Enhancing of COD Treatment in the Physico-chemical Stage of Refinery Wastewater Treatment Plants

CASEN PANAITESCU[1], MONICA EMANUELA STOICA[2]*

[1] Petroleum - Gas University of Ploiesti, Petroleum Processing and Environmental Engineering Department, 39 Bucharest Blv., 100680, Ploiesti, Romania

[2] Petroleum - Gas University of Ploiesti, Drilling, Extraction and Transport of Hydrocarbons Department, 39 Bucharest Blv., 100680, Ploiesti, Romania

The refinery wastewater treatment process involves constant changes depending on the quality of the influent. The present research aims at contributing to this issue by analysing the use of a new type of coagulant in the physico-chemical stage in order to reduce COD concentration upon both physico-chemical input and treatment plant output. The increase of wastewater treatment efficiency also represents a benefit for the refinery as it allows wastewater reusability as process water.

Keywords: wastewater, coagulant, COD, efficiency

Refinery wastewater treatment must be integrated in the context of process water reuse. Studies on environmental protection and especially oil pollution elimination highlight the necessity of treating all the environmental factors (air, water, soil) as equally important [1, 2].

Romania is compelled to implement and comply with the stipulations of Directive 91/271/EEC on wastewater treatment [3]. Because of ineffective treatment procedures or procedures incompatible with the real possibilities of the influent, what is necessary is not just the rehabilitation of the treatment plants, but also the finding of new reagents [4- 8]. Their use must have a minimal impact on the environment. Refinery wastewater treatment represents a current problem [9-11] that must be integrated into the local communities concerns to reduce generated waste and enhance treatment quality [12-15].

Taking into consideration that Prahova County is an area that features two major refineries and qualitatively sensitive surface water [14], it goes without saying that there is a serious need of advanced wastewater purification. Lately the general tendency has been to completely replace process water with treated water. The adoption of this concept represents the implementation of the zero-discharge European legislation [16].

The present paper attempts to find practical solutions on enhancing the wastewater treatment process by focusing on COD (chemical oxygen demand) elimination in the physico-chemical stage via new reagent use. It should be noted that this indicator was chosen because it surpassed the maximum permissible values upon input compared to the design indices, as well as plant output compared to the provisions of NTPA 001/2005 [17].

Experimental part

The examined refinery wastewater treatment plant was labelled "A". The top priority of the present paper was to determine the actual influent quality. The studied physico-chemical parameters: *p*H, conductivity, temperature, COD and total suspended solids (TSS). As shown in table 1, the analysis of these factors was conducted with the proper equipment as stipulated by the legislation in force [18- 20].

Wastewater quality monitoring in the physico-chemical stage, as well as treatment plant input and output were performed throughout a calendar year, more specifically from May 2013 to April 2014. The values listed in the paper are the recorded minimum monthly values. The CCO-Cr treatment process enhancement study relied on analysing the coagulation process. The two phases of coagulation were studied in detail [20- 22]:

- phase 1: peri-kinetic coagulation – characterised by coagulant hydrolysis and microfloc formation (rapid stirring process); this is the phase where the negative charge of the colloidal impurities is compensated;
- phase 2: orto-kinetic coagulation – stirring time is very important in this phase; it has to be as slow as approx. 15-30 min for highly sedimentary flocs to appear having the same dimensions as those that form in the industrial decanter.

In order to obtain correct information on the size and stability of the flocs depending on the selected reagent, the electrokinetic potential, also known as the zeta potential (Z), was studied [21].

The zeta potential occurs because of a surplus of particles formed by the partial involvement of the diffuse layer of moving fluid [21-25]. The zeta potential is

Table 1
SPECIFIC EQUIPMENT AND PHYSICO-CHEMICAL DETERMINATION STANDARDS

Physic-chemical indicators	Measure units	Methods	Specific equipment
pH	pH units	SR ISO 10523-97	pH-metru Burette
Conductivity	mS	-	Conductometer HANNA
Temperature	°C	-	HANNA 9300
COD	mg/l	SR ISO 6060/96	DR 5000

* email: monicastoica20022002@yahoo.com

Coagulants	Caracteristics
FLR 507	Copolymers epiclorhidrina şi dimetilamina. Cationic polymer.
ZETAG	Hexanedioic acid.
$FeCl_3$	Liquid, (40-42%)
MO-PAC14HB	Poli-hidroxi-clorurasulfat de Al. Polimer cationic în soluţie.
FR1131	Acrylamide. Cationic polimer.

Table 2
COAGULANTS CHARACTERISTICS USED

influenced by: changes in *p*H, conductivity (salt concentration or type) and component concentrations. The determination of this potential was carried out using a ZETASIZER NANO SYSTEM. In terms of result interpretation, it can generally be considered that the high values of Z are indicative of dispersion increased stability. Low stability dispersion has a zeta potential ranging between +30mV and - 30mV.

The efficiency of the coagulation process is influenced by the following factors: stirring time; *p*H; quantity - coagulation agent; temperature; floc size; floc stability [24, 26].

Based on these parameters, suitable coagulant choice was made by studying the following:

-the relation between the zeta potential and particle size evolution over time;

-the relation between the zeta potential and particle size/ temperature/*p*H.

In order to find the optimal solution of coagulation, a total number of twenty coagulants were tested, out of which only five were relevant, namely FLR 507, ZETAG 7587, $FeCl_3$ (Ferric chloride), MO-PAC 14HB, FR1131. Their characteristics are presented in table 2.

The coagulant and flocculant optimal amount tests were based on the JAR TEST method. The JAR TEST method represents a laboratory scale modelling of the coagulation process. Thus a number of four cups were filled with 100 mL of wastewater, each sample being then treated with different doses of the coagulant. Afterwards, by analysing the amount of flocs and the other parameters involved in the process, the optimal dose of necessary coagulant can be selected [27].

For coagulants whose zeta potential values indicated coagulation process stability, the CCO-Cr recovery level dependent on the concentration of the added coagulant was determined using the following equation (1):

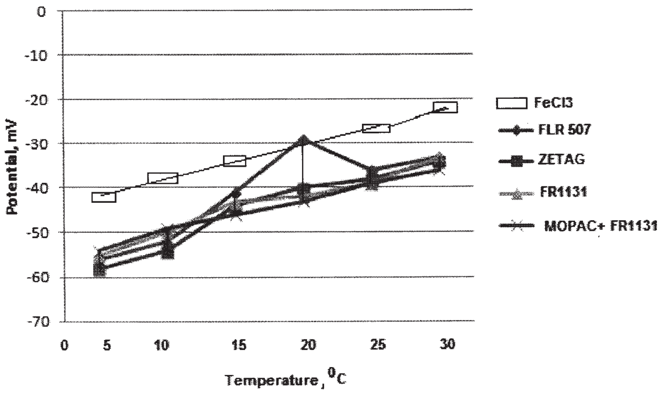

Fig. 1. Zeta potential variation depending on temperature

$$GE = \frac{C_{INTR.CCO-Cr} - C_{IES.CCO-Cr}}{C_{IES.CCO-Cr}} \cdot 100 \qquad (1)$$

where:

GE represent COD efficiency;

$C_{INTR.\ CCO-Cr}$- COD influent – wastewater treatment plant;

$C_{IES.\ CCO-Cr}$- COD effluent – wastewater treatment plant.

Results and discussions

Figure 1 lists zeta potential variation depending on temperature for the coagulants whose zeta potential registered the best values.

At the beginning of this experiment it can be observed that the highest coagulation process stability is offered by MO-PAC14HB and FR 1131, having a zeta potential of approximately -56 mV. The The optimal amount was 0.069 kg/m^3, as shown in figure 2.

As floc size is very important and affects the stability of the treatment process, especially in the case of coagulant MO-PAC14HB+FR1131, its variation in size was studied. The results showed that after the first 15 min the dimensions remained constant at about 170 μm – an adequate value in the case of floc physical chemical treatment (fig. 3.).

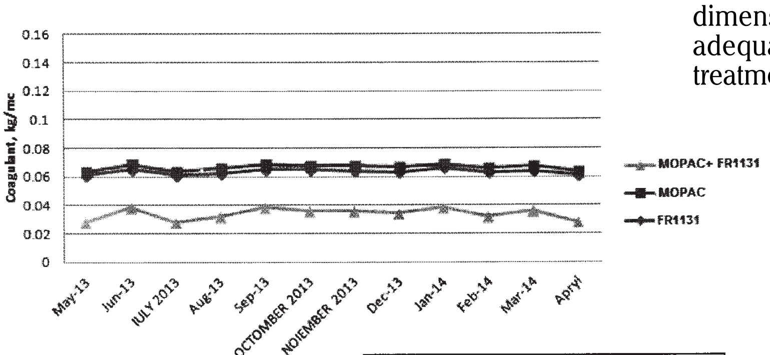

Fig. 2. Coagulant quantity variation (MO-PAC14HB and FR 1131) depending on influent quality

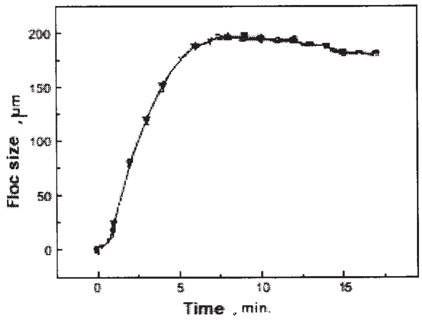

Fig. 3. Over time floc size variation upon MO-PAC14HB + FR1131 use

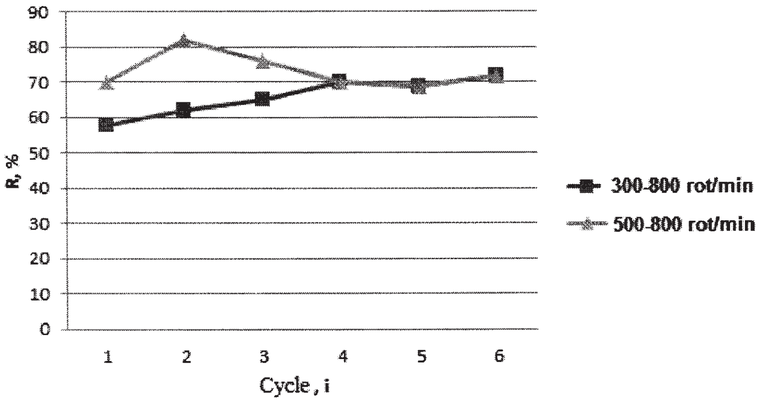

Fig. 4. Variation of reflocculating index in terms of cycles numbers at different stirring intensity

Table 3
VALUE OF COD AND EFFICIENCY BEFORE AND AFTER TREATMENT WITH COAGULANT

Month/Year	COD, mg/l influent	COD, mg/l effluent physico-chemical stage	COD, mg/l Effluent wastewater treatment plant		Eficiency, [%]	
			Before treatment	After treatment	Before treatment	After treatment
MAY 2013	1132	594	484	119	57	89
JUNE 2013	1001	534	240	89	76	91
IULY 2013	1527	569	203	75	87	95
AUGUST 2013	2743	831	353	120	87	96
SEPTEMBER 2013	2473	478	316	108	87	95
OCTOMBER 2013	2325	465	357	114	84	95
NOIEMBER 2013	2186	424	348	74	84	96
DECEMBER 2013	2634	591	413	97	84	96
JANUARY 2014	2566	462	358	82	86	96
FEBRUARY 2014	2602	435	376	78	85	93
MARCH 2014	2786	447	357	91	87	96
APRYL 2014	3099	562	557	106	85	96

For high water velocity is possible to appear the floc instability. That's why was studied reflocculating index given by equation (2) [17]:

$$R = \frac{A_{i+1} - B_{i+1}}{A_i - B_i} \cdot 100 \quad (2)$$

where:

R represent reflocculating index, %;

A_i, floc size-lower stirring intensity;

B_i, floc size-higher stirring intensity.

The variation of R in terms of cycles numbers at different stirring intensity is shown in figure 4. It is found that the value of R is greater than 60 % for reduced stirring intensity, and greater than 80% for higher stirring intensity for the same numbers of cycles. This shows that the choice of the coagulant mixture is correct.

Study of the flocs size should be done with determining efficiency in terms of the suspended solids after adding MO-PAC 14HB + FR1131.

After adding the optimal coagulant dose, COD concentration was monitored at treatment plant input, as well as both physico-chemical stage and treatment plant output. The recorded values are presented in table 3.

Upon treatment plant output the recorded values varied between 74 and 120 mg/L below the maximum threshold allowed by NTPA 001/2005 (125 mg/L), for extensive periods in October 2013, December 2013 and January 2014. Monitoring of *p*H and turbidity, figure 5, values indicated that the use of a new MO-PAC14HB and FR 1131 coagulant type leads to values between 6.9 and 7.8, respectively 8…25 NTU (fig. 5). They must not be tampered with as water values must vary between 6.5 and 8.0 during the biologic treatment process.

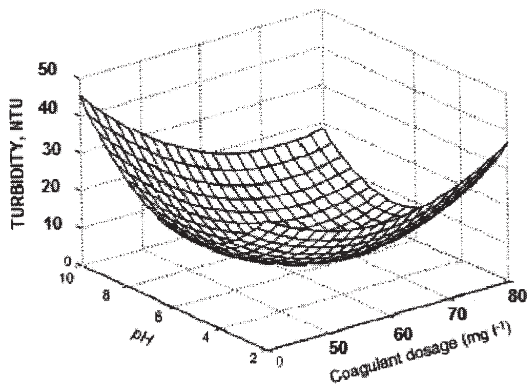

Fig. 5. *p*H and turbidity correlated with coagulant dosage (MathlabR2013b)

The assessment of the treatment process was done quantitatively on the entire station and was based on the obtained COD purification levels. Thus, after COD concentration monitoring in the physico-chemical stage input and output, treatment levels of approximately 9% were recorded. These levels are higher than those recorded before adding the new coagulant (max.87%). Upon treatment plant output, COD treatment level improved from 57 to 94% (the maximum admissible treatment plant output limit of 125 mg/L imposed by NTPA 001 being respected). For a value of 0.069 mg / L of coagulant, TSS value decreased from 750 mg/L to 300 mg/L.

Conclusions

The present study showed that using a suitable coagulant and an optimal dose can lead to the enhancement of COD treatment levels from 57 to 94%. Measurement of floc size and stability must constitute an important criterion when choosing the appropriate coagulant and flocculant.

*p*H is very important in the operating in the physico-chemical stage, hence it is recommended that it should be permanently adjusted close to 8, thus aiming not only at increased efficiency in terms of COD, but also at the proper management of oxidation in an alkaline environment.

Provided the content of dissolved inorganic matter still records high values, the intense chemical precipitation phenomenon via the chosen MO-PAC14HB and FR1131 should not be stopped so that the biological stage input should remain under the maximum permissible load. If upon treatment plant entry COD concentration values exceed 1500 mg/L, it is recommended polimer should be used. If turbidity conditions are not met or an increase in COD occurs, it is recommended that FR powder coagulants should be used. The treatment enhancement post-physico-chemical stage leads to the discharging of the biological stage of further loads, which means that the resulting treated water will have the necessary indicators that allow it to be used as process water.

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