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Study of the efficiency of polyelectrolytes in the treatment of liquid effluents resulting from hot-dip galvanizing

H. Arroub and A. Elharfi

Laboratory Agro-Resources, Organic Polymers and Process Engineering (LRGP)/Team Organic Chemistry and Polymer (ECOP), Department of Chemistry, Faculty of Science, Ibn Tofail University BP133, 14000 Kenitra, Morocco

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- ✓ BOD_5.
- ✓ *PVAs*
- ✓ *PVAc*

arroubhana30@gmail.com
Phone: +21279664493

Abstract

In this study, the treatment of liquid effluents from industry hot-dip galvanizing was made by the process coagulation/flocculation. The optimization of this process has shown that the *physical-chemical* and *biological* parameters indicating the degree of pollution have been recorded in the following abatement rates: (72.85%) for *conductivity*, (98.80%) for *turbidity*, (97%) for *suspended solids*, (98.88%) for the *chemical oxygen demand* and (98.96% for the *biochemical oxygen demand* in the case of treatment with the couple *lime/PVAs*. However those obtained during the treatment with the couple *lime/PVAc* we obtained only a removal: (67.76%) of *conductivity*, (98%) of *turbidity*, (96%) of *suspended solids*, (98.28%) of the *chemical oxygen demand*, (98.68%) of the *biochemical oxygen demand*. According to the results obtained by this study, we have shown that the treatment of residual waters by the *coagulation/flocculation* process is more efficient when using the *lime/PVAs* compared to the *lime/PVAc* and with respect to the reference method employ company level hot dip galvanizing.

1. Introduction

The industrial liquid effluents from the metallic coating are in most cases treated by the physicochemical processes. Among which is the coagulation/flocculation process [1-2-3-4-5]. The latter has wide use in the treatment of wastewater loaded with inorganic micro pollutants [6], organic [7] and organometallic [8-9] which are harmful to health and the environment. These methods are suitable for reducing colloidal materials [1-2-10]. Coagulation is the first step in this process of treating industrial wastewater; it consists in neutralizing or reducing the electrical charges and thus promoting the approximation of colloidal particles [1-2-10].]. The most used coagulants are lime ($Ca(OH)_2$), aluminum salts ($Al_2(SO_4)_3$ and $AlCl_3$) and iron salts ($FeCl_3$, $Fe_2(SO_4)_3$) [11], etc. Flocculation is the process that directly follows coagulation and promotes contact between the destabilized colloidal particles to form agglomerates requiring flocculants such as *polyacrylamides* [12], *polyacrylamides* anionic, cationic, *polyvinyl alcohol* [13] and *chitosan* [14] etc ...

The objective of this study is to treat residual waters from industrial hot-dip galvanizing to reduce pollutants by the coagulation/flocculation process according to the *lime/PVAc* [1] and *lime/PVAs*. First, we have compared optimal doses of used flocculants, and in a second step, we evaluated the purifying power of this flocculant.

2. Material and Methods

2.1. Residual waters sampling

The residual waters used in this study are of residual waters from different stages of the hot dip galvanizing of Galvacier Company (city of Kenitra, Morocco). Samples of these waters were taken from the inlet of the neutralization station, in vials capacity one liter high density polyethylene (HDPE).

2.2. Coagulant/flocculants

The coagulant used to perform the step of flocculation is an emulsion of lime (Ca(OH)2) of 97% purity and flocculants used are the following organic polyelectrolytes:

Ferrocryl® 8723 powder with a purity of 98%, of the family of polyacrylamides whose chemical formula is (C3H5NO.C3H4O2)n, of anionic character, the commercial polyvinyl alcohol(PVAc) provided by the company Shanghai Kaidu Industrial Development Co, Ltd. And synthesized polyvinyl alcohol (PVAs) with the chemical formula -(CH2CHOH)n.

2.3. Optimization the process of coagulation/flocculation

In order to make reliable the treatment of liquid waste neutralization bath station and increase the rate of reduction of pollutant parameters, we have optimized the process of coagulation/flocculation at laboratory scale, in a system Jar-test (ISCO Model RPM/OPM).

2.4. Doses Optimization of flocculants PVAc and PVAs

To optimize the doses of flocculants, we injected increasing doses of each flocculant prepared from 0.1g/l to 0.5g/l which method is described by the data sheet of liquid effluents neutralization station of the Galvacier society and secondly, we have successively diluted 1g/l, 2g/l, 3g/l, 4g/l and 5g/l of PVAc and PVAs. Next, we conducted flocculation of our samples (in 5 liter beakers volume) with a speed of 200tr/min for 3 min. Finally, 10 ml of each dose of the previously prepared solutions of flocculants were added sequentially to each beaker other than the control. After stirring for 5 minutes at a speed of 20TR / min, the samples were left to settle for 30 minutes to remove the supernatant.

2.5. Optimization of sample pH to deal

To optimize the pH of samples of residual waters to be treated, we worked with the same optimal doses of flocculantused and varying the pH from 6 to 9. Aqueous solutions of coagulant and flocculant used were successively prepared at a concentration of 40g / l for the lime and 3g/l et 2g/l for the flocculants PVAc and PVAs. Samples residual waters were collected from 4 beaker having a capacity of one liter, after adjustment of the pH to the values 6,7,8 and 9 with lime, which is in this case the coagulant used. The samples obtained were subjected to oxidation by means of H_2O_2. The flocculation process was conducted for 3 min with a stirring speed estimated by 200tr / min, during which we added 10ml of each flocculant prepared beforehand in each beaker is then reduced the stirring speed 20TR / for 5 min. Before measuring the pH of each preparation, we decanted hang 30min.

2.6.Comparative evaluation of the efficacy of the PVAcand PVAs

In order to compare the performance efficiency of the PVAs compared to PVAc, we conducted flocculation of our samplesconsist of a liter of residual waters collected at the upstream of the station whose pH been previously adjusted to 8 and 6.32 which are optimal doses subsequently oxidized with $H_2O_2$and injected at using a syringe, a mass concentration of 4g/L of coagulant with a speed of 200rpm for 3 min (rapid step of coagulation). While flocculants PVAc and PVAs were added to the previous preparations with a mass concentration successively of 3g/L, 2g/L and let the helices rotate at 20tr/min for 5 min (slow step of flocculation).The preparations obtained are then left to settle before making measurements of the following parameters: pH, temperature, COD, BOD5, TSS, turbidity and electrical conductivity.

3. Results and discussion

3.1. Characterization of poly acetate vinyl: after hydrolysis

IRFT spectra shown in figure 1 showed us several bands among which are the band that lies at 2943.89cm^{-1} corresponding to the CH bond of carbon SP_3, the band that lies at 1453.65cm^{-1} corresponding to CH_2 group, the band that lies at 1085.31cm^{-1} corresponding to the C-OH bond , the band that lies at 1571.83cm^{-1} corresponding to the C-C bond and the band that lies at 3347.64cm^{-1} corresponding to the OH function, which confirms the structure of the polyvinyl alcohol.

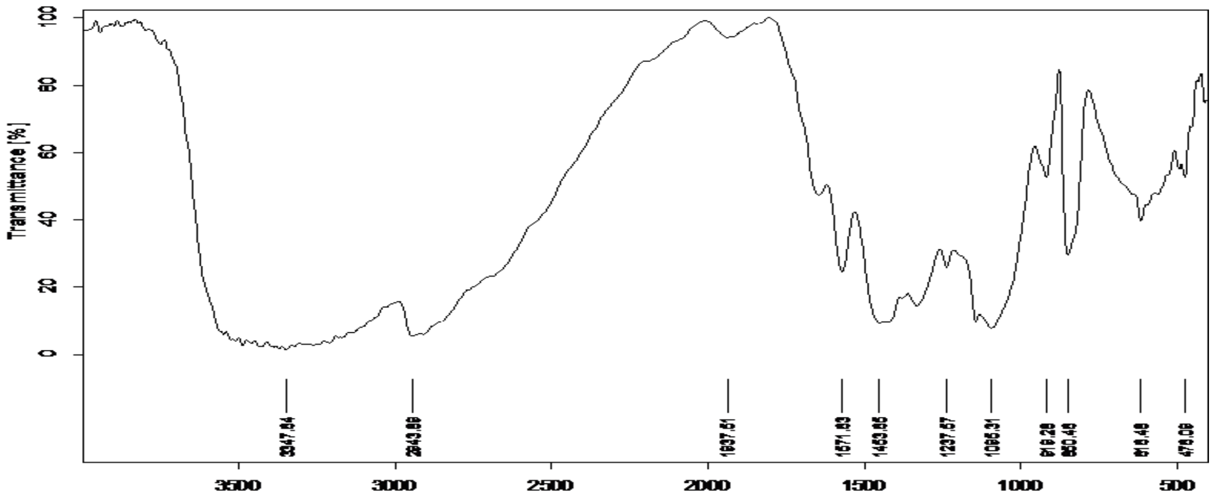

Figure1: Spectrum of poly acetate vinyl obtained by Fourier Infrared Spectroscopy after hydrolysis.

3.2. Assessment of physico-chemical parameters and biological residual waters neutralization station

Table 1 summarizes the average values of the physicochemical and biological parameters of raw water used in this study.

Table 1: Mean values of physico-chemical and biological parameters of the raw water taken from the inlet of the neutralization station.

Analyzed parameters	pH	T(°C)	Turbidity (NTU)	TSS (mg/l)	Conductivity (µs/cm)	DCO (mg/l)	DBO_5 (mgO_2/l)
Measured values below neutralization station	4.01	17.5	560	570	184.3	2862	602
Values measured upstream neutralization station	3.56	25	346	515	07.12	2075	546

3.3. The effectiveness of the optimal doses of the two flocculants PVAc and PVAs

The results of analysis of physico-chemical and biological parameters of flocculated water (ferrocryl® 8723, PVAc and PVAs) using lime as a coagulant are represented in the following figures:

- *Turbidity*

The variation in turbidity as a function of the dose of the flocculants applied is shown in figure

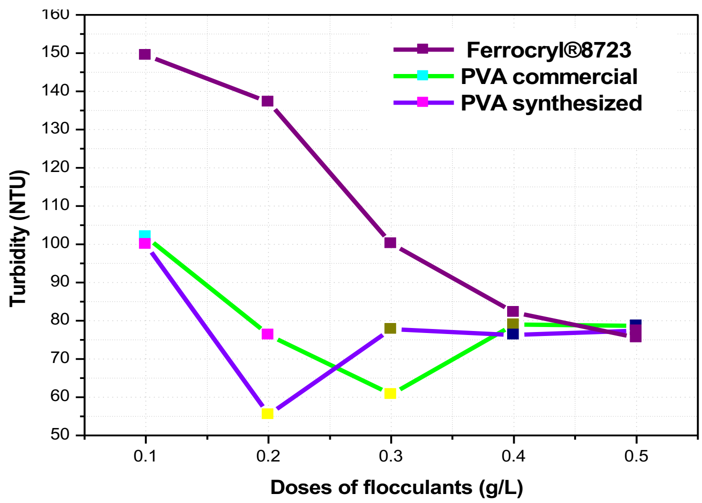

Figure 2: variation of turbidity according to the doses of flocculants

From the results obtained, we noticed that effluent turbidity decreases rapidly from 560NTU to minimum values of 75.6 NTU for a dose of 0.5g/l for ferrocryl®8723, 60.75NTU for a dose of 0.3 g/L for PVAc and 55.5NTU for a dose of 0.2g/L for PVAs.

➢ *Conductivity:*

The variation of the conductivity according to the doses of flocculants used ferrocryl®8723, PVAc and PVAs is represented in figure 3:

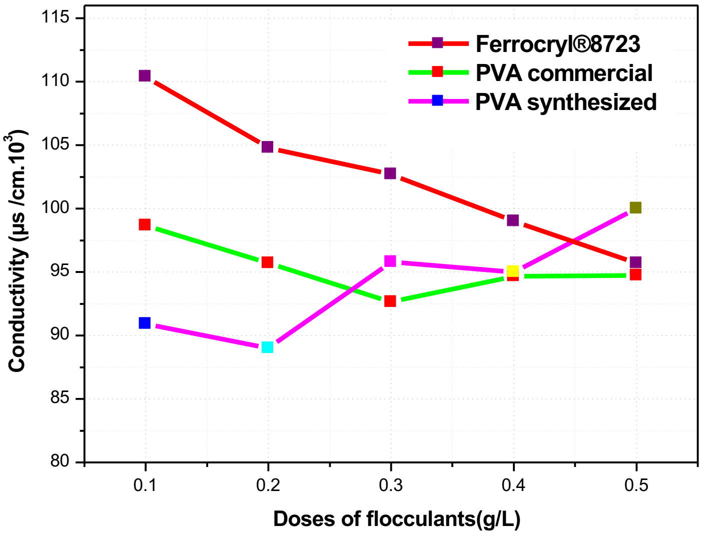

Figure 3: variation of the conductivity according to the doses of flocculants

From figure3, we found that the electrical conductivity of treated effluents gradually decreases for the three flocculants used. It increased from 184.3mg/L to 95.7 mg/L for a dose of 0.5g/l ferrocryl® 8723, 92.64 mg/L for a dose of 0.3g/L PVAc and 89 mg/l for a dose of 0.2g/L of PVAs.

➢ *TSS*

The variation TSS depending on the dose of flocculants ferrocryl® 8723, PVAc and PVA are shown in Figure 4:

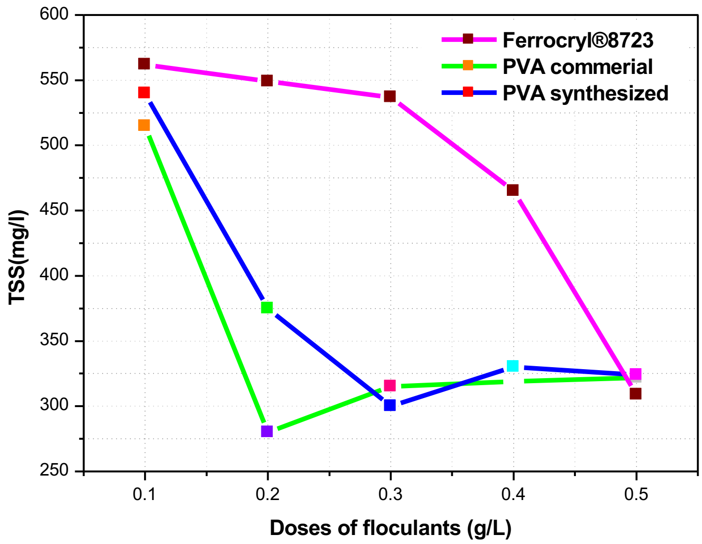

Figure 4: variation of the TSS according to the doses of the flocculants

From this figure, he showed us that a strong presence of TSS in treated effluents decreases as flocculant concentrations increase. In fact, these TSS were increased from 570 mg/l to minimum values recorded in 309 mg/l for a dose of 0.5g/l using ferrocryl®8723 flocculant, in 300 mg/l for a dose of 0.3g/l of PVAc and in a minimum value of 280 mg/l for a dose of 0.2g/l using PVAs.

- *COD*

The variation of the COD as a function of the dose of the flocculants is represented in figure.

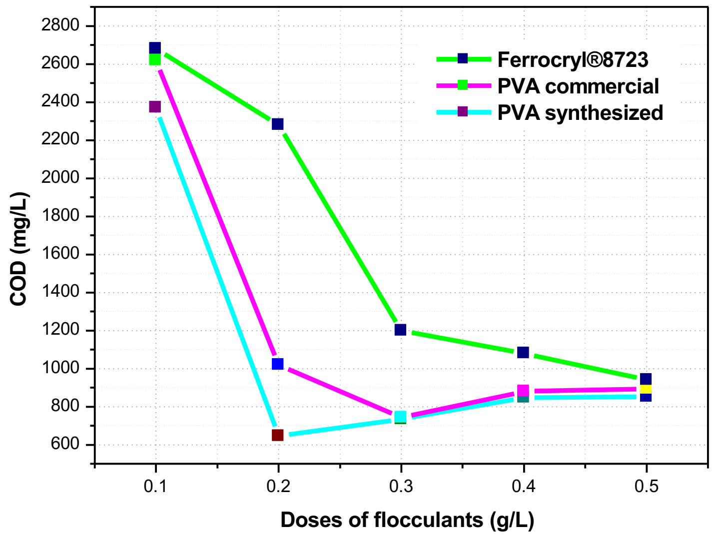

Figure 5: variation of the COD according to the doses of the flocculants

According to the curves shown in figure 5, we perceived that the COD rate of the treated effluents decreased progressively until constant residual values of 940mg/L, 742mg/L and 645mg/L respectively using ferrocryl®8723 at the optimal dose 0.5g/L, PVAC at the optimal dose 0.3g/L and PVAs at the optimal dose 0.2g/L. Indeed, the COD before the treatment was significant in the order of 2862 mg/L. This is due to the high load of raw water in oxidizable organic matter.

- *BOD_5:*

The variation of the BOD_5 as a function of the dose of PVAc and PVAs flocculants is represented in figure 6:

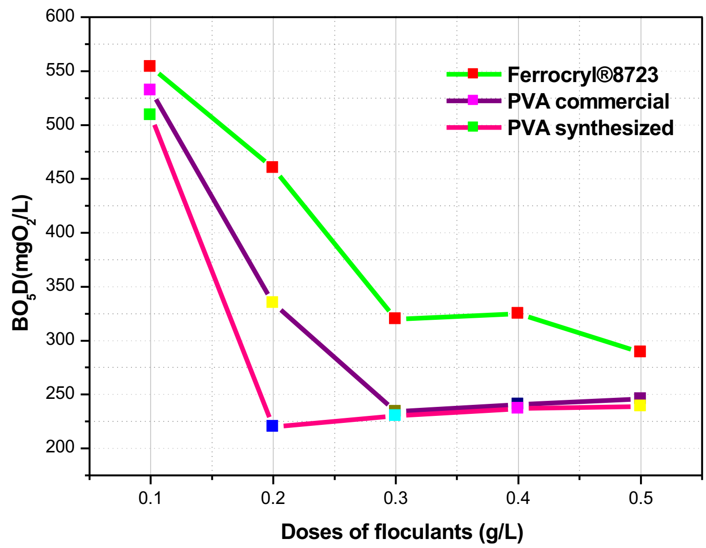

Figure 6: variation of BOD_5 as a function of flocculant doses

According to this figure, we found that the BOD_5 decreased from 602 mg/l to minimum values which are of the order of 289 mgO_2/L for an optimal dose of 0.5g/L of ferrocryl®8723, 234 mgO_2/L for an optimal dose of 0.3g/L of PVAc and of the order of 220mgO_2/L for an optimal dose of 0.2g/L of PVAs.

➢ *COD/BOD₅*

The variation of the ratio COD/BOD_5 is well represented in figure 7:

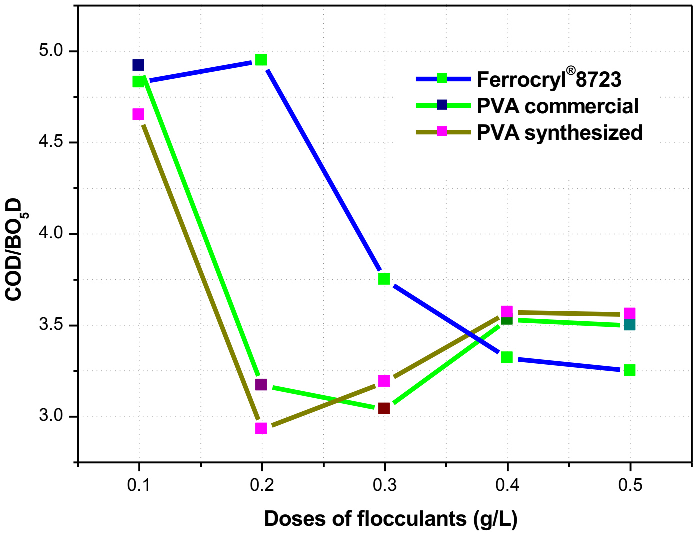

Figure 7: Variations of the ratio COD/BOD_5 according to the doses of the flocculants.

The evaluation of the COD/BOD_5 ratio according to the different doses of the flocculants applied shows that these waters are hardly biodegradable. This ratio was recorded in a minimum value of 3.5 for a 0.5g/L dose of ferrocryl®8723, 3.17 for a 0.3g/L dose of PVAc and in 2.93 for a 0.3g/L dose of PVAs.

3.4. Evaluation of the purifying power of flocculants used in the treatment of liquid effluents from hot dip galvanizing

3.4.1. Effluent analysis results treated by lime/ferrocryl®8723, lime/PVAc and lime/PVAs.

The physicochemical and biological characteristics of effluents treated with ferrocryl®8723, PVAc and PVAs are shown in figure 8:

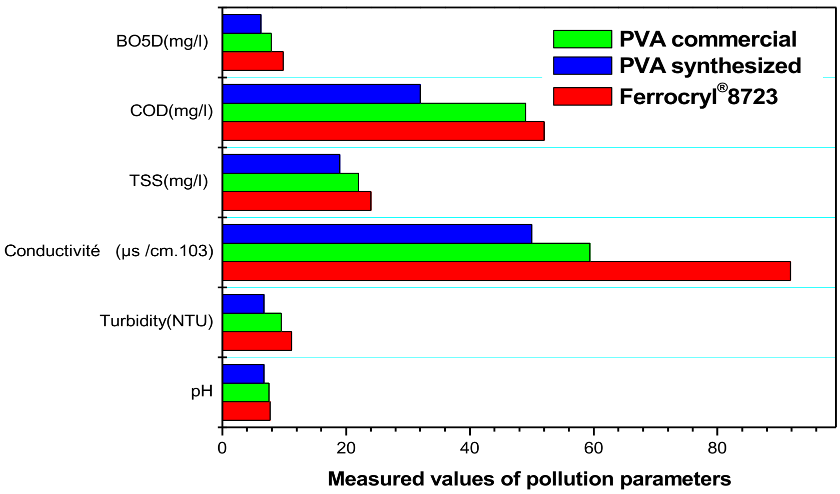

Figure 8: Physicochemical and biological characteristics of the effluents treated by lime/ferrocryl®8723,lime/PVAc and lime/PVAs.

➢ *pH*

At the end of effluent treatment with ferrocryl®8723, PVAc and PVAs, the pH of the effluents obtained was recorded in the values of 7.7, 7.5 and 6.7, respectively, which is more or less neutral.

- *Conductivity, turbidity and TSS*

Based on the results shown in Figure 8, the turbidity, conductivity and suspended solids parameters showed a remarkable decrease after effluent treatment with the three flocculants ferrocryl®8723, PVAc and PVAs. Such that the turbidity increased from 560 NTU in raw water to 11.2NTU in ferrocryl®8723 treated water, 9.52NTU in PVAc and 8.72NTU in the case of PVAs. The conductivity also passed from a value of 184.3µs.cm.10^{-3} to a value of 91.8µs.cm.10^{-3} in the case of raw water treatment with ferrocryl®8723, at a value of 59.4 µs .cm.10^{-3} in the case of PVAc and at a value of 50.02µs.cm.10^{-3} in the case of PVAs. The TSS values increased from 570 mg/L in untreated waters to 24 mg/L for ferrocryl®8723, 22 mg/L for PVAc and 19 mg/L for PVAs treatment.

- *COD and BOD_5*

According to the results of treatment with ferrocryl®8723, PVAc and PVAs, the COD and BOD_5 were significantly reduced to below the expected limit of 1000 mg/l for COD and 500 mg/l for the BOD_5.

Indeed, the COD has increased from a value of 2862mg/L in raw water to a value of 52mg/L in the case of treatment with ferrocryl®8723, to a value of 49mg/L in the case PVAc and of 32mg/L for PVAs, treatment as well as BOD_5 increased from 602mg/L to 9.85mg/L in the case of treatment with ferrocryl®8723 at a value of 7.92mg/L in the case of treatment with PVAc and 6.25mg/L in the case of treatment with PVAs.

3.4.2. Comparison of the purifying performances of flocculants ferrocryl®8723, PVAc and PVAs

Table 2 shows the different cleaning performances of the flocculants used for the treatment of effluents taken from the neutralization station of Galvacier:

Table 2: Rate of abatement of the pollution parameters treated by flocculants.

	Conductivity(NTU)	**Turbidity(mg/l)**	**TSS(mg/l)**	**COD(mg/l)**	**BOD_5(mg/l)**
Ferrocryl®8723(0.5g/L)	50.18%	98%	95.78%	98.18%	98.36%
PVA_C (0.3g/L)	67.76%	98.30%	96.14%	98.68%	98.68%
PVA_S(0.2g/L)	72.85%	98.80%	97%	98.88%	98.96%

The comparison of the three flocculants showed us a very significant effect on the removal of pollutant loads by PVAs compared to PVAc. In fact, the PVAs treatment was able to eliminate 72.85% of the conductivity, 98.80% of the turbidity, 97% of the suspended solids, 98.88% of the chemical oxygen demand and 98.96% of the biochemical oxygen demand. However, treatment with ferrocryl®8723 and PVAc resulted in only 50.18% removal of conductivity, 98% turbidity, 95.78% suspended solids, 98.18% chemical oxygen demand, 98.36% the biochemical oxygen demand in the case of ferrocryl®8723 and 67.76% of the conductivity, 98.30% of the turbidity, 96.14% of the suspended solids, 98.28% of the chemical oxygen demand, 98.68% of the biochemical oxygen demand in the case of PVAc.

According to the study, wastewater from hot-dip galvanizing using the lime/PVAs pairing method was more efficient than the lime/PVAc and compared lime/ferrocryl®8723.

Conclusion

During this study, we conclude that the results obtained in our study by the coagulation/flocculation process such as the lime/PVAs couple were very encouraging compared to the results of the lime/PVAc and with respect to the process standard carried out at the neutralization station of Galvacier. The comparative values of the experimental parameters obtained are as follows:

Lime/ferrocryl®8723 at a dose of 0.5g/L:

Turbidity (98%), Conductivity (50.18%), TSS (95.78), COD (98.18%) and BOD_5 (98.36%).

Lime/PVAc at the 0.3g/L dose:

Turbidity (98.30%), conductivity(67.76%), TSS (96.14%), COD(98.28%) and BOD_5(98.68%).

Lime/PVAs at a dose of 0.2g/L:
Turbidity (98.80%), conductivity (72.85%), TSS (97%), COD(98.88%) and BOD_5(98.96%).
This is the latest to show this encouraging lime/PVAs compared to lime/ferrocryl®8723 and lime/PVAc.

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References

[1]. H. Arroub, A. Elharfi, *M.J.Chem*, 3(3) (2015)525-530.
[2].H. Arroub, A. Elharfi *, J. Mater. Environ. Sci,*9(9) (2018)2645-2651
[3]. H. Arroub, A. Elharfi, *Inter. J. Ch.Tech Res*, 11(3)(2018) 334-341.
[4]. R. Han, J. Zhang, W.Zou, J. Shi, H. Liu, *J. Harz. Mater*. 125(2005)266.
[5]. H. Arroub, A. Elharfi, *Med. J. Chem*, 7(3)(2018)183-197
[6]. M. Allali-Hassani, O. Dusart, M. Mazet. Water Res, 24(6)(1990)699-708.
[7]. R.L. Valladares, V.Y. Quintanilla, Z. Li, G. Amy, *Recher.Eau*.45(2011)6737-6744.
[8]. C. L. Jenkins., *Arch. Environ. Health* 40 (1978)7-12.
[9]. R. A. Damodar, K. Jagannathan, T. Swaminathan, *Sol. Energ*, 81(2007)1-7.
[10]. R. Braz, A. Pirra,, S. Marco, J. Lucas, A. Peres, *Desalina*, 263(2010)226-232.
[11]. K.E. Lee, M. Norhashimah, T. Tjoon, P. Beng Teik, *Chem. Eng. J*, 203(2012)370–386.
[12]. J. Labanda, J. Lorens, *Chem. Eng. Process*, 47(2008)1061-1068.
[13]. M.I. Aguilar, J. Saez, M. Loriens, A.Soler, J.F.Ortuno, *Water. Res*, 37(2003)2233-2241.

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