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(RECOMMENDED CITATION)

SOLUTIONS IN THE COAGULATION OF OIL WASTEWATER

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ABSTRACT. Coagulation is one of the most important stages of the oil wastewaters pre-treatment. Oil wastewaters coagulation that we have studied and which had a content of 95.9-270.6mg Total Petroleum Hydrocarbon (TPH)•L^{-1} required optimal doses of polyaluminum chloride (PAC) coagulant between 12.0-16.4mgAl•L^{-1}. In the PAC coagulation, the use of various coagulants aids with absorbent properties, such as: indigenous volcanic tuff, charcoal, anaerobic biologic sludge led to: 1. The PAC dose reduction with 30-50%; 2. Turbidity, Total Organic Carbon (TOC), TPH and absorbance at wavelength 254 nm, A254, of treated samples in the presence of aids and reduced PAC doses were similar vs. samples treated with non-reduced PAC doses in aids absence. The use of indigenous volcanic tuff as coagulation aid led to coagulation sludge which are able to sediment with faster than the sludge obtained with PAC coagulation but without aid. More the volume of the coagulation sludge obtained is reduced with 50% vs. one obtained in other variants. By adding coagulation aids there was a reduction of coagulation reagent costs up to 50%. The correlation between A254 and TPH parameters can be useful in establishing on-line relationships that could ease the operators' activity in wastewater treatment plants.

Keywords: *Total Petroleum Hydrocarbons, wastewater coagulation, polyaluminum chloride, coagulant aids, costs*

INTRODUCTION

It is well known that a lot of wastewaters loaded with organic pollutants result from the oil processing operations. Out of them there are large amounts of oil compounds, among which a high percentage consists of aromatic compounds. Out of these oil compounds, the Total Petroleum Hydrocarbons (TPH), is very toxic in water and more than this they persist in the environment [1-6].

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It was noticed a decrease of algae productivity in natural water when oil compounds are found. The presence of these compounds often causes the alteration of the natural colour, taste and odour of water surfaces. More than this, the oils and the fats present in the wastewater tend to agglomerate on the water passages, in the premises units, on the side parts causing odour formation as a result of anaerobic degradation. Furthermore, TPH cause severe corrosion of the passages or of the storage units. As a whole, oil wastewaters are carcinogenic, causing a series of hazards for the natural water ecosystem components even extending onto the human health [2, 7-8].

There are methods of treating the oil wastewaters with physical / chemical treatments, such as: settling, filtration, centrifugation, foaming and coalescing, adsorption, coagulation, chemical oxidation and biological techniques. However, there are new technologies mentioned in the specialty literature [9-12], such as: membrane processes, catalytic oxidation, etc.

There are certain treatment methods, such as: adsorption, coagulation, flocculation, membrane processes etc. through which pollutants are transferred from one medium to another; this step is necessary because it eliminates the organic compounds from water. The organic compounds are removed from water in several concentrated phases that can be subsequently stored, processed, monitored.

The biological techniques have serious limitations caused by the presence of recalcitrant compounds, low speed biodegradation, voluminous treatment units, etc. However in the literature there are reported, good efficiencies in the reduction of TPH from wastewater by the coagulation processes associated with adsorption phenomena [13-15].This is the reason for which the authors used Al or Fe salts as coagulation reagent and associated materials as aids: polymeric compounds, natural gums, polyacrylamides, substances that contain sequences of carbohydrates and/or polysaccharides and proteins such as chitin, chitosan, together with various plant debris, such as: cane sugar, shredded coconut shells, charcoal, cellulose, etc. [7,16-19]. The aids addition in coagulation stage with coagulation reagent determines the formation of coagulation aggregates as flocks. The adding of the coagulation aids causes the absorption phenomena of TPH, and thus contributes to the increase of the flock’s size and the efficient separation of the pollutants. The analytical control of the coagulation stage has an important role in the management and the optimization of the processes involved in the industrial oil wastewater treatment plants. The control parameters are the following: pH, TPH, Chemical Oxygen Demand (COD), Total Organic Carbon (TOC), suspensions, etc. [3, 10, 17-18, 20]. The process control can be supplemented with specific parameters such as the ultraviolet absorbance at a wavelength of 254 nm (A254) [21-23].

The purpose of this study is to identify the natural materials that can be used as aids in the coagulation processes with PAC agent in the context of the oil wastewaters pre-treatment. The study monitored the efficiencies of the TPH reduction from wastewater by coagulation variants with: 1. the Optimal Dose (OD) of Al^{3+} salts, using PAC coagulant agent, 2. the low dose (LD) of Al^{3+} salts *vs.* OD using PAC coagulant agent and the coagulation aids with absorbent properties, such as: indigenous volcanic tuff, charcoal, biological sludge, 3. the correlation of the conventional control parameters TPH of treated/ untreated waters with the unconventional spectrophotometric parameter - absorbance at 254nm wavelength, A254, 4. the improvement of the coagulated sludge settling rate, 5. coagulant agent costs analysis.

RESULTS AND DISCUSSIONS

Table 1 shows the initial characteristics of the oil wastewaters. The conditions of discharging the treated oil wastewater into the sewerage networks of localities and directly in wastewater treatment plants are in compliance with HG 352/2005 NTPA 002 [24]. The pH of the wastewaters ranges between 7.16-8.2 (admissible values according to HG 352/2005 - NTPA 002 [24]). COD of wastewaters range between 161.3-376.5mgO_2·L^{-1} and do not exceed the values admitted by current norms of 500mgO_2·L^{-1} [24/]. It is known that the substances with aromatic character cannot oxidize by dichromate oxidation of organic compounds in strong acidic medium; and the oil wastewaters under study are heavily loaded with aromatic hydrocarbons.

Table 1. The initial characteristics of the oil wastewaters (three repetitions for each treated variants)

No	Parameters	Wastewaters		
		WW 1	WW 2	WW 3
1	pH	8.20±0.5	7.85±0.3	7.16±0.2
2	Turbidity [° NTU]	65.2±2.5	64.0±2.0	33.5±0.7
3	COD [mgO_2·L^{-1}]	376.5±32.5	230.4±27.5	161.3±12.5
4	TPH [mg·L^{-1}]	270.6±35.4	160.6±25.5	95.9±22.3
5	TOC [mgC·L^{-1}]	101.3±16.3	59.7±13.7	32.7±9.5
6	* Absorbance A254 [cm^{-1}]	2.235±0.5	1.031±0.7	0.89±0.2

** Samples filtered through filtering paper.*

The turbidity of the wastewaters ranges between 33.5-65.2°NTU and the TOC of wastewaters between 32.7-101.3mgC·L^{-1}. As for A254 of wastewaters this ranges between 0.890-2.235cm^{-1}. We have to mention that the TOC and the A254 are not set by national regulations. As it can be seen the TPH of wastewaters ranges between 95.9-270.6 mg·L^{-1} while the amount of TPH exceeds by 19.2 to 54.0 times the amount of 5mg TPH·L^{-1} admissible, according to HG 352/2005 - NTPA 002. [24]. The pre-treatment of WW 1, WW 2 and WW 3 wastewaters with PAC coagulant agent, at the optimal dose (OD) performed by the Jar-Test method, has determined a significant reduction of the efficiencies for COD, turbidity, TPH, TOC and A254.

Table 2 presents the characteristics of the water samples treated with optimal doses (OD) of PAC coagulation agent as far as the reduction efficiencies of turbidity and the organic loading are concerned; such as COD, TOC and A254. It can be observed that the reduction efficiency of the turbidity is high: from 68.2 up to 80.7%. The residual turbidity is ≤12.5 o NTU. It can also be seen that the reduction efficiency of the total organic load is high, from 46.8 to 63.9% for TOC, between 65.2 to 74.1% for TPH and for A254 between 15.7-39.0%.

Table 2. Characteristics of the treated water samples with OD of PAC coagulant agent [mgAl·L^{-1}] (three repetitions for each variants)

Wastewaters		**Parameters**	**Treated water samples**	
Type	**OD of PAC coagulant agent [mgAl·L^{-1}]**		**Residual values**	**Removal efficiency [%]**
WW1	16.4	Turbidity [º NTU]	12.5±3.5	80.7
		TPH [mg·L^{-1}]	39.7±5.3	74.1
		TOC [mgC·L^{-1}]	37.2±3.9	63.1
		* Absorbance A254 [cm^{-1}]	1.58±0.05	39.0
WW 2	16.0	Turbidity [º NTU]	12.5±5.3	80.5
		TPH [mg·L^{-1}]	67.6±6.6	67.0
		TOC [mgC·L^{-1}]	21.5±4.8	63.9
		* Absorbance A254 [cm^{-1}]	0.72±0.02	30.1
WW 3	12.0	Turbidity [º NTU]	10.75±3.3.	68.2
		TPH [mg·L^{-1}]	33.5±5.2	65.2
		TOC [mgC·L^{-1}]	17.6±1.9	46.8
		* Absorbance A254 [cm^{-1}]	0.75±0.01	15.7

**water samples filtered through filtering paper*

It can be seen that the residual TOC is up to 37.2mgC·L^{-1}, while the residual TPH up to 67.6mg·L^{-1}. It is worth mentioning that the coagulation variants applied caused the removal from the wastewater WW 1 of a high quantity of TPH·L^{-1}, *i.e.:* 230.9mg·L^{-1}; from wastewater WW 2 was removed 103.0mgTPH·L^{-1}, and from the polluted waters WW 3 the total quantity removed was 62.6mg TPH·L^{-1}. However, the TOC and the TPH residual values of the treated samples water were high. The TPH residual was 4.3-7.9 times higher than the national norms limits. In order to improve the reduction efficiency of the total organic compounds in the WW 1-WW 3 wastewaters at the stage of coagulation various inorganic or organic aids were added: indigenous volcanic tuff, charcoal, anaerobic biological sludge.

In tables 3, 4 and 5 there are presented the residual values of the turbidity, COD, TOC, A254 parameters in treated samples, at the coagulation stage, with reduced doses (RD) of PAC coagulant agents and coagulation aids. It is observed that the addition of aids in the coagulation stage with PAC led to:

1. Reductions of PAC coagulant agent dose by 30-50% vs optimal dose;

2. The turbidity in treated samples water with RD of PAC coagulant agent and indigenous volcanic tuff aid was 8.3-15.5 ° NTU, a RD of PAC coagulant agent and the charcoal were 4.5-5.5 ° NTU, a RD of PAC coagulant agent and the *biological* sludge were 7.5-10.5 ° NTU. Treated waters have had a turbidity which is below a 15.5° NTU and can be downloaded into the sewerage networks of localities and directly in wastewater treatment plants [24]

3. TOC in treated samples water with RD of PAC coagulant agent and indigenous volcanic tuff aid were 13.3-24.5mgC·L^{-1}, with RD of PAC coagulant agent and charcoal aid were 18.6-30.1mgC·L^{-1}, RD of PAC coagulant agent and biological sludge aid were 14.7-23.7mgC·L^{-1}.

4. TPH in treated samples water with PAC coagulant agent doses, RD, in aids presence were: for and indigenous volcanic tuff in the range 5.0-46.2mg·L^{-1}, for charcoal in the range 6.5-29.7mg·L^{-1}, and for biological sludge in the range 4.2-27.4mg·L^{-1}.The lowest residual concentrations TPH were within the range of 4.2-6.5mg·L^{-1}, which were obtained in case WW 3. It is worth mentioning that the water WW 3 indicated the lowest initial loading with petroleum products. Residual values of 4.2-5.0mg TPH·L^{-1} in WW 3 treated water with RD of PAC coagulant agent and indigenous volcanic tuff or biological sludge on can be discharged in accordance with the current Romanian rules. Even so, residual values of TPH = 6.5mg•L^{-1} in WW 3 treated with RD of PAC coagulant agent and charcoal were above the limit admitted at discharge [24].

It can be seen in tables 2, 3, 4, 5 that the efficiencies to reduce turbidity and TOC were similar for PAC coagulant agent used at OD or RD in coagulation stage in absence/presence of coagulation aids.

Figure 1 shows the results in the TPH reduction efficiencies, in WW 1 - WW 3 samples treated PAC coagulant agent used at OD or RD in coagulation stage in absence/presence of coagulation aids. It can be seen that by applying the coagulation variants with PAC coagulant agent RD and the indigenous volcanic tuff we can obtain the highest TPH reduction efficiencies, within the range of 88.6-94.5%. Also, high TPH reduction efficiencies in WW 1 - WW 3 samples treated with the PAC coagulant agent RD and biological sludge and charcoal were obtained in the range 64.3-93.2%. The TPH reduction efficiencies, in WW 1 - WW 3 samples treated PAC coagulant agent used at OD in coagulation stage in absence aids were under 72%.

Table 3. Treated samples WW 1 with RD of PAC coagulant agent and coagulate aids (three repetitions for each variants)

No	Treated variants WW 1	Parameters		
		Turbidity [º NTU]	TPH [mg·L^{-1}]	TOC [mgC·L^{-1}]
1	RD of PAC coagulant agent 11.5 mgAl·L^{-1} Coagulation aids: indigenous volcanic tuff 0.5mg·L^{-1}	8.3±1.6	46.2±4.8	24.5±3.2
2	PAC coagulant agent RD= 11.5 mgAl·L^{-1} Coagulation aids: charcoal 0.5 mg·L^{-1}	5.5±0.8	18.6±2.3	18.6±1.0
3	PAC coagulant agent RD= 11.5 mgAl·L^{-1} Coagulation aids: biologic sludge (0.4g·L^{-1} D.M.)	8.5±1.8	41.2±5.3	23.7±3.4

Table 4. Treated samples WW 2 with PAC coagulant agent RD and aids (three repetitions for each treated variants)

No	Treated variants WW 1	Parameters		
		Turbidity [º NTU]	TPH [mg·L^{-1}]	TOC [mgC·L^{-1}]
1	PAC coagulant agent RD=8.0 mgAl·L^{-1} Coagulation aids: indigenous volcanic tuff 0.5mg·L^{-1}	15.5±1.8	18.0±4.2	20.4±2.8
2	PAC coagulant agent RD=8.0 mgAl·L^{-1} Coagulation aids: charcoal 0.5 mg·L^{-1}	4.5±0.5	29.7±2.6	30.1±4.3
3	PAC coagulant agent RD=8.0 mgAl·L^{-1} Coagulation aids biologic sludge (0.4g·L^{-1} D.M.)	10.5.±1.6	27.4±3.9	23.7±3.5

Table 5. Treated samples WW 3 with RD of PAC coagulant agent and coagulate aids (three repetitions for each treated variants)

No.	Treated variants WW 1	Parameters		
		Turbidity [°NTU]	TPH [mg·L^{-1}]	TOC [mgC·L^{-1}]
1	PAC coagulant agent RD=8.4 mgAl·L^{-1} Coagulation aids: Indigenous volcanic tuff 0.5mg·L^{-1}	8.5±1.5	5.0±3.3	13.3±4.0
2	PAC coagulant agent RD=8.4 mgAl·L^{-1} Coagulation aids: charcoal 0.5 mg·L^{-1}	5.5±1.4	6.5±1.6	20.2±3.2
3	PAC coagulant agent RD=8.4 mgAl·L^{-1} Coagulation aids: biologic sludge (0.4g·L^{-1} D.M.)	7.5±0.9	4.2±0.8	14.7±2.4

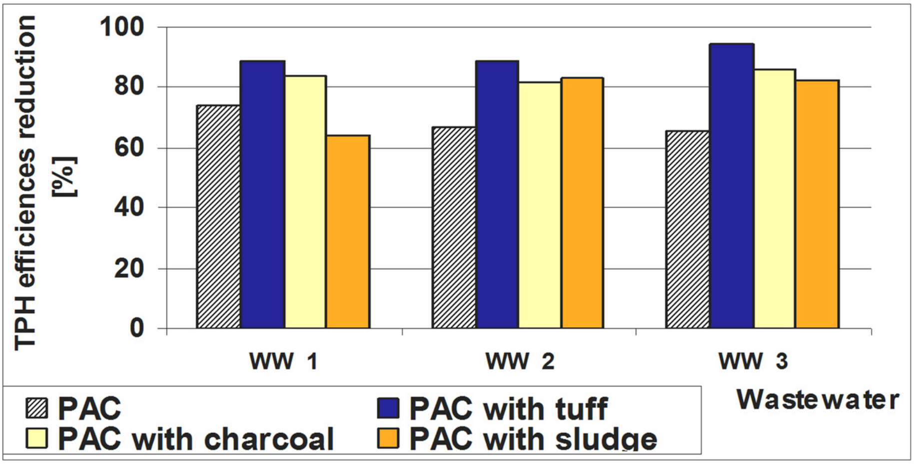

Figure 1. TPH reduction efficiency in WW 1- WW 3 samples treated with PAC coagulant agent used OD or RD in coagulation stage in absence/presence of coagulation aids.

In figures 2, 3 and 4, UV absorbance (A254) determined for WW 1-WW 3 untreated/treated waters are presented. The addition of PAC coagulant agent RD in coagulation stage in presence of coagulation aids led to the reductions absorbance *vs.* absorbance determinated for PAC coagulant agent OD in coagulation stage in absence of coagulation aids.

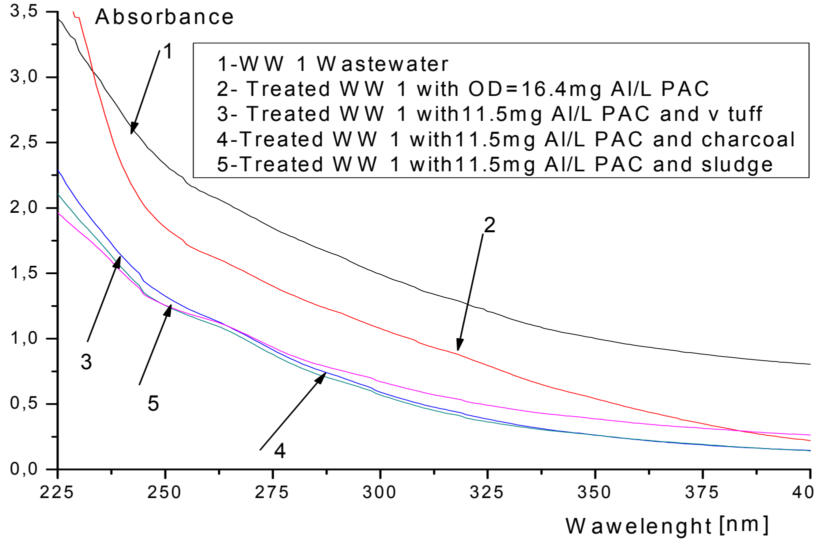

Figure 2. Selective UV VIS spectrum for untreated/treated WW 1 waters

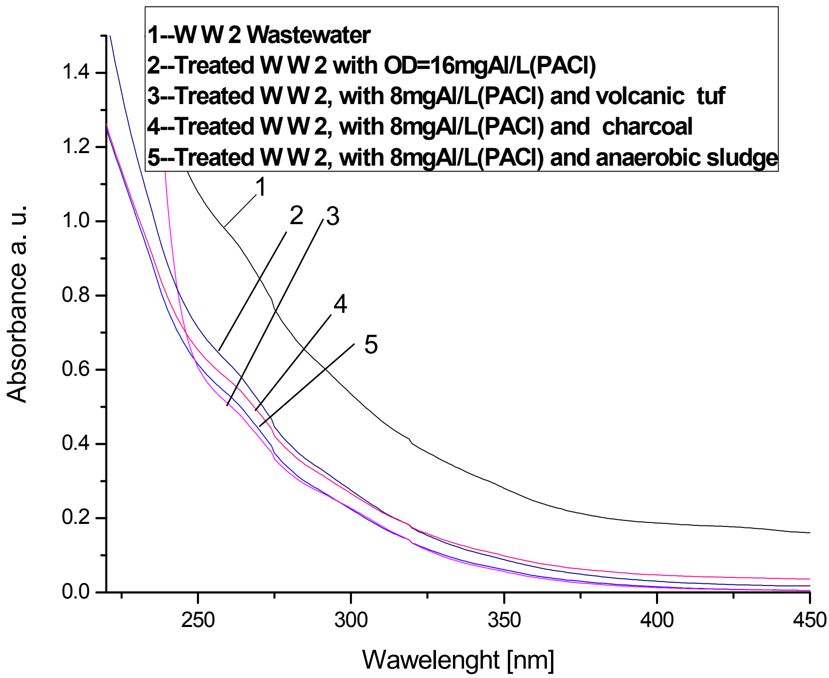

Figure 3. Selective UV VIS spectrum for untreated/ treated WW 2 waters

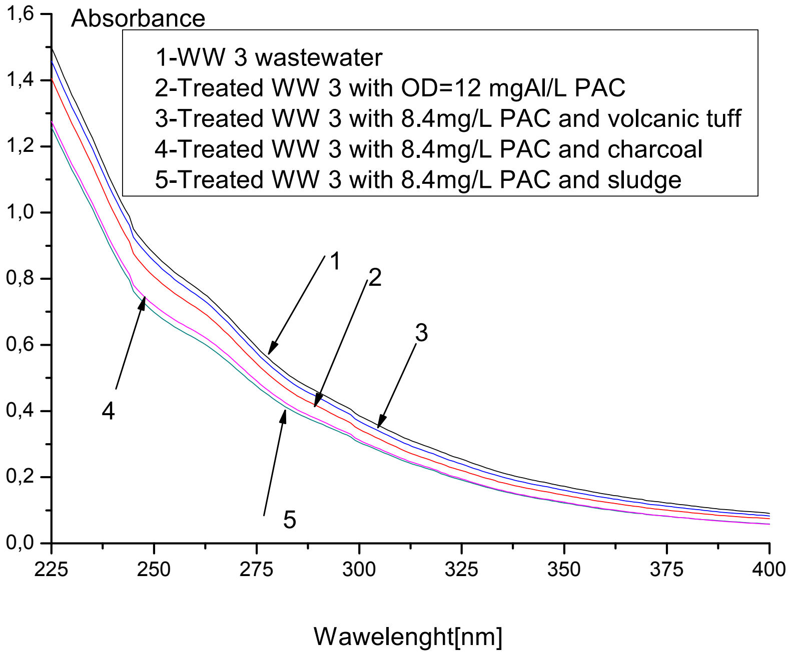

Figure 4. Selective UV VIS spectrum for untreated/ treated WW 3 waters

From figure 2, 3 and 4 the resulting reduction of global parameter A254 was:

- 11.7-44.1% at treating wastewater WWW 1-3 with PAC coagulant agent RD in coagulation stage in presence of coagulation aids indigenous volcanic tuff,
- 25.8-46.5% after treatment with PAC coagulant agent RD in coagulation stage in presence of coagulation aids biological sludge,
- 26.0-46.0% after the treatment of PAC coagulant agent RD in coagulation stage in presence of coagulation aids charcoal.

A254 reduction efficiencies was similar when wastewaters it were treated with PAC coagulant agent OD in coagulation stage in absence of aids. The absorbance variation was correlated with the variation of TPH.

Given the correlations between the two parameters TPH and A254, A254 parameter can be used as an indicator of untreated/treated water quality. A254 can be determined quickly without altering the water quality; thus the time spent for water analysis by classical procedure can be reduced. The correlation between A254 and TPH parameters can be useful in establishing on-line relationships that could ease the operators' activity in wastewater treatment plants.

Table 6 presents the quantities of coagulated sludge from water samples treated with PAC coagulant agent OD or RD in coagulation stage in absence/presence of coagulation aids. We have to state that in the samples treated with PAC coagulant agent RD in coagulation stage in presence of coagulation aids such as indigenous volcanic tuff and biological sludge, in the sedimentation stage, the coagulation flocs were large and heavy. Coagulation with PAC coagulant agent RD and indigenous volcanic tuff or biological sludge aids after 30 minutes have determinated the sludge sedimentation and the clear supernatant (see Jar Test settles flocs coagulation in the stage of sedimentation). Samples treated with PAC coagulant agent RD and charcoal aid require filtering operation for separating sludge coagulation. The flocks that do not sediment are to be removed when filtering.

Table 6. Quantities of sludge from water samples treated with PAC coagulant agent OD or RD in coagulation stage in absence/presence of coagulation aids

No	Wastewater treatment with PAC coagulant agent	Sedimentation time [min]	Sludge quantities [$ml \cdot L^{-1}$]	Observation
1	Optimal dose (OD)	30	40-60	Large and light flocs sediment
2	RD=0.7 OD PAC coagulant agent + indigenous volcanic tuff	10	20-30	Large and heavy flocs sediment
3	RD=0.5 OD PAC coagulant agent + charcoal	30	40-60	partially settled some float
4	RD=0.5 OD PAC coagulant agent + biological sludge	30	28-45	medium flocs sediment

In Table 6 it can be observed that the addition of indigenous volcanic tuff to PAC coagulant agent OD caused the formation of heavy flocs; they settle three times faster than those formed with PAC coagulant agent OD in the absence of coagulation aids. The addition of indigenous volcanic tuff has determined a high reduction of coagulated sludge, i.e. 50% (in volumes).

Table 7 presents a comparison between the costs of the coagulant agents for wastewaters treated with PAC coagulant agent OD or RD in coagulation stage in absence/presence of coagulation aids [Euro•m^{-3}].

Table 7. Coagulants cost comparison

No	Coagulant type	Cost of coagulants for wastewaters treated with PAC coagulant agent OD or RD in coagulation stage in absence/ presence of coagulation aids [Euro•m^{-3}]		
		WW 1	WW 2	WW 3
1	PAC coagulant agent OD	89.1	87.9	65.9
2	PAC coagulant agent RD with indigenous volcanic tuff aid	63.4	45.0	47.1
3	PAC coagulant agent RD with charcoal aid	64.5	46.1	48.2
4	PAC coagulant agent RD with biological sludge aid	62.4	44.0	46.1

The addition of the coagulation aids reduces the cost of coagulation agents needed to achieve efficacy as following: with 27.6-30% when the dose was reduced by 30% PAC coagulant agent; with 47.55-50% if the PAC coagulant agent was reduced by 50%.

To the waters treated with PAC coagulant agent RD in coagulation stage in presence of coagulation aids the next stage can be applied, i.e: gravitational separation (sedimentation) or filtration. The cost of the industrial sedimentation and filtration are calculated based on: the water flow, the types of decanters, filters, process time, etc. The filtering operation is estimated as being 1.62- 1.89 more expensive than sedimentation [25].

The advantages and disadvantages in using aids are determined by nature and their behaviour in the coagulation process:

- for charcoal is a better water treatment quality; but the sludge separation (filtering) operation is more expensive than settling;
- for volcanic tuff is high capacity of sedimentation (compacting the coagulation sludge) and a reduced processing cost in a subsequent stage;
- for the biological sludge is a industrial waste recycling and the capacity of sedimentation [26].

CONCLUSIONS

The optimal dose of PAC coagulant determined for the studied wastewaters ranged from 12.0 -16.4 [mg·L^{-1}] Al. Reduction efficiencies were high: 68 to 80.7% for turbidity, between 46.8 to 63.9% for TOC, for TPH between 65.2 to 74.1%, from 15.7.to 39.0% for A254. However, residual values of global parameters, *i.e.* TPH and TOC of treated water samples, have remained high. TPH have remained above the allowed limit of 5 mg·L^{-1}, being exceeded by 4.3-7.9 times vs. Romanian regulations. The use of adjuvants for wastewater coagulation has determined: 1. Reductions of the PAC coagulation dose by 30-50%; 2. Efficiencies of reduction of turbidity and TOC it was higher than the reduction efficiencies obtained for the coagulation with optimal dose in the absence of adjuvants; 3. TPH reduction efficiency was 64.3-94.5%. 4. Reduction efficiencies of A254 were 11.7-46.5%; The absorbance for treated water correlated with the TPH content. The correlation between A254 and TPH can be useful in establishing relationships that could ease the operators' activity in wastewater treatment plants. The addition of indigenous volcanic tuff in PAC coagulation has determined the formation of heavy and large flocs which settled three times faster than those formed at the coagulation with optimal dose of PAC in adjuvant absence, and the coagulated sludge volume was reduced by 50%. Moreover, the addition of coagulation aids has reduced costs coagulation reagents necessary to obtain optimum efficiency [7, 25, 26].

EXPERIMENTAL SECTION

Materials

1. Coagulation agents: polyaluminum chloride coagulant (PAC), from B.A.D.S. Brasov. Characteristics: name PAC 17 with 17.2% Al_2O_3; 2. Coagulation aids: indigenous volcanic tuff from Cemacom Zalau with ground particle size < 0.2 mm; charcoal from Letea Energo Prest SRL, Pitesti; anaerobic biological sludge (8.3 mg·L^{-1} D.M.) from a municipal waste plant; 3. Sources of wastewaters. Wastewaters were taken periodically from drilling wells in operation. Wastewaters were stored at 4°C.

Methods

Coagulation was performed with a stirrer equipped with variable speeds (Phipps & Bird Company, USA). The PAC coagulant agent OD or RD in coagulation stage in absence/presence of coagulation aids for maximum pollutant removal were done by Jar Test method (in three steps: rapid stirring, slow stirring and gravitational settling). Rapid stirring time of water sample with the optimal amount of coagulant in the presence / absence of aids was 3 minutes; Slow stirring time was 15 minutes; Settling time of coagulated water sample was 30 minutes;Coagulation pH =7.3. The wastewaters were introduced in 6 coagulation vessels. The volume of each sample coagulated it was 250 ml.

In the separated supernatant from coagulated samples were analyzed according to conventional parameters of the standard rules: pH determined pH-meter model 290A ORION RESEARCH USA, turbidity caused by Micro 100

Laboratory Turbidimeter, Scientific Inc. USA, COD (Chemical Oxygen Demand) determined by hot dichromate oxidation in strongly acidic medium of K. TOC (Total Organic Carbon) was determined by TOC Analyzer Multi N/ C 2100 Analytik Jena, Germany. Non-conventional parameter absorbance at wavelength 254 nm, A 245, was analyzed by UV VIS spectrophotometer, Specord 205, Analytik Jena, Germany. UV VIS Samples were filtered through Sartorius filter papers FT 2-206

TPH were determined according to the Romanian standardized norms by solvent (tetrachlorethylene) extraction with (SR 7877-1) *i.e.* TPH is extracted from a volume of wastewater corrected to pH=1 with hydrochloric acid d=1.19 $g \cdot L^{-1}$, (V) by mixing with solvent. Extracts number is four. Solvent extracts dried by passing through a filter with anhydrous Na_2SO_4 p.a. Then solvent extracts are placed in capsule C1, with m_1 [g]. The solvent is evaporated and weigh the capsule with TPH residuum, C2 m_2 [g]. Calculate the amount of TPH, TPH $g \cdot L^{-1} = [(m_2 - m_1) \cdot V^{-1} \cdot 1000$. Studied waters must have the characteristics required by national norm [24] to be discharged into the sewerage networks of localities and directly in wastewater treatment plants.

The volume of sludge it was determined after a period of 30 minutes sedimentation in cones Imhoff [27].

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