



Evaluation of the effectiveness of the new couples Aluminum sulphate/PVAc and aluminum sulphate/PVAs in the clarification of wastewater: case of treatment of liquid effluents resulting from hot galvanization by coagulation-flocculation

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- ✓ BOD₅.

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Abstract

During this work, we treated the effluents from hot-dip galvanizing. For this we used the coagulation/flocculation process using *aluminum sulphate* as coagulant and flocculants which are *PVAc and PVAs*. From the results obtained, we observed that the effluent rate values of treated effluents were recorded at 96.18% for *suspended solids*, 98.35% for *turbidity* and 98.94% for *conductivity* ($\mu\text{s}/\text{cm}$), 98.38% of the *chemical oxygen demand* and 98.50% of the *biochemical oxygen demand* in the case of treatment with the *aluminum sulphate/PVAs*. However, treatment with the *aluminum sulphate/PVAc*, we obtained 95.83% removal for *suspended solids*, 98.17% for *turbidity*, 67.57% for *conductivity* ($\mu\text{s}/\text{cm}$), 98.48% for the *chemical oxygen demand* and 98.48% of the *biochemical oxygen demand*.

1. Introduction

In the galvanizing industries, polluting discharges [1-2] cause serious problems on the environment [3-4] because of their high levels of organic materials that are difficult to biodegrade (detergent, surfactants, etc.), and inorganic materials [4] and organometallic [5-6]. The increase in the demand for water and the evolution of the legislation on discharges require the use of very efficient processes for the treatment of polluted water. Numerous studies have been carried out in order to treat these effluents by identifying economic treatment methods, such as biological treatments [7-8], oxidation [9-10], membrane processes [11-12], adsorption on materials [13], electro coagulation [14-15] and coagulation-flocculation [16-17-18]. Except that, this process is the most used in the treatment of wastewater discharged by the galvanizing and metal coating industries with a view to the substantial reduction of colloidal material [19]. Coagulation is the first step in this process of industrial wastewater, it is to neutralize or reduce electrical charges and thus promote reconciliation between the colloidal particles for their agglomeration. This stage results from the addition of chemical reactive in the aqueous dispersals in order to assemble larger aggregates. The most commonly used coagulants are lime ($\text{Ca}(\text{OH})_2$), aluminum salts ($\text{Al}_2(\text{SO}_4)_3$ and AlCl_3), aluminum sulphate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) [18-20] and iron salts (FeCl_3 and $\text{Fe}_2(\text{SO}_4)_3$) [21], etc.. Flocculation is the process directly following the coagulation and promotes contact between the colloidal particles to form agglomerates destabilized requiring flocculants such as polyacrylamides [22], anionic polyacrylamides, cationic, polyacrylic acid and polyvinyl alcohol [23] etc... Polyvinyl alcohol is an important water-soluble polymer, and is extensively used in industries due to its excellent chemical and physical properties, non-toxicity, good chemical resistance, good film formation capacity, biodegradability and high crystal modulus [24].

During this work, we opted for the treatment of effluents from hot-dip galvanizing by the coagulation/flocculation process using the aluminum sulphate/PVAc and the aluminium sulphate/PVAs.

2. Material and Methods

2.1. Sampling

The experimental study was carried out using rejects from the company Galvacier (city of Kenitra, Morocco). The samples of these discharges were taken from two different points of the company's wastewater treatment plant, which are successively the entry and exit of the station, into bottles whose capacity is based on a high density of polyethylene (HDPE).

2.2. Coagulant/flocculants

The coagulant used during this work for the coagulation/flocculation processes is aluminum sulphate ($(\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O})$) with a purity of 99%. However the polyelectrolytes used for the flocculation are the commercial polyvinyl alcohol (PVAc) supplied by Shanghai Kaidu Industrial Development Co., Ltd and polyvinyl alcohol synthesized (PVAs) whose chemical formula - $(\text{CH}_2\text{CHOH})_n$.

2.3. Comparative evaluation of the efficacy of the new couples aluminum sulphate/PVAc and aluminum sulphate/PVAs.

In this part of the work we have compared the efficiency of the new pairs of aluminum sulphate/PVAc compared to that of aluminum sulphate/PVAs. For this we proceeded to the coagulation/flocculation of our samples composed of one liter of effluent taken at the entrance of the neutralization station whose pH was previously adjusted to 9 and subsequently oxidized by H_2O_2 and injected at using a syringe, a mass concentration of 0.5g/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 0.3g/L, 0.2g/L and let the helices rotate at 20tr/min for 5 min (slow step of flocculation). 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:

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

With Ci: initial concentration of X in the wastewater.

andCf: final concentration of X in the waste water.

2.4. Physico-chemical parameters analyzed

The physico-chemical parameters analyzed are determined from the samples taken at the level of the liquid effluent from the hot-dip galvanizing process. These parameters are:

- pH, temperature, and conductivity are determined using a multiparameter parameter Consort C535.
- Turbidity is determined by a HACH2100 Turbidimeter.
- Suspended solids (TSS) are determined by filtration of a volume of waste water on cellulose filters (0.45 μm) according to Rodier.
- The Chemical Oxygen Demand (COD) is determined by a COD meter CR 2200.
- The BOD_5 is determined by the respiratory method using a WTW DBO-meter model 1020T according to the technique described by DIN.

3. Results and discussion

3.1. Characteristic of the physico-chemical parameters of the hot dip galvanizing rejects

Table 1 summarizes the average physico-chemical parameters of the liquid effluents used in this study.

Table1 : The average values of the physico-chemical parameters of the liquid effluents taken at two different points.

Analyzed parameters	Measured values downstream of the neutralization station	Measured values upstream of the neutralization station
pH	4.02	3.56
T(°C)	17.5	25
Turbidity (NTU)	560	65
TSS (mg/l)	570	515
Conductivity ($\mu\text{s/cm}$)	184.3	107.12
COD (mg/l)	2862	2075
BOD ₅ (mg/l)	602	546
COD/BOD ₅	4.75	3.80

3.2. Efficacy of optimal doses of flocculants PVAc and PVAs

Optimal doses of flocculants PVAc and PVAs are determined by determining a number of pollution parameters for these releases.

The results obtained from analysis of the sample physico-chemical parameters as a function of the optimal doses of the flocculants PVAc and PVAs are represented in the figures 1 to 5:

- *Conductivity* :

From the results obtained from the physico-chemical parameters, we found that a remarkable decrease in conductivity. It went from a value of 184.3 $\mu\text{s.cm}$ in raw water to values of 92.64 $\mu\text{s.cm}$ for a 0.3g/L dose of PVAc and 88.5 $\mu\text{s.cm}$ for a 0.2g/L dose of PVAs.

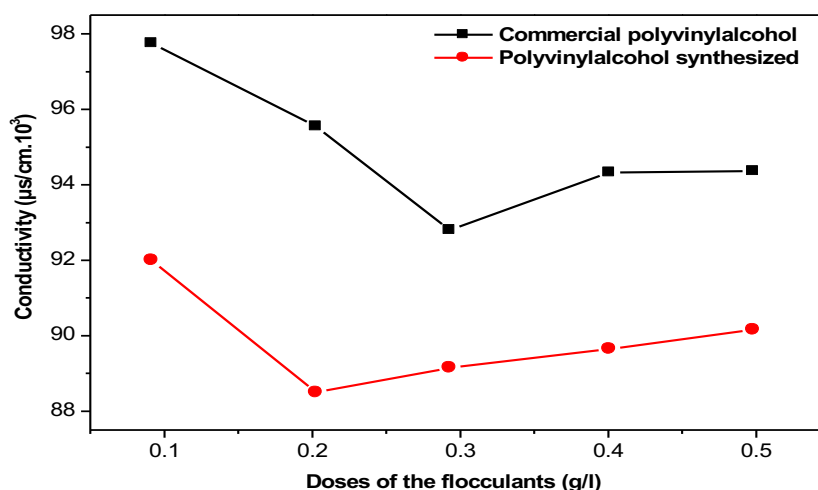


Figure 1: Effect of optimal doses of flocculants on the reduction of conductivity.

- *Turbidity* :

From the curve shown in figure 2, we observed that: Optimal flocculant doses reduce turbidity from 560NTU in raw water to 60.75NTU for 0.3g/L PVAc and 59NTU for a dose of 0.2g/L of PVAs.

- *TSS*:

According to the curves of the Figure 3, we found that: The results of analysis obtained also showed a strong presence of TSS in the treated waters which decrease as. The mass concentration of TSS reaches a minimum of 300mg/L and 290mg/L for a dose of 0.3g/L of PVAc and for a dose of 0.2g/L of PVAs.

- *COD*:

From the curve, we noticed that: A considerable decrease in COD. In fact, the COD dropped from a maximum value of 2862mg/L to 742mg/L for PVAc at a dose of 0.3g/L and 725mg/L for PVAs at the dose 0.2g/L.

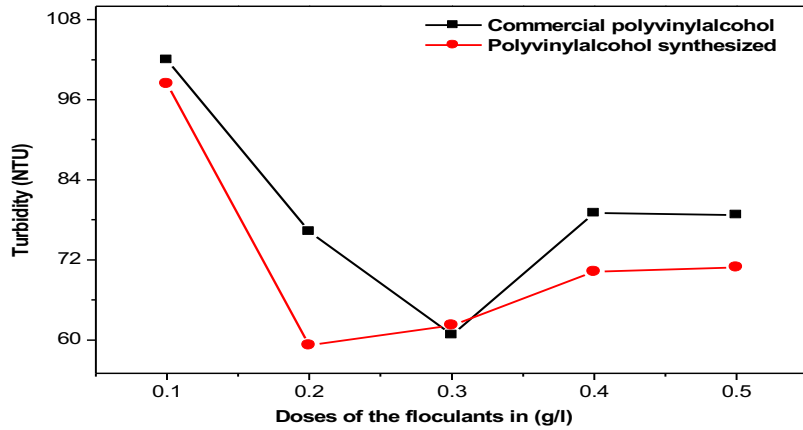


Figure 2: Influence of optimum flocculants doses on turbidity.

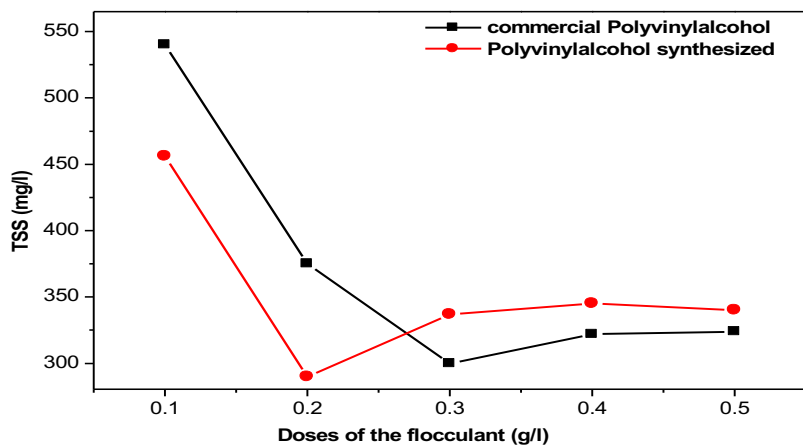


Figure 3: Influence of optimal doses of flocculants on the TSS.

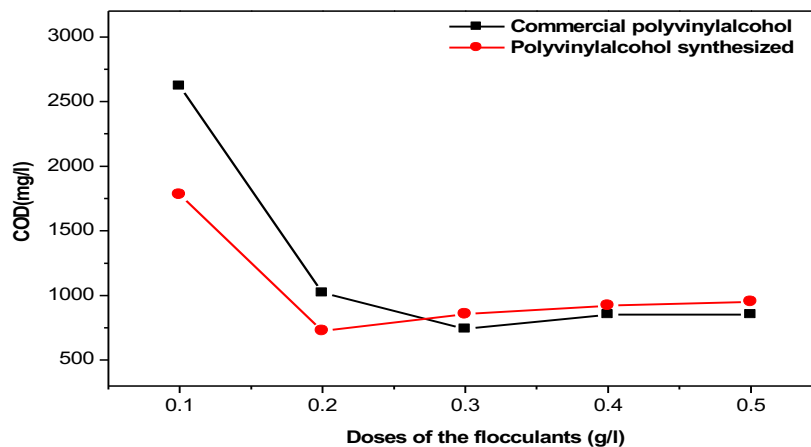


Figure 4: Effect of optimal doses of the flocculants on reduction of COD.

- *BOD₅*:

In view of the results shown in Figure 5 we have seen that: *BOD₅* increased from 602mg/L to 234mg/L for a dose of 0.3 of PVAc and 210mg/L for PVAs at a dose of 0.2g/L.

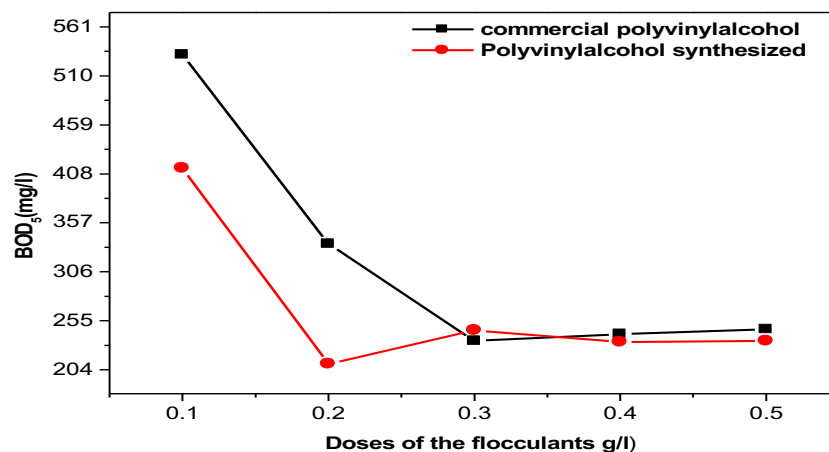


Figure 5: Influence of optimal doses of flocculants on BOD₅

- *DOC/BOD₅:*

The evaluation of the COD/BOD₅ following different doses of applied flocculants shows that these waters are easily biodegradable. This ratio varies from 3.04 to 4.29 in the case of PVAs and 3.17 to 4.92 in the case of PVAc. This report has been registered in a minimum value of 3.17 for a dose 0.3g/L for PVAc and 3.04 for a dose of 0.2g/L of PVAs.

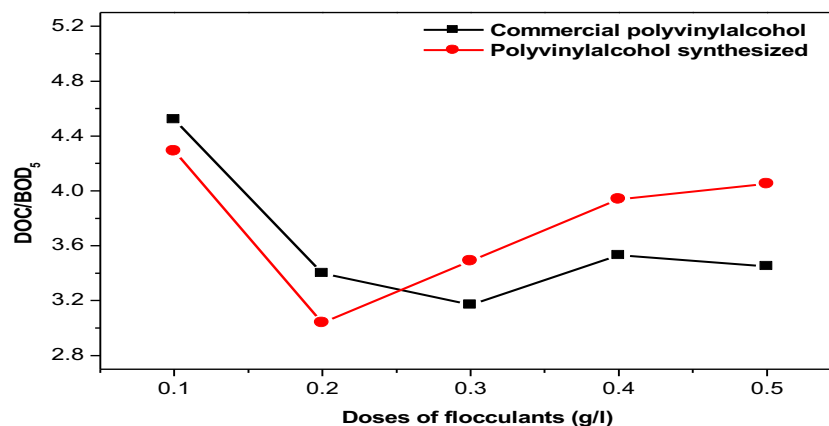


Figure 6: Changes in the COD/BOD₅ based doses of flocculants.

3.3. Comparative study of the effectiveness of aluminum sulphate/PVAc and aluminum sulphate/PVAs couples.

3.3.1. Treatment analysis results from both aluminum sulphate/PVAc and aluminum sulphate/PVAs couples.

The physico-chemical characteristics of the water treated by the two pairs are recorded in Table2:

PH

The pH at the end of the effluent treatment by the aluminum sulphate/PVAc and aluminum sulphate/PVAs, the pH values obtained were recorded respectively in the values of 7.4 and 7, 5 which is more or less neutral.

Conductivity, turbidity and TTS

Based on the results shown in Table 2, the turbidity, conductivity and suspended solids parameters showed a remarkable decrease after treatment with both aluminum sulphate/PVAc and aluminum sulphate/PVAs. For example, turbidity increased from 560NTU in raw water to 10.2NTU in the case of aluminum sulphate/PVAc treatment and 9.24NTU in the case of sulphate aluminum/PVAs. The conductivity also passed from a value of 184.3µs.cm to a value of 59.76µs.cm in the case of aluminium sulphate/PVAc and to a value of 57.24µs.cm in

the case of aluminum sulphate/PVAs. The MES increased from 570mg/L to 23.75 mg/l in the case of aluminum sulphate/PVAc and 21.95mg/L in the case of aluminum sulphate/PVAs.

Table 2: Physico-chemical characteristics of the effluents treated by the aluminum sulphate/PVAc and aluminum sulphate/PVAs .

Nature of couple Parameters	Aluminum sulphate (at the optimal dose 0.5g/L)/PVAc(at the optimal dose 0.3g/L)	aluminum sulphate (at the optimal dose 0.5g/L)/PVAs(at the optimal dose 0.2g/L)
TSS (mg/l)	23.75	21.95
Turbidity(NTU)	10.2	9.24
Conductivity (µs/cm).10	59.76	57.24
BOD ₅ (mg/l)	9.15	9
COD (mg/l)	46.3	43.24
PH	7.4	7.5
T(°C)	17	17

COD and BOD₅

Based on the results of treatment with the two aluminum sulphate/PVAc and aluminum sulphate/PVAs, the COD and BOD₅ were significantly reduced to below the expected limit is 1000mg/L for COD and 500mg/L for BOD₅. Indeed, the COD has increased from a value of 2862mg/L in raw water to a value of 46.3mg/L in the case of aluminum sulphate/PVAc and to a value of 43.24mg/L in the case of aluminum sulphate/PVAs as well as the BOD₅ went from a value of 602mg/L to a value of 9.15mg/L in the case of aluminum sulphate/PVAc and at a value of 9mg/L in the case of aluminum sulphate/PVAs.

3.3.2. Comparison of the efficiency of aluminum sulphate/PVAc and aluminum sulphate/PVAs couples in reducing physico-chemical parameters.

The effectiveness of aluminum sulphate/PVAc and aluminum sulphate/PVAs couples in reducing pollution parameters with their optimal doses (aluminum sulphate equals 0.5g/L, PVAc equals 0.3g/L and PVAs equals 0.2g/L) and at the optimum dose of pH equal to 8 are shown in Figure 6.

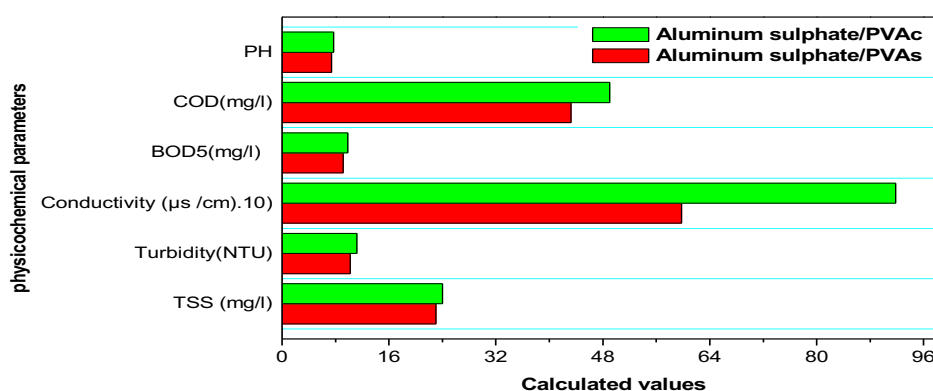


Figure 6: Influences of couples on the reduction of physico-chemical parameters.

The comparative results of the two pairs of aluminum sulphate/PVAc and aluminum sulphate/PVAs showed us a very significant effect on the reduction of the pollutant load. In fact, treatment with aluminum sulphate/PVAs was able to eliminate 96.18% for suspended solids, 98.35% turbidity, 98.94% conductivity (µs/cm), 98.50% of demand biochemical oxygen and 98.48% of the chemical oxygen demand. However, treatment with aluminum sulphate/PVAc, we obtained a 95.83% removal for suspended solids, 98.17% for turbidity 67.57% of conductivity (µs/cm), 98.48% of the biochemical oxygen demand and 98.38% for the chemical oxygen demand.

Conclusion

This work aims to treat liquid waste from hot dip galvanizing by the combined process of coagulation / flocculation. The results obtained in this work show that:

The maximum reduction of the degree of pollution of the studied parameters (the TSS, the BOD₅ the COD, the turbidity, the conductivity) situate in the case of use the couple aluminum sulphate/PVAs such as:

Suspended solids 96.18%, turbidity 98.35%, Conductivity (µs/cm) 98.94% chemical oxygen demand 98.38% and biochemical oxygen demand 98.50%.

However, in the case of using the aluminum sulphate/PVAc, we obtained an elimination of 95.83% for suspended solids, 98.17% for turbidity 67.57% for conductivity (µs/cm), 98.48% for chemical oxygen demand and 98.48% for biochemical oxygen demand. This is probably due to the adjuvant for stabilizing commercial PVAc.

In addition, the results obtained by the aluminum sulphate/PVAs couple are more interesting than those found by the reference torque used in the galvanizing industrial unit, namely the lime/ferrocryl[®]8723[16]. This is probably due to the nature and chemical structure.

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