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## Synthesis, modification by epichlorohydrin and characterization of a natural polyelectrolyte polymer and its application in the treatment of hot dip galvanizing water by coagulation/flocculation

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### Keywords

Coagulation/flocculation, polyelectrolyte, polymer, hot dip galvanizing, chitosan (S), chitosan-ECH, epichlorohydrin (ECH).

### Abstract

The purpose of this work is to synthesize and modify by epichlorohydrin (ECH) a natural polyelectrolyte chitosan. Its purpose is also the treatment of liquid effluents from hot-dip galvanizing, where the treatment is based on the coagulation/flocculation process. The synthesized and modified polymer was characterized by Fourier Transform Infrared Spectroscopy and Polarizing Optical Microscope. The result obtained concerning the microstructural characterization confirms the structure of chitosan<sub>(S)</sub> and chitosan-epichlorohydrin.

The treatment of effluent samples by means of chitosan<sub>(S)</sub> and chitosan-ECH allowed us to obtain interesting values concerning the physicochemical parameters.

These results obtained are translated into minimum values of the physical-chemical parameters. Indeed, treatment with lime/chitosan-ECH, could remove of 97.30% suspended solids; 99.20% of chemical oxygen demand; 98.45% of biochemical oxygen demand; 88.76% zinc ion and 83.68% copper ion. However treatment with lime/chitosan<sub>(S)</sub> we obtained only a removal of 97% suspended solids; 99% of chemical oxygen demand; 98.31% of biochemical oxygen demand; 78.88% of zinc ion and 72.64% of copper ion.

## 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, Cu, Ni and Zn

[2] 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), nano filtration (NF) [3-4] and polyelectrolytes [5], etc. The physicochemical treatment processes such as adsorption [5-6] coagulation/flocculation [6-7] are suitable methods to reduce colloidal materials [8]. 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 ( $\text{Ca}(\text{OH})_2$ ) [9], 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 [10], anionic polyacrylamides, cationic, polyacrylic acid and polyvinyl alcohol [11] and chitosan[12] 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 flocculants used, and second, we evaluated the purifying power of a new flocculants other than that, the chitosan<sub>(S)</sub> and chitosan-ECH.

## **2. Materials and experimental 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. Cross linking and coagulation agent**

During this work, the materials used is epichlorohydrin crosslinking agent, have been supplied by Aldrich Chemical Co. and concerning the coagulation/flocculation process of reference, the initial coagulant used is lime ( $\text{Ca}(\text{OH})_2$ ) of 97% purity.

### **2.3. Preparation of chitosan**

Preparation of chitosan is simply deacetylation of chitin in alkaline medium.

In order to prepare the chitin, we started by washing, drying and grinding the fish scales and then treated 100g of the latter with 1L of 2N hydrochloric acid for 5h. Then, we washed and filtered residues and attacked these residues with 1L of sodium hydroxide (10%) in a water bath for 4h. Afterwards, we filtered and washed chitin with distilled water, ethanol and ether. Finally, we dried the chitin in the oven at 40°C.

To obtain chitosan we treated the chitin with sodium hydroxide (50%) in a water bath for about 4 hours. Then we filtered and washed chitosan to neutral pH; lyophilization of chitosan. The structure illustrated in Fig.1.

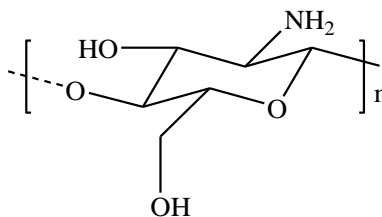


Fig.1. chemical structure of chitosan

## 2.4. Preparation of chitosan-epichlorohydrin

### 2.4.1. Chitosan solution

We introduced a mass of 5g of chitosan in 250 ml of distilled water and then we carried out the reaction of dissolution of chitosan by the addition of a volume of 2.9ml of acetic acid (99%) then we maintained the mixture thus obtained with stirring (600 rpm) until a well homogeneous gel.

### 2.4.2. Chitosan-ECH

We mixed the gel obtained after dissolving the chitosan with a volume of epichlorohydrin, and then we kept the mixture thus obtained under magnetic stirring at 50°C for 4 hours, then we added a trim ethylamine base to the reaction mixture with magnetic stirring for 3 hours at 40°C. The solvent is then removed using the rotary evaporator. Finally, we got a raw viscous product. The latter was treated with a solvent/non-solvent set by the solubilization/precipitation technique in order to obtain the purified final product. The structure illustrated in Fig.2.

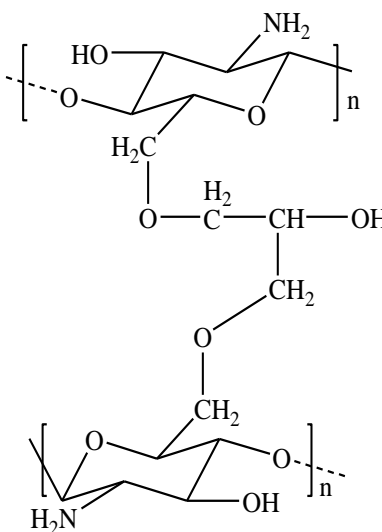


Fig.2. chemical structure of chitosan-ECH

## 2.5. Optimization of the process of the coagulation/flocculation

### 2.5.1. Optimization of samples pH

The wastewater treatment by the coagulation / flocculation process was conducted using a Jar test (ISCO Model RPM/PMS). Aqueous solutions of the used coagulants and flocculants were successively prepared at a concentration of 0.2g/L for the lime and 0.2g/L for the chitosan (s) and chitosan-ECH flocculants. The samples were taken downstream and upstream of the station and filled into 4 beakers having a capacity of one liter after adjusting their pH to the values 6, 7, 8 and 9 with lime which is in this case the used coagulant. The obtained samples were subjected to

oxidation with  $\text{H}_2\text{O}_2$ . The flocculation process was conducted for 3 min with a stirring speed estimated by 200tr/min, during which we added 10 ml of the flocculant previously prepared in each beaker, and then reduced the stirring speed to 20TR/min for 5 min. Before measuring the pH of each preparation, we decanted it for 30min.

#### **2.5.2. Optimization of the Chitosan<sub>(S)</sub> and Chitosan-ECH flocculants dose**

On the one hand, the optimization of the flocculant dose of chitosan<sub>(S)</sub> and that of chitosan-ECH was carried out at the pH optimized at 8 and at the increasing doses of the percentage weight flocculants from 0.1% to 0.5% with the method described by the data sheet of wastewater treatment of the neutralization station. On the other hand, we diluted successively 0.1g/L, 0.2g/L, 0.3g/L, 0.4 g/L and 0.5g/L of chitosan<sub>(S)</sub> and chitosan-ECH. In the end, we carried out the flocculation of our samples (in 5 beakers whose volume is 1 liter) with a speed of 200tr/min for 3 min. Next, 10mL of each dose of the flocculant solutions previously prepared were added sequentially to each beaker other than the control. After stirring for 5min with speed of 20tr/min, the samples were left to settle for 30 minutes to eliminate the float.

#### **2.6. Measurement of flocculant power chitosan<sub>(S)</sub> and chitosan-ECH**

In order to compare the performance epurative chitosan-ECH compared to chitosan<sub>(S)</sub>, we conducted flocculation of our samples consist of a liter of waste water collected at the entrance of the station whose pH been previously adjusted to 8 and subsequently oxidized with  $\text{H}_2\text{O}_2$  using these two flocculants with a mass concentration of 0.2g/L. While the coagulant lime was added to the fore going preparations with a mass concentration of 0.4g/L. The preparations obtained are then left to settle before making measurements of the following parameters:  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$ .

#### **2.7. Characterization and analysis**

##### **2.7.1. Infrared spectroscopy**

Fourier Transform Infrared Spectroscopy, SHIMADZU) FTIR8201PC whose frequency range is between 500 and 4000  $\text{cm}^{-1}$ , was used to determine the functional groups responsible for the adsorption of metals.

##### **2.7.2. Polarizing optical microscopy**

Polarizing optical microscopy is an optical instrument with an objective and an eyepiece that magnifies the image of a small object and separates the details of the image so that it can be seen by human eye.

##### **2.7.3. Metals Analysis by FAAS**

Water samples were analyzed for metals using Flame Atomic Absorption Spectroscopy (FAAS). Operational parameters such as wavelength, energy, lamp and burner alignment and slit width for  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  were adjusted according to the working standards.

### **3. Results and discussion**

#### **3.1. Characteristic of the physical-chemical parameters of the hot-dip galvanizing rejects used in this study**

Table 1 summarizes the average values the effluent physical-chemical parameters used in this study.

**Table. 1** The average values of the physical-chemical parameters of the liquid effluents taken at two different points and limit values retained.

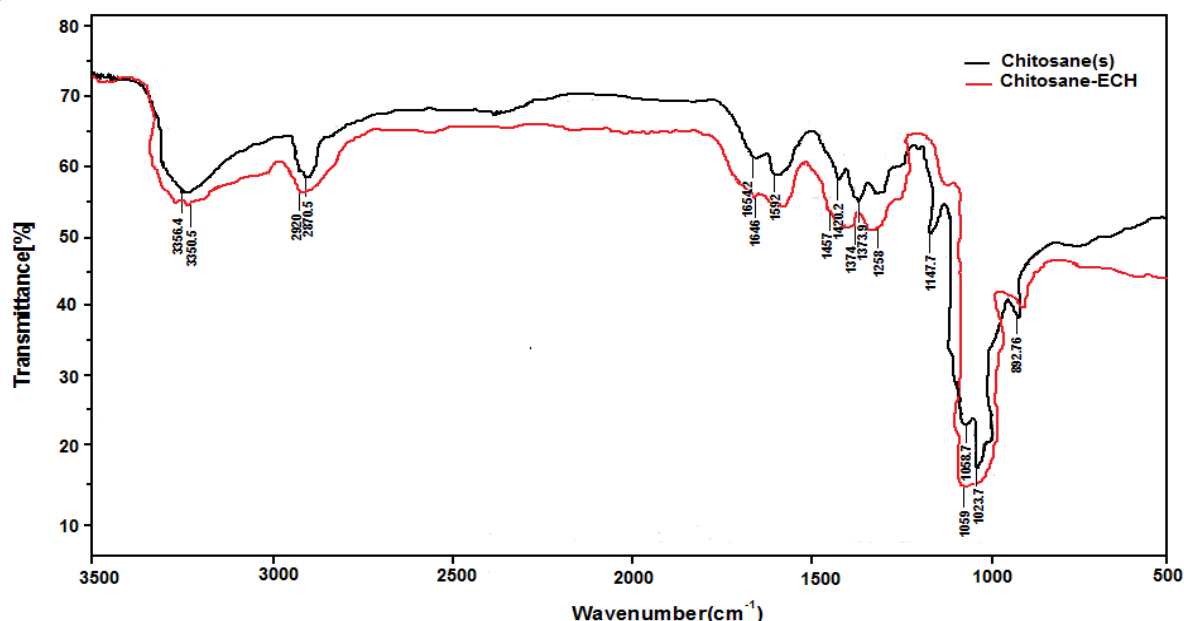
Analyzed Parameters	Measured values downstream of the neutralization station	Measured values upstream of the neutralization station	Limit values retained[13]
pH	4.01	3.56	6-9
Zn(mg/L)	11.75	11.19	10
Cu(mg/L)	6,25	6.12	4
TSS(mg/L)	570	562	50
COD(mgO <sub>2</sub> /L)	2862	2132	500
BO <sub>5</sub> D(mgO <sub>2</sub> /L)	602	532	100

From the Table 1 we noticed that the liquid effluents of hot-dip galvanizing provide values of major physical-chemical parameters that relatively exceed the general values limits for the "hot-dip galvanizing" branch [13].

### 3.2. Characterization

#### 3.2.1. Infrared spectroscopy

Fourier transforms infrared spectroscopy analysis of chitosan, and the main bands are shown in Fig.3.

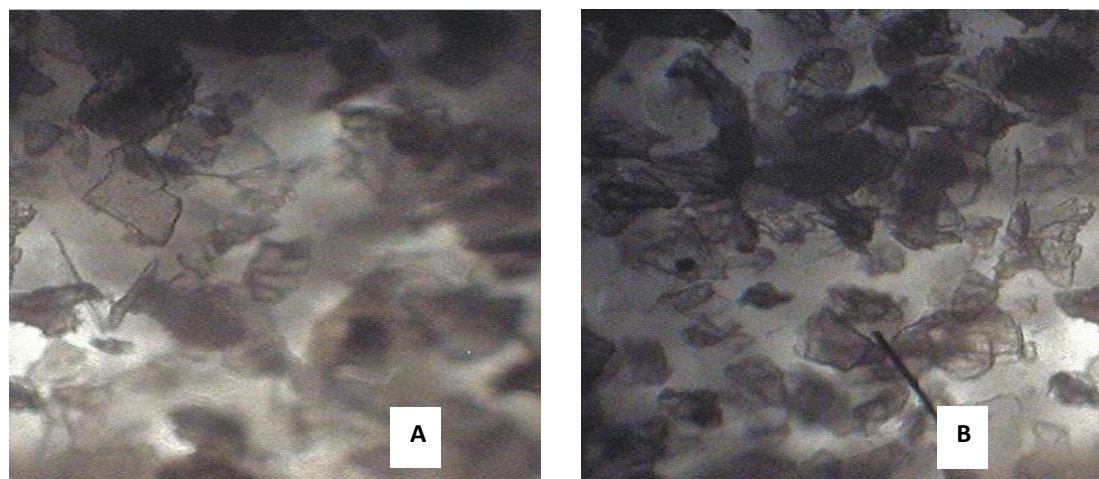
**Fig. 3.** IRTF Spectrum of Chitosan<sub>(s)</sub> and Chitosan-ECH.

From Fig.3 we found that the main peaks found at  $3356.4\text{cm}^{-1}$  for chitosan beads were assigned to the stretching vibration of OH and NH groups. The peak at  $2870.5\text{cm}^{-1}$  was due to stretching of the CH vibration.  $-\text{CONH}_2$  stretching in the secondary amide groups was observed at  $1654.2\text{cm}^{-1}$  while the peak at  $1592\text{cm}^{-1}$  was attributed to NH bending in the primary amine ( $\text{NH}_2$ ) groups. The deformation vibration of NH in  $\text{NH}_2$  was represented by the peak at  $1420.2\text{cm}^{-1}$ . Other peaks observed chitosan beads were found at  $1373.9\text{cm}^{-1}$  stretching vibration of ( $-\text{CN}$ ),  $1147.7\text{cm}^{-1}$  asymmetric stretching vibration of ( $\text{COC}$ ),  $1058.7\text{cm}^{-1}$  vibration of symmetric stretching ( $\text{COC}$ ) and  $1023.7\text{cm}^{-1}$  stretching vibration ( $\text{CO}$  in  $\text{COH}$ ). The  $892.76\text{cm}^{-1}$  band was assigned to the

absorption peaks of  $\alpha$ -(1, 4) glycoside in chitosan. These results confirm that the experimentally prepared chitosan was identical to that of the chitosan structure [14].

On the spectrum of the Chitosan-ECH mixture, the peak at  $3350.5\text{cm}^{-1}$  attributed to the peak of vibration absorption by stretching -OH appeared, whereas it was shifted to a lower wavenumber, which indicates that the hydroxyl groups of the chitosan molecules are involved in the crosslinking reaction. The peak that appears at  $1457\text{cm}^{-1}$ , corresponds to the deformation of  $\text{CH}_2$ . The peak at  $2920\text{cm}^{-1}$  was due to stretching of the C-H vibration. The peak at  $1646\text{cm}^{-1}$  corresponds to the vibration of valence C=O. The  $1374\text{cm}^{-1}$  band was assigned to the elongation vibration of the C-N bond. The band at  $1258\text{cm}^{-1}$  was attributed to the (C-O-C) elongation vibration. It can be seen that the adsorption peak of the hydroxyl group (C-OH) on the chitosan molecules at  $1059\text{cm}^{-1}$  also shifted, which showed that the hydroxyl (C-OH) group of the chitosan molecules reacted with epichlorohydrin.

### 3.2.2. Polarizing optical microscopy



**Fig.4. Morphology of chitosan<sub>(s)</sub> (A) and chitosan-ECH (B) seen by polarizing optical microscopy at x100**

According to this figure, it was noticed that extracted chitosan exhibited flake layers, and in the same sense, it was observed an increase in pores density in some areas, as in the studies of Kucukgulmez and al [15] which simulated this work. While the cross-linked chitosan surface was very rough. There were many particles on the surface of cross-linked chitosan, which demonstrated that cross-linked chitosan is a new polyelectrolyte.

## 3.3 Optimization

### 3.3.1. pH Optimization

The measurements obtained concerning the pH (optimized and treated water), the formation time of the flocs, the shape of the flocs and the clarification and/or quality of the treated water are collated in the table.



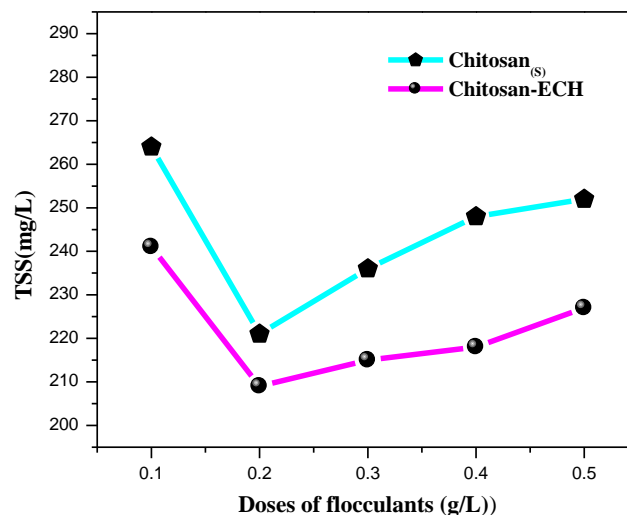
**Table 2 Characteristics of the effluents treated by the couples lime/chitosane<sub>(s)</sub> and lime/chitosane-ECH**

N° Container	1	2	3	4	
Characteristics					
Optimized PH of the raw water	6	7	8	9	Chitosane <sub>(s)</sub>
					Chitosane-ECH
PH of the treated water	6.07	6.10	7.22	7.17	Chitosane <sub>(s)</sub>
	6.56	6.84	7.55	7.14	Chitosane-ECH
Form of the flocs	small	small	Average	Average	Chitosane <sub>(s)</sub>
	Average	small	high	high	Chitosane-ECH
Time( min )flocs formation	15	13	12.45	9.5	Chitosane <sub>(s)</sub>
	16.15	15	14.22	12	Chitosane-ECH
Form the flocs Quality of float	disorder	clear	clear	clear	Chitosane <sub>(s)</sub>
	clear	clear	clear	clear	Chitosane-ECH

From the values shown in the table, we have shown that the time of flocs formation is very fast at pH to 9 for chitosan<sub>(s)</sub> and chitosan-ECH. Apart from this value and for pH values of less than or equal to 8, treatment with lime/chitosan<sub>(s)</sub> and lime/chitosan-ECH combinations is disadvantageous

### 3.3.2. Dose Optimization of flocculants chitosan<sub>(s)</sub> and chitosan-ECH

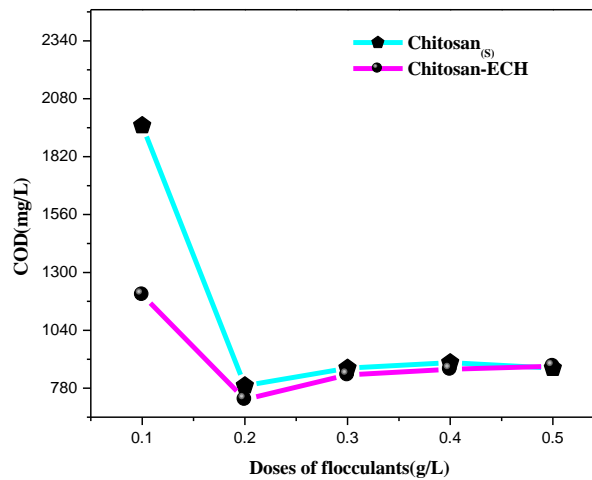
The analysis results of the physicochemical parameters of water treated by chitosan<sub>(s)</sub> and chitosan-ECH using lime as coagulant is represented in the following figures:



**Fig.5. Variation of the TSS following the doses of flocculants.**

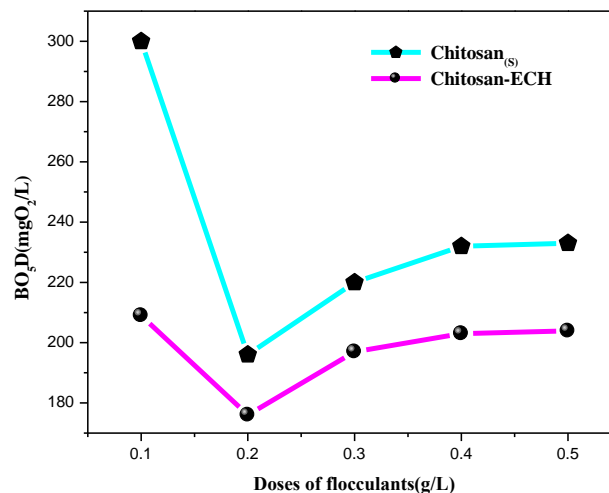
From this figure, it shows a strong presence of TSS in the treated water that decrease progressively as the concentrations of flocculants increase. Indeed these TSS were increased from 570mg/L at

the minimum values stored in 221mg/L in the case of chitosan<sub>(S)</sub> at dose of 0.2g/L and 209mg/L for chitosan-ECH at dose of 0.2g/L.



**Fig. 6. Variation of the COD following the doses of flocculants.**

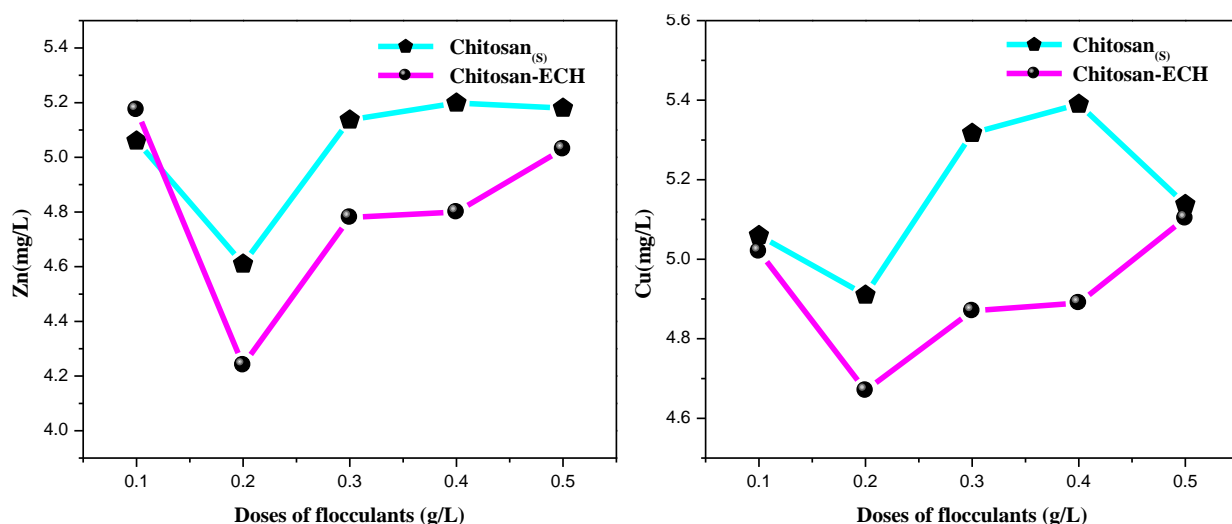
From the curve shown in Fig.6, we perceived that the effluent COD decreases progressively to constant residual values of 791; 730mg/L at a dose of 0.2g/L for both flocculants (chitosan<sub>(S)</sub> and chitosan-ECH) successively. Indeed, the COD before the treatment was important of the order of 2862mg/L.



**Fig.7. Variation of the BO<sub>5</sub>D following the doses of flocculants.**

From the figure, we found that BO<sub>5</sub>D decreased from 602mg/L to minimum values that are in the order of 220; 197mgO<sub>2</sub>/L for a dose of 0.2g/L of chitosan<sub>(S)</sub> and chitosan-ECH successively.



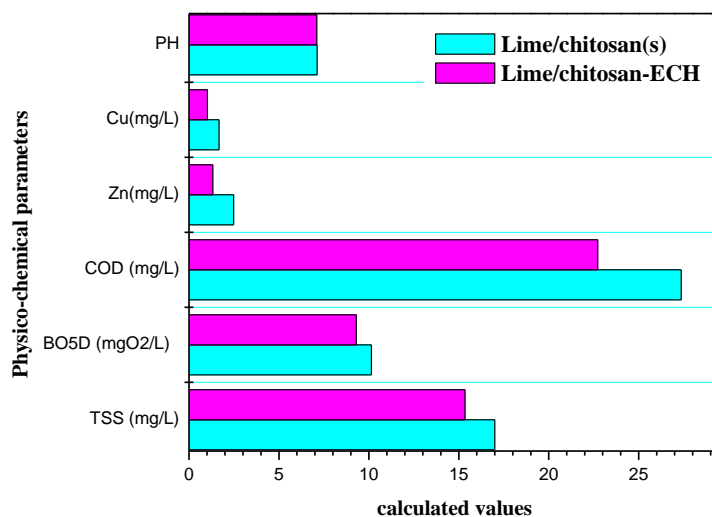


**Fig. 8. Variation of the zinc and the copper according to the dose of flocculants.**

From the curves illustrated in the figure, we have observed that the gradual increase in the doses of the flocculants applied slightly reduces the zinc and copper contents of the treated effluents, such as the Zn and Cu values, were recorded respectively in 4.61; 4.24 at dose of 0.2 g/L of chitosan<sub>(S)</sub> and 4.91; 4.67mg/L at dose of 0.2g/L chitosan-ECH.

### 3.4. Results of analysis of liquid effluents with couples lime/chitosan<sub>(S)</sub> and lime/chitosan-ECH

The effectiveness of lime/chitosan(S) and chitosan-ECH couples in for the treatment of waste water taken from hot-dip galvanizing, with their optimal doses (lime equals 0.4g/L, chitosan(S) ,chitosan-ECH equals 0.2g/L) at the optimum pH value (pH equals 8) are shown in Fig.9.



**Fig.9. Influences of couples on the reduction of physico-chemical parameters**

Results of treatment the liquid effluents by the couples used shows that there is a very significant effect on the elimination of pollution loads by the lime/chitosan-ECH compared to the lime/chitosan<sub>(S)</sub>. Indeed, treatment with lime/chitosan-ECH, could remove of 97.30% suspended solids; 99.20% of chemical oxygen demand; 98.45% of biochemical oxygen demand; 88.76% zinc

ion and 83.68% copper ion. However treatment with lime/chitosan<sub>(S)</sub> we obtained only a removal of 97% suspended solids; 99% of chemical oxygen demand; 98.31% of biochemical oxygen demand; 78.88% of zinc ion and 72.64% of copper ion. This is probably due to the nature and the chemical structure, as well as the size grading of used polyelectrolytes.

## Conclusion

This work was designed to treat waste water from the hot dip galvanizing of steel and to optimize the coagulation/flocculation process used in this treatment according to the new polyelectrolytes chitosan<sub>(S)</sub> and chitosan-ECH.

From the obtained results, we can that:

- The pH is an important factor that should be taken into account for the success of the coagulation/flocculation process in the hot dip galvanizing.
- The chemical structure of the polyelectrolyte used in the couple coagulant/flocculant is very important in removing the pollutants.
- The optimal dose of flocculants plays an essential role in the agglomeration of the destabilized materials.
- The treatment by the chitosan-ECH ends in convincing and more advantageous results than that used by the chitosan<sub>(S)</sub>.
- At the end, the change of the chemical nature of the polyelectrolyte stays one of our perspectives.

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