International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.11 No.03, pp 334-341, 2018

Comparison of the effectiveness of new couples in the treatment of effluents from hot-dip galvanizing

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Abstract : The treatment of industrial effluents by the coagulation/flocculation process is widely used internationally. This treatment makes it possible to reduce the pollution parameters (MES, COD, BOD5, turbidity, conductivity, pH, etc.). The effluent treatment tests from Galvacier various hot-dip galvanization stages by the three pairs used, have shown that these pairs used would make it possible to reduce the pollution parameters but the best treatment result is obtained by the application couple lime/chitosan (s) at a dose of 0.2g / l with a reduction of 97.01% of suspended solids; 98.83% of the turbidity, 79.92% of the Conductivity (µs/cm), 99.19% of the chemical oxygen demand and 99.14% of the biochemical oxygen demand.
Key words : new couples, effluents, , hot-dip galvanizing.

Introduction

Currently, the metallurgical industry uses the hot-dip galvanization process that protects the steel against corrosion. The use of this process generates a very large and considerable volume of effluents loaded with[1-2-3] inorganic organic matter[4-1-3], and organ metallic[5-1-3] and so on. Thus undesirable for humans and the environment because of their toxicity [6-7] and the difficulty of their biodegradability [8-9]. This requires treatment before being discharged into the receiving medium.

Mainly, there are several conventional techniques for treating liquid effluents. Among these are the adsorption process [10], the membrane techniques [12] and the coagulation/ flocculation process [11-13] and so on. The choice of the effluent treatment method depends essentially on the chemical nature of the organic material to be removed. Combined flocculation techniques are commonly used for this type of pollution.

Coagulation-flocculation [14-1-3] is one of the most important physicochemical treatment steps in the treatment of industrial wastewater to reduce colloidal material [15-1-3]. suspended solids, turbidity and also responsible for the reduction of organic matter which contributes to the BOD_5 and COD of wastewater[16-17], and are generally

DOI : http://dx.doi.org/10.20902/IJCTR.2018.110345

carried out by adding chemicals such as coagulant and flocculant Inorganic coagulants most used are lime ($Ca(OH)_2$ aluminum salts (Al_2 $(SO_4)_3$ and $AlCl_3$) and iron salts ($FeCl_3$, $Fe_2(SO_4)_3$)[18-1-3], etc. thus, among the synthetic organic flocculants used are anionic or cationic polyacrylamides [19-1-3], polyacrylic acid and / or polyvinyl alcohol [20-1-3].

The objective of our work is the study of the wastewater treatment of hot-dip galvanization in order to reduce the pollution parameters by the process of coagulation / flocculation according to the couples (lime $Ca(OH)_2$/ferrocryl®8723) and (lime $Ca(OH)_2$/chitosan(c) and (lime$(OH)_2$/ chitosan (s).

2. Material and method

2.1. The study area

The experimental study area was defined using the wastewater from different stages of the hot-dip galvanizing of Galvacier (city of Kénitra, Morocco).

2.2. Sample

The sample was taken from the downstream and upstream of the neutralization station, in bottles whose capacity is one liter based on a high density of polyethylene (HDPE).

2.3. Coagulant/flocculant (s)

The coagulant used during this work for coagulation/flocculation processes is lime (Ca $(OH)_2$) with a purity of 97%. The polyelectrolytes used for the flocculation are ferrocryl®8723 powder with a purity of 98%, of the polyacrylamides family, whose chemical formula is $(C_3H_5NO.C_3H_4O_2)n$ and the molecular weight between 11.10^6 and 12.10^6g/mol, of anionic character and which was provided by Henkel Metallchemie and chitosan (commercial and synthesized) is a cationic polymer that can be obtained by the acetylation of chitin [21- 22] whose chemical formula $(C_6H_9NO_4)n$.

2.4. Physico-chemical parameters analyzed

The physicochemical parameters are determined from the samples taken at the liquid effluent of Galvacier de Kenitra.

- The pH, the temperature and the electrical conductivity are determined using a multi parameter Analyzer of Consort type C535.

- The BOD5 is determined by the respiratory method using a BOD-meter brand WTW model 1020T according to the technique described by DIN.

- The COD is determined by a COD meter CR 2200.

- Turbidity is determined by a HACH2100 Turbid meter.

- The MES are determined by filtration of a volume of wastewater on cellulose filters (0.45 μm) according to Rodier [23].

2.5. Assessment of the power of new couples lime/chitosan (c) and lime/ chitosan (s)

In this part of work we evaluated the power of the new flocculants "chitosan (c) and chitosan (s)". The demonstration of the effectiveness of these flocculants, from the point of view of reducing the pollutant load, was carried out thanks to a comparative study with ferrocryl®8723 which is the reference flocculant at the neutralization station. we proceeded to flocculation of our samples composed of one liter of waste water taken downstream of the neutralization station whose pH was previously adjusted to 8 and subsequently oxidized by H2O2 using these three flocculants with optimal doses successively of 0.3g/l, 0.2g/l and 0.5g/l. While lime coagulant was added to previous preparations with a mass concentration of 0.4g/l. The resulting preparations are then decanted before the following pollution parameters are measured: pH, temperature, TSS, turbidity, electrical conductivity, COD and BOD_5.

The treatment efficiency was assessed analytically by monitoring the abatement rate of the pollution parameters.

The calculation of the abatement rate of a parameter X, expressed as a percentage, is based on the following formula:

$$\% \text{ abatement } (X) = \frac{Ci(X) - Cf(X)}{Ci(X)} \times 100$$

With Ci: initial concentration of X in the wastewater.

and Cf: final concentration of X in the waste water.

2. Results and Discussion

2.1. Characteristics of the liquid effluents of the neutralization station Table 1 summarizes the average of the effluent pollution parameters used in this study.

Table 1: The average values of the pollution parameters of the liquid effluents taken at two different points.

Analyzed parameters	pH	T(°C)	Turbidity (NTU)	TSS (mg/l)	Conductivity (µs /cm)	COD (mg/l)	BO_5D (mg/l)	COD/BO_5D
Measured values downstream of the neutralization station	4.02	17.5	560	570	184.3	2862	602	4.75
Measured values upstream of the neutralization station	3.56	25	65	515	107.12	2075	546	3.80

2.2. Comparison of optimization results of different doses of applied flocculants

The results of the analysis of the pollution characteristics of the samples as a function of the doses of the flocculant ferrocryl®8723, chitosan(c) and chitosan(s) are represented in the figures below:

Conductivity:

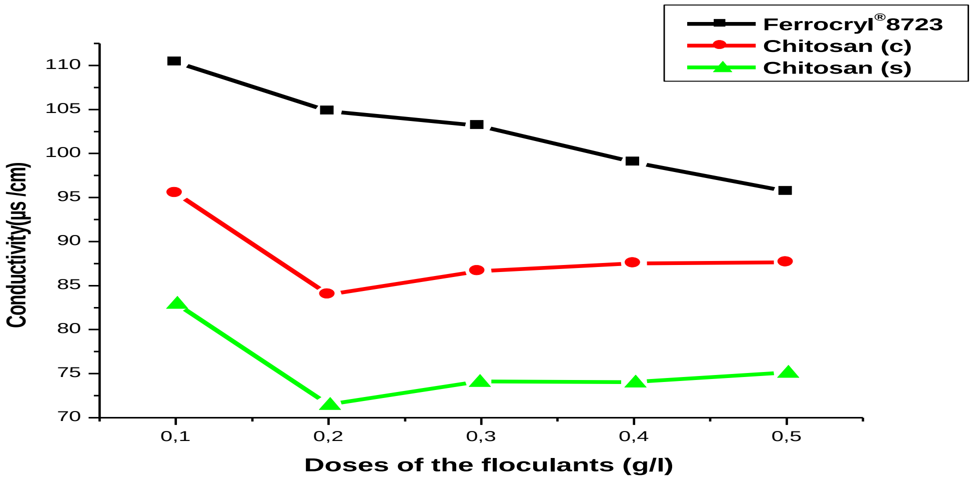

Figure 1: Effects of the optimal dose of floculants on the conductivity

From the results obtained from the pollution parameters, we have shown that:

A remarkable decrease after the treatment of liquid effluents by lime/ferrocryl®8723, lime /chitosan (c) and lime/chitosane(s). Indeed, the conductivity has passed respectively from a value of 184.3µs.cm in the raw water to the following values: 95.7 µs.cm , 84 µs.cm and 71.5 µs.cm.

Turbidity:

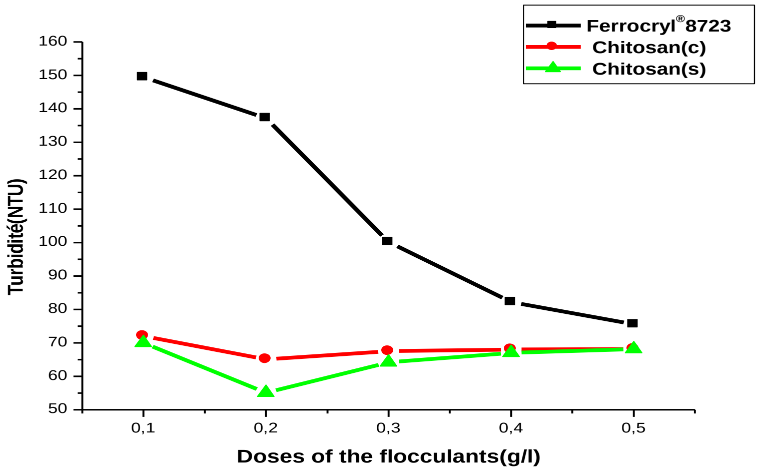

Figure 2: Effects of the dose optimal of floculants on the turbidity

From the curve shown in Figure 2, we find that:

The optimum doses of the flocculants applied reduce the turbidity as it successively passed from a value of 560 NTU in the raw water to values of 75.6 NTU, 65.12 NTU and 55.1 NTU in the treated water.

TSS:

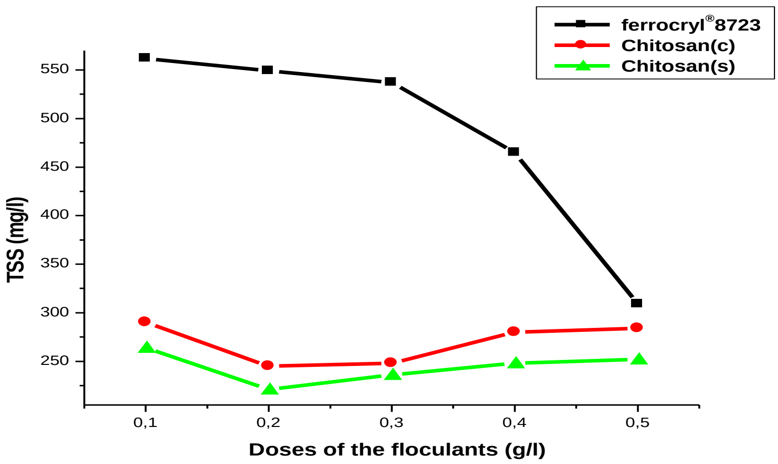

Figure 3: Influence of the dose optimal of floculants on the TSS

From the results of analyzes obtained we have recorded that:

The TSS was increased respectively from 570 mg/l in liquid effluents to values of 309 mg/l, 245 mg/l and 221 mg/l.

COD:

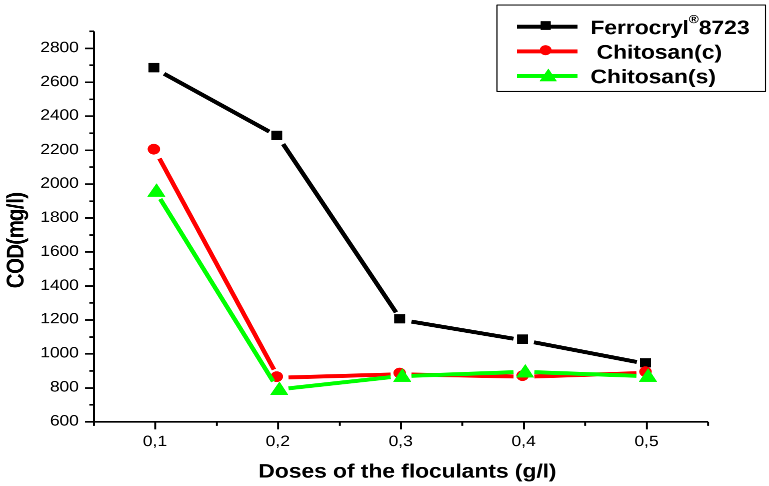

Figure 4: Influence of the optimal doses of floculants on the DCO

From the results obtained we noticed that:

A considerable reduction of the COD, Indeed the value of 2862 mg/l in the raw water has successively dropped to 940 mg/l, 860 mg/l and 791 mg/l.

BO_5D

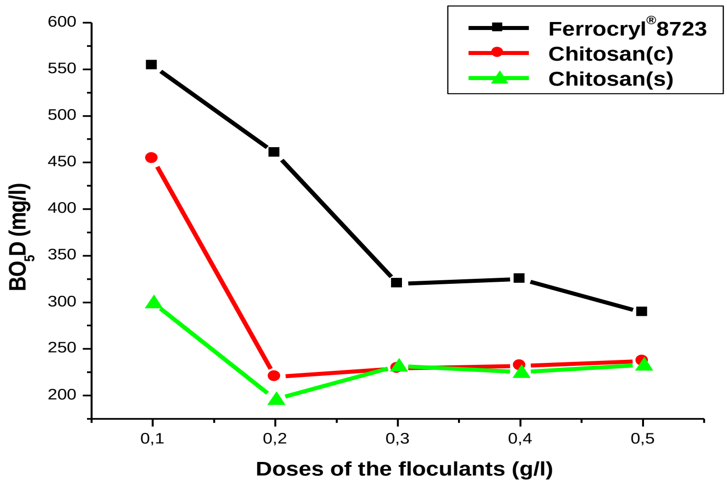

Figure 5: Effects of the optimal doses of floculants on the DBO_5

In view of the results shown in Figure 5 we have seen that:

BOD_5 increased from 602 mg/l to 289 mg/l, 220 mg/l and 196 mg/l, respectively.

COD/BO$_5$D

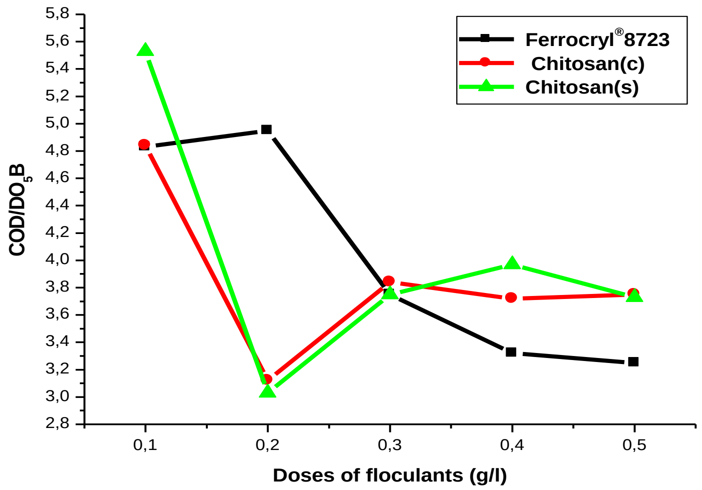

Figure 6: Changes in the COD/BOD$_5$ based doses of flocculants.

The evaluation of the COD/BO$_5$D following different doses of applied flocculants, shows that these waters are easily biodegradable. These ratios vary from 3.03 to 5.53 in the case of chitosan (s), varies from 3.12 to 4.84 in the case of chitosan (c) and from 3.25 to 4.95 in the case of ferrocryl®8723. These ratios were recorded in a minimum value of 3.25 for a 0.5g/l dose of ferrocryl®8723, 3.12 for a dose of 0.2g/l of chitosan (c) and in 3.03 for a dose of 0.2g/l of chitosan (s).

2.3. Assessment of the épuratif power of the couples lime/ferrocryl®8723, lime/chitosane(c) and lime/chitosan(s)

2.3.1. Treatment results by the couples used

The characteristics of the effluents treated by the different pairs are recorded in Table 2:

Table 2: Characteristics of the pollution parameters of treated effluents.

Nature of couple / Parameters	Lime/ferrocryl®8723	Lime/chitosan (c)	lime/chitosan (s)
TSS (mg/l)	24	20	17
Turbidity(NTU)	11.2	8.76	6.54
Conductivity (µs /cm).10)	91.8	50.01	37
BO$_5$D (mg/l)	9.85	7.04	5.14
COD (mg/l)	49	34	23
PH	7.7	7.6	7.12
T(°C)	17.4	16.2	16.32

• ***pH***

After the couple treatment, the couples lime/ferrocryl®8723, lime/chitosan(c) and lime/ chitosan (s), the pH values respectively recorded in the values of 7.7, 7.6 and 7.12.

• *Conductivity, turbidity and TSS*

According to the results obtained from physicochemical parameters such as turbidity, conductivity and suspended solids, the lime/ferrocryl®8723, lime/chitosan(c) and lime/ chitosane(s) showed a remarkable decrease. In fact, the turbidity has successively passed from a value of 560 NTU in the raw water to the values of 11.2 NTU, 8.76 NTU and 6.54 NTU in the treated water. When the conductivity has passed from a value of 184.3µs.cm to the values of 91.8µs.cm, 50.01µs.cm and 37µs.cm. In the end, the recorded TSS increased from 570 mg/l to 24 mg/l, 20 mg/l and 17 mg/l .

• *COD and BOD$_5$*

According to the results of treatment with lime/ferrocryl®8723, lime/chitosane (c) and lime/chitosan (s), we noticed a considerable decrease in COD. Indeed, the value of 2862 mg/l in raw water dropped to 49mg/l, 34mg/l and 23mg/l. BOD$_5$ increased from 602 mg/l to 9.85 mg/l, 34 mg/l and 7.04 mg/l.

2.3.2. Comparison of the effectiveness of applied couples

The effectiveness of lime/ferrocryl®8723, lime/chitosan(c) and lime/chitosan(s) couples in reducing pollution parameters with their optimal doses (lime equals 0.4g/l, ferrocryl®8723 equals 0.5g/l, chitosan (c) equals 0.2g/l and chitosan (s) equals 0.2g/l) at the optimum pH value (pH equals 8) are shown in Figure 7 and Table 2

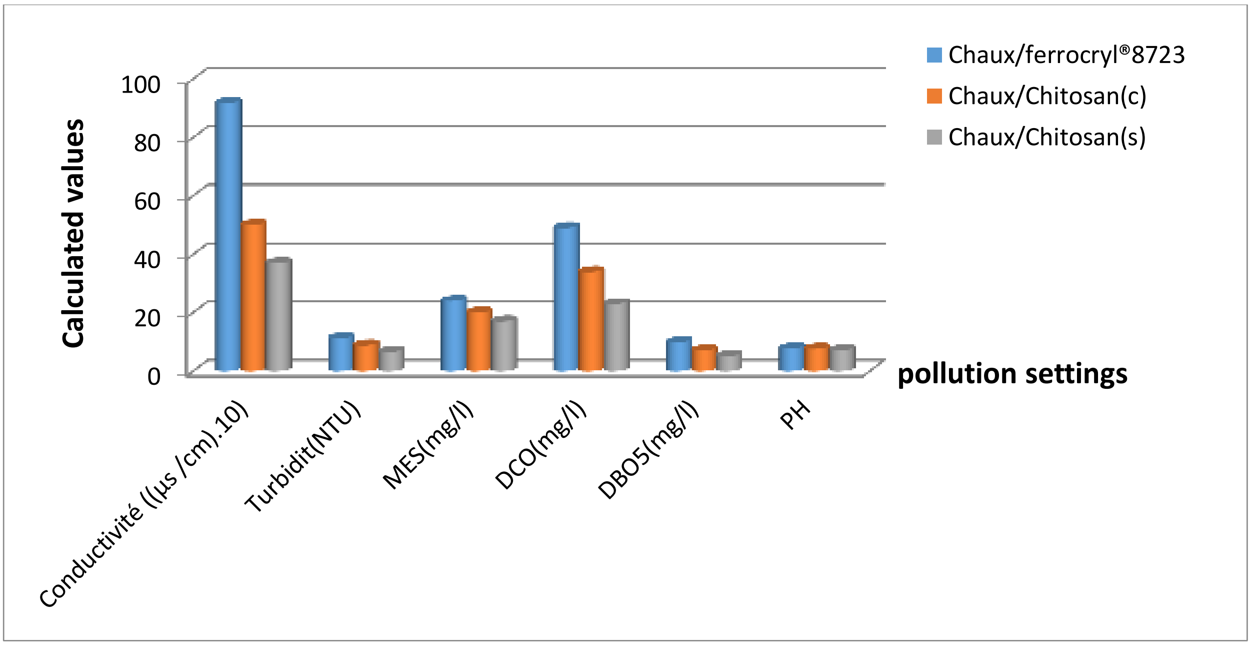

Figure 7: Comparison of the effectiveness of couples

Comparative results of three couples; lime/ferrocryl®8723, lime/chitosan(c) and lime/chitosan (s) used with their optimal doses and at the optimum pH value showed us a very significant effect on reducing the pollutant load. Indeed, treatment with lime/chitosan(s) was able to eliminate 97.01% of suspended solids; 98.83% of the turbidity, 79.92% of the conductivity (µs/cm), 99.19% of the chemical oxygen demand and 99.14% of the biochemical oxygen demand. However, the lime/chitosan treatment(c), we obtained a 96.49% removal for suspended solids; 98.43% for turbidity 72.86% for conductivity (µs/cm), 98.81% for chemical oxygen demand and 98.83% for biochemical oxygen demand; However, the lime/ferrocryl®8723 couple treatment achieved only a 95.78% reduction in suspended solids; 98% for turbidity 50.18% for conductivity (µs/cm), 98.18% for chemical oxygen demand and 98.36% for biochemical oxygen demand.

Conclusion

This work aims to treat the liquid discharges resulting from the hot-dip galvanizing of steel by the combined process of coagulation flocculation by means of a Jar-test system, using the flocculants (ferrocryl®8723 at the

0.5g dose). Chitosan (c) at a dose of 0.2g/l and chitosan (s) of 0.2g/l the results obtained in this work show us that:

The maximum reduction of degree of organic pollution of the studied parameters (the TSS, the BOD_5 the COD, the turbidity, the Conductivity) situate in the case of use the couple lime/chitosan (s) such as: the turbidity (98.83%), the MES (97.01%) of the Conductivity (µs/cm)(79.92%), the BOD_5 (mg/l)(99.14%) and the COD(mg/l)(99.19%) for the couple lime/chitosan (s). This is probably due to the nature and the chemical structure, as well as the particle size of the coagulant/flocculants used: chitosan (s), chitosan (c) and ferrocryl®8723.

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