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STUDY ON OIL WASTEWATER TREATMENT WITH POLYMERIC REAGENTS

Rodica Bucuroiu[1*], Marius Petrache[2], Viorel Vlasceanu[1], Marius Gabriel Petrescu[1]

[1]Petroleum-Gas University of Ploiesti, Faculty Mechanical and Electrical Engineering/Department Mechanical Engineering, Bvd. Bucharest, no. 39, Ploiesti, 100680, Romania
[2]Petroleum-Gas University of Ploiesti, Faculty of Petroleum and Gas Engineering/Department Mines, Oil and Gas, Bvd. Bucharest, no. 39, Ploiesti, 100680, Romania

*Corresponding author: rodica.bucuroiu1957@gmail.com

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Abstract: Used the polymeric reagents in oil wastewater treatment is an effective method of eliminate hydrocarbons. The present study aims to finding reagents that lead to lowering of extractible (EXT), suspended solids (SS) and chemical oxygen demand (COD) of industrial wastewater from washing cars in loading ramps petroleum products. For this purpose five reagents were tested, namely: polyamines, cationic polyacrylamides, polydiallydimethyl ammonium chloride (PolyDADMAC), melamine formaldehyde polymer resin and polydicyandiamide polymer resin. Obtaining removal degrees over 80 % justifies using this method in the industrial practice.

Keywords: *chemical oxygen demand, extractible, hydrocarbons, polymeric regents, suspended solids, wastewater*

INTRODUCTION

Water pollution by oil products is a current issue because of the stability of pollutants and their action on the environment [1]. Finding solutions in wastewater treatment must prevent decomposition of organic substances which would result in compounds that can pollute the soil, water and air [2 – 4]. Therefore it is necessary to decrease the hydrocarbon content and suspended matter. This may be achieved by physical-chemical treatment of wastewater with coagulants and flocculants [5]. A current trend is to take over treatment of chemical engineering processes based on chemical reactions in the presence of catalysts [6]. But choosing the optimal solution treatment have to take into account the quantities of sludge obtained and automating the process [6, 7].
The coagulation stage can be considered an intermediate stage destabilizing the role of the particles. After the coagulation stage next stage which involves adding flocculation reagents in order to increase the flocks' particle sedimentation rate. There are lots of factors that influence coagulation process: nature of the coagulant; coagulant quantity; *p*H; water alkalinity; chemical composition of wastewater; quality of suspended solids; physico-chemical process, quantity of flocks, electrocinetic potential Zeta (PZ); temperature of wastewater [8, 9].
The main classical coagulants used in industrial practice are: aluminium salts, iron salts, iron (II) sulphate [$FeSO_4 \times 7H_2O$], iron (III) sulphate [$Fe_2(SO_4)_3 \times 9H_2O$]; ferric chloride [$FeCl_3 \times 6H_2O$]. The choice of coagulant depends on *p*H. In generally was known the optimum domain for coagulant use. In Table 1 were presented the optimum domains for several coagulants used in wastewater treatment process [5, 10 – 13].

Table 1. *Optimum domain for coagulant used*

Coagulant	***p*H**
$Al_2(SO_4)_3 \cdot 18H_2O$	4.0 –7.0
$FeSO_4 \cdot 7H_2O$	>8.5
$Fe_2(SO_4)_3 \cdot nH_2O$	3.5 – 7.0
$FeCl_3$	7.2
$FeCl_3$ and chitosan	5.5
Chitosan	5.3
Aluminum chlorohydrate	> 8.5

Currently there is a tendency of using polymeric reagents type in order to have double role: flocculation and coagulation. This occurred due to the need to reduce the cost of wastewater treatment.
The presence in wastewater of certain types of pollutants that prevent most often achieve cleansing physico-chemical, made this study to explore the possibility of obtaining degrees sewage largest in the physico-chemical treatment for all quality indicators involved in this process [14 – 19]. The present study aims to find reagents that lead to lowering of extractible (EXT), suspended solids (SS), chemical oxygen demand (COD) and sulphonic acid (SA) of industrial wastewater from washing cars in loading ramps petroleum products.

MATERIAL AND METHODS

Analysis of wastewater physico-chemical indicators

The experimental determination consisted in taking of a total 10 samples channeling where it was collected wastewater from washing wagons in ramps of petroleum products. This sampling was made according to the standards. Physico-chemical analyze and analysis methods used are shown in Table 2. For this study was prepared the sample with medium value, obtained from 10 samples analysed before. The analysis methods of these indicators have complied with applicable standards.

Table 2. *Analysis methods for wastewater quality indicators*

Parameters	Analysis methods
*p*H	WTW *p*H-meter
Extractible [20]	SR7587- 96
Suspended solids [21]	SR EN 872 :2005
Chemical oxygen demand [22]	SR EN 6060 :1996

Analyzing the amount of very fine particulate and colloids from wastewater of the individual samples under laboratory examination it has been found that these exceed the value of 20 %. From literature studies it is known that over this value is indicated the use of coagulation and flocculation processes.

Establishing the optimal dose of reagent required for physicochemical treatment

For choice of reagents coagulation - flocculation needed it was rated a plan for experimental study was based on the Jar-test method and aimed to analyze factors that influence the coagulation - flocculation *p*H, the optimal dose of coagulant, temperature.
Coagulation - flocculation reagents used were as follows: polyamines, cationic polyacrylamides, polydiallydimethyl ammonium chloride (PolyDADMAC), melamine formaldehyde polymer resin, polydicyandiamide polymer resin [17, 18].
The synthesis of these reagents was made in the laboratory. The reagents used were Sigma Aldrich. The synthesis reactions used are shown in Figures 1 - 5.

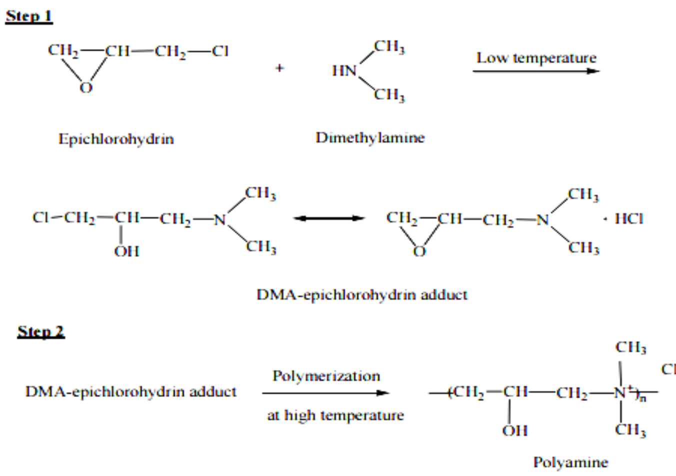

Figure 1. *Synthesis of polyamines (PAM)*

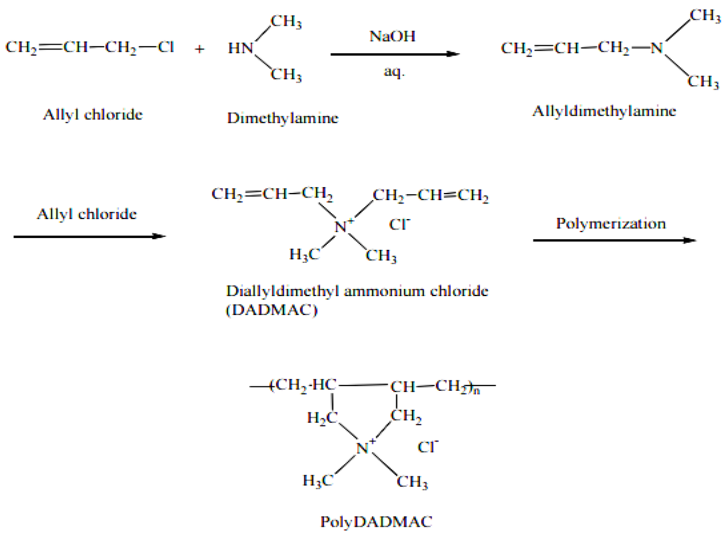

Figure 2. *Synthesis of polydiallydimethyl ammonium chloride (PolyDADMAC)*

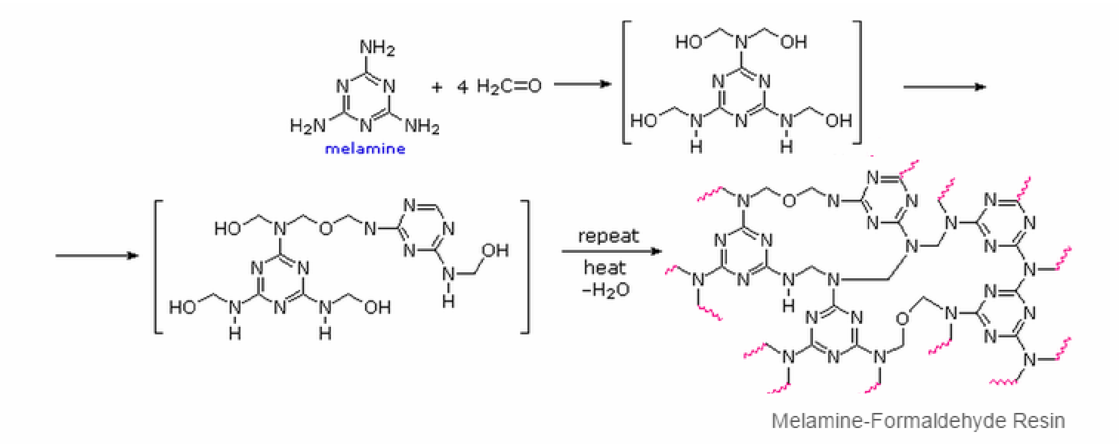

Figure 3. *Synthesis of melamine formaldehyde polymer resin (MFP)*

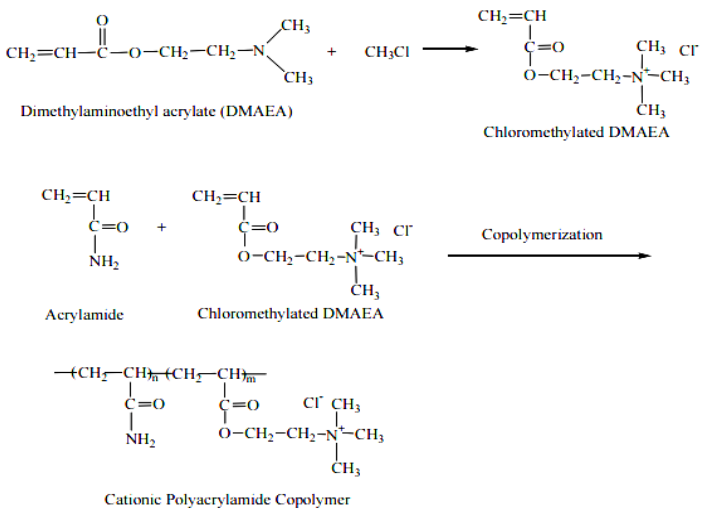

Figure 4. *Synthesis of cationic polyacrylamides (PAC)*

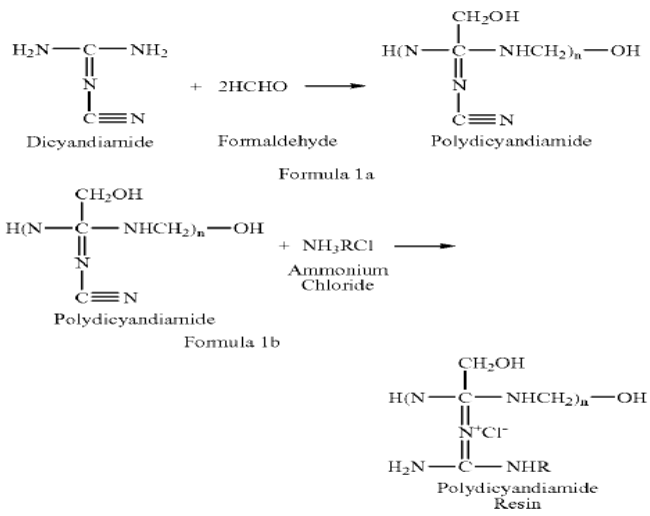

Figure 5. *Synthesis of polydicyandiamide polymer resin (PDC)*

The dose of reagent was selected to range between 0.5 mg·L^{-1} and 1.4 mg·L^{-1}. This range was chosen because it has been observed that below 0.5 mg·L^{-1} did not exist coagulation phenomenon. Above the 1.4 mg·L^{-1} reagent addition does not change the quality of wastewater.
The removal degree of ETX, SS, COD from wastewater is shown in equation (1) [9, 19]:

$$RD = \frac{c_i - c_f}{c_i} \times 100 \quad (1)$$

where:
RD – represent the removal degree for ETX, SS, COD, [%];
c_i – initial concentration of ETX, SS, COD, [mg·L^{-1}];
c_f – final concentration of ETX, SS, COD, [mg·L^{-1}].

RESULTS AND DISCUSSION

Analysis of quality indicators water samples collected from entering the treatment plant is presented in the Table 3.

Table 3. *Wastewater indicators value*

Indicators	Value
*p*H [*p*H units]	7.6
Extractible [mg·L^{-1}]	196
Suspended solids [mg·L^{-1}]	281
COD [mg O_2·L^{-1}]	712

Applying the Jar-test method in order to find the optimal amount of coagulant in physico-chemical treatment led to the results presented in the Figures 6 - 8.
The variation of *p*H was not presented in this work, because this variation is limited in a small domain, namely 7.6 - 7.8.

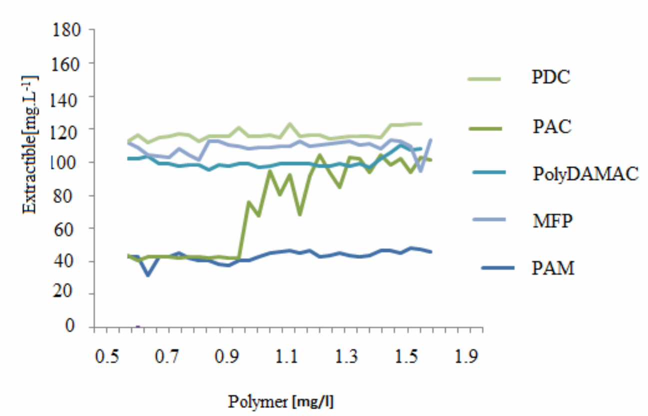

Figure 6. *ETX concentration after treatment with polymers*

The explanation of the ETX rising content by adding PAC is that the concentration is decreasing at 45 mg·L$^{-1,}$ after that the flocks formed by mixing, becomes unstable and breaks in the individual systems with a low speed, remaining in forms of fine particles.

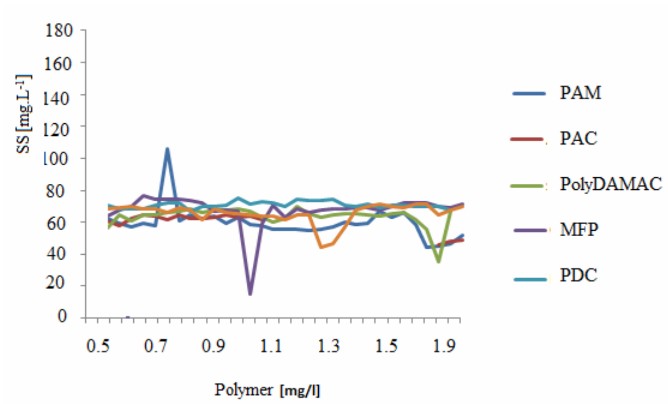

Figure 7. *SS concentration after treatment with polymers*

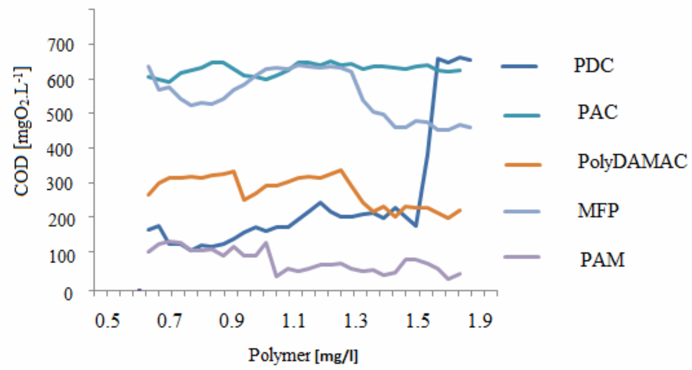

Figure 8. *COD concentration after treatment with polymers*

The elimination of flocs formed, was based on the combination of mixing and agitation process that led suspensions aggregation by forming classical flocs.
It can be noted that good results are obtained in the case of using PAC: EXT decrease to 21 mg·L^{-1}, SS up to the value of 19 mg·L^{-1} and COD value to 3.4 mg·L^{-1}. The use of the reagent of PolyDAMAC yielded the following final values: *p*H - 8.1, ETX – 95 mg L^{-1},

SS - 114 $mg \cdot L^{-1}$, and COD - 240 $mg \cdot L^{-1}$. The intermediate results were obtain also for the MFP and PMC reagents.
From the five tested reagents, two were chosen, namely PAM and MFP. For these, the removal rates for ETX, COD and SS were determinated. The removal rates obtained by using of PAM and MFP reagents are shown in Figure 4.

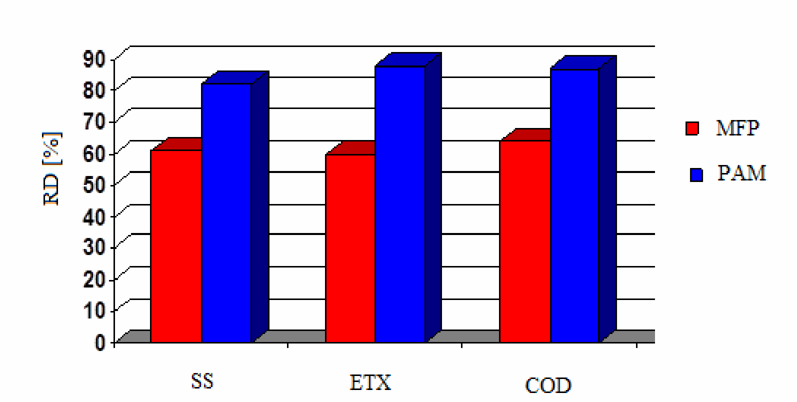

Figure 9. *The removal rates for SS, ETX and COD*

Obtaining the best removal rates when using PAM was explained by increasing floc sedimentation velocity separation from wastewater. For SS the removal rate was by 62 % for MFP and 83 % for PAM. The ETX reduction was 60 % by using MFP and 89 % in the case of PAM using. COD was reduced by 62 % with MFP and by 88 % with PAM.

CONCLUSIONS

In this paper the possibility of treating wastewater with a high content of hydrocarbons was studied. The determined values for wastewater samples indicate a very high concentration of ETX (196 $mg \cdot L^{-1}$), high suspended solids (281 $mg \cdot L^{-1}$) and high COD (712 $mg \cdot L^{-1}$).
In this way was tested the reagents: polyamines (PAM), cationic polyacrylamides (PAC), polydiallydimethyl ammonium chloride (PolyDADMAC), dimelamine formaldehyde polymer resin (MFP), polydicyandiamide polymer resin (PDC).
Using of PAC has an effect on sedimentation rate, because the polyelectrolyte favors the congestion and increases flocks size formats. The decreased concentration of pollutants in wastewater is significant when treating samples with PAM, according to the obtained removal rates.

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