in paper pulp and thus, it increasing the dispersion rate of the filler, and more than that, it stabilizes the dispersion rate at its optimal value. [30÷32].

In addition, sodium aluminate influence continues to grow in fields like lithography for the production of printing inks and print forms, as well as, in the detergent, varnish and paints industries, in textiles field as a mordant in dyeing and printing cloth and in numerous other domains. Its capabilities include inhibiting glass etching by alkaline solutions, safeguarding steel and aluminium surfaces during galvanizing, enhancing dyeing quality and the antistatic properties of polyester synthetic fibres or acting as an additive in foundry sand melds and cores. Moreover, it finds a role as a binder in the ceramics industry, raising its significance across the industrial landscape. The enamels industry benefits from the incorporation of sodium aluminate into enamel mixtures to achieve low-melting covers [32÷42].

The purpose of this paper is the evaluation of sodium aluminate uses as raw material, and to choose some examples of application, available for valorization of the sodium aluminate as secondary product in technology of dried, milled and classified aluminum hydroxide.

MATERIALS AND METHODS

The experimental research presented in this paper refers to 2 important applications of sodium aluminate, namely:
- removing silica from the water during the water softening process;
- removal of suspended matter and global organic materials from waste water coming from leather manufacturing (after advanced reduction and separation of chromium VI).

The analytical determinations for the characterization of the sodium aluminate samples were performed following the standard methods presented in the tables 1 and 2 and the results were compared with the maximum admitted values (MAVs) according to in force legislation [43].

Table 1. Standard characterization of the sodium aluminate resulting from Bayer process
(well clarified liquid after long time settling, Type A)

Parameters	Units	Sample code / Results		MAVs according to [43]			Methods
		A1	A2	Type 1	Type 2	Type 3	
Dried matter	%	43.1	50.41	-	-	-	STAS 6953/1981
Insolubile materials	g/kg Al	1.23	0.95		8		STAS 6953/1981
Density	g/cm^3	1.498	1.487		1.5		SR EN ISO 11272/2017
Al_2O_3	%	19.94	19.75	-	-	-	Internal standard
$Na_2O_{caustic}$	%	18.93	21.10	-	-	-	Internal standard
Na_2O/Al_2O_3	mol/mol	1.56/1	1.75/1		-		-
Al	%	10.56	10.46		10÷13.2*		SR EN ISO 17294/2:2023
Fe	g/kg Al	0.048	0.012		0.8		SR EN ISO 17294/2:2023
As	mg/kg Al	0.22	0.11	14	40	100	SR EN ISO 17294/2:2023
Cd	mg/kg Al	0.05	0.08	3	50	100	SR EN ISO 17294/2:2023
Cr	mg/kg Al	1.59	0.64	30	700	1000	SR EN ISO 17294/2:2023
Hg	mg/kg Al	0.09	0.14	4	10	20	SR EN ISO 17294/2:2023
Ni	mg/kg Al	0.61	0.46	20	700	1000	SR EN ISO 17294/2:2023
Pb	mg/kg Al	0.60	0.20	40	200	800	SR EN ISO 17294/2:2023

*Interval for aluminum content in usual sodium aluminate commercial products

Table 2. Standards for characterization of the sodium aluminate resulting from Bayer process (normal fluid from Bayer process, Type B)

Parameters	Units	Sample code / Results		MAVs according to [43]			Methods
		B1	B2	Type 1	Type 2	Type 3	
Dried matter	%	42.72	45.17	-	-	-	STAS 6953/1981
Insolubile materials	g/kg Al	0.98	0.73		8		STAS 6953/1981
Density	g/cm^3	1.514	1.526		1.5		SR EN ISO 11272/2017
Al_2O_3	%	21.06	19.52	-	-	-	Internal standard
$Na_2O_{caustic}$	%	19.17	22.21	-	-	-	Internal standard
Na_2O/Al_2O_3	mol/mol	1.50/1	1.87/1		-		-
Al	%	11.15	10.433		10÷13.2*		SR EN ISO 17294/2:2023
Fe	g/kg Al	0.011	0.019		0.8		SR EN ISO 17294/2:2023
As	mg/kg Al	13.85	12.0	14	40	100	SR EN ISO 17294/2:2023
Cd	mg/kg Al	0.12	0.22	3	50	100	SR EN ISO 17294/2:2023
Cr	mg/kg Al	3.57	3.72	30	700	1000	SR EN ISO 17294/2:2023
Hg	mg/kg Al	1.20	0.44	4	10	20	SR EN ISO 17294/2:2023
Ni	mg/kg Al	0.99	0.39	20	700	1000	SR EN ISO 17294/2:2023
Pb	mg/kg Al	0.43	0.30	40	200	800	SR EN ISO 17294/2:2023

*Interval for aluminum content in usual sodium aluminate commercial products

Removing silica from the water in the softening process

In order to carry out the experiments, two samples of the Danube water (after pre-settling, marked D1, D2) which were used as a source of raw water by company Alum SA Tulcea were taken and characterized by physical and chemical parameter measurements. The obtained results, compared with the parameters required for raw water used as source for water intended for human consumption [44], are presented in table 3.

Table 3. Physical-chemical characterization of raw samples of water in pre-settling stage

Indicators	Units	Sample		Highest concentrations admitted in the treated waters [44]
		D1	D2	
pH	-	8.00	8.02	10.0
Conductivity	μS/cm	371	432	259
Turbidity	NTU	5.14	4.30	1.00
Alkalinity m	mval/L	3.10	3.40	0.70
Alkalinity p	mval/L	0	0	0.50
Total hardness (D_T)	°dGH	9.80	10.94	4.40
Cl^-	mg/L	30.53	23.79	30.0
SO_4^{2-}	mg/L	25.42	32.16	-
HCO_3^-	mg/L	195.2	207.4	-
Ca^{2+}	mg/L	50.10	56.10	-
Mg^{2+}	mg/L	12.15	13.40	-
Na^+	mg/L	18.0	14.2	-
Al^{3+}	mg/L	0.80	0.70	-
SiO_2 total	mg/L	21.80	6.40	-
SiO_2 ionic	mg/L	6.44	4.24	3.00
Permanganate index	mgO$_2$/L	2.81	2.26	6.32

The use of lime in combination with sodium aluminate is an alternative for the advanced silica removal of from any kind of waters with significant content of both temporary and permanent hardness. In this case, the lime induces the precipitation of amorphous $Mg(OH)_2$, which acts as an adsorbant for the colloidal silica. Further succesive reactions between colloidal silica and aluminum, calcium and magnesium ions lead to precipitation of insoluble, amorphous or crystalline, alumino-

silicates. A comparison was done with the test results using the existing industrial process-water softening flow-sheet (lime + $FeSO_4$ or lime only), including the applied reagent doses.

In this context, the influence of the doses of lime and sodium aluminate (expressed in term of Al^{3+} concentration) on the removal efficiency of Ca^{2+} and Mg^{2+} ions, as well as silica (total and ionic) from raw water samples D1 and D2 was carefully studied. The doses of reagents applied were the following ones: 78 mg/L CaO and 15 mg/L Al^{3+}. Dosing of the reagents in the water samples was done under stirring, and the reaction time was 30 minutes.

The influence of the dose of lime and the dose of Al^{3+} on the treatment process of sample D1 was studied, as well as the influence of the pH and the doses of CaO and Al^{3+} on treatment process for the sample D2.

Removal of suspended matter and the global organic load accumulated in the waste waters, following chemical treatments from the tannery industry, after the advanced reduction and separation of chromium VI

In the following experimental tests, there will be compared the efficiency of coagulation-flocculation processes in case of tannery wastewater treatment with sodium aluminate, aluminum sulphate and iron chloride. All coagulants were tested together with two types of synthetic polymers as flocculants (cationic and anionic). Aluminum sulphate and ferric chloride were bought from the reagent market, but sodium aluminate was produced in Romania as secondary product at alumina factory Alum SA Tulcea. The experiments of coagulation-flocculation were performed in order to identify the optimal parameters (pH, coagulant dose and flocculants doses) for a constant settling time of two hours.

Coagulant doses were computed as total aluminum doses with specific ratios between aluminate and sulphate in the range of 50÷1000 mg Al/L respectively 0.3÷6.1 mL sodium aluminate (sodium aluminate type B with 25 times dilution factor). Aluminate type B has the following main characteristics: 20.54% Al_2O_3, 19.10% Na_2O, 1.495 g/cm3 specific weight. Both flocculants have 0.1% active substance. Two additional tests with aluminum sulphate (sample T10) and iron chloride (sample T11) were also performed. For these additional samples the doses of coagulant were similar with optimal doses for sodium aluminate, respectively, 100 mg Al/L. The pH corrections was performed at pH = 9 for total precipitation of Cr^{3+} and pH = 7 for coprecipitation of chromium, aluminum and iron had been done with H_2SO_4 1N (for the tests with sodium aluminate) and NaOH 10% (for the tests with aluminum sulphate). Table 4 shows the experimental conditions for the treatment of tannery waste water (after Cr^{6+} reduction).

Table 4. Operating conditions of tannery wastewater treatment by coagulation-flocculation

Experimental parameters	Samples											
	T1	T2	T3	T4	T5	T6	T7	T8	**T9**	**T10**	**T11**	T12
pH, initial						8.5						
Sodium aluminate dose, mg Al/L	1000	500	500	200	-	100	100	100	100	-	-	50
Al_2SO_4 dose, mg Al/L	-	-	-	-	200	-	-	-	-	100	-	-
$FeCl_3$ dose, mg Fe/L	-	-	-	-	-	-	-	-	-	-	100	-
V_{H2SO4},1N, ml/L	11	9	9	3	-	3.2	3.2	3.2	6	-	-	4
V_{NaOH},10%, ml/L	-	-	-	-	9	-	-	-	-	7.3	8.4	-
pH coagulation-flocculation	9	9	9	9	9	9	9	9	7	7	7	7
Coagulation time, minutes	30	30	30	30	30	30	45	60	45	45	45	45
Cationic flocculant dose, ml/L	5	5	-	5	5	5	5	5	5	5	5	5
Anionic flocculant dose, ml/L	-	-	5	-	-	-	-	-	-	-	-	-
Flocculation time, minutes	5	5	5	5	5	5	5	5	5	5	5	5
Settling time, minutes	120	120	120	120	120	120	120	120	120	120	120	120

The initial main characteristics of wastewater (the effluent of Cr^{6+} reduction phase) were: COD = 2860 mg O_2/L, BOD_5 = 1030 mg O_2/L, extractable substances with petroleum ether = 22 mg/L, TSS = 1050 mg/L, total chromium = 30.4 mg/L.

The residual concentration (after coagulation-flocculation and settling) were compared (Table 9) with admitted limits for discharging to the sewer).

RESULTS AND DISCUSSION
A. Removing silica from water in the softening process
The lime dosage influence on the efficiency in the treatment process of raw water sample D1
Considering that sodium aluminate allows to reduce the temporary hardness of water by precipitating calcium and magnesium in the form of carbonate and respectively hydroxide, it was aimed to reduce the dose of lime in the context of treatment process with lime and alumina. According with this opportunity, the experiments were carried out at a constant dose of aluminate, and the dose of lime was ranged between the currently applied one (100mg/L) and respectivly, 78% of it. The applied dose of Al^{3+} (29.7mg/L) corresponds to a 10% excess compared to the stoichiometric requirement for total removal of Mg^{2+} from raw water, because for 1 mol of Mg^{2+} there are required only 2.22 moles of Al^{3+}. The obtained results, presented in Table 5 are highlightening six important conclusions presented in the next paragraphs.

Table 5. The influence of CaO dose to the efficiency of D1 sample treatment for 29.7 mg Al^{3+}/L

CaO, mg/L	pH	Conducti vity µS/cm	Turbidity NTU	Alkalinity m/p, mval/L	D_T, °dG H	Ca^{2+}, mg/L	Mg^{2+}, mg/L	Al^{3+}, mg/L	Na^+, mg/L	SiO_2 total, mg/L	SiO_2 ionic, mg/L
-	8.00	371	5.14	3.10/-	9.80	50.1	12.2	0.80	18	21.8	6.44
100	10.4	336	5.00	2.00/1.25	1.94	12.0	1.20	0.47	62.5	2.04	1.73
86.8	9.80	279	5.79	1.60/0.85	1.96	10.0	2.43	0.85	61	2.54	1.90
78.1	9.50	281	3.16	1.50/0.4	3.36	12.2	7.29	0.56	56.3	3.60	2.92
100*	10.4	265	-	1.05/-	4.48	16.0	9.72	0.80	18	8.20	5.05
100**	10.7	270	5.61	1.25/0.85	4.76	16.0	10.93	0.80	18	8.45	5.40

* The existing industrial softening process, raw water treated with CaO and $FeSO_4$ (1.2mg Fe^{2+}/L);
** The existing industrial softening process, raw water treated only with CaO.

First, in the presence of sodium aluminate, an increase in the removal efficiency of the total water hardness (D_T) was recorded and the level of this indicator in the treated samples (< 3.4 °dGH) is 29% ÷ 44% lower than the one achieved in the currently applied process-water softening process using 100 mg CaO/L and $FeSO_4$ (1.2 mg Fe^{2+}/L).
Second, the above indicators were obtained using a significant lower dose of lime, around 22%, respectively from 100 to 78 mg CaO/L compared to the existing water softening process. Also, it was noted the final treated water pH effect, with a significant decreasing the precipitation efficiency of Mg hydroxide (a fact highlighted by the 6-fold increase of the concentration of Mg^{2+} in soluble form), however the residual Mg^{2+} level remains 1.3 times lower than the current one (9.72 mg/L).
Positive effect of the aluminate dosing is also reflected in relation to the removal of colloidal and ionic silica; the remaining level of ionic silica is 2.6÷2.9 times lower than that currentlly obtained, for the application of doses of lime ≥ 87% of the current dose.
The low level of the remaining concentrations of Al^{3+} in the soluble phase of sample is located below 1mg/L. Alongside with the systematic decrease of soluble Mg this is suggesting that, in the treating process using aluminate, other precipitation reactions than those associated with formation of aluminum hydroxide were also involved, possibly hydrotalcite precipitation.
In this case, considering that the pH of the treated samples (>9.5) exceeds the optimal one (pH=7.5÷8) for hydroxide precipitation, the presence of ionic silica in significant concentrations (part of it resulting from the solubilization of colloidal silica in alkaline pH) favors the formation of insoluble aluminosilicates, a fact confirmed by the advanced removal of silica.
In case of reagent dosages of 29.7 mg Al^{3+}/L and 87 mg CaO/L, the total hardness and ion silica levels are reduced by 5 time and 3.4 times respectively, relative to raw water. Compared to the limits for the softened water, the hardness and ionic silica are 2.2 times, respectively 1.6 times lower. In this

case the optimal selected dose of lime remained 87 mg/L, and the optimal dose of Al^{3+} had to be adopted after a new test-work reevaluation.

The influence of Al^{3+} dose on the treatment process efficiency of the raw water sample D1
The purpose of the experiments was to evaluate the variation of the dose of sodium aluminate, expressed as $Al^{3+,}$ on the efficiency of removing hardness and silica from raw water in the process of treatment with lime and sodium aluminate. The results are presented in table 6.

Table 6. The influence of Al^{3+} dose to the efficiency of D1 sample treatment for 86.8 mg CaO/L

Al^{3+}, mg/L (D/S)	pH	Conducti vity µS/cm	Turbidity NTU	Alkalinity m/p, mval/L	D_T, °dGH	Ca^{2+}, mg/L	Mg^{2+}, mg/L	Al^{3+}, mg/L	Na^+, mg/L	SiO_2 total, mg/L	SiO_2 ionic, mg/L
-	8.00	371	5.14	3.10/-	9.80	50.1	12.15	0.80	18.0	21.8	6.44
29.7 (1.1)	9.80	279	5.79	1.60/0.85	1.96	10.0	2.43	0.85	61.0	2.54	1.90
27.0 (1)	9.60	242	4.33	1.20/0.50	1.68	10.8	2.17	0.79	58.6	1.72	1.25
24.3 (0.9)	9.40	236	3.72	1.00/0.40	2.64	12.7	3.78	0.55	51.7	3.93	2.61

The experiments indicate a positive effect reflected by the total hardness level, which is 1.6 times lower than in the sample treated with a dose of 27 mg/L Al^{3+}, compared to the sample treated with a dose of 24.3 mg/L Al^{3+}.
The desilication process is also favored by the excessively use of aluminate, probably because of the increase in the precipitation yields of alumino-silicates, as a result of the increase in pH of the samples.
The colloidal silica is predominantly present in raw water and it turns easily into ionic silica by solubilization in alkaline pH, and accordinly, this behavior is reflected by the decrease to half of the remaining total and ionic silica in the treated samples, when the dose of Al^{3+} increases from 24.3 to 27 mg/L.
It can be considered that, in the case of waters with high total hardness (9.8 °dGH) and high content of total silica (21.8 mg/L), the application of the treatment process with lime and sodium aluminate can ensure a high yield of softening) (83%) and advanced desilication (94%), under the following operating conditions: pH = 9.6; dose of $Na_2Al_2O_4$ equivalent to Al^{3+} =27 mg/L; dose of CaO = 87mg/L; reaction time = 30 min.
The use of lime together with sodium aluminate in the water softening process, under the operating conditions established as optimal, ensures the following levels of the remaining concentrations: the total hardness (1.68 °dGH) and ionic silica (1.25 mg/L). These indicators are lower than 2,7 times and respectively, 4 times than those obtained by the currently applied treatment process.

The influence of CaO and Al^{3+} doses on the efficiency of softening process of D2 raw water samples
Since the level of impurities concentration influences the yield of any water treatment process, there have been performed softening experiments on the D2 raw water samples, which, unlike the D1 sample, shows a level about 3 times lower in total silica, mainly, due to a low content of colloidal silica (table 7).
The experiments were carried out at three doses of lime located between 87% of the currently applied dose and 10% excess compared with 100% currently applied dose. For each dose of lime tested, the dose of sodium aluminate, expressed as Al^{3+}, was varied between 15 and 36 mg/L, corresponding to concentrations between 50% of the stoichiometric requirement for Mg^{2+} removal and an excess of 20%, compared to the same refference value. In addition, a softening experiment was carried out, only by treatment with lime and with the currently applied dose of 100 mg/L. The characteristics of treated sample have been used, as a reference element for the evaluation of all treatments performance in the lime - sodium aluminate system, under different operating conditions.

The analysis of the experimental results presented synthetically in table 7, indicate some important conclusions.

The same positive effect of increasing the doses of lime and aluminate on the processes of removing total hardness and silica was recorded, as in the case of sample D1.

At similar reagent doses (CaO = 87 mg/L; Al^{3+} = 27 mg/L), the total hardness removal yields are similar (82% ÷ 83%), for the two raw water samples (D1 and D2), which also present a comparable level of loading for this indicator.

A different situation was recorded in relation to the removal of total silica under identical operating conditions. Thus, the desilication process proceeds with lower efficiency for sample D2 (84%) with low silica content, compared to sample D1 (92%). When treating sample D2 with any of the doses of lime tested as before and doses of Al^{3+} higher than the stoichiometric requirements, the levels of total hardness and residual ionic silica are below 2 °dGH and 0.6 mg/L respectively. These values are at least 2 and respectively, 6 times lower than the ones obtained by treating with lime at the currently applied dose (100 mg/L).

Table 7. The influence of CaO and Al^{3+} doses to the efficiency of D2 sample treatment

Al^{3+}, mg/L (D/S)	CaO mg/L	pH	Conductivity µS/cm	Turbidity NTU	Alkalinity m/p, mval/L	D_T, °dGH	Ca^{2+}, mg/L	Mg^{2+}, mg/L	Al^{3+}, mg/L	Na^+, mg/L	SiO_2 total, mg/L	SiO_2 ionic, mg/L
-	-	8.00	432	4.30	3.40/-	10.94	56.10	13.40	0.80	14.2	6.40	4.24
26.8 (0.9)		9.80	274	5.14	1.70/0.60	2.01	8.45	3.63	9.91	45.2	0.98	0.61
29.8 (1.0)	87	9.90	296	4.30	1.60/0.80	1.73	7.68	2.84	10.35	48.0	0.66	0.55
32.8 (1.1)		10.1	303	3.85	2.00/0.70	1.44	6.62	2.23	13.63	51.0	0.54	0.46
35.8 (1.2)		10.2	307	4.40	2.10/1.20	1.26	6.31	1.65	15.15	53.8	0.53	0.46
-		9.50	245	4.70	1.45/0.70	4.62	15.72	10.51	-	-	5.40	3.95
14.9 (0.5)		9.70	260	4.10	1.50/0.45	2.75	11.12	5.20	6.80	37.2	2.85	2.45
20.9 (0.7)		9.75	262	4.51	1.60/0.55	2.25	9.63	3.91	5.15	39.8	0.94	0.77
26.8 (0.9)	100	10.0	289	5.30	1.80/0.60	1.49	7.25	2.78	8.51	43	0.64	0.54
29.8 (1.0)		10.1	300	4.80	1.90/0.70	1.23	5.26	2.15	10.77	46.9	0.58	0.48
32.8 (1.1)		10.2	304	5.50	2.00/0.70	1.13	5.20	1.76	13.85	52.7	0.51	0.43
35.8 (1.2)		10.3	308	4.82	2.20/1.10	1.09	5.25	1.55	15.57	54.5	0.49	0.43
14.9 (0.5)		10.0	275	4.50	1.70/0.40	2.10	8.36	4.02	8.60	35.6	2.30	1.98
20.9 (0.7)	110	10.1	284	4.20	1.85/0.40	1.86	7.42	3.55	9.85	38.2	1.10	0.93
29.8 (1.0)		10.5	308	5.00	1.80/0.80	120	6.58	1.23	11.41	48.3	0.53	0.44

The application of treatment with lime and aluminate to sample D2 leads to residual concentrations of soluble aluminum of the order of tens of mg/L, which suggests that the precipitation of insoluble alumino-silicates is disfavored by the low level of silica.

The removal of silica in the case of sample D2 is carried out predominantly by adsorption on the precipitate of $Mg(OH)_2$, whose formation is favored by the shift of the pH in the strongly alkaline range (10-11), a fact which is highlightehing also, by the low level of the remaining $Mg^{2+} \leq 2mg/L$ concentration, only for the samples treated with doses of Al^{3+} higher than the stoichiometric requirement.

On the basis of experimental results, it is estimated that in the case of water with a high level of total hardness (11°dGH) and a low content of total silica (6.4 mg/L), the application of the treatment process with lime and sodium aluminate can ensure softening ($\eta = 89\%$) and advanced desilication ($\eta = 91\%$) under the following operating conditions: pH = 10.15; dose of $Na_2Al_2O_4$ equivalent to Al^{3+} = 29.8 mg/L; doze of CaO = 100 mg/L; reaction time = 30 min.

The influence of pH on the removal of Al^{3+} from sample D2 treated with lime and sodium aluminate
As is known, $Al(OH)_3$, due to its amphoteric nature, dissolves in strongly acidic or strongly alkaline environments. Consequently, for the precipitation of Al^{3+} from alkaline solutions, as is the case with softened water, it is necessary to lower the pH of the filtered sample by dosing acid. To establish the operating conditions that ensure the advanced removal of Al^{3+}, the influence of pH on precipitation efficiency, has to be studied for any particular case.
For this purpose, the precipitation experiments were carried out at three pH values between 9÷7.5, by adding different doses of H_2SO_4 located between 2.5÷13 mg/L, with a reaction time of 15 minutes. The treated samples were filtered and characterized, according to the quality indicators followed for softened water, with the exception of total silica. The results are presented in table 8.

Table 8. The influence of H_2SO_4 dose to Al^{3+} removal from demineralized D2 sample

H_2SO_4, mg/L	pH	Electric cond. µS/cm	Turbidity NTU	Alkalinity m/p, mval/L	D_T, °dGH	Ca^{2+}, mg/L	Mg^{2+}, mg/L	Al^{3+}, mg/L	Na^+, mg/L	SiO_2 ionic, mg/L
-	10.1	300	0.92	1.90/0.70	1.23	5.26	2.15	10.8	46.9	-
2.40	9.02	306	0.82	1.80/-	1.11	4.46	2.11	8.47	45.2	2.40
10.0	8.00	315	0.75	0.95/-	1.12	4.39	2.05	2.63	43.6	10.0
12.9	7.50	320	0.75	0.70/-	1.02	4.07	1.97	1.98	38.8	12.9

The results indicate that the decrease of final pH of the treated samples between slightly alkaline and neutral ensures the increase of the Al^{3+} precipitation yield from 21 to 82%.
The dose of 10 mg/L H_2SO_4 was selected because at final pH 7.5÷8 the precipitation yields were relatively close, for ensuring the removal of Al^{3+} up to a level of remaining concentration of 6 mg/L, which does not affect the process of demineralization applied with the new water treatments with calcium hydroxide and sodium aluminate.

B. Removal of total suspended matter and global organic load from tannery wastewater (after reduction and advanced separation of Cr^{6+})
In case of coagulation at pH = 9 (recommended value by our previous tests [45] and confirmed by literature data), the increase of coagulant dose – sodium aluminate led to a slight decrease of TSS removal efficiency (83% for sample T4 and 77% for sample T1) and to doubling of chromium concentrations. In the next comparative samples (table 9), the coagulant dose has been diminished to a lower value (200 mg Al/L in the samples T4 and T5).
Comparing of residual values of organic and inorganic loads (filtrate residue and chromium concentrations) emphasized a similar evolution of removal efficiencies and the compliance with the admitted limits just for TSS and extractable substances. But, the rest of parameters concentrations (COD, Al^{3+} and filtered residue) had higher values, over admitted limits.
Concerning characterization of treated effluents, below were presented some important conclusions.
The increase of coagulation time up to 60 minutes for aluminate dose of 100 mg Al/L (samples T6, T7, T8) led to diminishing of organic load as COD up to 810 mg O_2/L, but the removal efficiency raised with 12% for 100 mg Al/L and 45 minutes coagulation time (sample T7 vs sample T4). The coagulation tests at pH = 7 were done in order to reduce organic load and residual aluminum. Also, the coagulation at pH = 7 had positive influence to organic and inorganic load removal.

Table 9. Characterization of the treated effluents (tannery treated wastewater)

Indicators	Samples												
	Initial	T1	T2	T3	T4	T5	T6	T7	T8	**T9**	**T10**	**T11**	T12
COD, mg O_2/L	2860	2460	2510	2596	1144	1056	860	810	920	**490**	**520**	**660**	620
CBO$_5$, mg O_2/L	1030	-	-	-	-	-	-	-	-	**295**	**464**	**480**	-
Extractable substances, mg/L	32.0	20.0	25.0	26.0	25.0	23.0	23.0	22.0	22.0	**20.0**	**18.0**	**15.0**	27.0
TSS, mg/L	1050	235	200	220	180	196	172	153	164	**79.0**	**68.0**	**72.0**	94.0
Filtered residue, mg/L	5850	-	-	-	7420	8122	-	-	-	**11000**	**10520**	**10720**	-
Conductivity, mS/cm	10.3	-	-	-	17.0	18.0	-	-	-	**15.6**	**28.4**	**25.1**	-
Cr, mg/L	30.4	0.55	0.56	0.88	0.20	0.20	0.22	-	-	**0.10**	**0.02**	**0.27**	-
Al, mg/L	15.9	-	-	-	7.00	6.00	-	-	-	**0.74**	**0.95**	**0.09**	-
Na, mg/L	2740	-	-	-	-	-	-	-	-	**2730**	**2400**	**1865**	-
Dried substance, %	-	-	-	-	-	-	-	-	-	**3.62**	**3.40**	**3.91**	-

Regarding the comparative tests with aluminum sulphate (sample T10), iron chloride (sample T11) and sodium aluminate – lower doses of 50 mg Al/L (sample T12), results presented in table 9, the experimental data indicated that the removal efficiencies of organic load increased with 11% (sample T9, pH = 7, ηCOD = 83% vs sample T7, pH = 9, ηCOD = 72%). The diminishing of organic load as BOD$_5$ was 71%m, which means the treated effluent is biodegradable (Symons ratio BOD/COD = 0.6) [46]. There for, is recommended an additional biological treatment phase.

The removal yield of chromium was 99.7%, (0.1 mg/L residual chrome in case of sample T9 with sodium aluminate, below the sample T11 where the residual chromium was 0.27 mg/L), but over the value for the sample treated with aluminum sulphate. The same evolution was observed in case of residual aluminum. The diminishing of coagulant dose – sodium aluminate (sample T12) led to higher residual organic load in the treated water. After two hours settling the dried substance (d.s.) of the sludge was higher for the sample which was treated with sodium aluminate (3.62% for sample T9) than sample which was treated with aluminum sulphate (3.40% for sample T11).

Figures 1 and 2 show the settling velocities for samples T9 (coagulation with sodium aluminate) and T10 (coagulation with aluminium sulphate).
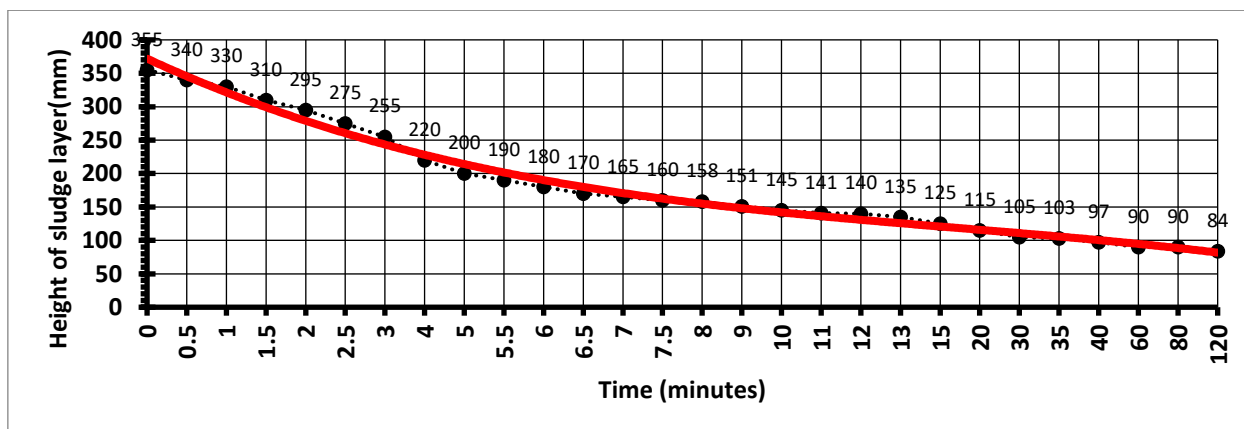
Fig. 1. Settling velocity of suspended matters (coagulation-flocculation of tannery wastewater)

These comparative graphics emphasized that the sludge layer height is 84 mm for sodium luminate vs 50 mm for aluminum sulphate (aluminum sulphate - better settling of the sludge for the same time of 120 minutes), but the dry substance of the sludge is with 0.2% higher in case of sodium aluminate.
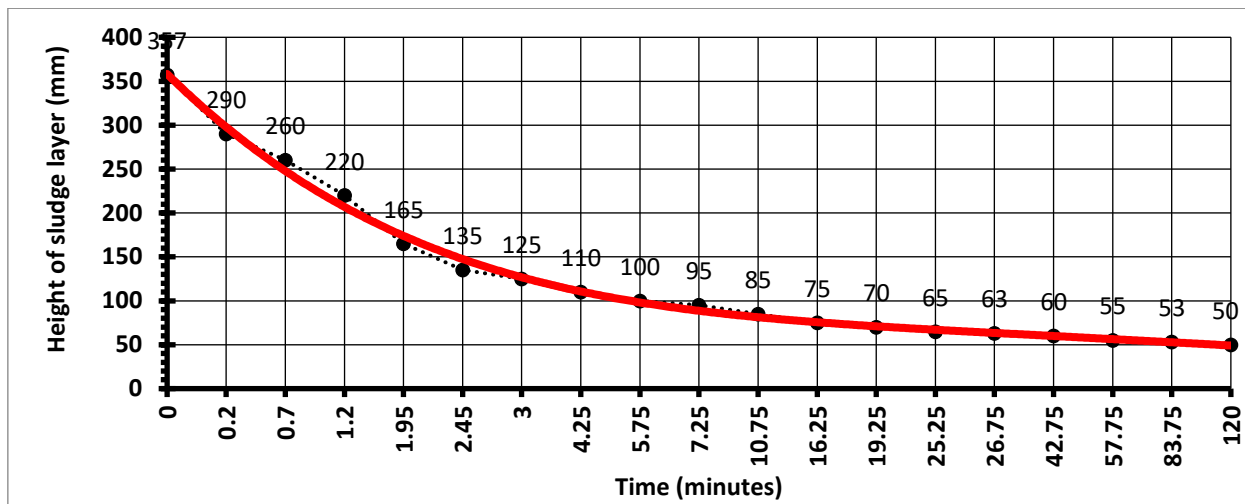
Fig. 2. Settling velocity of sodium sulphate (coagulation-flocculation of tannery wastewater)

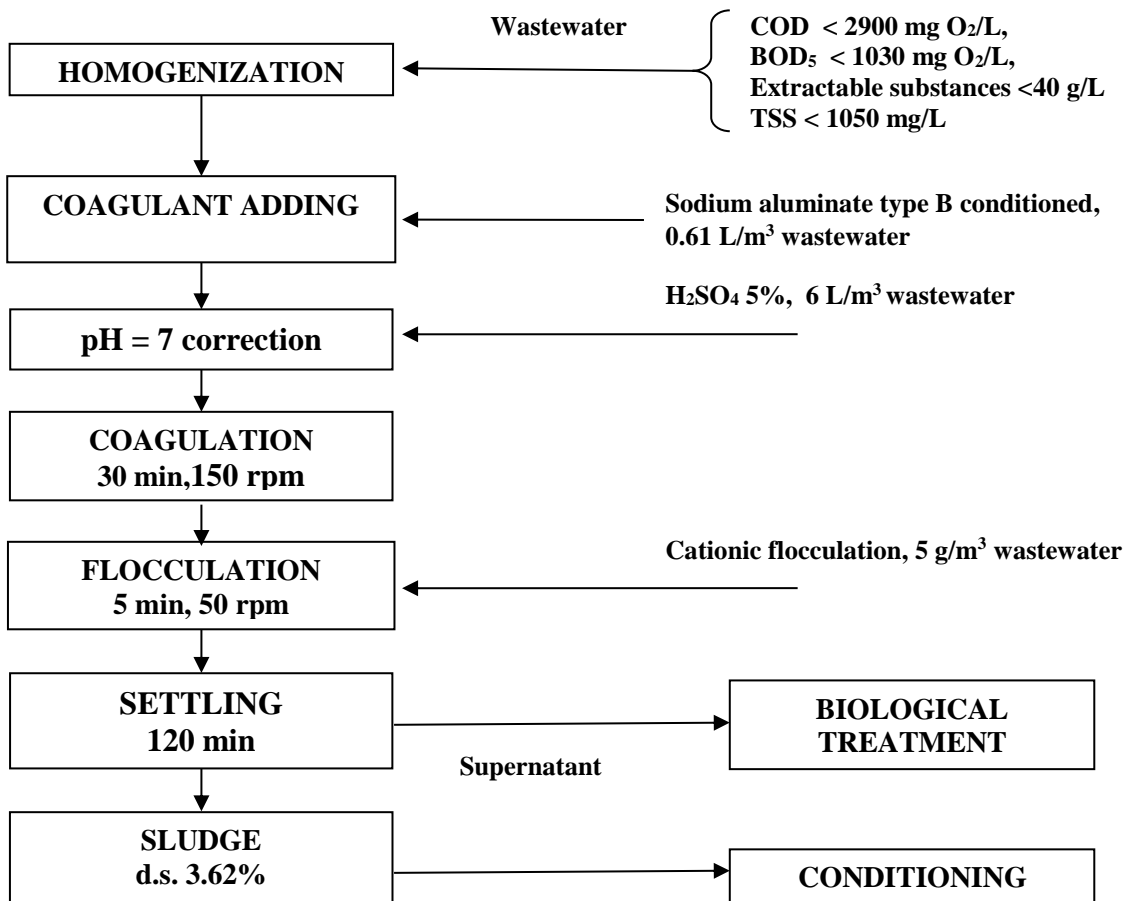Taking into account the above presented results, a common treatment flow chart was proposed in figure 3.

Fig. 3. Pretreatment flow by coagulation-flocculation with sodium aluminate of tannery wastewater

CONCLUSIONS

This paper demonstrated that replacing aluminum sulphate and aluminum poly-chloride with sodium aluminate may lead to similar results in water softening and silica precipitation (potabilization), as well as in waste water (from tannery) advanced treatments. In both cases, the sodium aluminate is the cheapest raw material for waters treatments, because sodium aluminate is a common intermediary product in Bayer alumina production and in recycling material in non-metallurgical alumina products,

manufactured at Alum SA Tulcea. Also, in both cases sodium aluminate is precursor, in both manufacture of aluminum sulphate and aluminum poly-chloride manufacture.

The results concerning the chromium removal from waste waters are in good agreements with our previous results about inertization chromium in the mixtures of alumino-silicate compounds.

REFERENCES
[1] KADUK, J.A., SHIYOU, P., J. Solid State Chem., **115,** no. 1, 1955, p. 126.
[2] MARTEN, G., BARKER, M.G., GADD, P,G., BEGLEY, M.J., J. Chem. Soc., **6**, 1984, p. 1139.
[3] TOSSEL, L.A., Am. Mineral, **84**, no. 10, 1999, p. 1641.
[4] KRUPINSKA, I., Molecules, **25**, no. 3, 2020, p. 6415.
[5] SHEWA, W.A., DAGNEW, M., Sustainability, **12**, no. 15, 2020, p. 5928.
[6] SHARMA, S., AHAMMED, M.M., Heliyon, **9**, no. 5, 2023, p. e15796.
[7] FOTOOHI, E., MOKHTARIAN, N., FARAHBOD, F., Appl. Water Sci,. **14**, no. 2, 2024, p. 27.
[8] HAN, J., WANG, K., SHI, J., WANG, Y., Constr. Build. Mater. J.*,* **64**, 2014, p. 342.
[9] LIU, Y., ZHANG, Y., DONG, B., WANG, Y., Constr. Build. Mater J.*,* **368**, 2023, https://doi.org/10.1016/j.conbuildmat.2023.130446.
[10] CHEN, B., WANG, J., ZHAO, J., Adv. Mater. Sci. Eng., 2021, p.1, https://doi.org/10.1155/2021/6658588.
[11] SITHOLE, N.T., MAGAGE, B., IOP Conference Series: Earth and Environmental Science, **1048**, 2021, p.1, https://doi.org/10.1088/1755-1315/1048/1/012002.
[12] MARAVIĆ, T., MAZZITELLIM, C., MANCUSO, E., DEL BIANCO, GF., JOSIĆ, U., BRESCHI, K., MAZZONI, A., J. Esthet. Restor. Dent., **35**, 2023, p. 1085.
[13] HEBOYAN, A., VARDANYAN, A., KAROBARY, M.I., MARYA, A., AVAGYAN, T., TEBYANIYAN, H., MUSTAFA, M., ROKAYA, D., AVETISYAN, A., Molecules, **28**, no. 4, 2023, p. 1619.
[14] GIEŁZAK, J., DEJAK, B., SOKOŁOWSKI, J., BOCIONG, K., *Coatings,* **13***, no.* 2, 2023, p. 244.
[15] XIAO, J., HAN, N., LI, Y., ZHANG, Z., SHAH, S.P., Front. Struct. Civ. Eng., **15**, no. 5, 2021, p.1.
[16] KROPYVNYTSKA, T.P., KAMINSKYY, A.T., SEMENIV, R.M., CHEKAYLO, M.V., IOP Conference Series: Material Science and Engineering, **708**, 2019, p.1, https://doi.org/10.1088/1757-899X/708/1/012091.
[17] KANG, H., KANG, S., LEE, B., MATIKAS, T.F., THEODORE, E., Materials, **14**, no.18, 2021, p. 5407.
[18] MITROVIĆ, A., NIKOLIĆ, D., MILIČIĆ, L., DRAGAN BOJOVIĆ, D., *Teh. Vjesn.*, **4**, no. 20, 2013, p. 683.
[19] SUN, X., DONG, J., Membranes, **13**, no. 3, 2023, p. 305.
[20] VOGRIN, J., SANTINI,T., PENG, H., ZHAO, L., VAUGHAN, J., Appl. Clay Sci., **244**, no. 107106, 2023, p.1.
[21] DERBE, T., TEMESGEN, S., BITE, M., Adv. Mater. Sci. Eng., 2021, p. 1, https://doi.org/10.1155/2021/6637898.

[22] CATALDO, E., SALVI, L., PAOLI, F., FUCILE, M., MASCIANDARO, G., DAVIDE MANZI, D., COSIMO MARIA MASINI, C.M., MATTI, G.B., Agronomy, **11**, 2021, p. 1547.

[23] PATRIKEEV, V.A., PAVLOV, M.L., KUTEPOV, B.I., Russ. J. Appl. Chem., **80**, 2007, p. 498.\

[24] NIKOLOV, A., Spis. B Lgarskoto Geol. Druz., **83**, 3, 2022, p. 27.

[25] BELVISO, C., CAVALCANTE, F., Materials (Basel)., **13,** no. 21, p. 4780

[26] BENAISSA, S., CLAPPER, D.K., PARIGOT, P., DEGOUY, D., International symposium on oilfield chemistry, Houston, Texas, February 1997, https://doi.org/10.2118/37268-MS.

[27] AKKOUCHE, A., BENMOUNAH, A. GUECIOUER, A., CHALAH, K., *Egypt. J. Petrol.*, **29**, no. 2, 2020, p. 127.

[28] QUINTERO, L., J. Disper. Technol., **223**, no. 1-3, 2002, p. 393.

[29] LIU, J. Y., QIU, Z.S., HUANG, W., J. Pet. Eng., **135**, 2015, p. 433.

[30] SHEN, J., SONG, Z., QIAN, X., LIU,W., BioResources, **4**, no. 3, 2009, p. 1190.

[31] HUBBE, M.A., GILL, R.A., BioResources, **11**, no. 1, 2016*, p.* 2886.

[32] YUE, X., DU, X., XU. Y., BioResources, **12**, no. 4, 2017, p. 9357.

[33] XU, Y., ZHANG, W., YUE, X., ZHANG, D., BioResources, **10**, no 4, 2014, p. 7704.

[34] WAN, T., YU, P., LUO, Y., WANG, S., LUO, Y., Energ. Fuel, 23, no. 2, 2009, p. 1089.

[35] PAMPARARO, G., DEBECKER, D.P., ACS Sustainable Chem. Eng., 11, no. 28, 2023, p. 10413

[36] KEOGH, J., DESHMUKH, G., MANYAR, H., Fuel, **310**, Part C, 2022, p. 122484.

[37] LOGHMAN, Z.M, FATTAH-ALHOSSEINI, A., GASHTI. S.O., Anal. Bioanal. Electrochem., **10**, 2018, p. 1247.

[38] HORSTH,D.F.L., PRIMO, J.O., DALPASQUALE, M., BITTENCOURT, C., ANAISSI, F. J., J. Clean. Prod., **5**, 2021, p. 100313.

[39] ORNA, M., FONTANI, M., Colorants, **1**, 2022, p. 307.

[40] HORSTH,D.F.L., PRIMO, J.O., ANAISSI FAUZE. J., BITTENCOURT, C., RSC Sustain., **1**, 2023, p.159.

[41] ROSSI, S., RUSSO, F., CALOVI, M., J. Coat. Technol. Res., **18**, 2021, p. 39.

[42] DU, B., ZHOU, S. S., LI, N.L., Procedia Environ. Sci. Eng. Manag.*,* **10**, 2011, p. 807.

[43] SR EN 882/2016: Chemical reagents for drinking water treatment. Sodium aluminate, https://magazin.asro.ro/ro/standard/246182 [20.05.2024].

[44] Government Decision 100/2002, NTPA 013 regarding surface water quality used as a source of raw water for water intended for human consumption, Official Monitor of Romania no.130/19.02.2002, https://legislatie.just.ro/Public/DetaliiDocument/34145 [20.05.2024].

[45] NICULESCU, M., IONITA, A. D., FILIPESCU, L., UPB Scientific Bulletin, Series B: Chem. Mat. Sci., **72**, no. 3, 2010, p. 99.

[46] SYMONS, M.C.R., Acc. Chem. Res, **14**, no. 6., 1981, p. 179.