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Article

OIL WASTEWATERS COAGULATION USING AIDS

Smaranda Masu [1♣] Mariana Albulescu [2], Maria Popa [3]

[1]National R & D Institute for Industrial Ecology ECOIND,Branch of Timisoara, 300004, 1 Regina Maria Square, Timisoara, Romania

[2] West University of Timisoara, Advanced Environmental Research Laboratory, 4 Oituz Street, Timisoara, Romania

[3] "1 Decembrie 1918" University of Alba Iulia, Faculty of Sciences, Nicolae Iorga, 11-13, Alba Iulia, 510009, Romania

ABSTRACT

Oil is composed of organic compounds with varied molecular structure; in water suppress the respiration of plants and animals, and have toxicity effects on flora and fauna. An important pretreatment step for the water containing oil is coagulation with optimal dose of coagulant such as polyaluminum chloride (PAC). The addition of coagulating aids had reduced the PAC optimal dose for by 25-50%. The UV analysis of the treated/untreated water showed significant preferential adsorption for total petroleum hydrocarbons at 254nm wavelength (A254) and the correlation of this parameter with conventional control parameters - total organic carbon (TOC) and chemical oxygen demand (COD).

Keywords: Total petroleum hydrocarbons, wastewater, polyaluminum chloride, coagulant aids.

1. INTRODUCTION

Water polluted with petroleum hydrocarbons cannot be discharged into the environment, they must be treated by a pretreatment plant which generally provides a stage of decantation containing three successive settling basins where hydrocarbons are separated and recovered. Volatile petroleum hydrocarbons that reach the water evaporate quickly. Their toxicity cannot therefore manifest acutely, but these compounds present a particular disadvantage because they alter the taste, or, if in larger amounts, they pose the risk of explosion and fire. Heavy petroleum hydrocarbons are very slightly soluble, present as films and/or emulsions thus

♣ Correspondent author: tel.: +4035600822:, Fax:+40256220369, E-mails:smarandamasu@yahoo.com

having significant, dangerous toxicity. Their toxicity is manifested up to the living cell level. Internal rules on water protection impose a frequent control of the operation of clarifiers if having frequent rainfall. If the decantation step is not sufficient to remove total petroleum hydrocarbons (TPH) from the wastewater so that when released into the emissary be respected internal rules of NTPA.002, then, in the pretreatment process there must be introduced additional treatment steps such as coagulation. Protection of surface and ground water is severely regulated as the penetration in the layers of soil to groundwater causes changes in water taste. For the groundwater protection must be carried out works to optimize the working conditions regarding the security against loss of petroleum hydrocarbons in the environment [1-3]. Waters polluted with petroleum hydrocarbons contain organic/inorganic suspensions and stable droplets of oil-in-water emulsions. Suspension systems and emulsions can be destabilized by acidification or by adding aluminum or iron salts or suitable poly-electrolytes. There have been numerous experiments that have confirmed the effectiveness of aluminum and iron salts. The addition of Al^{3+} salts (pre-hydrolyzed, pre-polymerized) has major effects; they neutralize the negative charges of the colloids and destabilize droplets of non polar products. At the introduction of the coagulation agent based on Al in the aqueous phase, heavy, sedimentable flocks are formed and a whole variety of complex ions. A net result of this action causes destabilization of the emulsion, their coalescence and destabilization of colloids. In the case of a low pH, the precipitate of aluminum hydroxide in aqueous solution forms a complex that raises turbidity. At alkaline pH greater than 8, the species present at equilibrium is gibbsite which is an anionic monomer $Al(OH)^{4-}$. At pH<6, the dominant species at equilibrium with the gibbsite is the monomeric cation Al^{3+}. At pH<6.5 the solubility of the compounds of Al is less than 10^{-6} mol $\cdot L^{-1}$. If the pH were adjusted to 6.5 then the solubility of the aluminum hydroxide and turbidity would determine an optimum in the chemical pre-treatment [3-8]. The addition of natural materials with adsorbent characteristics as coagulation aids result in the increase of the removal efficiencies of petroleum compounds from wastewater [9-10]. Analytical control of influents and effluents plays an important role in the management and optimization of processes involved in treatment plants of industrial wastewater containing petroleum hydrocarbons. It is obvious that in the design of these technologies, the real possibilities for reducing pollutants in each stage have to be known. Control parameters are pH, TPH, organic load parameter expressed by chemical oxygen demand (COD), biochemical oxygen demand (BOD), suspensions and others [8, 11]. UV analytical results for petroleum hydrocarbons have led to the identification of a spectro-photometric parameter, A254, which can evaluate globally, qualitatively and quantitatively, the petroleum compounds. This parameter refers to the absorption of a large number of petroleum hydrocarbons at 254nm wavelength. A254 analyzes allowed the characterization of global pollution from wastewater, six times faster than COD analyzes. A254 values for influent and effluent water must be measured on unfiltered and filtered (filter 0.45) water. Correlations between A254 and turbidity showed an average growth of unfiltered A254 of 0.004 cm^{-1} per1 °NTU [12]. This study monitored the efficiencies of TPH removal from wastewater, by coagulation with:

1. The optimal dose (OD) of Al^{3+} using polyaluminum chloride (PAC),
2. Reduced doses of Al^{3+} using polyaluminum chloride (PAC), *vs.* OD and the addition of aids with adsorbent properties: indigenous volcanic tuff, Kieselgur charcoal, biological sludge,

3. The correlation of the conventional control parameters of treated / untreated waters with the unconventional spectrophotometers parameter - absorbance at 254 nm wavelength, A254.

2. METHODS

Materials:

1. Coagulation agents: prepolymerized aluminum salt *i.e.* polyaluminum chloride coagulant (PAC), molar ratio OH / Al = 2.4;

2. Coagulation aids: indigenous volcanic tuff from Marsid/Zalau quarry with size < 0.2 mm, Kieselgur (Dicalite 4200 Agromar 99 SRL, Focsani), charcoal (Letea Energo Prest SRL. Pitesti), biological sludge (Sewage sludge with 8.3 $mg \cdot L^{-1}$ DM from municipal wastewater treatment plant);

3. Waters A1- A3 wastewaters taken from decantation basin of a PETROM deposit.

Methods: Coagulation has been performed with a stirrer equipped with variable speeds (Phipps & Bird Company, USA). The optimal dose of coagulation agents, in the absence / presence of adjuvant for maximum pollutant removal, has been assessed by Jar Test method. The coagulation pH was the pH of the studied wastewater samples. (Coagulation required no corrections with acids or bases). The wastewater used for treatment was in volumes of 250 ml in coagulation vessel; time for rapid stirring = 3 min; slowly agitation= 15 minutes; gravitational sedimentation = 30 minutes. In the supernatant separated from the treated samples, conventional parameters were analyzed according to the standardized norms: pH determined by pH-meter model 290A ORION RESEARCH USA, turbidity with Micro 100 Laboratory Turbid meter, Scientific Inc. USA; COD by hot K dichromate oxidation in strongly acidic medium; TOC by TOC Analyzer with Multi N/C 2100 Analytic Jena, Germany. The absorbance – the unconventional parameter, at 254 nm wave length, A245, was analyzed by UV VIS spectrophotometer, Specord 205, Analytic Jena, Germany. Samples filtered through paper filter Sartorius filter papers FT 2-206. Total petroleum hydrocarbons (TPH) have been determined according to the Romanian standardized norms by extraction with tetrachlorethylene, Merck (SR 7877-2/95), *i.e.* TPH is extracted from a volume of wastewater corrected to pH<5 with hydrochloric acid, (1:3 vol:vol) (V), by mixing with solvent. Extracts number is four. Solvent extracts dried by passing through a silicagel filter the determination was performed at a wavelength of 2930 cm^{-1} with Infrared Spectrophotometer Model 500, Buch Science. The optimal dose was determined according to standard procedure, depending on the minimum turbidity obtained in the sample treated with coagulating agent. Studied waters must have the characteristics required by national norm HG 352/2005 - NTPA 002 to be discharged into the sewerage networks of localities and directly in wastewater treatment plants [13]. pH = 6.5-8.5, TPH ≤5 $mg \cdot L^{-1}$, C≤ 500 $gO_2 \cdot L^{-1}$.

3. Results and Discussions

3.1. Results

Table 1 shows the characteristics of the investigated A1, A2 and A3 wastewaters. Wastewater containing petroleum hydrocarbons, (TPH), are brownish-yellow apparent color and slight yellow real color. Waters have a strong smell of petroleum products. They present petroleum hydrocarbons spots and/or emulsified stable droplets. Waters had turbidity ranging from 27.2 to 47.5°NTU, pH in the range of 7.15 -7.68 and TPH in the range of 6.03-8.33mg·L^{-1}. TPH exceed the permissible value of the current standards NTPA 002/2005 of 5 mg/l for discharging them in the local sewerage networks and wastewater treatment plants directly. The organic load expressed by COD parameter exceeds the values allowed by the norms for waters A2 and A3, with 18-26%.

Table 1. Characteristics of the investigated wastewaters

No.	Parameters	Oil wastewater		
		A1	**A2**	**A3**
1	Apparent color	Brownish-yellow	Yellow	Brownish
2	Real color	Slightly yellow	Slightly yellow	Slightly yellow
3	Smell	Petroleum products	Petroleum products	Petroleum products
4	Aspect	Film and emulsions	Film and emulsions	Film and emulsions
Wastewater characteristics after gravitational separation				
5	pH	7,68	7,15	7,56
6	Turbidity[^{o}NTU]	27,2	34,9	47,5
7	COD [mgO_2·L^{-1}]	221,5	676,4	608,8
8	TPH [mg·L^{-1}]	6,03	8,33	7,42
9	TOC [mgC·L^{-1}]	21,2	89,7	72,0
10	* Absorbance A254 [cm^{-1}]	0,80	1,65	2,59

* Samples filtered

The organic load was expressed by TOC parameter, ranging from 21.2 to 89.7 mg C/l. The spectra drawn in the UV-VIS were performed on filtered water. Analyzing the spectra, these waters show a range of absorption in the ultraviolet range at 240-260 nm and in the visible range at 430-450 nm. Absorbance at a wavelength of 254 nm, referred to as A254 has been selected for the study as a control parameter. This wavelength has been selected as a number of organic compounds with conjugated double bonds or aromatic nature absorb water in the bands B and K. The values of the parameter for the studied waters had A254 in the range of 0.80 to 2.78 A.U. (Absorbance units). A254 values were taken as such without correction due to a computational color because the signals in the visible domain 430-450, represent 2-5% of the 254 [12].

Table 2-4 show the characteristics of the water treated samples A1-A3 by:

1. The optimal dose (OD) of Al^{3+} using polyaluminum chloride (PAC),
2. Reduced doses of Al^{3+} using polyaluminum chloride (PAC) and coagulant aids with adsorbent properties: indigenous volcanic tuff, Kieselgur charcoal, biological sludge

Table 2. Treated samples A1 characteristics with the optimal dose and low dose of PAC+ aids

No.	Parameters	PAC Optimal dose OD=3,6 [mgAl ·L^{-1}]	Low dose of PAC + aids			
			0,7 OD PAC + volcanic tuf 0,5 [mg·L^{-1}]	0,75 OD PAC + kieselgur 0,5 [mg·L^{-1}]	0,7 OD PAC+ caorchal 0,4 [mg·L^{-1}]	0,7 OD PAC+ biological sludge 20 [ml·L^{-1}]
1	Turbidity [^{o}NTU]	9,5	10,5	9,5	6,5	9.5
2	COD [mgO$_2$·L^{-1}]	152	128,0	117,5	126,5	146
3	TPH [mg·L^{-1}]	3,97	4,19	4.07-	3.87	3.5
4	TOC [mgC·L^{-1}]	15,8	13,2	15,2	12,6	15.3

Table 3. Treated samples A2 characteristics with the optimal dose and low dose of PAC+ aids

No.	Parameters	PAC Optimal dose OD=16,4 [mg Al ·L^{-1}]	Low dose of PAC + aids			
			0,5 DO PAC+ Volcanic tuf 0,5 [mg·L^{-1}]	0,75 DO PAC+ kieselgur 0,5 [mg·L^{-1}]	0,5 DO PAC+ caorchal 0,4 [mg·L^{-1}]	0,5 DO PAC + biologic sludge ,20 [ml·L^{-1}]
1	Turbidity [^{o}NTU]	9,2	6,5	7.2	3.3	9,0
2	COD [mgO$_2$·L^{-1}]	465	426,5	425	312	386,2
3	TPH [mg·L^{-1}]	5,48	5,05	4.88	3.6	4,16
4	TOC [mgC·L^{-1}]	73,2	71,3	63.3	54.7	65,5

Table 4. Treated samples A3 characteristics with the optimal dose and low dose of PAC+ aids

No.	Parameters	PAC Optimal dose OD=8,4 [mg Al·L^{-1}]	Low dose of PAC + aids			
			0,5 DO PAC + Volcanic tuf 0,5 [mg·L^{-1}]	0,75 DO PAC + kieselgur 0,5 [mg·L^{-1}]	0,5 DO PAC+ caorchal 0,4 [mg·L^{-1}]	0,5 DO PAC + biologic sludge 20 [ml·L^{-1}]
1	Turbidity [^{o}NTU]	7,5	9,7	9,5	5,5	4,0
2	COD [mgO$_2$·L^{-1}]	436	426,5	478	316,5	416,2
3	TPH [mg·L^{-1}]	3,8	3,8	4,0	3,15	2,56
4	TOC [mgC·L^{-1}]	53,8	56,3	57,8	53,9	65,3

3.2. Discussion

Tables 2-4 show that the optimal dose of PAC was determined by the composition and concentration of pollutants in the investigated wastewater. Optimal doses of coagulant for the 3 waters were between 3.6-16.8 mg Al·L^{-1}. Tables 2-4 show that the reduction of the dose of PAC was determined by the nature of coagulant aids. For the wastewater A1, PAC quantity reduction was of 25-30% compared to the optimal dose in the absence of the aids and for the wastewaters A2 and A3, PAC reduction was of 25-50% compared to the optimal dose. The residual values from samples treated with PAC in the presence/absence of the aids are similar and rank, generally, in the standardized norms.

The exception was water A3 when treating it with the optimal dose of PAC, the TPH supernatant containing an amount of TPH which exceeded by 8.75% the amount allowed by standards. The use of aids determined that substances by their adsorbing properties to reduce TPH from the investigated water under the limits imposed by standards. When using charcoal as aid, the supernatant of the treated samples contains suspended coal, for which a further filtering is required if this option is chosen.

From the aids used, the biologic sludge stands out, determining highest efficiencies of removal of TPH in the investigated waters. Figure 1a and 1b show the compared efficiencies to reduce TPH and COD load of water treated with CAP in the presence/absence of aids, sewage sludge.

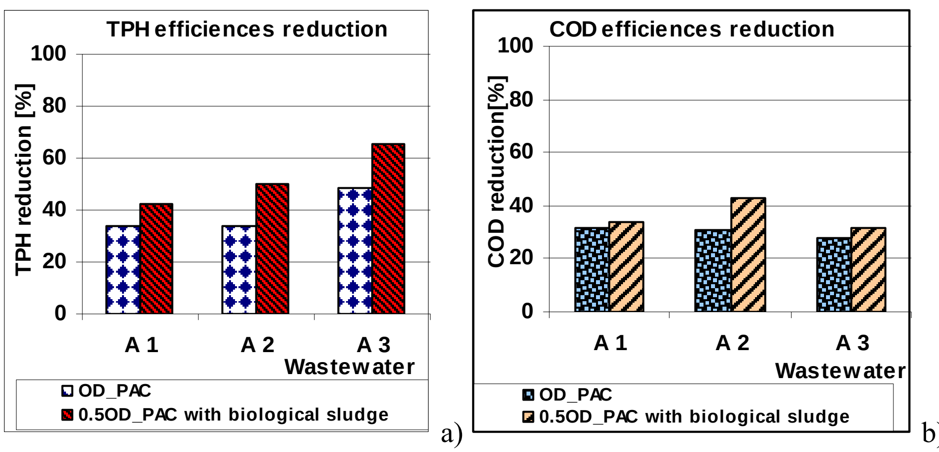
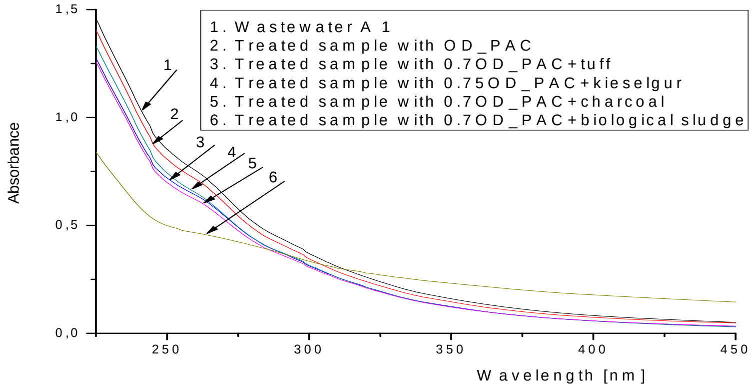
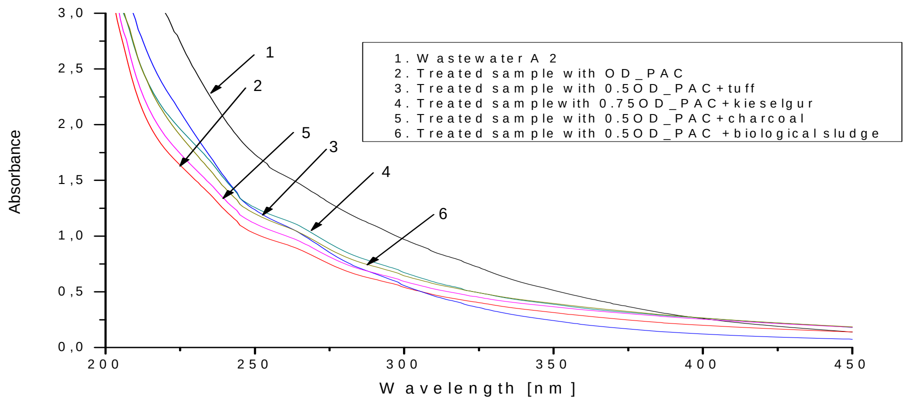


Figure 1. Reduction efficiency of the organic load of wastewater when using the optimal dose of PAC, of the reduced dose of PAC and of sewage sludge as aids a) TPH, b) COD

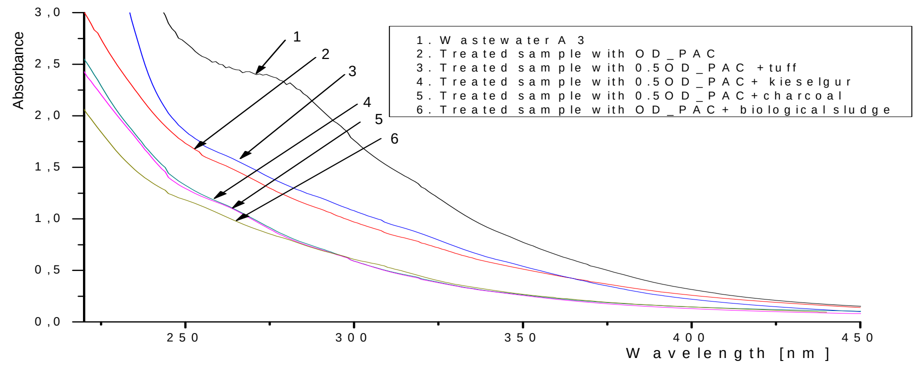
TPH reduction efficiencies in the treated samples were between 34-48.8% when using the optimal dose of PAC and 42.0-65.5% for low-dose of PAC and sewage sludge aid. COD decreased by 28.4-31.4% when using the optimal dose of CAP and between 31.5-43.0% when using the reduced dose of PAC and the sewage sludge as aids. Figure 2 shows the variation of absorbance determined for the untreated/treated samples. The use of coagulation agents caused the decrease in the absorbance of the analyzed UV domain. Studying these nonspecific global parameters one can assess how the coagulating agents interact with dissolved organic matter in wastewaters. The absorbance at a wavelength of 254 nm, as shown by the curves in Figure 2a, 2b and 2c, indicates the formation of a concentration plateau A 254 nm parameter is an indicator that can be used in monitoring the efficiency to remove TPH.



a)



b)



c)

Figure 2. Selective UV VIS spectrum untreated/treated waters with PAC in aids absence/presence: a) wastewater A 1, b) wastewater A 2, c) wastewater A3.

Studies have been conducted in this regard on wastewaters from a motorway service station in California. Wastewaters contain a mixture of petroleum hydrocarbons, natural organic material, soil, sand, road salt, rainfall water and microorganisms. In this context, the control parameter of the treated water, analyzed as an indicator of absorption of total petroleum hydrocarbons (TPH) was the absorbance in UV at a wavelength of 254 nm (A254) [12]. Figures 2a-2c show that from the aids used, the organic materials, i.e. sewage sludge and charcoal, led to better efficiencies to reduce the oil content in the wastewater. It demonstrates that these adsorbent materials exercise in the case of studied wastewaters their capabilities to adsorb TPH.

CONCLUSIONS

The use of a coagulation stage in the pre-treatment process of the studied wastewaters with variable content of oil, was accomplished with prepolymerized salts of Al, polyaluminum chloride with a ratio OH/Al = 2.4. The used coagulation agent, in optimal doses, resulted in a reduction of the organic load, expressed as chemical oxygen demand, total organic carbon and total petroleum hydrocarbons. Reduction efficiencies were between 34.0-48.8% for TPH, 28.4-31.4% for COD and 34.1-49.7. % for TOC. The residual TPH concentrations in the treated wastewaters have not been in all cases below the maximum allowed by current standards of 5 $mg \cdot L^{-1}$. The use of coagulation aids, with adsorbent properties of organic nature *i.e.* sewage sludge, has reduced the optimal dose of polyaluminum chloride by 30-50%. TPH reduction efficiencies were higher, between 42.0 and 65.5% and between 31.6 and 42.9 for COD. TPH and COD amounts in the treated waters were in all cases below the maximum allowed by current regulations. By the study of some global nonspecific parameters, such as UV absorbance at 254nm wavelength, A254, it has been possible to assess how the coagulation agents interact with the dissolved organic matter in wastewaters, and their reduction in the treated waters. Parameter A254 may be an indicator used more quickly and effectively in monitoring the efficiency to remove petroleum compounds.

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