

Treatment of hot-dip galvanization by coagulation-flocculation, adsorption and by new hybrid process coagulation-flocculation/adsorption using lime-(chitosan-epichlorohydrin)/activated carbon based on dates stones

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Received 23 April 2019,

Revised 30 Aug 2019,

Accepted 05 Feb 2020.

Abstract

In this work, we conducted a study that is to bleach wastewater loaded with ions, while using and optimizing the process of hybridized treatment of liquid effluents by of coagulation-flocculation/adsorption (CF-ADS). According to the separate optimization of flocculation processes (optimum dose of the flocculant (chitosan cross-linked by epichlorohydrin (chitosan-ECH))) and adsorption (activated carbon based on dates stones), we combined the two methods in order to increase performance fading exploited wastewater. The results of the rate of elimination separated by the methods of coagulation-flocculation, adsorption and are respectively of the order of 88.17% and 96.17% for the zinc and of the order of 83.68% and 95.4% for copper. While the results of the bleaching obtained by the hybrid method CF-ADS have shown that the bleaching rate was calculated as around 99.14% for zinc and of the order of 96.8%, for the copper, obviously very interesting with respect to the coagulation-flocculation(CF) and adsorption(ADS) used separately.

Keywords: coagulation-flocculation (CF), adsorption (ADS), chitosan-ECH, activated carbon, epichlorohydrin

1. Introduction

The technique of hot dip galvanizing is one of the most used techniques in the metallurgical industries. This technique requires a very large amount of water during its stages, which generates a considerable volume of effluents loaded with inorganic micro pollutants (heavy metals) such as Cd, Cr, Cu, Zn and Fe[1] etc... These pollutants have the ability to concentrate along the food chain and accumulate in certain organs of the human body. It is therefore essential to totally eliminate these toxic elements present in the various industrial effluents or to reduce their quantity below the admissible thresholds defined by the standards of rejections. In an attempt to solve the problem and in order to better respond to the problem raised, there are several types of treatment have been used, physical, chemical and physical-chemical processes have been widely used for the treatment of this type of pollution. In the case of physicochemical treatment, we find membrane separation techniques[2-3], among which, we can first mention the ultra filtration (UF) [4], nano-filtration (NF)[5-6] and in a second time, there are the processes of coagulation/flocculation[7-8-9] precipitation [10-11] and adsorption[12-13] on some materials are the most used and etc ... In order to improve the performance of industrial wastewater treatment, some authors have combined these treatment processes[14-15] with highlighting the adsorption/ultra filtration [16] and coagulation/flocculation/adsorption[17]... The latter method is the most commonly used for wastewater treatment because of their ease of implementation. The interest of this work is to increase the performance of wastewater loaded with inorganic micro pollutants, by using the combined coagulation-flocculation-adsorption process after optimization of each separate method, by determining the optimal doses of flocculant and adsorbent used.

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 agent, coagulant/flocculant and adsorbent

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 ($\text{Ca}(\text{OH})_2$) of 97% purity [18], chitosan-epichlorohydrin which used as a flocculant and activated carbon prepared from dates stones

2.3. Preparation of chitosan-epichlorohydrin

The cross linking of chitosan achieve in stages: the first step begins with the preparation of chitosan ($\text{chitosan}_{(S)}$) from the chitin; the second step is the preparation of a $\text{chitosan}_{(S)}$ gel, the third step, and focus on obtaining chitosan-epichlorohydrin (chitosan-ECH):

2.3.1. Preparation of chitosan from the chitin

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 ($\text{chitosan}_{(S)}$). The structure illustrated in figure 1.

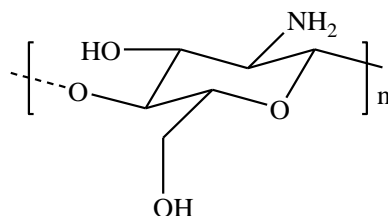


Figure 1: chemical structure of chitosan_(s)

2.3.2. Chitosan_(s) solution

We introduced a mass of 5g of chitosan_(s) 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.

2.3.3. Chitosan-ECH

We mixed the gel obtained after dissolving the chitosan(s) with a volume of epichlorohydrin, 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 figure 2.

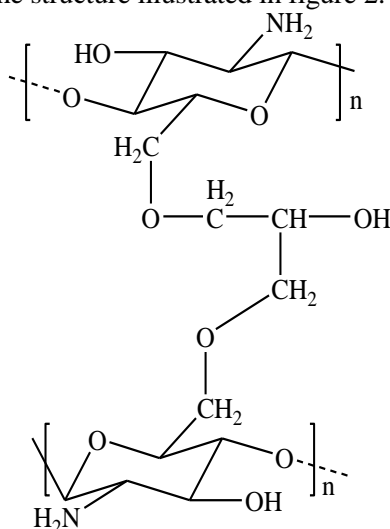


Figure 2: chemical structure of chitosan-ECH

2.4. Preparation of Activated Carbon

In this study, the carbon stones samples were chemically treated with acid phosphoric. The latter is the most preferred because of the environmental and economic concerns.

After separation of the dates stones, they are washed, and then put in an oven at 105°C for 24 hours and then ground. The ground material retained and kept protected from the air in tightly closed bottles. The carbonization is carried out in an electric four. The resulting carbon is put in closed porcelain capsules. The carbonization was between 400 and 800°C in a furnace at 1h to 3h. The samples are chemically treated with H₃PO₄ (40%) for 10h at 25°C. They are then washed with distilled water until the pH is neutral, and finally dried at 105°C for 24 hours. . Figure 3 the necessary steps for obtaining activated carbon.

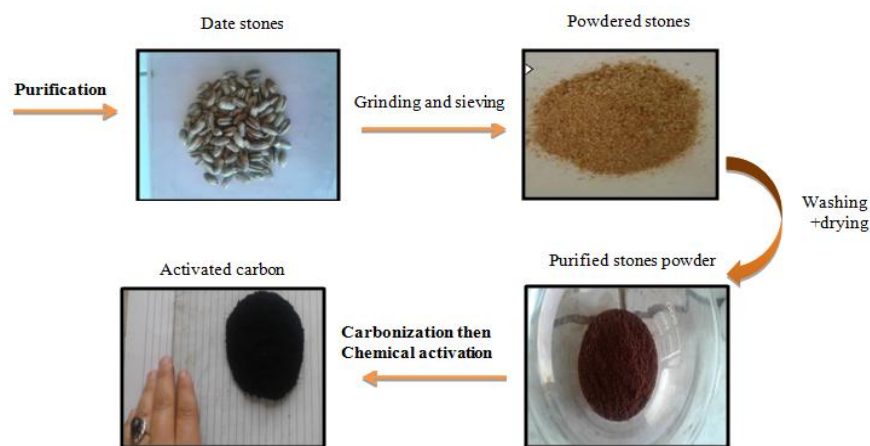


Figure 3: Activated carbon preparation.

2.5. Characterization

2.5.1. 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.

2.5.2. 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.

2.6. 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.

2.7. Optimization the process of coagulation-flocculation and adsorption

2.7.1. Dose optimization of flocculant chitosan-ECH

To optimize the dose chitosan-ECH, we used firstly the optimum pH in the range of 8 then we injected increasing concentrations of each flocculant prepared from 0.1% to 0.5% which method is described by the data sheet of wastewater neutralization station of the Galvacier society and secondly, we have successively diluted 0.1g/L, 0.2g/L, 0.3g/L, 0.4g/L and 0.5g/L of chitosan-ECH. Next, we conducted flocculation of our samples (in 5 liter beakers volume) with a speed of 200tr/min for 3 min. Finally, 10mL of each dose of the previously prepared solutions of flocculant were added sequentially to each beaker other than the control. After stirring for 5 minutes at a speed of 20TR/ min, the samples were left to settle for 30 minutes to remove the supernatant.

2.7.2. Adsorbents mass

Effect of the adsorbent dose was studied by agitating 50mL of different concentration of ions with different doses of adsorbent (0.1 to 0.5g/L) for a time greater than their equilibrium time at their natural pH . Experimental conditions were selected to assess the effect of adsorbent dose.

2.8. Treatment of the liquid effluents by coagulation-flocculation, adsorption and combined process coagulation-flocculation/adsorption

2.8.1. Coagulation-flocculation experiments

To study the power of chitosan-ECH, we proceeded to the coagulation-flocculation of our samples composed of a liter of waste water taken at the entrance of the station whose pH was previously adjusted to pH 9 using a coagulant with a mass concentration of 0.4g/L, and then oxidized with H₂O₂. While the flocculant was added to previous preparations with optimal concentration 0.2g/L.

2.8.2. Batch adsorption experiments

To study the activated carbon power, we added an optimal mass 0.5g/L in a volume (1L) of solution of metal ions whose concentrations of Zn²⁺ and Cu²⁺ successively equal 11.75mg/L and 6.25mg/L. The adsorption was carried out at pH equal to 6 at a stirring speed of the order of 500 rpm for 3 h and at 30°C.

2.8.3. Combined process coagulation-flocculation/adsorption experiments

Firstly, we proceeded to coagulate our compound samples in one liter of a solution of effluents of Zn²⁺ and Cu²⁺ ions whose concentrations equal to 11.75 mg/L and 6.25 mg/L respectively and the pH was previously adjusted to 6 and subsequently oxidized with H₂O₂, with a speed of 200 rpm for 3 min, during which 10 ml of the dose of solutions of lime and chitosan-ECH prepared beforehand with a mass concentration of were added 0.4g/L and 0.2g/L respectively in each beaker, then reduce the stirring at 60 rpm for flocculation, for 20 min. After the coagulation/flocculation steps we added 0.5 g/L of the adsorbent (activated carbon) and stirred at 150 rpm for 30 minutes (adsorption step). Finally, the samples were allowed to decant for 30 min before making measurements of the physical-chemical parameters.

The evaluation of the effectiveness is carried out by the determination of the rate of abatement noted E of elimination of the metal and expressed in percentage, is based on the following formula [19]:

$$E(X)\% = \frac{C_i(X) - C_f(X)}{C_i(X)} * 100$$

Where C_i is the initial ions concentration put in contact with the adsorbent (mg L⁻¹) and C_f is the ions concentration (mg L⁻¹) after the batch adsorption procedure.

3. Results and discussion

3.1. Characteristics of the physical-chemical parameters of the hot-dip galvanizing rejects 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 [20] |
|---------------------|--|--|----------------------------|
| pH | 4.01 | 3.56 | 6-9 |
| Zn(mg/L) | 11.75 | 11.19 | 10 |
| Cu (mg/L) | 6,25 | 6.12 | 4 |

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 [20].

3.2. Characterization

3.2.1. Infrared spectroscopy

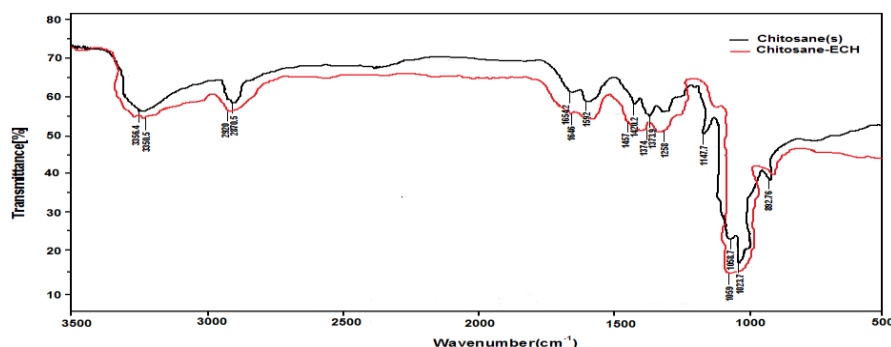


Figure 4: IRTF Spectrum of chitosan(s) and chitosan-ECH.

From figure 4 we found that the main peaks found at 3356.4cm^{-1} for chitosan beads were assigned to the stretching vibration of OH and NH groups. The peak at 2870.5cm^{-1} was due to stretching of the CH vibration. $-\text{CONH}_2$ stretching in the secondary amide groups was observed at 1654.2cm^{-1} while the peak at 1592cm^{-1} was attributed to NH bending in the primary amine (NH_2) groups. The deformation vibration of NH in NH_2 was represented by the peak at 1420.2cm^{-1} . Other peaks observed chitosan beads were found at 1373.9cm^{-1} stretching vibration of ($-\text{CN}$), 1147.7cm^{-1} asymmetric stretching vibration of (COC), 1058.7cm^{-1} vibration of symmetric stretching (COC) and 1023.7cm^{-1} stretching vibration (CO in COH). The 892.76cm^{-1} band was assigned to the absorption peaks of α -(1.4) glycoside in chitosan. These results confirm that the experimentally prepared chitosan was identical to that of the chitosan structure [21-22]. On the spectrum of the Chitosan-ECH mixture, the peak at 3350.5cm^{-1} attributed to the peak of vibration absorption by stretching $-\text{OH}$ 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 1457cm^{-1} , corresponds to the deformation of CH_2 . The peak at 2920cm^{-1} was due to stretching of the C-H vibration. The peak at 1646cm^{-1} corresponds to the vibration of valence $\text{C}=\text{O}$. The 1374cm^{-1} band was assigned to the elongation vibration of the C-N bond. The band at 1258cm^{-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 1059cm^{-1} also shifted, which showed that the hydroxyl (C-OH) group of the chitosan molecules reacted with epichlorohydrin.

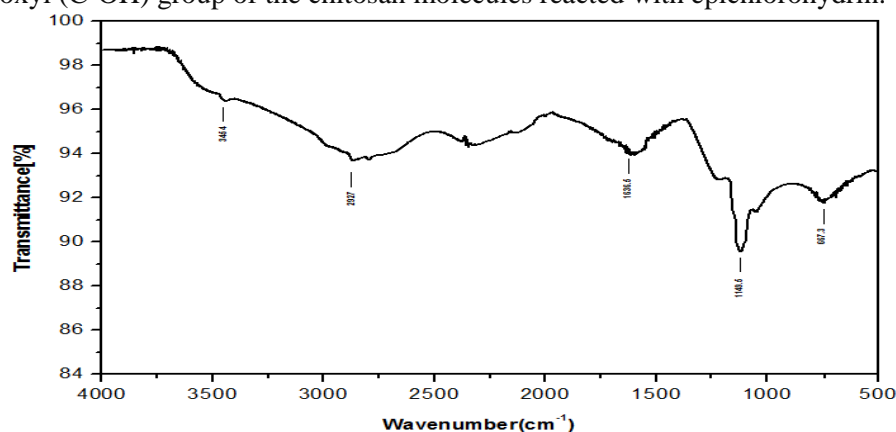


Figure 5: IRTF Spectrum of activated carbon

From the spectrum of FTIR we found that the main peaks found at 3454cm^{-1} for activated carbon were attributed to the hydrogen stretching vibration of the O-H hydroxyl groups (of carboxyls, phenols or alcohols) and adsorbed water [23]. It also corresponds to the O-H elongation vibration of cellulose, pectin and lignin [24]. The 2927cm^{-1} band was

attributed to the C-H elongation vibration of aliphatic molecules. The band observed in the 1636.5cm^{-1} region is attributed to the C=C bond of groups of pyrones[25] the peak at 1149.5cm^{-1} is assigned to the vibration of the C-O bonds [23]. The band of 667.3cm^{-1} corresponds to the vibration of the S-C bonds [26-27].

3.2.2. Polarizing optical microscopy

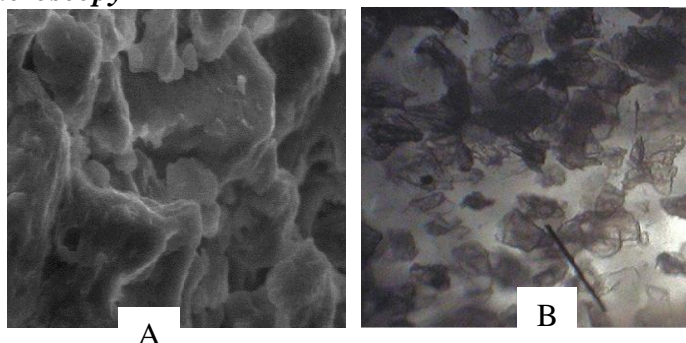


Figure 6: Morphology of activated carbon (A) and chitosan-ECH (B) seen by polarizing optical microscopy at (x100)

The image of the polarizing optical microscopy of the activated carbon (A) show a relatively heterogeneous surface rich of pores with large size situated in the mesoporous range, as well as the presence of cavities, which result from the reaction of the activating agent on the surface of the activated carbon as in the studies of Enaime al [28].

According the image (B), 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 Kucukgulmezand and al [29] which simulated this work.

3.3. Results of optimization of flocculant

From the curves shown in figure 7 we have found that the gradual increase in applied flocculant doses slightly decreases the zinc and copper contents of the treated effluents, such as the Zn and Cu values, respectively at values of 4.24 and 4.67mg/L at a dose of 0.2g/L and chitosan-ECH.

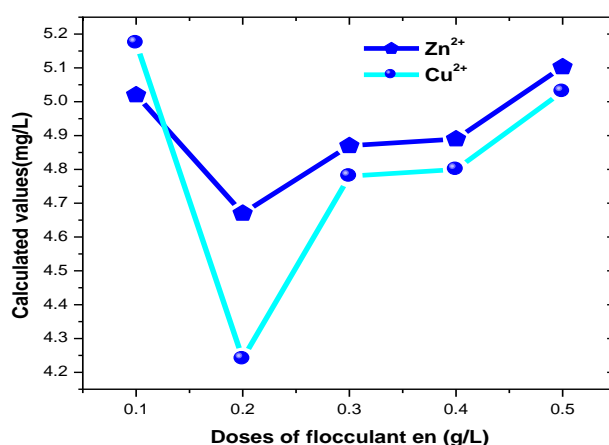


Figure 7: Variation of Zn^{2+} and Cu^{2+} according to the dose of chitosan-ECH.

3.4. Results of effects of adsorbent mass

The analysis results of the samples of treated water ions as a function of the increasing masses of the adsorbent (activated carbon) are represented in the following figure. From figure 8 we noticed that the adsorption capacity on the carbon decrease with the increase of the mass of adsorbent, such as the very high adsorption capacity at 0.1g of the adsorbents by cons very low to 0.5g adsorbents above this mass the adsorption rate became stable.

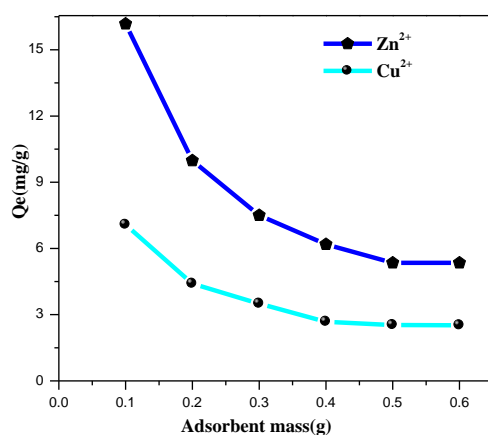


Figure 8: Influence of the mass of activated carbon on the adsorption of Zn²⁺ and Cu²⁺ ions

3.5. Results of analysis of water treated by CF, ADS and by the combined process CF-ADS

To better visualize the efficiency of the reduction of the metal ions, we made a comparison between the previously used processes CF, ADS and CF-ADS. The removal efficiencies of each metal after treatment by each process are shown in the figure above:

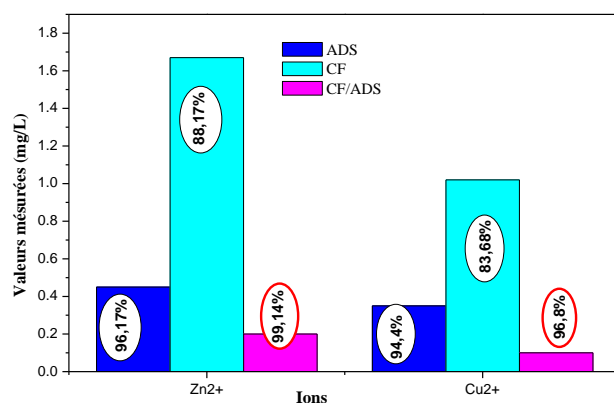


Figure 9: Removal rate of Zn²⁺ and Cu²⁺ ions by CF, ADS and CF/ADS

From the figure we have found that the comparison of the purifying power of the processes used has shown us a very significant effect on the elimination of the pollution load of the metals by the CF-ADS, unlike that of the CF, ADS. In fact, the treatment with CF-ADS was able to eliminate 99.14% of zinc and 96.8% of copper. However, treatment with CF and ADS we obtained successively only a reduction of 88.17% and 96.17% for zinc and 83.68% and 95.4% for copper.

4. Conclusion

This work is designed to improve the performance of water loaded with inorganic pollutants by combining coagulation-flocculation/adsorption with lime as a coagulant agent, thus chitosan-ECH as a flocculant and activated carbon as an adsorbent. The results obtained in this work, it shows us that:

- Optimization of the flocculant dose and the adsorbent improved the performance of the CF/ADS processes for the treatment of effluents loaded with inorganic micro pollutants.
- The elimination of ions by the CF/ADS combined process gives a very significant effect on the elimination of the polluting load of the metals.

- The CF/ADS combined process is more efficient than the other processes.

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