Wastewater Coagulation with Chitosan-Al-Compounds

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Abstract

The wastewater containing TPH (total petroleum hydrocarbons), can not be discharged untreated due to the toxic loading. These substances are potential sources of contamination of soil and water. Primary treatments of these waste waters require a coagulation stage. The classical coagulation agents reduce turbidity and partially, the dissolved substances content. In this study, optimized coagulation process was obtained through the use of metal salts and bioflocculants. Use of chitosan-Al-compounds has reduced by more than 50% of the dose for Al salts and has produced effective reduction of petroleum products by up to 10% higher.

Introduction

In recent years the demand for environment-friendly materials in coagulation / flocculation of wastewater is increasing. The bioflocculants are materials that seem to be a very good alternative to replace synthetic treatment agents. Until now, the bioflocculants were applied as adjuvant in coagulation of wastewaters combined with the following usual coagulating agents: ferric chloride, ferric sulfate, aluminum sulfate, Al polymerized salts. Certain categories of bioflocculants were most studied: chitosan, tannin, gums etc. Chitosan is one of the most promising polymer because of its positive charge at acidic pH. It is described as a cationic polyelectrolyte and is expected to coagulate negatively charged suspended particles found in natural waters with increased turbidity. [1-4] Chitosan is a linear copolymer of D-glucosamine and Nacetyl-D-glucosamine produced by the deacetylation of chitin, a major component of the shells of crustaceans such as crab, shrimp, and crawfish. Chitin and chitosan polymers are natural aminopolysaccharides having unique structures, multidimensional properties, highly sophisticated functions and wide ranging applications. [5] Chitosan is insoluble in water or organic solvents, but is soluble in diluted organic acids such as acetic acid, formic acid, etc.. At pH 5 is a cationic polymer chitosan with acidic charge density. In these circumstances it becomes a clotting agent that can remove contaminants in suspended or dissolved state. Wastewater treatment with chitosan facilitate electrostatic interactions between the polymer chains and the negative charges of the anions of metals, organic compounds etc. In this study are reported the results of treatment of wastewater containing TPH with clotting agents based on Al polymerized salts in the absence / presence of a bioflocculant, respectivelly chitosan. Among all the available coagulants, aluminum salts are the most widely used because of their competitive costs, effectiveness and handling. However, the obtained sludge lead to aluminum accumulation in the environment and they are some concerns about the residual aluminum which may be present in the final, treated water [4]. Therefore aluminium dose reduction is important in water coagulation.

Experimental

In this study, wastewater from petroleum oil extraction unit were collected. Wastewater is pretreated by coagulation process. The coagulation was performed with a stirrer with variable speeds (Phipps & Bird Company USA). The coagulants used were poly-aluminum chloride (PAC) and complex agent chitosan: poly-aluminum chloride in two variants 1.chitosan: Al=0.3 and 2 .chitosan: Al=0.6. The optimal dose (OD) of PAC coagulant in the absence /presence of chitosan was assessed by Jar Test method. Chitosan with average molecular weight was obtained by courtesy of Advanced Environmental Research Laboratories, West University Timisoara. Poly-aluminium chloride, PAC was obtained by reaction of aluminium salts with a base under carefully controlled conditions of ECOIND Laboratory, Branch of Timisoara. They are typically characterized by degree of neutralisation or alkalinity, expressed as “r”. “r” is the molar ratio OH: Al = 2.4[6]. Samples of 250 ml for wastewater with TPH were used. The working conditions were: slow stirring for 15 minutes and gravitational sedimentation for 30 minutes. In the supernatant, were analyzed the following conventional parameters: pH using pH-meter model 290A ORION RESEARCH USA, turbidity with Micro 100 Laboratory Turbid meter, Scientific Inc. USA, TOC by TOC Analyzer with Multi N/C 2100 Analytic Jena, Germany. The conventional parameter, the absorbance at 436 nm wave length (A436) and nonconventional parameter, the absorbance at 254 nm wave lengths (A245), was quickly analyzed by UV/VIS spectrophotometer, Specord 205, Analytik Jena, Germany. Total petroleum hydrocarbons were determined according to the Romanian standardized norms by extraction with carbon tetrachloride (SR 7877-1) *i.e.* TPH is extracted from a volume of wastewater at pH=1 corrected with hydrochloric acid, d= 1.19 $g \cdot L^{-1}$, (V), by mixing with solvent. The number of extracts was four. Solvent extracts were dried by passing through a filter with anhydrous Na2SO4 p.a. layer. Then, solvent extracts are placed in capsule, with weight m_1 [g]. The solvent is evaporated and the weight of capsule with TPH residuum, was noted m_2 [g]. The amount of TPH, was calculated with formula: TPH $g \cdot L^{-1}$= $[(m_2 - m_1)\ V^{-1} \cdot 1000$. 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. Correction of coagulation pH was made with mineral acid/base.

Results and Discussion

In Table 1 are shown the conventional parameters for untreated/ treated waters, *i.e.*: pH, turbidity, TOC, TPH and the nonconventional parameter - absorbance at λ = 254nm, PAC optimal dose (OD) and coagulation efficiencies. PAC optimal dose (OD), established by Jar Test, was: OD = 64.0 mg Al $\cdot L^{-1}$. Wastewater shows shocking high content of TPH, 580.0 ± 26.5mg ·L. The loading with organic matter, TOC, was de145.6 ± 7.5mg C · L. Absorbance A254 was 2.590± 0.23cm^{-1}. The waters are tinted yellow; A436 was 0.180 ± 0,018cm^{-1}. By using the optimal dose of PAC as coagulation agent in the absence of chitosan, the reduction of TPH was 79.8%, of TOC- 59.8% and of A254 - 63.7%. The use of a coagulation agent based on chitosan and poly-aluminum chloride has reduced dose of Al and increased efficiencies for reducing the organic charging expressed by parameters such as TPH, TOC, at a higher level than those obtained in the absence of chitosan coagulation. In Table 2 are shown the conventional parameters *i.e.*: pH, turbidity, TOC, TPH and the nonconventional parameter - absorbance at λ = 254nm (A254) and color (A436) of the chitosan: Al optimal dose (OD) treated samples and the coagulation efficiencies, as well. It is seen from Table 2 that the use of chitosan determined the reduction of optimal dose for aluminum by more than 50%. Efficiencies in reduction of organic load when low doses of Al were used are similar or up to 10% higher than the efficiencies obtained when PAC was used as clotting agent, in the absence of chitosan.

Table 1. The characterization of untreated / treated wastewater with PAC and coagulation efficiencies. PAC optimal dose for treated samples was OD = 64.0 mg Al $\cdot L^{-1}$

No	Parameters	Wastewater	Treated water samples	Efficiencies [%]
1	pH	7.53	6.5	
2	Turbidity [^{o} NTU]	68.3±5.0	12.5±2.5	81.7
3	*Absorbance at 436 nm, A436[cm^{-1}]	0.180±0.018	0.034	81.1
4	TPH [$mg\cdot L^{-1}$]	580.0±26.5	117.,6±8.5	79.8
5	TOC [$mgC\cdot L^{-1}$]	145.6±7.5	58.5±5.6	59.8
6	*Absorbance at 254 nm, A254[cm^{-1}]	2.590±0.23	0.94	63.7

* Samples filtered through filter paper

Table 2. The characterization of wastewater samples treated with chitosan : Al at optimal dose (OD) and coagulation efficiencies

No	Parameters	Chitosan:Al = 0.3		Chitosan:Al = 0.6	
		Treated water samples	Efficiencies [%]	Treated water samples	Efficiencies [%]
1	Optimal dose	28.0	-	28.0	-
2	pH	6.5	-	6.5	
3	Turbidity [^{o} NTU]	12.5	81.7	11.5	83.2
4	* A436[cm^{-1}]	0.02	88.9	0.047	73.9
5	TPH [$mg\cdot L^{-1}$]	97.9	83.1	68.9	88.1
6	TOC [$mgC\cdot L^{-1}$]	57.7	60.4	51.7	64.5
7	*A254[cm^{-1}]	1.15	55.5	1.147	55.7

* Samples filtered through filter paper

It is seen from Table 2 that the use of coagulation agent chitosan: Al = 0.6 caused a slight increase efficiencies in reduction of TPH and TOC values versus efficiencies obtained using coagulation agent chitosan: Al = 0.3. Figure 1 shows the variations of the A254 in determining the optimal dose of coagulation agent chitosan: Al = 0.6. It is seen from the figure 1 that with increasing dose of Al, from 14mg $\cdot L^{-1}$ to 28mg $\cdot L^{-1}$, decreases the absorbance value from 1.15 to 1.147 cm^{-1}. Further increasing the dose of clotting agent, increase of the absorbance A254 was observed, since the organic load increases, perhaps because of higher proportion of chitosan. In Figure 1 it can seen that the optimal dose of coagulation agent chitosan-Al compounds may be determined in conjunction with the varying spectra of water treated with different doses of coagulating agent. Chitosan: Al optimal dose for wastewater coagulation process was 28.0 [$mgAl\cdot L^{-1}$].

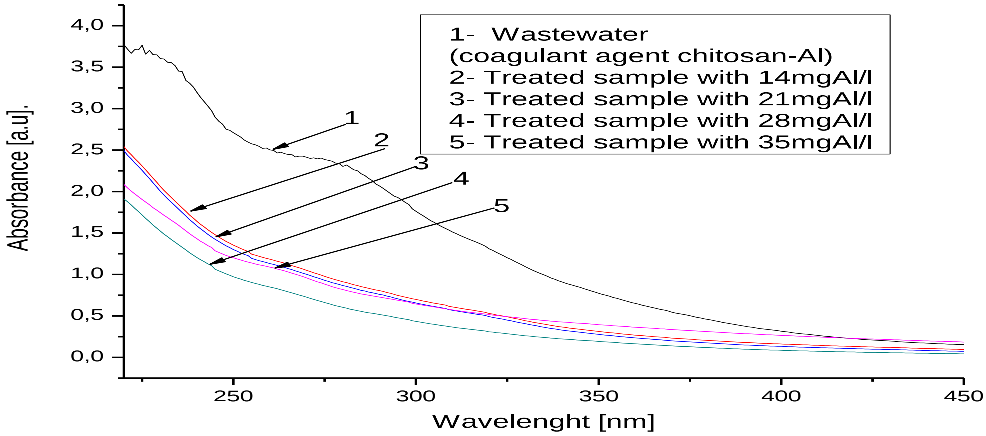

Figure 1 Selective absorbance spectrum evolution after Jar test application to establish the optimal dose for wastewater treatment with coagulation agent chitosan: Al = 0.6

Conclusions

The use in the coagulation stage of wastewaters with petroleum hydrocarbons of coagulation agents type chitosan : Al, caused a dose reduction of over 50% for Al and increased efficiencies in reduction of organic load, TPH and TOC.The greatest efficiencies of the coagulation process of water containing TPH were obtained when ratio chitosan: Al = 0.6 was used.. At the same time, it must also mention that the use of aluminum in the presence of chitosan, reduces costs and the sludge deposits containing aluminum which depending on quality of it may be considered or not a dangerous deposit for environment.

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