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Synthesis, modification and characterization of a polyelectrolyte polymer and its application in wastewater treatment by coagulation/flocculation process

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ABSTRACT: *The aim of this work is to synthesize a polyelectrolyte polymer (polyvinyl alcohol (PVA)) through radical means and vinyl acetate as a vinylic monomer followed by hydrolysis and modify the polyelectrolyte with epichlorohydrin (ECH).Its aim is also the treatment of liquid effluents from hot-dip galvanizing, where the treatment is based on the process of coagulation/flocculation.*
The synthesized and modified polymer was characterized by Fourier Transform Infrared Spectroscopy (IRFT) and Polarizing Optical Microscope. The result obtained concerning the micro structural characterization confirms the structure of polyvinyl alcohol ($PVA_{(S)}$) and polyvinyl alcohol-epichlorohydrin (PVA-ECH).
The treatment of effluent samples by means of $PVA_{(S)}$ and PVA-ECH allowed us to obtain interesting values concerning the physicochemical parameters. These results are translated into minimum values of the following parameters, 19mg/L for suspended solids, 15.25mgO_2/L for biochemical oxygen demand, 37mg/L for chemical oxygen demand, 3.07mg/L for zinc contents and 2.93mg/L for copper contents in the case of lime/$PVA_{(S)}$ and 18.78mg/L for suspended solids, 13.04mgO_2/L for biochemical oxygen demand, 30mg/L for the chemical oxygen demand, 2.62mg/L for zinc contents and 2.73mg/L for copper contents in the case of lime/PVA-ECH.
KEYWORDS *polyelectrolyte, polymer, epichlorohydrin, polyvinyl alcohol, PVA(s), PVA-ECH, coagulation/flocculation, hot-dip galvanizing, physical-chemical*

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I. INTRODUCTION

Industrial liquid effluents from the hot-dip galvanizing are in most cases handled by physicochemical processes which include the coagulation/flocculation process [1-2-3-4-5]. The latter having a wide use in the treatment of waste water loaded with inorganic micro pollutants [6] organic [7] and organometallic [8-9] are harmful to health and the environment. These are suitable methods to reduce colloidal materials [1-2-10].

Coagulation is the first step in this process of treatment of industrial waste waters. It is to neutralize or reduce electric loads and thus promote the approximation of colloidal particles [1-2-10]. The most frequently used anti-coagulants are lime ($Ca(OH)_2$) [11], aluminum salts ($Al_2(SO_4)_3$ and $AlCl_3$) and iron salts ($FeCl_3$, $Fe_2(SO_4)_3$) [12], etc. Flocculation is the process which directly follows the coagulation and it promotes the contact between the destabilized colloid particles to form agglomerates requiring flocculants such as polyacrylamides [13], anionic polyacrylamides, cationic, polyacrylic acid and/or polyvinyl alcohol [14]. However, the polyvinyl alcohol was never used in the wastewater treatment type hot dip galvanizing.

On the one hand, the objective of our work is to synthesize, to modify by epichlorohydrin (ECH) and to characterize the new polyelectrolyte which is $PVA_{(S)}$ and PVA-ECH. On the other hand, is to treat liquid effluents from hot-dip galvanizing and to optimize the coagulation/flocculation process used in this treatment according to the couples (lime $Ca(OH)_2$/$PVA_{(S)}$) and (lime $Ca(OH)_2$/PVA-ECH).

II. MATERIALS AND EXPERIMENTAL METHODS

II. 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).

II.2. Cross linking and coagulation agent

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

II. 3. Synthesis and modification of the PVA

In a bath thermostat, we placed 5g of vinyl acetate in a tube, and then we added the initiator AIBN at a temperature of 80°C. The product obtained is first dissolved in chloroform and then precipitated in methanol to remove the oligomers. The polymer obtained is recovered by filtration under vacuum and then dried at room temperature. Then we placed in a reactor with a magnetic stirrer and surmounted by a coolant 10g polyvinyl acetate and 150cm3 anhydrous methanol, then we heated the mixture to reflux of methanol (65°C) and the polymer is completely dissolved, then we introduced 4 to 5 pellets of potash and maintained the reflux 90 min, such that the reaction mixture obtained is cooled and filtered.

Finally we washed the obtained polymer with methanol and redissout hot in 37ml of water and we precipitated in 70 to 80 ml of acetone (non-solvent). Our polymer is filtered and washed with acetone and finally dried in an oven. The molecular structure of the resin thus obtained is shown in Fig.1.

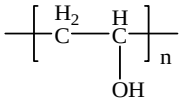

Fig.1. Chemical structure of $PVA_{(S)}$

We introduced a mass of 5g of polyvinyl alcohol in 250ml of distilled water and then we kept the mixture thus obtained with stirring (600 rpm) until a well homogeneous gel was obtained. Then we condensed the polyvinyl alcohol with an excess epichlorohydrin with magnetic stirring at 70°C for 4 hours, and then we added a tri-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 molecular structure of the resin thus obtained is shown in Fig.2.

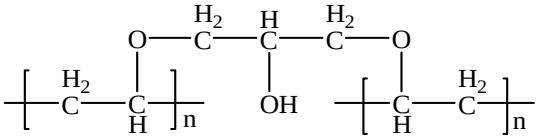

Fig.2. Chemical structure of PVA-ECH

II. 4. Characterization

II.4.1. 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.

II.4.2. Infrared spectroscopy

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

II.4.3. 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 Zn^{2+} and Cu^{2+} were adjusted according to the working standards.

II.5. Optimization of the process of the coagulation/flocculation

II.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 4g/L for the lime and 2g/L for the $PVA_{(S)}$ and PVA-ECH flocculants. The samples were taken downstream and upstream of the neutralization 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 H_2O_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 5min. Before measuring the pH of each preparation, we decanted it for 30min.

II.5.2. Optimization of the $PVA_{(S)}$ and PVA-ECH flocculants dose

On the one hand, the optimization of the flocculant dose of $PVA_{(S)}$ and that of PVA-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 1g/L, 2g/L, 3g/L, 4g/L and 5g/L of $PVA_{(S)}$ and PVA-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.

II.6. Measurement of flocculant power $PVA_{(S)}$ and PVA-ECH

In order to compare the performance epurative PVA-ECH compared to $PVA_{(S)}$, 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 H_2O_2 using these two flocculants with a mass concentration of 2g/L.While the coagulant lime was added to the fore going preparations with a mass concentration of 4g/L. The preparations obtained are then left to settle before making measurements of the following parameters: pH, temperature, COD, BO_5D, TSS, Zn^{2+} and Cu^{2+}.

III. RESULTS AND DISCUSSION

III.1. Characteristic of the physical-chemical parameters of the hot-dip galvanizing rejects

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[15]
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_2/L)	2862	2132	500
BO_5D(mgO_2/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 [15].

III.2. Characterization

III.2.1. Polarizing optical microscopy

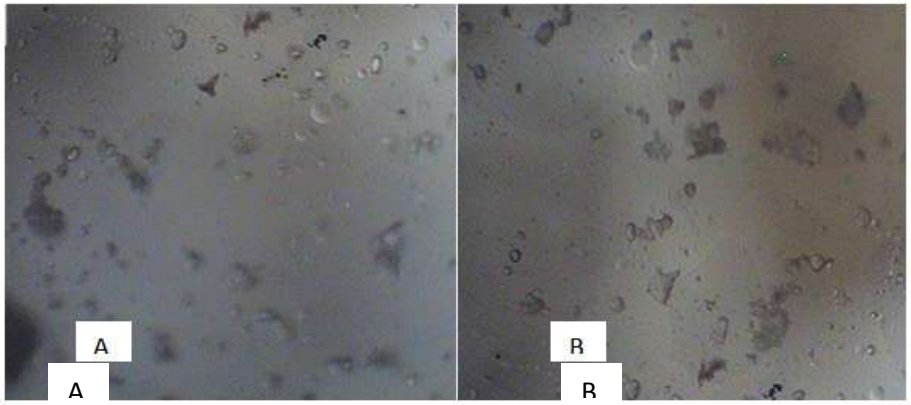

Fig.3.Morphology of $PVA_{(S)}$ (A) and PVA-ECH (B) seen by polarizing optical microscopy at (x100)

From the figure we observed that the surface of PVA-ECH(B) shows a micro porous and rough surface structure, against the surface of $PVA_{(S)}$(A) has a relatively smooth surface and therefore less porous. These illustrations can show us that indeed the PVA has been chemically modified by the cross linking agent used.

III.2.2. Infrared spectroscopy

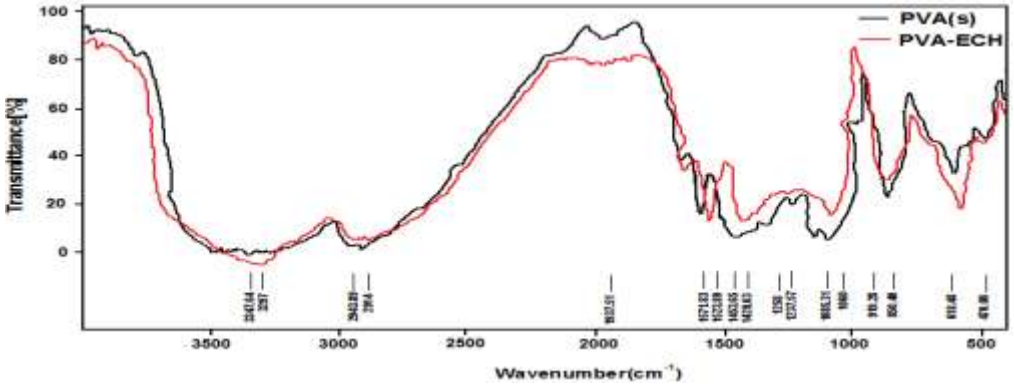

Fig.4. IRTF Spectrum of $PVA_{(S)}$ and PVA-ECH

The FTIR spectra presented in figure 4 showed us several bands among which we find the wide band on the spectrum of $PVA_{(S)}$ which appears at 3347.64cm^{-1} corresponds to the OH function, the band which is at 2943.89cm^{-1} corresponds to the CH bond, the band that exists at 1453.65cm^{-1} corresponds to the CH_2 group, the band that exists at 1085.31cm^{-1} corresponds to the C-OH bond, the band that exists at 1571.83cm^{-1} corresponds to the C-C bond. The peak at 3297cm^{-1} corresponds to the OH function is more intense than that which appears in the spectrum of $PVA_{(S)}$, which may suggest a decrease in crystallinity after modification of PVA by ECH. The peak at 2914cm^{-1} corresponds to the C-H bond. The peak that appears at 1523.89cm^{-1} corresponds to the C-C bond. The band that exists at 1420.63cm^{-1} corresponds to the C-C bond.
The intensity of the peak at 1060cm^{-1}which relates to the C-C binding in the PVA-ECH spectrum decreases, demonstrating the binding of ECH to the OH position of the PVA. The peak that appears at 1258cm^{-1} corresponds to the C-O-C bond.

III.3. PH values optimized by flocculants used

Table2. Shows the characteristics waters treated by the two flocculants $PVA_{(S)}$ and PVA-ECH.

N° Container / Characteristics	1	2	3	4		
Optimized PH of the raw water	6	7	8	9	$PVA_{(S)}$	**Flocculants**
					PVA-ECH	
PH of the treated water	6.37	6.12	7.03	7.23	$PVA_{(S)}$	
	6.74	6.74	7.75	7.54	PVA-ECH	
form des flocs	small	small	Average	Average	$PVA_{(S)}$	
	Average	small	high	high	PVA-ECH	

Tim (min) flocs formation	15	13	9.5	12.45	$PVA_{(S)}$	
	16.15	15	12	14.22	PVA-ECH	
Form the flocs Quality of float	disorder	clear	clear	clear	$PVA_{(S)}$	
	clear	clear	clear	clear	PVA-ECH	

From the values shown in Table 2, it shows that the time of the flocs formation is very fast at the optimum pH to 8 for the two flocculants used using a single coagulant which is lime. Apart from this value and for pH values above or below 8, treatment with combinations of lime/$PVA_{(S)}$ and lime/PVA-ECH are disadvantageous.

III.4. Dose Optimization of flocculants $PVA_{(S)}$ and PVA-ECH

The analysis results of the physicochemical parameters of water treated by $PVA_{(S)}$ and PVA-ECH using lime as coagulant is represented in the following figures:

✓ The variation TSS depending on the dose of flocculants $PVA_{(S)}$ and PVA-ECH is shown in figure 5.

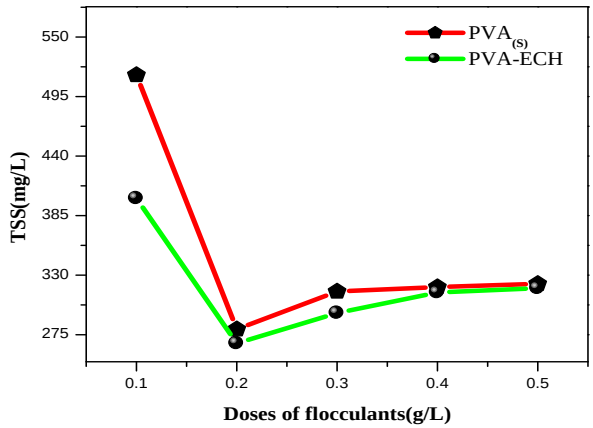

Fig.5. Evolution of the TSS of effluents treated with $PVA_{(S)}$ and PVA-ECH

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 280mg/L and 267mg/L for a dose of 0.2g/L in the case of $PVA_{(S)}$ and PVA-ECH successively.

✓ The variation of COD as a function of dose of $PVA_{(S)}$ and PVA-ECH is shown in figure 6.

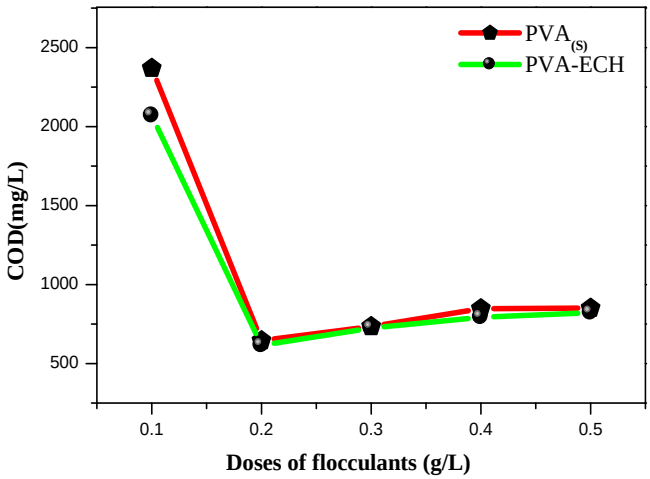

Fig.6. Variation of COD by the growth in doses of $PVA_{(S)}$ and PVA-ECH

According to the curves shown in figure 6, we have seen that the rate of the COD of the treated water decreases progressively until constant residual values of 645mg/L and 615mg/L respectively using $PVA_{(S)}$, PVA-ECH for optimum flocculant dose equal to 0.2g/L. In fact, the COD before treatment was significant in the order of 286 mg/L.

✓ The variation of BOD_5 depending on dose $PVA_{(S)}$ and PVA-ECH is shown in figure 7:

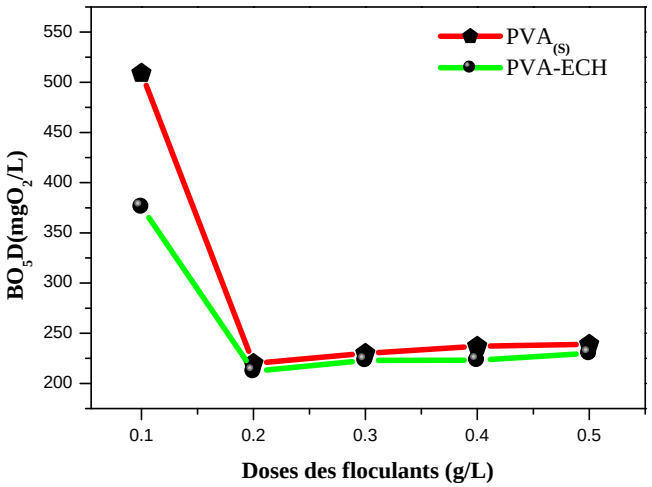

Fig.7. Variation of BO_5D based doses of flocculants

From this figure, we found that BO_5D has decreased from 602mg/L to minimum values of the order of 220; 212mgO_2/L for optimal dose of 0.2g/L the $PVA_{(S)}$ and PVA-ECH successively.

✓ Variation des ions Zn^{2+} and Cu^{2+}

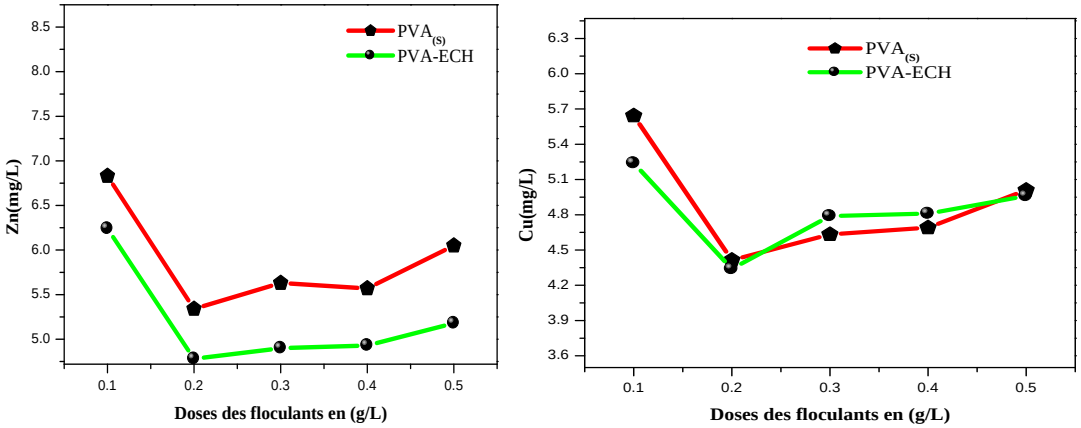

Fig.8. Variation of Zn^{2+} and Cu^{2+} based doses of flocculants

From the curves shown in Figure 8 we found that the gradual increase in flocculant doses applied, slightly decreases the zinc and copper contents of the treated effluents, such as the Zn^{2+} and Cu^{2+} values, were respectively recorded in 5.34; 4.78; and 4.414; 4.34mg/L at a dose of 0.2g/L $PVA_{(S)}$, PVA-ECH successively.

III.5. Evaluation of epurative power of flocculants used in wastewater treatment of Galvacier

III.5.1. Results of analysis of water treated with couples lime/$PVA_{(S)}$ and lime/PVA-ECH.

The physical-chemical characteristics of the treated water by the PVA(S) and PVA-ECH are recorded in table 3:

Table 3. Physical-chemical characteristics of the water treated by lime/$PVA_{(S)}$ and lime/PVA-ECH.

Couples / Parameters	Lime/$PVA_{(S)}$	Lime/PVA-ECH
TSS (mg/L)	19	18.78
BO_5D (mgO_2/L)	15.25	13.04
COD (mg/L)	37	30
Zn (mg/L)	3.07	2.62
Cu (mg/L)	2.93	2.73
PH	6.7	6.7
T (°C)	20.5	20.56
COD/BO_5D	2.42	2.30

In view of the results indicated in the table, the physicochemical parameters have experienced a remarkable decrease after the treatment of the effluents by couples lime/$PVA_{(S)}$ and lime/PVA-ECH. Such that the TSS, BO_5D, COD, Zn^{2+}, Cu^{2+}, pH and T ° passed successively at a 19mg/L, 15.25 mgO_2/L, 37mg/L, 3.07mg/L, 2.9 mg/L, 6.7, 20.5°C in the case of lime/$PVA_{(S)}$ and at a 18.78mg/L, 13.04 mgO_2/L, 30mg /L, 2.62mg/L, 2.73mg/L, 6.7, 20.56°C in the case of lime/PVA-ECH. These values are lower than those indicated in the industry-wide standard for hot dip galvanizing.

The average values of the COD/BO_5D ratio are 2.42, 2.30 respectively consistent with that of wastewater with COD/BO_5D ratio of less than3 [16]. So, we can conclude that even if the effluents of this discharge have a low organic load, it is relatively easily biodegradable.

III.5.2. Comparison of the effectiveness of applied couples

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

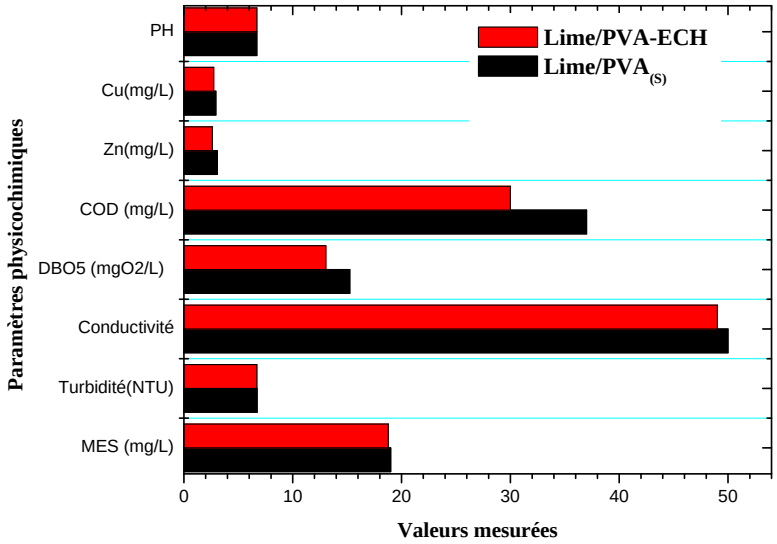

Fig.9. Performance of purifying $PVA_{(S)}$ and PVA-ECH.

Comparison of the purifying power of the couples used shows that there is a very significant effect on the elimination of pollution loads by the lime/PVA-ECH compared to the lime/$PVA_{(S)}$. Indeed, treatment with lime/$PVA_{(S)}$, could remove 96.66% suspended solids; 98.70% of the chemical oxygen demand, 97.46% of the biochemical oxygen demand; 73.87% of zinc ion and 53.12% of copper ion successively. However treatment with lime/PVA-ECH respectively we obtained only a removal of 96.70% suspended solids; 98.95% of the chemical oxygen demand, 97.83% of the biochemical oxygen demand; 77.70% zinc ion and 56.32% copper ion.

IV. 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 polyelectrolyte $PVA_{(S)}$) and PVA-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 a key role in the agglomeration of destabilized materials.
- This is the latest to show this encouraging lime/$PVA_{(S)}$ compared to lime/PVA-ECH.

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