Chapter

Characterization and Treatment of Real Wastewater from an Electroplating Company by Raw Chitin

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Abstract

The objective of this chapter is to study of the heavy metal removal in real waste water. The use of the raw chitin shows itself of big potential for the treatment of the liquid discharges of the studied unity. It showed itself capable to treating heavy metal loads superior to 200 mg/l by presenting percentage removal between 90 and 97%, as in the case of Cu^{2+}. After the study performed on the global discharge, we were interested in the local treatment that rinses out plating baths, and this is the aim to optimize the treatment process and develop a project of treatment plant, recycling in situ based on the adsorption technique on raw chitin. Examination of the results allowed us to save significant percentages of sewage treated for metals mainly copper. Raw chitin showed a high affinity toward heavy metals in rinsing water supply. According to this study, the design of a treatment facility of this type of release must include a waste water treatment by adsorption on chitin. The valuation of the raw chitin is situated in this context as an economically adsorbing material, which can be an interest at the level of the recovery of heavy metals in waste water.

Keywords: chitin, adsorption, heavy metals, current rinsing, global rejection, treatment, electroplating

1. Introduction

Generally, a chain of surface treatment consists of sequences of functions (pretreatment, treatment, finishing), consisted of several posts (treatment bath, rinsing, passivation ...). The composition of industrial waste water of treatment surface contains a lot of heavy metals such Cu, Zn, Ni, Cr, Cd and the other toxic materials such as the alkalines, the acids and the cyanides. More and more it contains several complexing agents which influence the used process Na^{+}, OH^{-}, SiO_3 and Na_2CO_3, These products are generated in the operations of rinsing of materials before treatment. A variety of acids, HCl, H_2SO_4, HNO_3, H_3PO_4, $HCrO_3$, etc. is used to eliminate the oxidized films. The rejection of the stage of electroplating deposit contains widely metals and the following anions: BO^{3-}, $CO^{2-}{}_3$, $Cr_2O^{2-}{}_7$, F^{-}, $PO_4{}^{3-}$, Cl^{-}, NO^{-3} and $SO_4{}^{2-}$. Generally, wastewater contains many heavy metals. The most important of cations are Cr^{6+}, it is reduced to Cr^{3+}, while CN-is oxidized in the preliminary treatment.

Different treatment techniques for wastewater laden with heavy metals have been developed in recent years both to decrease the amount of wastewater produced and to improve the quality of the treated effluent. Although various treatments such as chemical precipitation, coagulation-flocculation, flotation, ion exchange and membrane filtration can be employed to remove heavy metals from contaminated wastewater, they have their inherent advantages and limitations in application [1].

Chemical precipitation is widely used for the treatment of electroplating wastewater [2, 3]. It consists of adding a base followed by sedimentation. The pH is adjusted to the minimum solubility, so it is difficult to treat multiple metals simultaneously. Coagulation-flocculation has also been employed for heavy metal removal from inorganic effluent [4]. Sorptive flotation has attracted interest in Greece and the USA [5–7] for the removal of non-surface active metal ions from contaminated wastewater. In recent years, ion exchange has also received considerable interest in Italy and Spain [8, 9] as one of the most promising methods to treat heavy metals. Starch xanthate (XA) synthetic polymers resins grafted cellulose natural zeolites are used. This process is particularly effective for the recovery of metals, but the cost of the process is very expensive and often justified only metals are recovered [10]. Due to its convenient operation, membrane separation has been increasingly used recently for the treatment of inorganic effluent. There are different types of membrane filtration such as ultrafiltration, nanofiltration and reverse osmosis. Membrane filtration has used in Taiwan and in South Korea [11, 12].

The adsorption treatment is widely used with activated carbons, this process has several advantages: it is very effective in removing heavy metals even at low pH [13] with different adsorbent materials such as polymers [14–16] and clays [17–19]. Electrolysis is generally used to treat water with high metal content. One of the major obstacles encountered in this technique is the complexity of the environments to be treated that leads to a series of redox reactions [20]. In recent year, the clean Technology constituted preventive actions to review and question the production concept, these actions converge to a common point: Targeting the pollution source rather than its reverse vector example osmosis [21] and zero discharge principle [22, 23].

In general, control of water flow requires the establishment of means for counting and control flow at the entrance of each channel. In addition, it reduces the consumption of reagents and production of sludge treatment plant, which is a significant gain in operating costs. Several techniques exist to recover the flow pollutants at the source to mention a few key principles:

- The decrease in volumes trained by parts by adjusting the drainage time.

- The establishment of additional rinse tanks such as rinsing tank death after degreasing, pickling, hot metal deposition and passivation, it traps the metal salts which are then reassembled in the treatment bath to compensate for evaporation. Rinsing; in which the parts are dipped before and after the cold metal plating baths, it can recover from 30 to 50% of the entrained flow.

- Finally, the development of production lines to reduce pollution is an opportunity to optimize production (questioning of manufacturing ranges, the products used and streamlining the flow of parts) and improves quality and working condition.

The objective of this research was to study the ability of raw chitin to purify wastewater loaded with a mixture of heavy metals. This chapter first focused on the physicochemical characterization and the determination of heavy metals levels in wastewater followed by adsorption treatment. We started the study by the global rejection of the society then by the rinsing waters running at the exit of the electroplating baths. Finally, we have studied the comparison between the efficiency of the treatment of heavy metals by chitin shrimps - Ccre or chitin crab -Ccra thus analyzing the possibilities of in situ treatment and recycling.

2. Materials and methods

A study unit is MAFER located at CASABLANCA in MOROCCO. Its activity is surface treatment. The studied unit of surface treatment consists of five chains. Every chain is determined by the succession of tanks. The average capacity of baths varies between 950 and 1710 l. The majority of baths has a volume of 1440 l and is fed by well water except the bath of metallic deposit and the baths of rundown which are filled by the drinking water. Waters of the baths of the dead rinsing are recycled in the bath of metallic deposit. The water supply of well often matches 1 h a day. Whereas the drinkable water supply is made after draining of bath.

2.1 Preparation of the adsorbent

the shells of Shrimp (Ccre) and the shells of crabs (Ccra) are isolated at first by their mild part (protein) washed in bidistilled water then dried at 100°C during 48 h [17], then crushed and sieved. The size grading is understood between 100 and 125 μm.

2.2 Adsorption test

A mass of the adsorbent is placed in contact with the rejection to be treated (100 ml). The suspensions were stirred (500 rev/min) in constant temperature (25 ± 2°C) until adsorption equilibrium obtained for a duration of 4 h [17]. The supernatant is filtered and the equilibrium concentration (Ceq) is determined after mineralization by flame atomic absorption using a Philips type PU 900.

*Physico-chemical analysis of the rejection quality:

PH: Measured using a pH meter ORION RESEARCH type and a combined glass electrode.

Electrical conductivity (CE): measured using a conductivity type ORION RESEARCH mod 101 and a 1 cm cell.

Chemical oxygen demand (DCO): Determined according to AFNOR T90-101. The principle consists in oxidizing the organic matter contained in wastewater by an excess of silver sulfate.

Suspended solids (MES): Determined according to standard AFNOR T90-105, the filtering is done on Whatman paper (0.45 mm). The drying of the already weighed filter is done at 105°C for 1 h and weighed.

Dissolved oxygen (OD): Determined using a pulse oximeter, the assay is performed directly by immersing the electrodes in water for analysis. The oxygen reduction at the cathode generates a proportional current to the partial pressure of oxygen in the cell.

3. Characterization and treatment of global rejection by adsorption on raw chitin

3.1 Physical-chemical quality of wastewater to be treated

3.1.1 Physical-chemical quality

In order to determine the degree of pollution caused by this unit, we were brought during this work to study the physical–chemical quality of rejection to be treated. We will translate the physicochemical parameters evolution during a period of study 20 days, study period from 7 to 9-08 to 3-10-08 in **Figure 1** below.

*PH: It is an important physiological parameter which influences the development of numerous microorganisms [21] as well as speciation and the solubility of heavy metals. During followed laborers, the pH value of this discharge (**Figure 2b**)

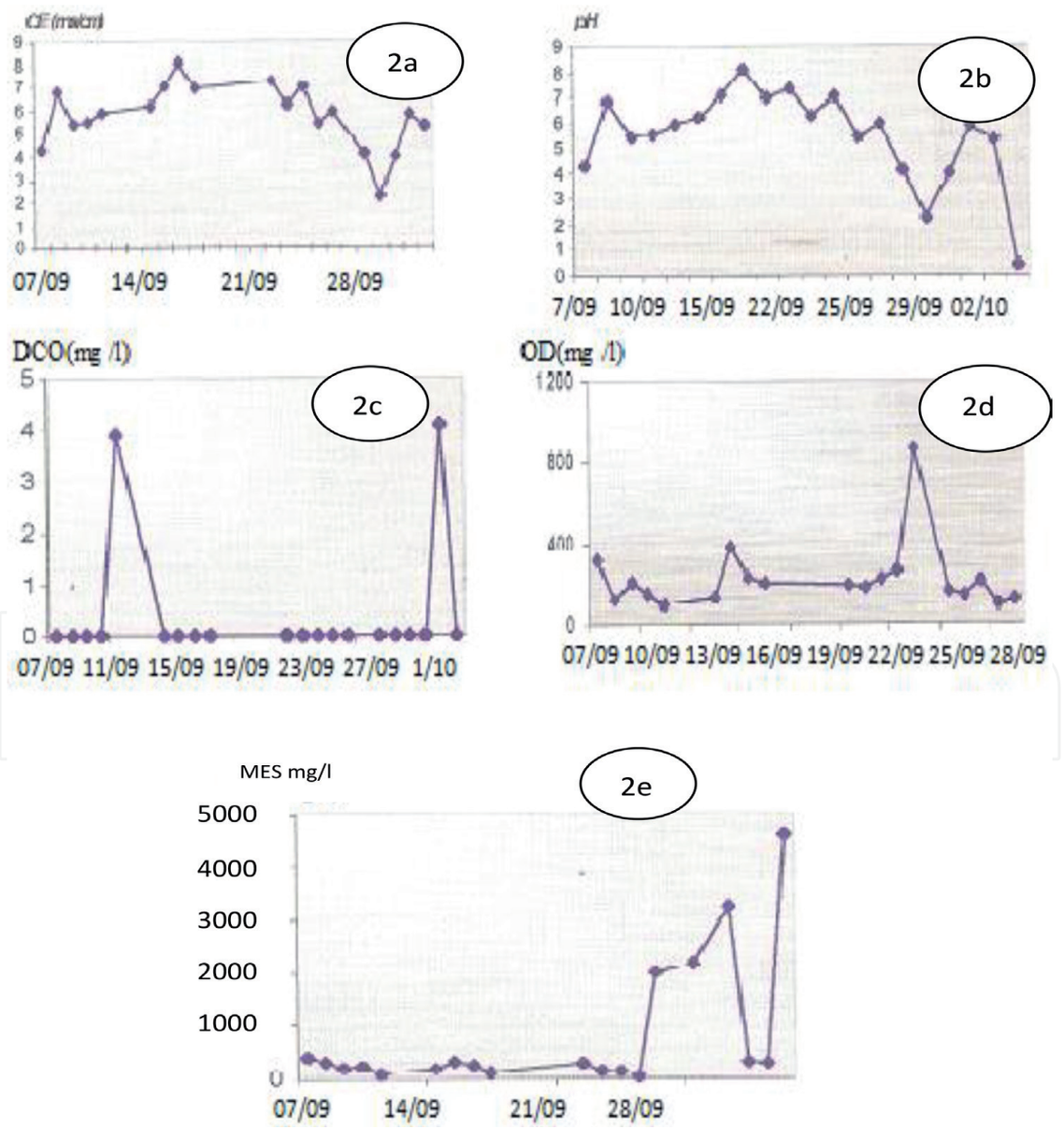

Figure 1.
Temporary follow-up of the physico-chemical parameters of the global rejection of surface treatment unity [(2a) CE, (2b) pH, (2c) DCO, (2d) OD, and (2e) MES].

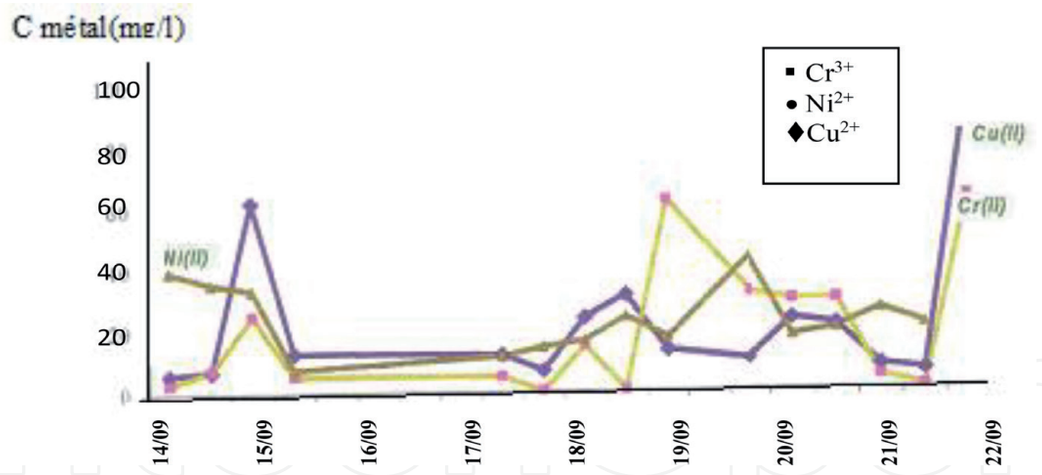

Figure 2.
Daily evolution of the heavy metals concentration in the discharge.

Sampling	Drain
22-9-08	Bath drain depassivation sulfuric
26-9-08	Bath chemical degreasing
29-9-08	Baths depassivation hydrochloric
30-9-08	Bath depassivation sulfuric Bath depassivation hydrochloric Bath anodic degreasing
3-10-08	Bath Accident at work, breaking of a pickling bath in full swing

Table 1.
Dates and the bath affected by drain.

fluctuate generally between 5 and 7, it is the optimal pH for the treatment by the raw chitin [22], except some exceptional cases such the case samples of days 22, 26, 29, 30. This is due to oil changes that have occurred in these samples (**Table 1**). Minimum values are recorded in these samples.

*CE: The electrical conductivity varies generally between 3 and 4 for all samples except that of the 3-10-98, which is very important. This value is effectively due to break of baths cleaning. The important values are recorded in the sampling days 22, 26 and 30. This drain of the baths shows that the degreasing depassivation waters of the baths are enormously salted. This salinity is essentially due to the high chloride concentration and to high acidity. The average value is of the order of 3.96 ms/cm.

*MES: The MES content confirms the statements made above. Levies where are oil changes occurring are charged by the MES. Indeed, the MES concentration is very high up to a maximum of 4.59 g/l and so exceed those generally encountered in domestic wastewater [23]. This result can be explained by the release of metallic waste and the solid deposits which accumulate at the bottom of a bath.

DCO: It present contents in variable organic matters from 96 to 3240 mg/l, but in general the value is situated near 200 mg/l, they are lower in standards dictated by the limits values of the indirect discharge [24].

OD: **Figure 2d** of OD brings to light an almost permanent state of anaerobiosis. The invalid contents of the oxygen in this discharge are due to the biological activity and to the absence of contributions in oxygen. A deficiency of this element in such

effluent can have serious implications for their treatment, fermentation, release of smell, etc. This characterization shows that the wastewater of the unit can be considered relatively stable if we eliminate the variations dictated by the draining. In other words the effluent can be easily handled if we avoid the draining or we get back them in the other pipe to treat them to part and thus insure a continuous treatment of the global discharge of the unit (**Table 1**).

3.1.2 Metallic pollution analysis

The global discharge contains numerous metals that cannot be separated. We focused our study on three metals Cu, Cr and Ni. The results of the analysis of heavy metals in the effluent are illustrated by the **Figure 2**.

Cu: The levels of Cu^{2+} vary from 5.12 mg/l to 97.76 mg/l (**Figure 2**), the temporary fluctuations in this element are much more pronounced. The registered minimal value exceeds 5 times the PVL (1 mg /l). The contents of Cu^{2+} achieve in average 22.21 mg/l. This is due to currents after plating rinses.

Cr: The concentrations of chromium fluctuate between a minimal value of 0.11 mg/l and a maximal value of 63.86 mg/l (**Figure 2**). The most values exceed the PVL of Cr (2 mg/l).

Ni: as far as the nickel is concerned, the registered concentrations are enormously important and far from being in compliance with national standards. The maximal content is registered the takings of 28-9-08.

From these results, we can identify the following points:

1. Among the three metals Cu, Ni and Cr no one presents normal means in comparison with the project national standards (PVL) and the international standards (FAO, EQO, etc.) This is due to the fact that, in general, the step of dead rinsing is often exceeded.

2. The average grade is the highest registered in the case of Ni (**Figure 2**). This is due on the one hand to the fact that the nicklage is in the most part of chains and on the other hand to the fact that the standards of the bath Ni (300 mg/l) are the most raised with regard to the other one baths of plating.

3. The temporary fluctuations in heavy metal contents are essentially explained by the following client commands. The bath can work hundreds of parts by hours, consequently current rinsing will strongly by loaded. The minimal values are recorded in the case of Cr.

It appears from these results that the effluent of this unit presents a big risk on the receiving environment; this is by accumulation along the food chain of the enormous quantities of rejected heavy metals [19]. During the study of the impact of the metallic pollution on the Casablanca coast, it showed that the dosage of metallic elements in the biological compartment crab *Eriphia spinifrons* of Fe, Cr, Pb, and Cd in bivalves *Mytilus* sp. *Mactra* and *Corallina* are rather high, which indicates a possible threat of the health because of the consumption of these mollusks (**Table 2**).

3.2 Treatment test for global rejection

The results for the Cu^{2+} are summarized in **Table 2**.

Figure 3 indicates the changes of removal rates of heavy metals with the change of added quantity of raw chitin. For every mass, the raw chitin reduces the residual amount of Cu^{2+} in all treated samples even if the used quantity is weak, quoting the example of 250 mg.

Ccre				Ccra			
Test 1 Co = 0.78 mg/l		**Test 2 Co = 1.31 mg/l**		**Test 1 Co = 0.78 mg/l**		**Test 2 Co = 1.31 mg/l**	
Weights (mg)	**Ceq (mg/l)**	**Weights (mg)**	**Ceq (mg/l)**	**Weights (mg)**	**Ceq (mg/l)**	**Weights (mg)**	**Ceq (mg/l)**
30	0.45	30	1.05	50	0.17	50	0.57
60	0.32	60	1.00	100	0.16	100	0.42
90	0.30	90	0.82	150	0.13	150	0.89
120	0.28	120	0.76	200	0.12	200	0.27
150	0.25	150	0.67	250	0.07	250	0.19
180	0.15	180	0.57	300	0.05		

Table 2.
Evolution of the equilibrium concentration according to the dose of the material to remove.

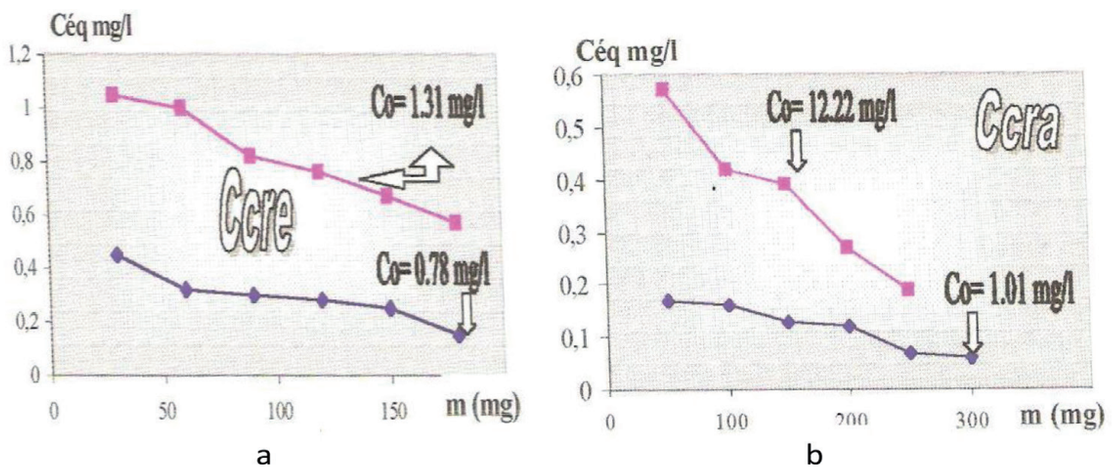

Figure 3.
(a) Variation of the Cu concentration as a function of added mass of Ccre. (b) Variation of the Cu concentration as a function of added mass of Ccra.

By calculating the average percentage removal of Cu for both materials (**Table 3**), we noticed that the highest percentages of elimination are marked for water treated by the Ccra. Whereas the percentages relative to Ccre are weaker than what is in agreement with [16].

For a given sample, when the mass of material increases, the percentage of reduction increases slightly. The variation of the percentage change can be considered constant from 250 mg (**Table 3**).

	Ccre		Ccra	
	Test 1	**Test 2**	**Test 1**	**Test 2**
Co mg/l	0.78	1.31	1.01	12.22
Ceq mg/l	0.25	0.67	0.13	0.39
%	67.95	48.85	87.13	96.80

Table 3.
Average removal percentages evolution of Cu for both materials.

Ni: To estimate the efficiency of the material for the treatment this wastewater, we followed the evolution of the residual concentration of the Ni according to the various injected doses. The optimal dose of the material is chosen according to the quality wished by the water treaty. It is generally obtained when the ratio of M^{2+} equilibrium/M^{2+} original becomes little bit constant.

Figure 4 shows that the residual amount of Ni after adsorption on the Ccre decreases gradually by increasing the dose of the material. For the Ccra the concentration in the equilibrium after treatment by 50 mg does not differ any more from that stayed after treatment by 150 or 200 mg. This results shows that the Ni shows an affinity important for Ccra. This is at the middle in evidence by the efficiencies on elimination which are maximums for Ccra.

Cr: The results of the dosage of the chromium before and after adsorption are included in **Table 4** below.

From this table, the removal efficiency increases as the Ccre metal concentration decreases. This agrees well with the isothermal studies [16], even if the physico-chemical quality of the water differs. We should note also that all the initial concentrations exceed the PVL fixed to 0.2 mg/l (**Table 5**). After treatment by the Ccra and by Ccre, the concentrations become lower than the standards. The hexavalent chromium is weakly eliminated by Ccre and

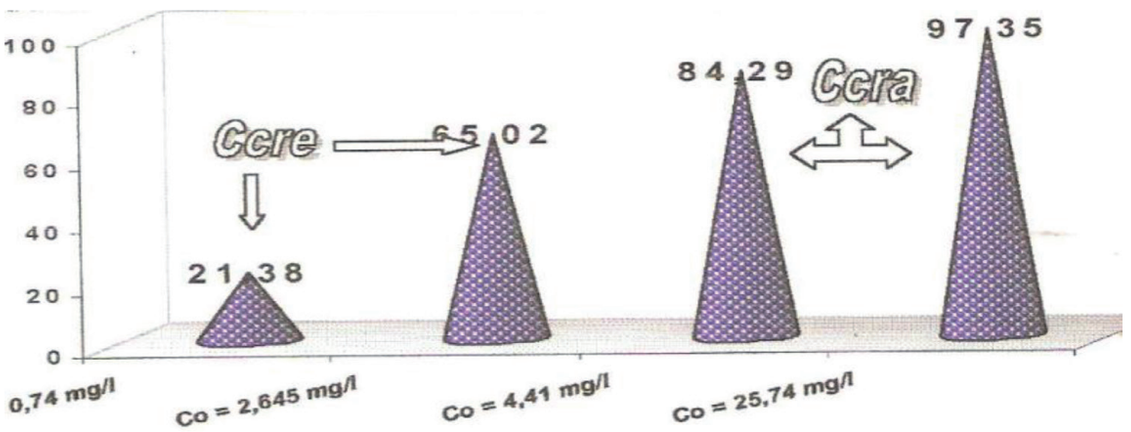

Figure 4.
Changes in removal efficiencies of Ni as a function of dose % of the material removal.

Ccra		Ccre			
Test 1 **Co = 3.204 mg/l**		**Test 1** **Co = 0.41 mg/l**		**Test 2** **Co = 0.56 mg/l**	
Weights (mg)	**Ceq (mg/l)**	**Weights (mg)**	**Ceq (mg/l)**	**Weights (mg)**	**Ceq (mg/l)**
	0.036	30	0.096	30	0.051
100	0.044	60	0.024	60	0.100
150	0.016	90	0.002	90	0.060
200	0.011	120	0.018	120	0.087
250	0.053	150	0.014	150	0.056
300	0.020	180	0.019	180	0.033

Table 4.
Evolution of the concentration of the Cr^{6+} according to the dose of the material.

	Ccre	Ccre	Ccra
Co (mg/l)	0,411	0,564	3,204
Ceq (mg/l)	0,024	0,100	0,044
PVL (mg/l)	0,2	0,2	0,2

Table 5.
Evolution of the concentration equilibrium Ceq according to the initial concentration C_o for a dose of 0.6 mg/l.

by Ccra [14, 16], yet in this discharge, the elimination of chromium is very important by both sources of the chitin.

4. Characterization and treatment of current rinsing by adsorption on raw chitin

4.1 Physical-chemical characterization

4.1.1 Physical-chemical

We have studied the characterization and the treatment of the rejects of the metallization baths of metals Cu, Zn, Cr and Ni. The physico-chemical rinses aware of four baths metallization (Cu, Zn, Cr and Ni) has been grouped by the following table:

pH: Because of degreasing, etching and galvanic deposition, we worked with solutions of different types of reactions. We have to avoid absolutely the training of the slightest traces of a solution in what is next. In addition, we must ensure that no residual solution in the emptiness or back of the room, because this residue would affect extremely, adversely the adhesion of a plating. According all to the possibilities the rinsing must be done in that is rinses current water which is characterized by a neutral pH, from **Table 6**, the recorded pH is more neutral. The pH of the rinsing current Cr is acidic. All rinses Cr acquire the characteristics of a flushing death. The same for the flushing power of Cu, since it works with an alkaline bath, the pH of the rinse is relatively high; it reached a maximum 8.33 for the collection of 11-9-08. In the case of current rinsing bath of Zn is acid so the pH values below 7. They reach 6.6 by the same observation was recorded in the case of power flushing Ni. Note that for the same type of rinsing, the pH does not change significantly from one chain to another.

CE: Electrical conductivity is the lowest recorded in the case of the Cu current rinsing, while the highest values are recorded for the zinc rinses (**Table 6**).

MES: rinses have higher levels of MES ranging from 162 to 740 mg/l respectively for Ni and Zn. MES in the rinses is much smaller than the global rejection [14]. The rinses of zinc are the most loaded (**Figures 5** and **6**).

DCO: Highest values of DCO are recorded in the case of rinsing the zinc in the chain II, while for the rinsing of Ni, Cu and Cr, they do not exceed by 400 mg/l, that value is less the limit values (PVL).

OD: it is large fluctuations, water bodies are generally well oxygenated (**Table 6**). Maximum values up to 17.8 mg/l are noted in the current Cu rinses. This contribution is due to the complete absence of a biological pollution in the rinse tanks. Besides all the settings in this collection are low, the DCO does not exceed 40 mg/l. For comparison the variation of average concentrations of these parameters depending on the type of metal rinsing are shown in **Figure 5** below.

	Day/ month	Chain	pH	CE (mS/cm)	MES (mg/l)	DCO (mg/l)	OD (mg/l)	S_{O4}^{2-} (mg/l)	Cl- (mg/l)	Ca^{2+} (mg/l)
	11/9	II	6.96	3.93	190	380	14.6	212	—	—
Ni^{2+}	15/9	II	6.81	3.66	162	—	16.6	348	537	—
	23/9	II	6.56	3.73	134	300	12	200	521	—
	3/10	II	6.72	4.00	—	340	10.0	64.8	507	736.2
	11/9	I	6.04	49.50	525	2960	4.9	631	—	688
Zn^{2+}	15/9	I	6.07	43.75	500	3920	6.41	556	—	—
	23/9	I	6.04	63.79	740	2800	5	500	—	785.8
	3/10	I	6.08	58.0	715	3760	6.6	424.8	724	883.4
	11/9	II	3.02	3.93	492	258	10.2	—	—	—
Cr^{6+}	15/9	IV	3.21	8.16	234	315	9.2	202	—	—
	29/9	II	4.12	3.05	138	418	5	353	—	—
	3/10	IV	2.5	17. 5	74	269	121.4	50.4	—	272
	11/9	II	8.33	3.04	88	480	8.5	—	597	112.1
Cu^{2+}	23/9	IV	7.51	2.13	138	40	17.8	37.9	239	192.1
	3/10	I	8.19	2.24	628	400	12.01	13.9	269	160.0
	3/10	I	7.97	3.74	190	240	14.7	—	726	288.1

Table 6.
Quality physical-chemical of rinses for the treatment.

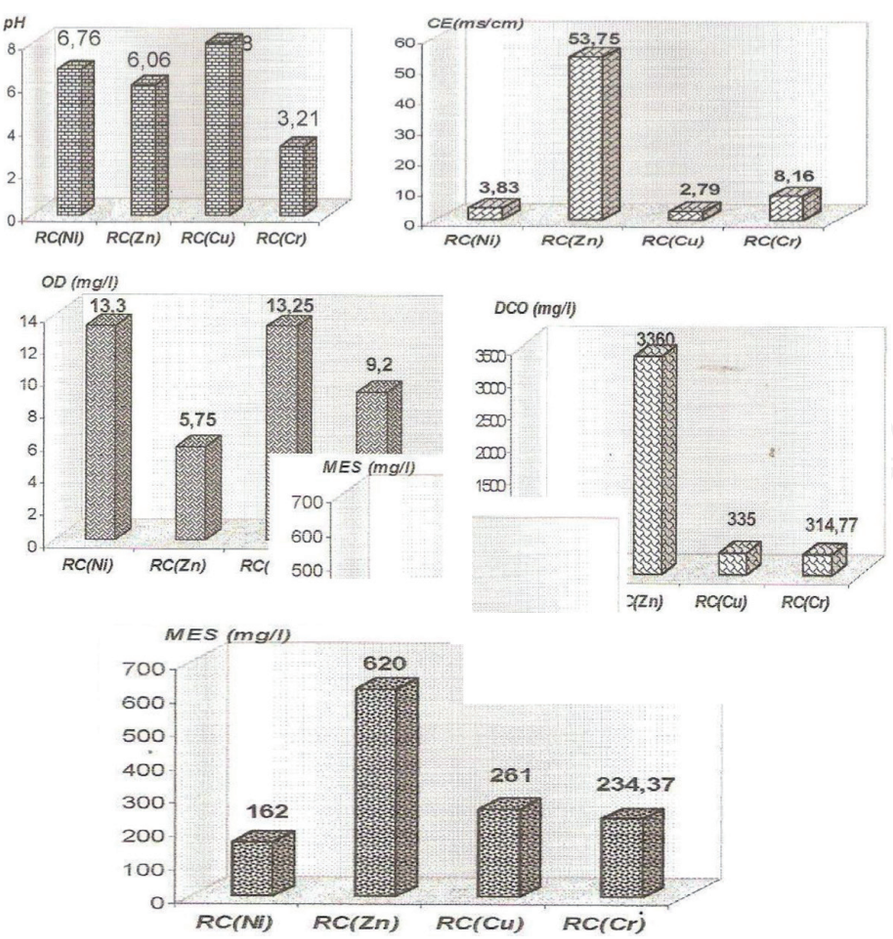

Figure 5.
Evolution of the physicochemical parameters pH, EC, MES, COD, DO according to the type of current rinsing [RC(Ni), RC (Zn), RC(Cu) and RC(Cr)].

4.1.2 Metal pollution

In order to assess metal pollution, we tried to assay the ion currents located in the rinsing after plating by Cu, Zn, Cr and Ni (**Figure 6**).

In the studied unit, the static rinse is used primarily to recover and recycle metal in the plating baths, but on the other hand, the current simple rinsing aims to clean the pieces. The determination of heavy metals in these rinses (**Table 7**) shows that the levels of metal ions are very high. They are generally higher than those found in the global rejection. Example, the levels of Cu^{2+} reach an average 22.21 mg/l [14].

In fact, some bath rinses as Ni and Cr are highly concentrated in the rinse tanks, there are many colored water after rinsing the metal: green for Ni, Cu and blue to yellow for Cr. These waters differ slightly from the dead rinses. These huge losses of metal ions are due to inadequate drainage time pieces and often exceeded the stage of rinsing death. For the case of Cu the maximum values are found in the flushing of the IV chain, while the levels of the chain I are relatively low, this is due to the number of work pieces and the capacity of each channel.

For the case of Ni the values fluctuate between 15 and 34 mg/l with an average of 24.51 mg/l. In the case of Zn, the maximum values are recorded in samples of 11-9 and 3-10.

It should be noted also that in the current flush of a metal there are traces of other metals, rinsing the Ni the chain of 3-10 II also contains Cu and Zn, Cu rinsing contains Cr, Cr rinse contains Ni and Cu (**Table 8**).

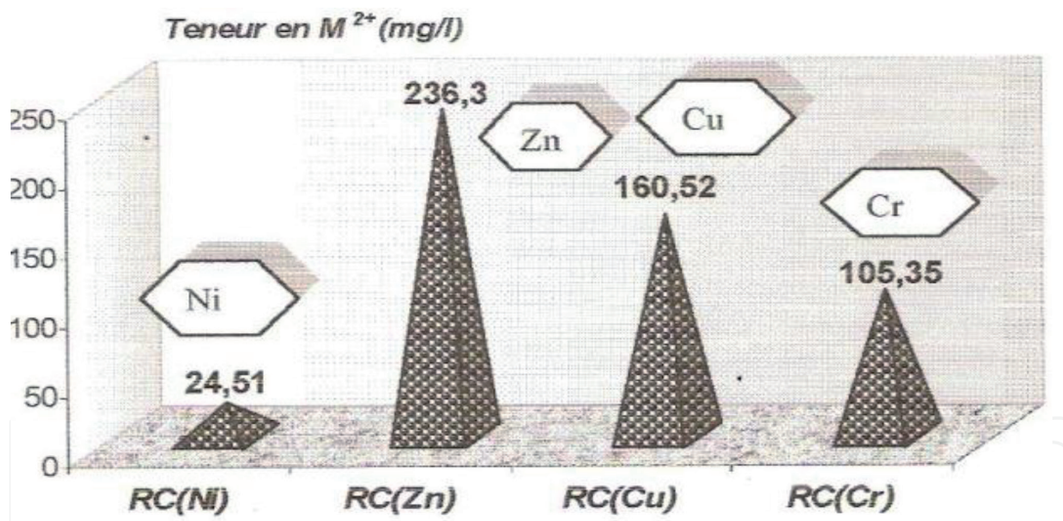

Figure 6.
Average levels of metal ions in the rinse currents.

	Nickel	Copper	Chrome	Zinc
11/9	34.21(II)	296.5(IV)	211.7(II)	201.1(I)
15/9	29.31 (II)	—	20.13(IV)	32.4(I)
23/9	19.02(II)	20.70 (I)	—	41.6(I)
29/9	—	—	0.96(II)	—
3/10	15.05(II)	256.6(IV)	—	670.1(I)
3/10	—	68.3(I)	188.6(IV)	—

Table 7.
Evolution of metal ion concentrations (mg/l) according to the type of rinsing in different chains.

	Ni	Cr	Zn	Cu
Current rinse of Ni	15.05	0.59	1.93	0
Current rinse of Cr	3.87	188.6	0	12.42
Current rinse of Cu	0	1.17	0	68.3
Current rinse of Zn	0	0	670.11	4.73

Table 8.
Concentration of metal ions in the rinse of metal in mg/l of sample 3/10.

4.2 Rinsing water treatment test common to plating baths

The current water rinses are treated the same way that releases overall. We studied the case of Cu, Ni, Cr and Zn. For each metal we have tried to work on two different samples. The results of this study are summarized in the **Table 9** below.

The expression of the calculation of the % of adsorption is 100 * C0-Ceq/C0.

Cu: The table shows that the removal efficiency increases as the mass of material increases especially for the rejection diluted. In general, treatment of rinse water is more effective than the treatment of Cu in the global rejection [6–8]. Indeed, the removal percentages do not exceed more than 63% in the global rejection while for flushing streams they reach 98.08%.

Ni: In the case of Ni, we see that the residual concentration decreased from 1.5 to 1.2 mg/l with a percentage reduction is very small compared to the percentage reductions in the case of total rejection [6], we can say that the presence of other metals does nothing, but increasing the removal of the Ni.

Cr: the removal yields is relatively low compared to those found in the overall rejection, it does not exceed 28% for the diluted rinsing and 25% for the concentrated rinsing.

		Weights of adsorbant (mg/l)	50	100	150	200
	1	C (mg/l)	1.99	2.69	3.99	0.43
		% of adsorption	92.23	89.49	84.45	90.17
Cu	2	C (mg/l)	0.59	0.54	0.31	0.12
		% of adsorption	71.64	74.06	84.98	94.39
	1	C (mg/l)	165.7	155.9	141.1	149.6
		% of adsorption	12.14	17.34	25.18	20.68
Cr	2	C (mg/l)	15.39	15.43	16.15	15.10
		% of adsorption	27.3	27.11	23.71	28.67
	1	C (mg/l)	63.66	—	16.52	6.54
		% of adsorption	4.99	—	16.83	90.23
Zn	2	C (mg/l)	0.290	0.051	0.039	0.033
		% of adsorption	—	—	—	—
Ni	1	C (mg/l)	1.2	—	—	—
		% of adsorption	66.27	—	—	—

Table 9.
Changes in percentage of the adsorption of metal ions of the current rinses depending on the dose of added material.

Zn: to achieve a removal efficiency of 90.23%, it is necessary to introduce a mass of 200 mg, Similar to Cu, the effect of the dose of the material added to the percentage reduction of micro metal is very pronounced for high concentrations of metals. This result confirms the results found by Boukhlifi et al. [17, 30, 31]. By comparing the removal efficiency of the four metals, it appears that the strongest removal is marked for the case of Cu [16].

5. Study flow of pollution

A chain consists of a set of tanks whose general functions are: surface preparation, processing and finishing of the piece part in question. Each tank is defined by three characteristics:

- The mode of treatment (pretreatment, metal deposition, stripping ...)
- The type of chosen treatment (e.g. a metal deposit: silver, chrome plating, copper plating, zinc plating, etc.)
- The operating conditions (for example, a zinc plating: alkaline non-cyanide, acid fluroborate not ...) including different chemicals concentrations, fluid flow, the rate of production, etc.

The unit of surface treatment under study is composed of five chains. Each channel is determined by the succession of tanks. The average capacity of baths varies between 950 l and 1710 l, but most of the bath has a volume of 1440 l, the majority of the baths is powered water wells except metal plating baths and degreasing baths, which are filled with drinking water, bathing water that is recycled in metal plating baths of rinses dead. Water supply wells are often for an hour a day, while drinking water is draining after a bath. Discharges baths is collected through pipes that lead to the aerated sewage. All discharges are evacuated in the rough, but the rejection of the flushing stream which is recycled zinc. We were interested in flushing power of Ni and Cr; we followed up daily flow rates of 7/9 to 3/10 in **Figures 7** and **8**.

We found that the high flow rates were recorded for Cr and Ni, the rate of flushing power of Cr can be up to 600 l/h and the neither flushing current reached a maximum of 841 l/h.

- The flow rates of Ni in the chain will fluctuate between 260 and 390 l/h, they will reach 389.21 l/h, a value which represents the 1/3 of the bath of treatment, that is to say that every day, the third of the rinsing bath is changed with a capacity of 1440 l. This during the fifth of the rinsing bath of Cr is changed. These waters are evacuated; this appears from the color of releases. Rejection of Cr is yellow while the rejection of Ni is green.

The Ni current rinsing flow varies from one channel to another varies from the average flow 389 l/h for channel II 738.8 l/h for the string I.

- The temporal variation of the flow does not follow a given order; it varies from day to day depending on water supplies that are directly related to the availability of water in the well. - We tried to compare these rates with those of other baths as bath chemical degreasing and pickling bath. The flow of degreasing bath is lower and messy, while the stripping is relatively constant and is around 400 l/h.

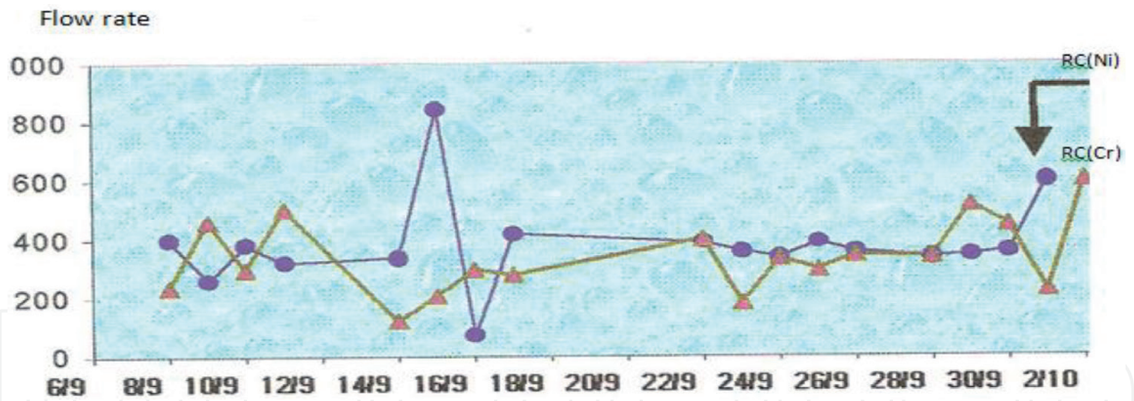

Figure 7.
Monitoring rinsing flow flows as a function of time.

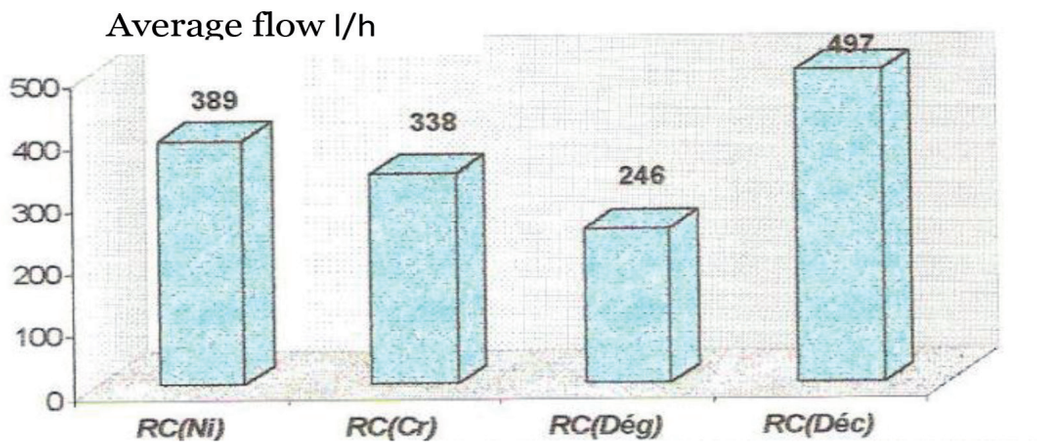

Figure 8.
Average flow rates of rinses for different metals.

From this study, it follows that the rates baths variation is random. This makes the adaptation of a method for processing or recycling of waste water very difficult. In conclusion, we must control the flow based on the minimum and maximum values recorded by installing a storage buffer.

6. Description of procedure for treatment

Handling treatment facilities are numerous, these some examples of treatment courses of this type of release:

Physical–chemical treatment is to continuously purify the various effluents as when they are produced to reject them in permanent rates.

The process is a combination of the following basic treatments:

- manure storage
- basic treatment
- additional treatment
- Final Control
- Physical–chemical batch which is to purify the effluent by tarpaulin, it is to say by successive and constant volume in the same reactor of suitable sequences [16].

- In general the combination of elementary processing is defined by the nature of the effluent to be treated. According to preliminary studies we conducted, only the rinse water can be recycled after treatment with raw chitin in particular rinses common metallization baths [25–28]. We therefore propose a processing rinses followed by a comprehensive treatment of rejection. The design of items of treatment plant is highly dependent on flow rates of each rinse that helps to estimate the reaction time stays easily adaptable.

- Reactors as a column filled with the material well-conditioned. Water to be treated flows from the bottom up by the effect of differences in level and then flows into the rinsing baths continuous overflow. Thus the heavy metal content in the total discharge will be reduced.

For the global rejection we prefer a continuous physical–chemical treatment. This principle (continuous) is used in preference to batch treatment by tarpaulin, where daily volumes in excess treat tens of m^3 even if the discontinuity of the process provides some security and facilitates the monitoring and treatment by visual inspection of each analytical or steps prior to discharge. It allows, if necessary, replacement of the entire process or just step failed. This treatment considered contains the following five basic treatments [27–31]:

1. Effluent Storage: The storage provides the interface between production facilities and the treatment plant so it performs the following functions:

   - A buffer role with regard to changes in volume and mass charges from workshops, and a reserve sufficient to accommodate the effluent during the treatment.

   - A perfect separation between the different components of the effluent.

   - A minimum hydraulic capacity, allowing the complete filling of the reactor treatment at the launch of the operation with the more regular flow of possible mergers with minimal variations.

   The storage to consider is divided into three types of storage:

   - Storage backup's role is to provide storage during an accident or during an overload of other storage.

   - Storage diluted normally receives all current daily rinsing of all pre-treatments and treatments.

   - Storage is focused especially on the garbage baths surface preparation or special cases.

The storage times are equipped with means for adjustment and control of flow injection in the treatment reactors.

2. liquid–solid separation step that gets rid of the effluent MES and some insoluble elements [31]; it is installed mainly concentrated after storage. The liquid–solid separation of sludge is achieved by settling, both phases are separately drained.

3. Neutralization, this phase is on the middle that is, the characterization studies have shown that most of the pH is close to 5.99 with an average 6.01 except a few exceptional cases. From then this step will be in most of the day exceeded even in the case of the neutralization of dilute effluents at the exit of treatment, discharge will be clarified concentrated alkaline after treatment and then joined the others in terms of diluted effluent neutralization.

4. Specific Treatment: The treatment methods are defined in terms of chemical elements in the flue. In most cases, the courses include.

- One or more stages of detoxification.
- A phase in dissolution-precipitation.
- A flocculation phase alternating.

But all these steps, we offer the reactors filled with raw chitin from shrimp processing is done in series with at least two reactors. Power through the discharge is from the bottom up to ensure the best conditions of contact. Similarly we must always place two reactors relief and it is also a book containing alternating chain also at least two presidents to keep the operation continues.

5-Treatment of sludge generated once the carrier material is saturated, the sludge is then pumped out regardless of the waters. This sludge can be regenerated by an acid or recycled in building materials [32], such transactions may take place after dehydration on a filter press which the design is based on the mass flows of raw material and insolubilized in the reactor.

7. Conclusion

In conclusion, and since the coast of Casablanca city is subjected to numerous anthropologic attacks, In front of such a situation, it is indispensable that every industrial unity must be equipped with a wastewater system treatment, to protect the environment and its resources. The treatment of the global discharge shows that there is competitive adsorption between metals. The nickel has more affinity toward crab raw chitin. The waste water treatment by raw chitin from shrimp entrains a decrease of heavy metals contents in the global rejection. The efficiencies on elimination are important and excess 99% for some metals. The use of the raw chitin shows itself of big potential for the treatment of the liquid discharges of the studied unity MAFER. It showed itself capable of treating heavy metals loads superior to 200 mg/l by presenting percentage removal between 90% and 97%, as in the case of Cu^{2+}.

The physic-chemical characterization shows that the currents rinses are greatly loaded with heavy metals far exceed the proposed limit values Morocco PVL. The adsorption test of heavy metals on raw chitin showed interesting results for the current rinses. Besides the rejection colored before adsorption (case of Ni, Cu, and Cr) becomes colorless after treatment with raw chitin. The study of the rinses currents treatment by raw chitin, we allowed the description of a treatment facility based on chitin. Consequently the adsorbing support raw chitin must be added in the treatment stations of the effluent of the units of surface treatment to eliminate the metallic pollution.

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