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Treatment of Fez City (Morocco) Effluent by Chemical Coagulation (CC) and Electrocoagulation (EC)

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***Abstract*—** Heavy metals are released in the environment with a heavy load due to rapid industrialization and thus become a major global concern.

At Fez city, chromium, zinc, copper, nickel, lead, antimony, and selenium, are often found in wastewater of artisanal industry (tanneries, pottery, copperware, etc).

These metals are mostly present in trace amounts, but their toxicity develops through bioaccumulation in organisms, causing short- and long-term deleterious effects on biodiversity and human health.

The objective of this work is the pretreatment of these effluents, to reduce or eliminate their metallic load by two methods: The coagulation-flocculation and ectrocoagulation using aluminum plates.The characterization of Fez city effluents demonstrates their highmineral and organic pollution load, that is non-biodegradable.Treating this effluent by coagulation flocculation under optimum operating conditions revealed an important reduction of the organic matter, cupric ions Cu^{II} and of chromium VI.

As for treatment by electrocoagulation, the elimination of chromium VI and color is total and the other pollutants have reached a reduction ratio which is almost the same as that obtained by the coagulation flocculation.

***Keywords*—** Heavy metals, Treatment, Coagulation -Floculation, Electrocoagulation.

I. Introduction

In the Mediterranean region, water is a scarce and In many developing countries, between 80% and nearly 90% of discharged wastewater is estimated to be raw and untreated. This wastewater has become increasingly huge because of industrial development, economic growth, population growth and high density urban areas [1]. In recent years the Fez region (Morocco) experienced a demographic development estimated at 1.088 million inhabitants with a 1.02% growth rate [2]. That generates approximately 130 000 m^3/d of domestic and industrial wastewater [3]. Main activities include tanneries, brewing, textiles, oil mills, canneries, blacksmiths and pottery. Several studies have shown that the quality of wastewater from the city of Fez (Morocco) does not respond to the direct discharge standards [4] due to strong industrial and craft activity of the city These effluents are the source of surface water and ground pollution. They constitute a danger to environment and human health [5].

This study aims at clarifying sewage of the most polluted area, recognized by many craft activity in the region of Fes (AinNokbi ,Old Medina), by conducting a comparative test of treatment by two techniques: The chemical coagulation(CC) and ectrocoagulation (EC) using aluminum plates . Which have proven their effectiveness on several types of effluents [6, 7, 8].

The optimization of CC and EC methods selected is searched under different experimental conditions obtained by changing key parameters including: pH, Doses, speed and time for the coagulant and flocculant process. Voltage and treatment time of electrocoagulation. The optimum values of these parameters are determined based on the efficiency of reduction of COD, Cupric ion Cu^{II} and hexavalent chromium Cr^{VI}.

II. Materials and Method

A. Wastewater Source and Characteristics

The wastewater was collected from Ain Nokbi district (Morocco, Fez) and surroundings collector, which group's domestic and industrial wastewater from tanneries, brassware and pottery. The flow of these effluents could reach up to 3560 m^3per day. It contained organic (COD, DBO_5, and dark brown color) and inorganic compounds (nitrogen, phosphorus, sulfate, cupric ion etc.). The wastewater was decanted for 24 h before being used for the subsequent studies. Characteristics of LFW were shown in Table 1.

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B. Analysis methodologies and used equipment

All controlled parameters were analyzed in the laboratory. Transportation and packaging of samples were made according to the AFNOR standards set by Rodier [9] The temperature, conductivity, and pH measured with a multi-parameter analysis type Consort Model C535, The COD was performed according to standard NF T90-101,Cu^{II} was determined by colorimetric method using sodium thiosulfate and the Cr^{VI} was measured according to standard NF T 90-043.

For pre-treatment testing, the experimental protocol followed in coagulation-flocculation is Jar-test; It is the oldest, cheapest and easiest method used. [22] The protocol generally comprises introducing into each beaker of a flocculator (*FISHER BIOBLOCK SCIENTIFIC*), 800 liter of water to be treated with a solution of commercial coagulant (aluminum sulfate ($Al_2(SO_4^{3-}),18H_2O)$) 10 $g.L^{-1}$ and commercial flocculant (Praestol650 ($C_{12}H_{24}ClN_3O_2$) 0.05$g.L^{-1}$. The optimization of the treatment method involves varying the pH of the effluent to optimum pH considering the pourbaix diagram, by addition of H_2SO_4 (0.01 M) or the base NaOH (0.01 M).The optimized parameters of wastewater treatment by aluminum sulfate are: Doses of coagulant and flocculant, Speed of the coagulation and flocculation Time of coagulation and flocculation. Whenever a parameter is optimized, it's taken into consideration for the remaining parameters.

Experiments of EC were conducted with similar operating conditions of CC. Batch experiments were carried out in a 1 liter borosilicate glass reactor containing 800 ml of solution. The effective surface area of Al electrodes was 40 cm^2. Six parallel electrodes were placed into the solution using an insulated clamp fixed to a stand. Electrode spacing was kept constant at 10 mm. Electrodes were connected to a regulated D.C. power source (Metrix AX 503). The desired cell current was supplied by changing the impressed voltage. The EC experiments were performed at the same agitation level of CC

TABLE I: THEARRANGEMENT OF CHANNELS

Physico-chemical parameters	Unit	(O.B 2013)
pH	8,05	5,5-8,5
Temperature (°C)	21,85	30
$\chi(\mu s.cm^{-1})$	1620,75	2700
MES ($mg.L^{-1}$)	685,5	30
COD ($mgO_2.L^{-1}$)	2114,5	120
DBO_5 ($mgO_2.L^{-1}$)	395,5	40
Cu^{II}($mg.L^{-1}$)	3,74	-
Cr^{VI}($mg.L^{-1}$)	2,54	0,1

III. RESULTS AND DISCUSSION

A. Optimum Conditions of Clarification of Wastewater by CC Treatment

The study of clarification by CC pretreatment proposed aims to reduce pollution load of wastewater of Ain Nokbi(Fez, Morocco) effluent. The organic and mineral reduction of wastewater by the addition of metal salts (CC), is to destabilize colloidal dissolved solids with negative charge in particulate insoluble form to be decanted .This reduction goes through the following mechanisms: trapping, adsorption, neutralization / destabilization charges and complexation / precipitation studied and cited by various references [10 , 11].

During treatment, we are seeing an instantaneous dispersion of trivalent metal salt Al (III) which neutralizes and destabilizes the colloidal particles to carry the floc formation.

$$3Al_2(SO_4)+ 18\,H_2O \longrightarrow 2\,Al^{3+} + 3SO_4^{2-} \quad (1)$$

$$Al_3 + 3H_2O \longrightarrow Al\,(OH)_{3s}+3H^+ \quad (2)$$

The pH in this type of treatment is very important since we seek to produce maximum of coagulant Al $(OH)_3$in the solution. As shown in figure 1, the reaction for producing this shape is optimum at pH between 6 and 7.5 [12].

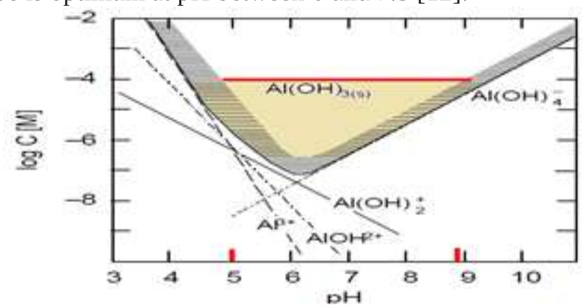


Fig. 1: Pourbaix diagram of aluminum

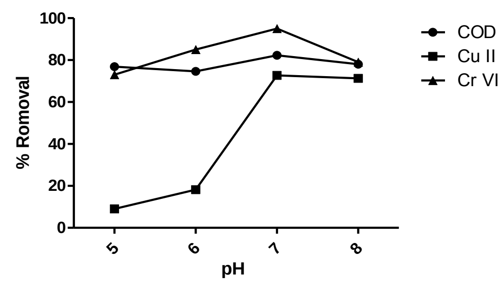


Fig. 2: Effect of pH on % of removal

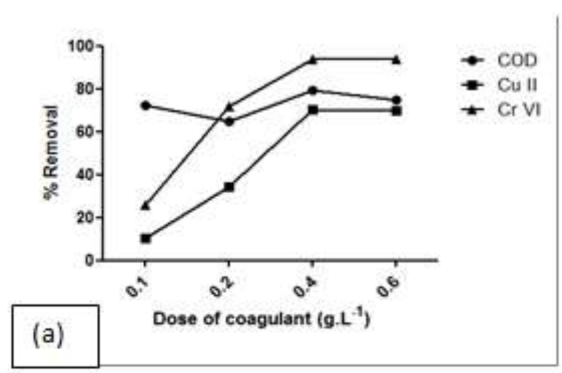
Obtained is 95% for Cr^{VI}, 72.73 % for Cu^{II} and 82.3% for COD, for an optimum pH of 7.3. This value is within the limits of the dominance area of the aluminum hydroxide (Fig.1), the range where dissolved form of Al^{3+} is almost nonexistent. This explains the shape of resulting curve. Indeed, at basic pH other forms of aluminum hydroxide is formed Such $Al(OH)_4^-$ (Eq.3). While in pH acid the formation of Al^{3+} is favored (Eq.4) thus reducing the effectiveness of treatment.

Acidic medium:

$$Al\,(OH)_3(s) + 3H_3O^+ \longrightarrow Al^{3+} + 6H_2O (3)$$

Basic medium:

$$Al\,(OH)_3(s) + HO^- \longrightarrow [Al(OH)_4]^- (4)$$



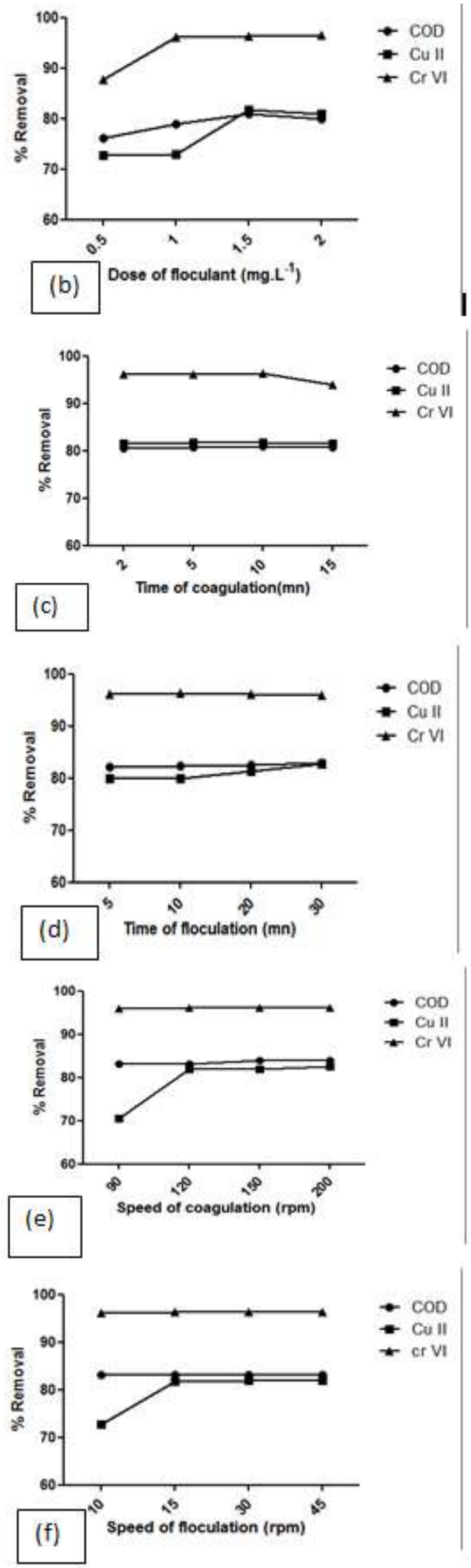


Fig. 3: Effect of the dose, time and speed of coagulation-flocculation on Cr^{VI} removal Cu^{2+}removal, and COD removal

Figure 3 illustrates the effect of dose, time and speed of the chemical coagulant and its dosage on Chromium, cooper and COD removals. As can be seen in the Fig. 3 (a), initially as the salt dosage of coagulant increases Cr^{VI} ,Cu^{II} and COD concentration decrease, and hence their corresponding percent removals increase. In fact, when the dosage of coagulant equals or exceeds 0.4 $g.L^{-1}$, there is no substantial improvement in the parameters reductions. This means that a chemical coagulant with a dosage of $0.4g.L^{-1}$is sufficient for optimal reductions of total Cr^{VI} , Cu^{II} and COD levels. The optimum dose of the flocculant is 1.4 $mg.L^{-1}$ Fig.3 (b). The dose where we have the maximum thickening flocs, results the highest removal.

On the other graphs figure 3 (c,d,e,f) we can observe that in optimum pH and dosage of coagulant and flocculant, the time and the speed of coagulation-flocculation have almost no influence on the quality of treatment. 2-5 min of rapid stirring (200 rpm) is enough for destabilization of colloidal particles in wastewater studied to reduce the same abatement rate of the 3 parameters and 10 min of slow stirring (45 rpm) Fig.3 (d) suffice to growth of flocs laden pollutants of the studied wastewater. After fixing all the optimum previous parameters, we obtained an optimal fast rate of coagulation on 120 rpm. And optimum slow stirring speed of flocculation on 20 rpm.

B. Optimum Conditions of Clarification of Wastewater by EC Treatment

Electrocoagulation is a process consisting of creating metallic hydroxide flocs within the wastewater by electrodissolution of soluble anodes, usually made of iron or aluminum. The generation of metallic cations takes place at the anode, due to the electrochemical oxidation of the iron or aluminum, whereas at the cathode the production of H^2 typically occurs [13]. This reduction goes through these mechanisms: electrooxidation , surface complexation , electrostatic attraction, adsorption, chemical modification [14] .Current density is an important parameter for controlling the reaction rate in most electrochemical processes such as the EC processes. Current density determines the rate of coagulant and bubble generation, its flocs size and distribution, and hence affects the growth of flocs$Al_2(OH)_{3(s)}$ coagulate particles in the EC process. In the EC the OH^- formation rate is controlled by the applied current density during the electrolysis. In this study, the efficiency of electrocoagulation in removing cupric, hexavalent chromium and COD from wastewater all following pHand conductivity of solution was investigated. The effects of the voltage for the treatment in the EC processes were studied in the range of 0–30 V at operating time of 30 and 60 min.

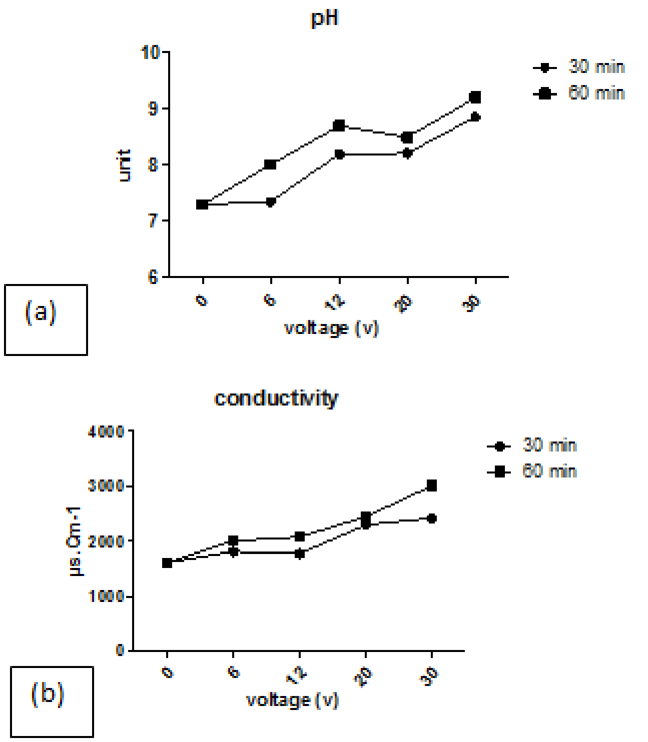


Fig.4 : Evolution of pH and Conductivity as a function of the electrical voltage.

Fig. 4a and b indicated that the initial pH and Conductivity of LFW before treatment is of 7.3 and 1600 µs.cm $^{-1}$ respectively ; after electrocoagulation , pH and conductivity increases with the voltage applied to the cell, so there is an increase of the value of the two parameters. Indeed the two phenomena of metal oxidation at the anode and water reduction at the cathode produce trivalent aluminum Al^{3+} (Eq.5) and several more metallic species hydroxide monomers : $Al(OH)^{2+}$, $Al(OH)^{+}_{2}$, $Al_2(OH)^{4+}_{2}$, et $Al(OH)^{-}_{4}$ and polymers : $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}O_4(OH)_{24}$, $Al_{13}(OH)_{34}^{5+}$ (Eq.7)) which consequently increases the conductivity of the solution with the elevation of the voltage and time. While the pH increase is mainly due to the production of OH^- on the cathode (Eq.6).

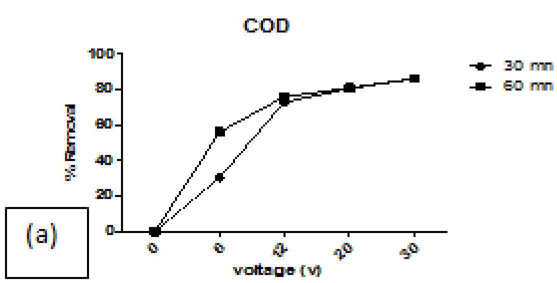
Anodic reaction:

$$Al \rightarrow Al^{3+} + 3e^- \quad (5)$$

Cathodic reaction:

$$H_2O + e^- \rightarrow 1/2\ H_2 + OH^- \quad (6)$$

$$xAl^{3+} + yH_2O \rightarrow Al_x(OH)_y^{3x-y} + yH^+ \quad (7)$$



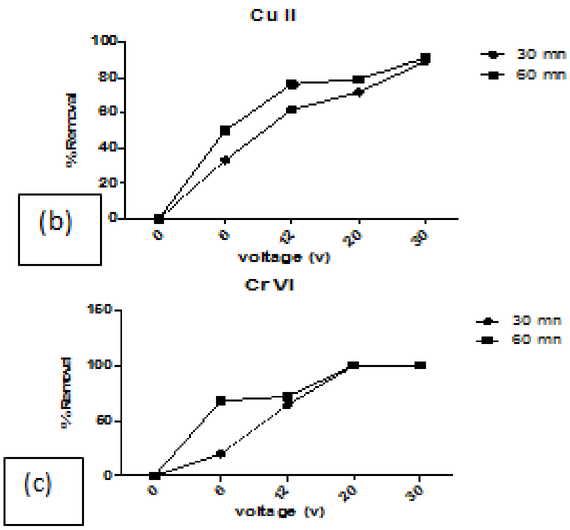


Fig.5: Evolution of the removal efficiency of COD, Cu^{II} and Cr^{VI} as a function of the electrical voltage.

The COD reduction levels increase as the voltage increases. Indeed on an electrical voltage of 20V and only 30 minute of treatment the efficiency of removal increases from 0 to 80.82%. The figure 5a shows also that although the processing time increases from 30 to 60 minutes on 20 or 30 V the removal efficiency does not improve; it changes from 80.82 to 81.13 % and from 86.31 to 86.45 to an electrical voltage of 20 and 30 V respectively. In fact, several studies have shown that the reduction rate of COD reaches a limit and even if we continue to raise the Voltage (electrical current) and / or the contact time remains constant [7, 8, and 15].

This clearance of solution is due to the fact that voltage affects the amount of aluminum ions produced, thus the coagulant Al $(OH)_3$ produced from electrodes. At high voltage, the extent of anodic dissolution of aluminum increases, resulting in a greater amount of precipitate for the removal of pollutants. Moreover, the bubble generations rate increases and the bubble size decreases with increasing voltage. These effects are both beneficial for high pollutant removal [15]

Fig. 5b and c illustrate the effect of electrical voltage on Cu^{II} and Cr^{VI} removal in EC process. As expected, it was found that, an increase in electrical voltage from 6 to 30 V yields an increase in the efficiency of Cu^{II} removal after 30 min from 33.2 to 89.46%. The Cr^{VI} was completely removed after 30 min of electrocoagulation at an electrical voltage of 20V. The removal of Cr^{VI} was total because it has a lower initial value than Cu^{II}.At higher electrical voltage (current density) the formation rate of $Al(OH)_3$ increased. The aluminum hydroxide flocs act as adsorbents for metal ions and eliminate them from the wastewater. Simultaneously, the hydroxyl ions which are produced at the cathode increase the pH of wastewater and may induce co-precipitation of Cu^{II} and Cr^{VI} in the form of their corresponding hydroxides, and releasing hydrogen that will assist in the removal of the pollutant by electroflotation (Eq.8) [7].

$$2Me + 6\ H_2O + 2\ OH^- 2 \longrightarrow Me\ (OH)_4^- + 3H^2 \quad (8)$$

IV. Conclusion

The present study attempted to investigate the applicability of an coagulation and electrocoagulation method in the treatment of wastewater of Ain nokbi district (Fez, Morocco). The influence of variables such doses, speed and time of coagulant and flocculant process. electrical voltage and electrolysis time for the electrocoagulation process on the removal of COD, Cu^{II} and Cr^{VI} was investigated. The results show that water from Ain Nokbi of Fez sewerage is slightly basic. Its characterized by a non-biodegradable organic load and a significant metallic luding cupric ions and chromium ions. The treatment of this wastewater by coagulation flocculation by aluminum sulfate allowed in optimum conditions 94% removal of hexavalent chromium, 82% removal of cupric and 85% removal of COD. The electrocoagulation treatment can effectively reduce COD and metal ions to a very low level. An EC process was able to achieve 86%COD, 89% Cu^{II} and 100%Cr^{VI} removal at an electrical voltage of 30V after an elecrocoagulation time of 30 min. The comparative study of pre-treatment of effluents from an industrial district of Fez city showed the possibility of using either method with satisfaction. Reduction rate of controlled parameters was very higher for both of methods.

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