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Optimization of the coagulation/flocculation process for the treatment of industrial wastewater from the hot dip galvanizing of steel

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Abstract
In this study, the treatment of wastewater from industry galvanizing was made by the process of coagulation/flocculation with a Jar-test. The optimization process coagulation/flocculation shows that the optimized parameters (conditions of treatment, sampling of raw water, the doses of coagulants and flocculant used) have a significant effect on the performance of this process. When treating water from galvanizing, we achieved significant returns on the disposal of polluting matter, namely: 98.24% for turbidity, 97.75% for chemical oxygen demand (COD), 97.02% for total suspended solids (TSS), 97.04% for zinc and 94.4% for iron, while using a new pair coagulant/flocculant is aluminium sulphate/Ferrocryl®8723.

Keywords: Coagulation/flocculation, Jar-test, treatment, wastewater, turbidity, COD, TSS, zinc and iron.

1. Introduction
The technique of hot-dip galvanizing is one of the techniques mostly used in metallurgical industries. It helps strengthen a piece of steel with zinc and protective coating to give the characteristics of the adhesion, the impermeability and the mechanical resistance. This technique requires a very large amount of water during its stages, which generates a large volume of wastewater loaded with the total suspended solids [1] and heavy metals such as Cd, Cr, Cu, Ni and Zn [2-3] which are harmful to health and the environment. To treat this industrial wastewater, several types of treatments have been used; we can mention a few methods such as physicochemical treatment techniques microfiltration (MF), ultrafiltration (UF), reverse osmosis (RO), nanofiltration (NF) [4-5-6] and complexation with benzimidazole derivatives [7], chelating [8] and polyelectrolytes [9], etc. The physicochemical treatment processes such as coagulation/flocculation [10] are suitable methods to reduce colloidal materials [11]. 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 reactives in the aqueous dispersals in order to assemble larger aggregates. The most commonly used coagulants are lime ($Ca(OH)_2$), aluminum salts ($Al_2(SO_4)_3$ and $AlCl_3$) and iron salts ($FeCl_3$ and $Fe_2(SO_4)_3$) [12], 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 **[**13**]**, anionic polyacrylamides, cationic, polyacrylic acid and polyvinyl alcohol [14], etc.
The objective of this study is to treat industrial wastewater in order to reduce pollutants and levels of some heavy metals, namely zinc and iron. At first, we optimized the dose of coagulants and flocculant used, and second, we evaluated the purifying power of a new coagulant other than that, the aluminum sulphate ($Al_2(SO_4)_3.18H_2O$) with respect to the lime ($Ca(OH)_2$), usually used in this galvanizing plant.

2. Materials and methods
2.1. Wastewater
The experimental study was conducted using wastewater of the Galvacier Company (city of Kenitra, Morocco). Samples of the water were taken from three different points of the treatment plant of the company, which are successively input, inside and out of the station, in flasks of one-liter capacity, based on high density polyethylene (hdPE), for 8 hours daily. The characterization of these waters has been carried out for a month to

ensure changes in the composition of the effluent; they change every day according to the percentage of the constituents of the galvanizing bath.

2.2. Coagulants/flocculant

The coagulants used in this work processes coagulation/flocculation, are lime ($Ca(OH)_2$) of 97% purity and aluminum sulphate ($Al_2(SO_4)_3.18H_2O$) with a purity of 99 %. The flocculant used for flocculation is the trade name Ferrocryl®8723 powder with a purity of 98%, is the copo - acrylamide - acrylic acid whose chemical formula $(C_3H_5NO.C_3H_4O_2)_n$ and the molecular weight between 11.10^6 and 12.10^6 g/mol, ionic and anionic character is provided by Henkel Metallchemie Company.

2.3. Optimization of the process of the coagulation /flocculation

2.3.1. Measuring the pH of the preparation after sample pretreatment by coagulation/flocculation

The wastewater treatment by the process of coagulation/flocculation was realized by means of a system Jar-test (ISCO Model RPM/OPM). The solutions of the lime and the Ferrocryl®8723 were successively prepared for mass concentration 40g/l and 3g/l. Wastewater samples taken directly from the input of the wastewater treatment plant (WWTP) in 4 beakers are filled with a capacity of one liter, after adjusting their pH values to 6, 7, 8 and 9 with lime which in this case the coagulant used. The samples obtained were subjected to oxidation by H_2O_2. The flocculation process was conducted for 3 min with a stirring speed of 200 rpm estimated, in which were added 10 ml of the previously prepared flocculant to each beaker and then decreases the speed of agitation at 20 rpm for 5 min. Before measuring the pH of each preparation, we decanted hang 30 min.

2.3.2. Optimization of the dose of the flocculant (Ferrocryl®8723)

On the one hand, the optimization of the dose of the used flocculant (Ferrocryl®8723) was performed at the pH optimized to 8 and increasing the doses of the flocculant of mass percentage going from 0% to 0.5% which method is described by specifications processing wastewater treatment plant. Moreover, the solutions of the Ferrocryl®8723 were prepared in the following concentrations by mass successively: 1g/l, 2g/l, 3g/l, 4g/l and 5g/l. In the end, we made the flocculation of our samples (6 beakers liter volume) with a speed of 20 rpm for 3 min. As a result, 10 ml of each dose of flocculant solutions prepared previously were successively added to each beaker other than the witness. After stirring for 5 min with the speed of 20 rpm, the samples were left to settle for 30 min to remove the supernatant.

2.3.3. Benchmarking power coagulant lime (WWTP) and aluminum sulphate

In order to compare the treatment performance of aluminum sulphate ($Al_2(SO_4)_3$.18H2O) compared to lime used at the station, we proceeded to the coagulation of our samples consisting of one liter of wastewater collected at the entrance of the station whose pH was previously adjusted to 8 and subsequently oxidized by H_2O_2 with both coagulants with a mass concentration of 40g/l. While Ferrocryl®8723 has flocculant was added to the previous preparations with a mass concentration of 5g/l preparations obtained are then left to settle before taking measurements of the following parameters: pH, COD, TSS, turbidity and levels of zinc and iron.

3. Results and discussion

3.1. Evaluation parameters of wastewater pollution of the WWTP

The Table 1 summarizes the average of the physical, chemical and physico-chemical wastewater exploited in this study taken from three different points.

Table 1: The average value of physical, chemical and physico-chemical wastewater collected at three different points.

Characteristics	Features the WWTP	Entrance the WWTP	Outlet of the WWTP
pH	4.67	6.71	6.67
Temperature (°C)	20	24	27
TSS (mg/l)	671	-	615
Turbidity [NTU]	522	-	40.16
COD (mg/l)	1820	-	1090
Iron (ppm)	6.25	-	4.02
Zinc (ppm)	6.75	-	4.67
Q (m^3/h)	11.4	-	11

3.2. Optimization the pH of the flocculation

The measurements on the pH (raw and treated water), the time flocks formation, the floc shape and the clarification and/or the quality of treated water are shown in Table 2.

Table 2: Characteristics of the water treated by the lime ($Ca(OH)_2$) according to the pH.

N° of container	pH of the raw water	Time (min) flocs formation	pH of the treated water	Form the flocs	Quality float
container 1	6	17	6,8	small	disorder
container 2	7	14	7,3	small	disorder
container 3	8	8	7,6	high	clear
container 4	9	10	8,1	high	clear

The results obtained in Table 2 shows that the formation of the flocs is very fast with the optimum pH at 8 and that the combination of the lime and the Ferrocryl®8723 is less advantageous in the pH higher or lower than this value. As a smooth process physicochemical treatment by coagulation/flocculation proved closely related to the pH of the wastewater from the hot dip galvanized steel.

3.3. Optimization of the dose of the flocculant Ferrocryl®8723)

The results of analysis of the physico-chemical characteristics of the samples of water treated according to the increasing doses of the flocculant Ferrocryl®8723 are represented in the figures below:

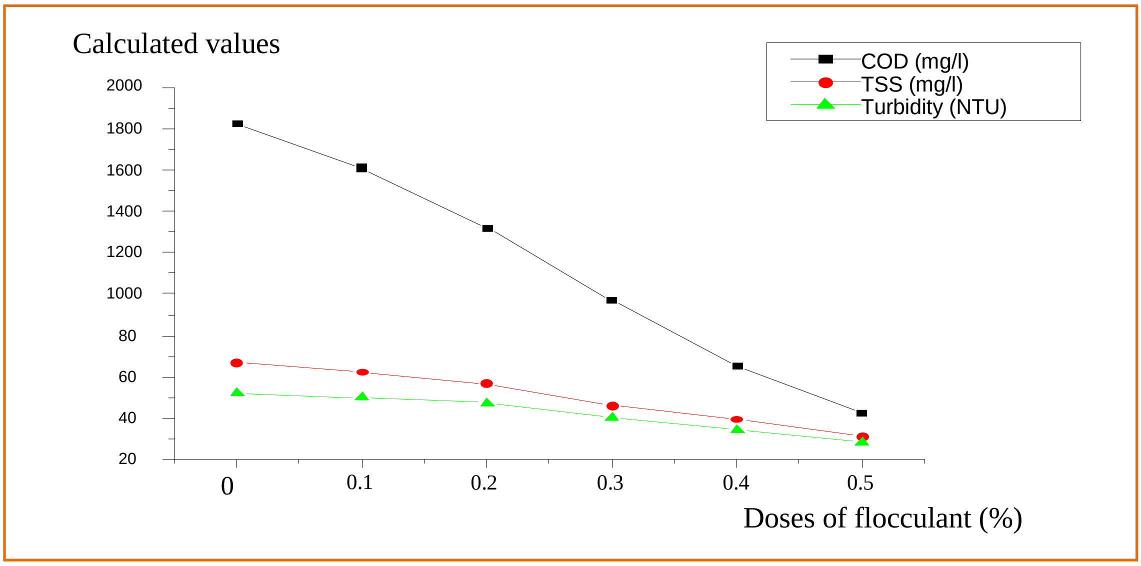

Figure 1: Variation of the DCO, the TSS and the turbidity following the doses of the flocculant.

According to the curves of the Figure 1, we notice that:

- ✓ The COD of the treated water decreases once the concentration of flocculant increases. Indeed, the COD before the treatment was important with the order of 1820 mg/l. This is due to the excessive load of raw water of oxidizable organic matters. The COD becomes more and weaker until it reaches a value of 423 mg/l for a dose of the flocculant is 0.5%. Beyond 0.5%, the solution becomes disordered, which requires the necessity of limiting itself to the percentages varying between 0 and 0.5%.
- ✓ The results of analysis obtained also showed a strong presence of TSS and of the turbidity in treated waters which decrease as the concentration flocculant increases. The mass concentration of TSS reached a minimum of 314 mg/l and the registered turbidity equals to 286 NTU for an optimal dose of the flocculant of 0.5%.

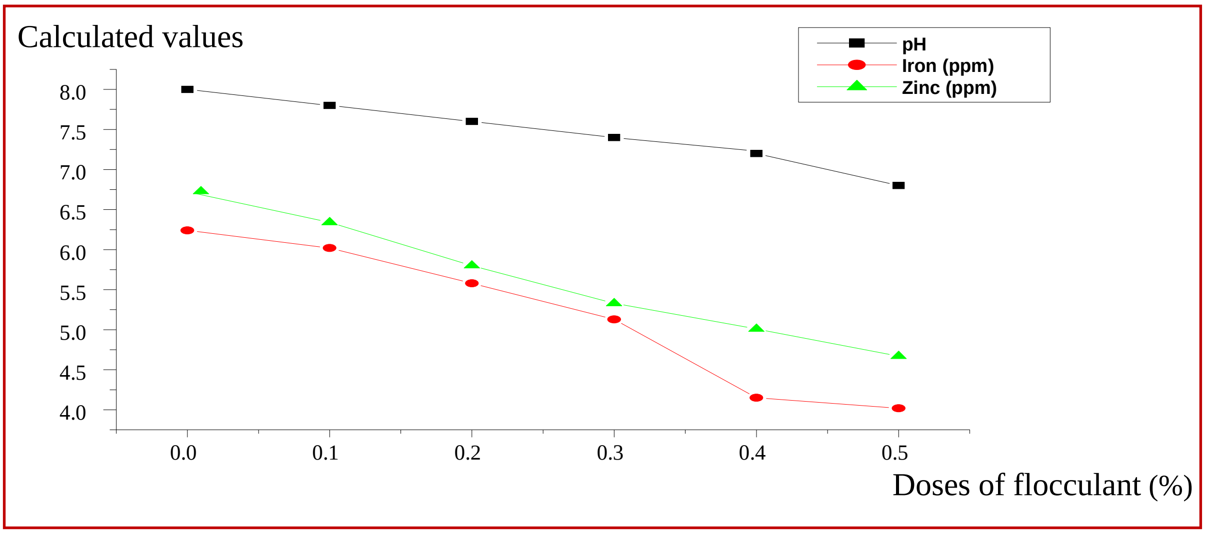

Figure 2: Variation of pH, levels of the zinc and the iron according to the percentages of the flocculant.

From the curves illustrated in Figure 2, we notice that the progressive increase of the doses of the applied flocculant decreases slightly the pH of treated waters, while staying in a more or less neutral pH, such that the pH values were recorded according to respectively increasing doses of flocculant Ferrocryl®8723 in 8, 7.8, 7.6, 7.4, 7.2 and 6.7. The analysis of the contents in zinc and in iron of treated waters shows that they decrease in a progressive way to values of 4.02 ppm for iron and in 4.67 ppm for zinc.
From the tests of Jar-test, the raw water and analysis of the results, the optimal dose of Ferrocryl®8723 to remove as much of the organic matter, total suspended solids and turbidity was obtained at 0.5%.

3.3. Evaluation of the power coagulation of the aluminum sulphate
3.3.1. Results of treatment by aluminum sulphate
The results of analysis of the treated water by the aluminum sulphate grouped in Table 3.

Table 3: Characteristics physico-chemical of the water treated by the aluminum sulphate.

Parameters	COD (mg/l)	TSS (mg/l)	Turbidity (NTU)	[Iron] (ppm)	[Zinc] (ppm)	pH
Initial values at the entrance to the WWTP	1820	671	522	6.25	6.75	4.67
Measured values	41	20	9.2	0.35	0.2	7.5

✓ *The COD*
After treating the wastewater resulting from the hot galvanization of the steel by means of the coagulant of aluminum sulphate, there was a considerable decrease of the COD. It went beyond 1820 mg/l in raw waters in a value of 41 mg/l in the treated water, with an important dejection of the organic matters (97.75%), which reveals the efficiency of our treatment by the aluminum sulphate.
✓ *The TSS and the turbidity*
With regard to the results indicated in Table 3, suspending materials and turbidity showed a remarkable decrease after the treatment by this type of coagulant. The matters in suspension moved from the value of 671mg/l in untreated waters to the value of 20 mg/l in the water treated by the aluminum of sulphate with a rate of registered dejection of 97.02%. The turbidity also moved at 522 NTU in raw waters in a value of 9.2NTU with a rate of diminution of 98.24%.
✓ *The contents in zinc and in iron*
The sulfate of aluminum revealed a perfect haste of zinc and iron. Indeed, the analysis of these metallic tracks in the treated water showed that these find themselves with percentages of dejection registered at the 97.04% value for zinc and 94.4 % for iron.
✓ *The pH*
The pH registered in the end of wastewater treatment by the sulfate of alumina is more or less neutral (7.5).

According to these obtained results based on the process of coagulation/flocculation ($Al_2(SO_4)_3.18H_2O$/Ferrocryl®8723) by the test of Jar-test of the raw water stemming from the industrial galvanization showed that:

- The optimal dose of Ferrocryl®8723 to eliminate the maximum of COD, of TSS and of the turbidity is of 5g/l that is 0.5%.
- The combination between aluminum sulphate and the Ferrocryl®8723 gave power in the elimination of a big part of the polluting material.

3.3.2. Comparison of the purifying performances of the applied coagulating agents

The results of the comparison of the purifying performances of aluminum sulphate ($Al_2(SO_4)_3.18H_2O$/Ferrocryl®8723) and some lime ($Ca(OH)_2$/Ferrocryl®8723) are represented in the Figure 3:

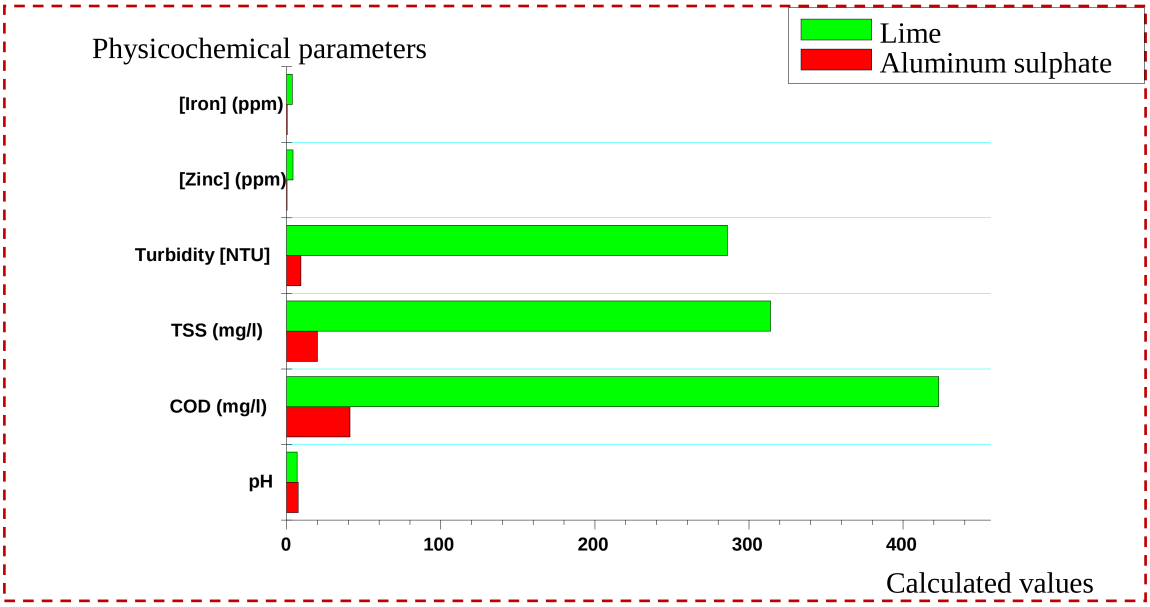

Figure 3: Comparison of the power purification of the coagulating agents in the presence of the same mass quantity of the Ferrocryl®8723.

The comparison of the purifying power of the used coagulants shows that there is a very significant effect on the elimination of the levels of pollution by the couple aluminum sulphate/Ferrocryl®8723, contrary to that of lime/Ferrocryl®8723. Indeed, the treatment by the aluminum sulphate was able to eliminate 97.02% of suspension materials, 98.24% of the turbidity and showed a rather important dejection for the chemical oxygen demand (97.75%). The sulfate of alumina also revealed a perfect haste of the zinc and the iron found in the treated water with the following rates of dejection: 97.04% for the zinc and 94.4% for the iron. However, the treatment by the lime as a regulator of the pH and coagulating agent is less advantageous. The registered dejections for the estimated parameters of pollution are 53.2% for suspension materials, 76.76% for the chemical oxygen demand, 45.21% for the turbidity, 35.68% for the iron and 30.81% for the zinc. This is probably due to the nature and the chemical structure, as well as the size grading of used coagulants: the sulfate of alumina and the lime, on one hand. As, for the addition of polyelectrolyte (Ferrocryl®8723) believes in a meaningful way the elimination of pollutant rate synergy of attraction between the latter and the flocculant charge used.

Conclusion

This work aims at treating the wastewater resulting from the hot galvanization of the steel and optimizing the process of coagulation/flocculation applied for this treatment.

Indeed, we managed at first to treat this wastewater by the process of the coagulation/flocculation by means of a system Jar-test and to optimize the doses of coagulants (aluminum sulphate and lime) and of flocculant (Ferrocryl®8723) and consequently the pH of the wastewater to be treated.

According to the obtained results we conclude that:

- ✓ The pH is an essential factor which it is necessary to take into account for the good progress of the process of coagulation/flocculation at the level of the water-treatment plant of the Galvacier Company.
- ✓ The chemical nature of used coagulants plays very important roles in the elimination of the polluting materials.
- ✓ The optimal dose of the flocculant (Ferrocryl®8723) plays an essential role in the agglomeration of the destabilized materials.
- ✓ The treatment by the sulfate of alumina ends in convincing and more advantageous results than that used by the lime.
- ✓ At the end, the change of the chemical nature of the polyelectrolyte stays one of our perspectives.

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