*p*H Variation in the Presence of the Coagulants used in Oil-well Industry Wastewater Treatment

MADALINA CARBUREANU, CATALINA GABRIELA GHEORGHE*
[1]Petroleum-Gas University of Ploiesti, 39 Bucuresti Blv., 100680, Ploiesti, Romania

This paper presents an analysis of pH variations in the presence of coagulants used in oil-well industry wastewater treatment. In order to accomplish this analysis, a mathematical model from literature was chosen for pH neutralization process. The analysis goal was to transpose the process' theoretical mathematical model in practice, the model confirmation through a set of tests and the determination of one of the process' titration curves in order to emphasize the process' strong nonlinear behaviour. Determinations were made regarding the variations in pH for samples with different composition in the presence of hydrated lime and sulphuric acid.

Keywords: pH, wastewater, hydrated lime, sulphuric acid, neutralization

In a wastewater treatment plant (WWTP) the *p*H neutralization process takes place in the plant physico-chemical step through the usage of some neutralizers such as hydrated lime ($Ca(OH)_2$) and sulphuric acid (H_2SO_4) [1]. This process is a dynamic one and it has a strong nonlinear behaviour as it will be demonstrated through the experiments and through the obtained titration curve which is similar to those from literature [2 - 5]. The titration curve is symmetrical in relation with the equivalence point (*p*H=7) and the *p*H value has an abrupt variation around this equivalence point. Also, there is a *p*H dependence only to acid concentration on the first part of the curve (until equivalence point is reached) and a *p*H dependence only to alkaline concentration on the second part of the curve (after passing of the equivalence point). Also a decreasing of the acid neutralizer concentration leads to *p*H variation decreasing around equivalence point [2 - 5].

After studying the literature, the model developed by R. Ibrahim in his Ph. D. Thesis [6] was chosen for the wastewater pH neutralization process.

The model main differential equations emphasize the process dinamic behaviour:

$$V\frac{d\alpha}{dt} = F_1C_1 - (F_1 + F_2)\alpha \tag{1}$$

$$V\frac{d\beta}{dt} = F_2C_2 - (F_1 + F_2)\beta \tag{2}$$

In equations (1) and (2), F_1 is the acid (H_2SO_4) stream flow rate, F_2 is the alkaline ($Ca(OH)_2$) stream flow rate, C_1 is the acid concentration in F1 flow, C_2 is the alkalinity concentration in F2 flow, V is the volume of the compartment where it takes place the pH neutralization (the second compartment of admixture-reaction tank from a plant) and α and β are the concentration of acid and alkaline components in the compartment (the non-reactant concentrations for acid and alkaline [6]).

In order to neutralise the acid *p*H, the calcium hydroxide in hydrated lime form ($Ca(OH)_2$) is used. Also to neutralise the alkaline *p*H, the sulphuric acid (H_2SO_4) is widely used. The powdered hydrated lime is diluted with water and injected through a lime pump in the first compartment of the admixture-reaction tank. The diluted solution of sulphuric acid is also injected through a separate sulphuric acid pump into the tank first compartment [7, 8].

Experimental part

For the experimental part, four samples of wastewater from a WWTP were used: one sample from the plant input, one from plant decanter, from the biological step and also from plant output.

The samples analysis bulletin is presented in table 1.

The equipment and the substances used in our experiments are as following: a conductometer, an electronic *p*H-meter, glass and calomel electrodes, burettes, droppers, Erlenmeyer and Berzelius recipients, warming plate with magnetic agitator, hydrated lime, sulphuric acid, distilled water and four wastewater samples from an oil-well industry wastewater treatment plant.

In order to determine the *p*H of an unknown solution, a glass electrode was used as a hydrogen electrode because the potential that appears between the glass membrane and the analysed solution is determined by the ions of hydrogen concentration determined during analyses. The internal reference electrode is a glass electrode (as shown in fig. 1), made from a special thin-walls glass pipe that

	Input [mg/l]	Decanter [mg/l]	Biological step [mg/l]	Output [mg/l]
Slops/Extractibles ([9])	132	42	11.5	5.4
Sulphonated acids/Synthetic detergents ([10])	9.4	4.7	1.8	0.5
Total suspended solids (SST) ([11])	4.7	51	64	16
Biochemical oxygen demand (CCO-Cr) ([12])	575.8	110	40.1	32.4

Table 1
SAMPLES ANALYSIS BULLETIN

---

* email: ghe.catalina@yahoo.com

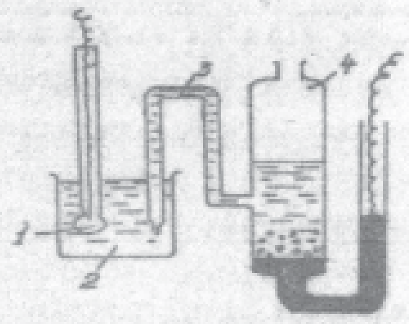

Fig. 1. 1 - glass electrode, 2 - analysed solution, 3- bridge of KCl saturated solution, 4- calomel electrode

contains a buffer solution with a known *p*H which assures the electrical contact.

In order to determine the hydrogen ions activity in the solution, a special cell was built from an indicator electrode and a reference electrode. The *p*H measuring cell is composed from an indicator electrode (glass electrode), a reference electrode (calomel KCl saturated/Hg_2Cl_2/Hg) submerged in the unknown *p*H sollution.

Work model: Using the experimental setup presented in figure 2, some determination were made regarding the *p*H variation for the samples presented in table 1 in the presence of hydrated lime with concentration C_2=10% and sulphuric acid with concentration C_1=40%.

Each sample was tested by adding consecutively 10 mL of hydrated lime ($Ca(OH)_2$) with concentration C_2=10%. After adding hydrated lime with such a concentration, the value of *p*H was recorded for each analysed sample.

Fig. 2. Experimental setup

Results and discussions

For the first set of experiments, a plant input sample was used (50mL filtered water) with the initial *p*H=7.05. After adding 0.2mL of H_2SO_4 the starting point was established at *p*H=2 units. By consecutively adding 10mL of hydrated lime, we obtained the experimental results shown in table 2 and the variations in *p*H according to figure 3.

Table 2
EXPERIMENTAL RESULTS

H_2SO_4 [ml]	$Ca(OH)_2$ [ml]	pH [units]
-	-	7.05
0.2	-	2
-	10	2.05
-	10	2.15
-	10	2.25
-	10	2.4
-	10	2.5
-	10	2.9
-	10	4.5
-	10	10.4

Table 3
EXPERIMENTAL RESULTS

H_2SO_4 [ml]	$Ca(OH)_2$ [ml]	pH [units]
-	-	7.8
0.2	-	2.8
-	10	3.3
-	10	9
-	10	9.3
-	10	9.5
-	10	9.8
-	10	10
0.2	-	2.9

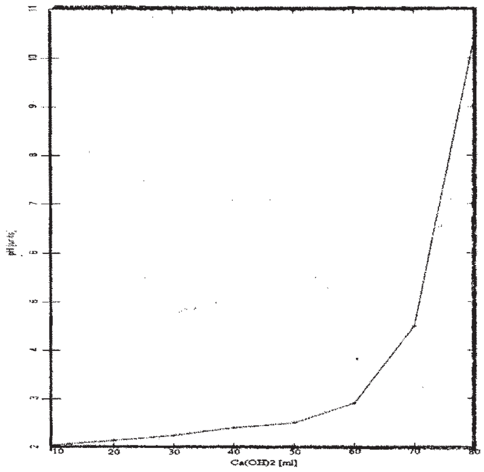

Fig. 3. *p*H variation (first set of experiments)

For the second experiments set, the decanter plant sample was used – 50mL of filtered water with measured *p*H of 7.8 units. Following the mathematical process model, we dosed 0.2mL of H_2SO_4 with concentration C_1=40%. The resulting *p*H was 2.8 units (fig. 4). By consecutively

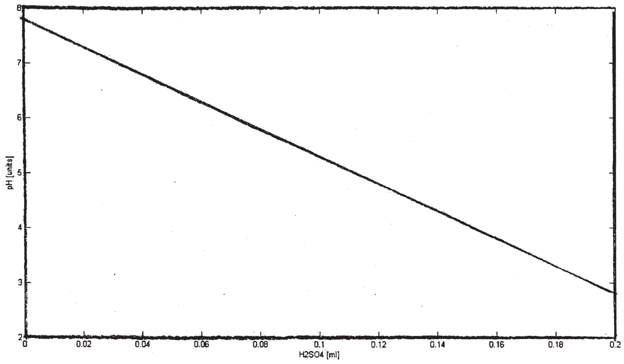

Fig.4. *p*H variation (second experiments set)

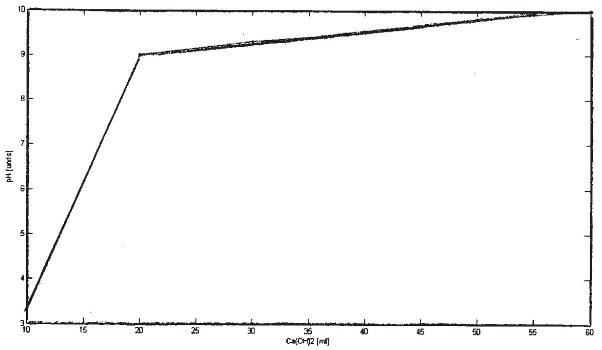

Fig.5. pH variation (second set of experiments)

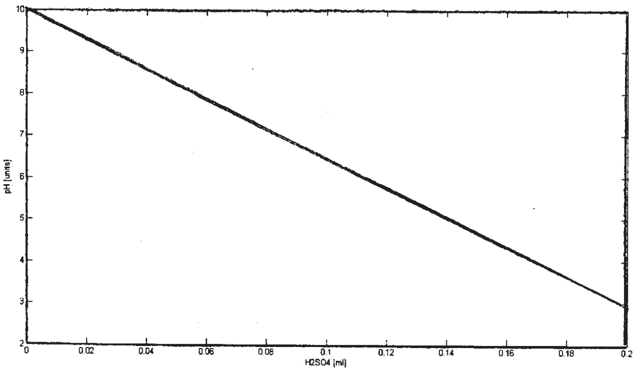

Fig.6. pH variation (second set of experiments)

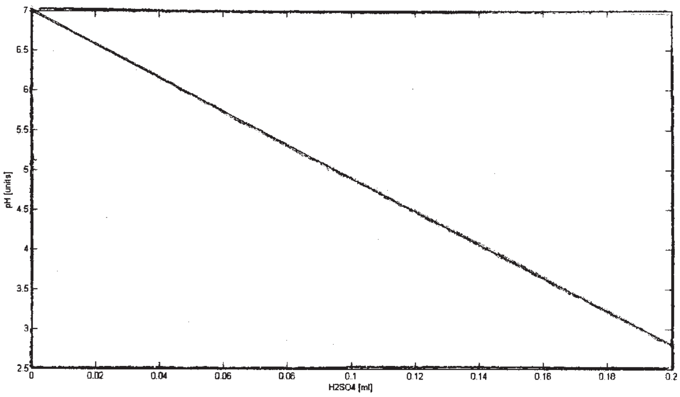

Fig.7. pH variation (set experiments no.3)

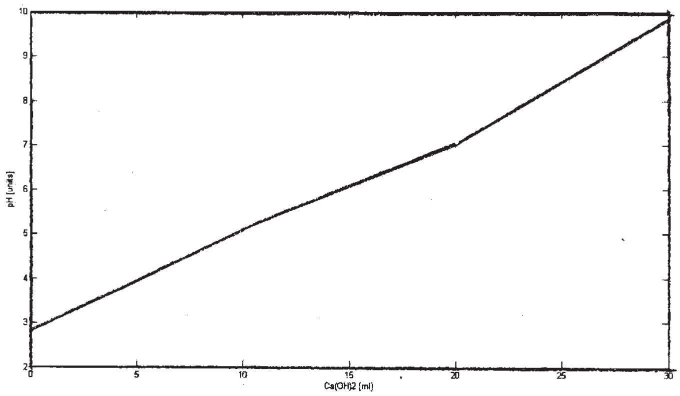

Fig. 8. pH variation (third experiments set)

Table 4
EXPERIMENTAL RESULTS

H_2SO_4 [ml]	$Ca(OH)_2$ [ml]	pH [units]
0.2	-	2.8
-	10	5.1
-	10	7
-	10	9.8

Table 5
EXPERIMENTAL RESULTS

H_2SO_4 [ml]	$Ca(OH)_2$ [ml]	pH [units]
0.2	-	2.6
-	10	2.8
-	10	6.3
-	10	10.9
0.2	-	2.9
-	10	6.1
-	10	10.7
0.2	-	2.6
-	10	2.7
-	10	3.1
-	10	6.15
-	10	10.1

adding hydrated lime, the experimental results were obtained according to table 3. The evolution in *p*H level is described in figure 5.

Following the experimental graphic representation above, after the initial *p*H value of 7.8 units through 0.2mL H_2SO_4 dosage with concentration C_1=40%, the *p*H abruptly descends to 2.8 units.

Following the mathematical model in [6] at initial *p*H of 3.3 units, we consecutively added 10mL of hydrated lime with C_2=10%. The variation in *p*H is described in figure 5.

For a solution with initial *p*H=10 units, according to the mathematical model [6] we added 0.2mL of H_2SO_4 with C_1=40%. The variation in *p*H is presented in figure 6.

As it can be observed in both figure 5 and figure 6, the *p*H value has an abrupt variation due to the process strong neliniarity.

The following set of experiments uses the sample from plant biological step (50 mL of filtered water) with 7 units *p*H level. To follow the model [6], 0.2 mL of sulphuric acid with C_1=40% were added, the *p*H evolution was obtained as in figure 7.

Within the solution with initial *p*H=2.8 units, 10 mL of $Ca(OH)_2$ with C_2=10% were added consecutively. The evolution of *p*H is presented in figure 8.

For the last set of experiments, the sample from the WWTP output (50 mL filtered water) with a *p*H=7.1 was used. After adding 0.2 mL of H_2SO_4 with C_1=40%, the *p*H value has been brought at *p*H=2.6 units. With the initial *p*H level at 2.6 units, 10 mL of $Ca(OH)_2$ with C_2=10% were consecutively added, the variation in *p*H level is presented in figure 9.

The solution with initial *p*H=10.9 was mixed with 0.2ml of H_2SO_4, C_1=40%, this way the *p*H value was brought down to *p*H=2.9 units. Then, having as starting point *p*H=2.9 units, by consecutively adding 10 mL of hydrated lime with C_2=10%, the *p*H value was brought up to 10.7 units. From 10.7 units by adding again 0.2 mL of H_2SO_4, the *p*H value was brought down to 2.6 units. Having *p*H=2.6 units as

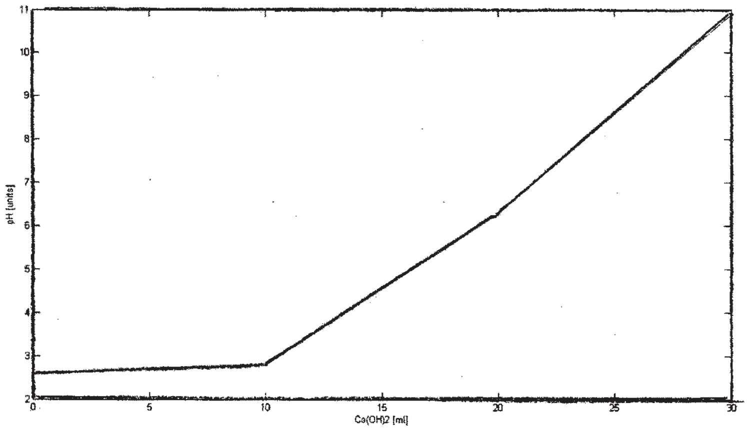

Fig. 9. *p*H variation (final experiments set)

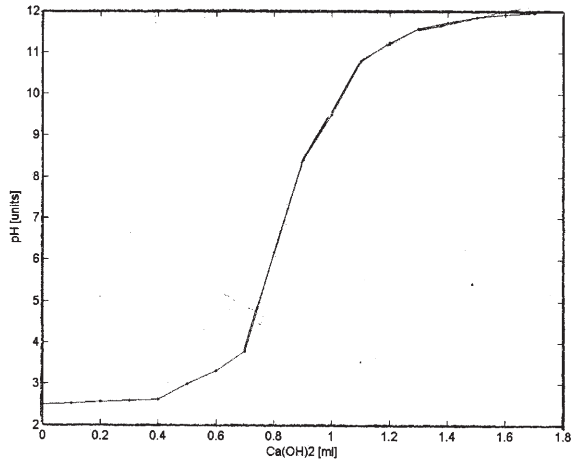

Fig. 10. The titration curve of *p*H neutralization process

Table 6
EXPERIMENTS FOR TITRATION CURVE DETERMINATION

$Ca(OH)_2$[ml] C_2=10%	pH [units]
0	2.5
0.1	2.52
0.2	2.56
0.3	2.60
0.4	2.62
0.5	3
0.6	3.32
0.7	3.8
0.8	6.18
0.9	8.42
1	9.51
1.1	10.79
1.2	11.24
1.3	11.59
1.4	11.73
1.5	11.86
1.6	11.92
1.7	11.97
1.8	12.02

starting point and adding consecutively 10 mL of hydrated lime of concentration C_2=10%, the obtained *p*H value was equal to 10.1 units.

In figure 10 the titration curve (the static characteristic) is presented for the set of experiments described in table 6.

Conclusions

Due to the results obtained in practice using the experimental set-up from figure 2, we can say at this point that our experimental results follow the theoretical mathematical model of the wastewater *p*H neutralization process. The results follow a model which has the same strong non-linear and unstable behaviour through the entire *p*H domain due to the strong variation in process amplification factor (the process amplification is extremely high as we are closer to *p*H≈7 - neutral *p*H). Also, the dosage precision for sulphuric acid is high, which may cause problems controlling the actuators (the dosage pump for sulphuric acid).

Through the chemical experiments, one of the titration curves (fig. 10) was determined for the neutralization process of an acid or alkaline *p*H. This titration curve (or the process static characteristic) has a strong nonlinear behaviour, being similar to the titration curves presented in literature [2-5]. As it can be observed in figure 10, the titration curve is symmetrical in relation with the equivalence point (*p*H=7) and the *p*H value has an abrupt variation around this equivalence point.

To conclude, the practical implementation of the wastewater *p*H neutralization mathematical model supplies results which follow those presented theoreticaly. Plus, the process is a complex one, has a strong non-linearity on the entire *p*H domain, fact that arise serious problems regarding the precision of the reactants dosage.

References

1. MACOVEANU, M., TEODOSIU, C., DUCA, GH., Advanced treatment of wastewater containing non-biodegradable organic compounds (Epurarea avansată a apelor uzate conţinând compuşi organici nebiodegradabili), Ed. Tehnică, Bucureşti, 1983;
2. SKOOG, D. et al., Fundamentals of Analytical Chemistry, Saunders College Publishing, New York, 1988, p. 182-230;
3. PIETRZYK, D. et al., Analytical Chemistry, Second Edition, Technical Press, Bucharest, 1989, p.111-160;
4. LITEANU, C. et al., Quantitative Analytical Chemistry, Pedagogic and Didactic Press, Bucharest, 1972, p. 178-185;
5. LUCA, C. et al., Analytical Chemistry and Instrumental Analysis, Bucharest, 1983, p. 136-146.
6. IBRAHIM, R., Practical modeling and control implementation studies on a pH neutralization process pilot plant, Ph. D. Thesis, Dept. Electronics and Electrical Engineering, University of Glasgow, 2008;
7. NEGULESCU, M. et al., Industrial wastewater treatment (Epurarea apelor uzate industriale), Ed. Tehnică, Bucureşti, 1978;
8. WITTHAUER, D.P., Biocoenosis and degradation in model wastewater-treatment plants, European Journal of Applied Microbiology and Biotechnology, Vol. 9, No. 2, 1980, p. 151–163;
9. *** SR 7587:1996 Water Quality. Determination of solvent extract;
10. *** ISO 7875-1:1996 Water Quality. Determination of surfactants. Part 1: Determination of anionic surfactants by means of methylene blue spectrometry;
11. *** STAS 6953-81 Surface water and wastewater determination in matters in suspension;
12. *** ISO 6060:1996 – Chemical demand

Manuscript received: 31.01.2014