# Contribution to Tannery Waste Water Treatment for Chromium Removal/Recycle by Means of Cation Exchange Resins

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This work deals with the methodology of choosing a combination of processes for optimal treatment of tannery waste water, aiming at chromium removal/recycle through adsorption and cation exchange. The methodology we have developed, under the form of an algorithmic procedure, consists of 22 activity stages and 8 decision nodes. A case example has been used to illustrate certain features of the functionality of this procedure, concerning the adsorption of $Cr^{3+}$ on and cation exchange with Amberlite IR 120-H (CAS: 39389-20-3, MSDS), a strongly acidic exchange resin of gel type, with sulphuric acid as functional group and styrene-divinylbenzene as matrix. The thermodynamic equilibrium of this process has been studied through adsorption isotherms and the kinetics has been examined by applying several models of various order under batch conditions while for the continuous flow regime the Bohart Adams model and its relevant modifications were used.

## 1. Introduction

The tanning media mostly applied in leather industry are the $Cr^{3+}$-salts. The liquid and sludge wastes (coming from the last six processes shown in Figure 1) contain the same metal in significant concentrations. Although traces of $Cr^{3+}$ may be beneficial for human health, there is evidence that the compounds of $Cr^{6+}$ are dangerous for human health, even at very low concentration. Since oxidation of $Cr^{3+}$ to $Cr^{6+}$ may occur in Nature, accelerated also by the catalytic action of common ores like $MnO_2$, the removal of such ions from tannery wastes is necessary to prevent water and soil contamination.

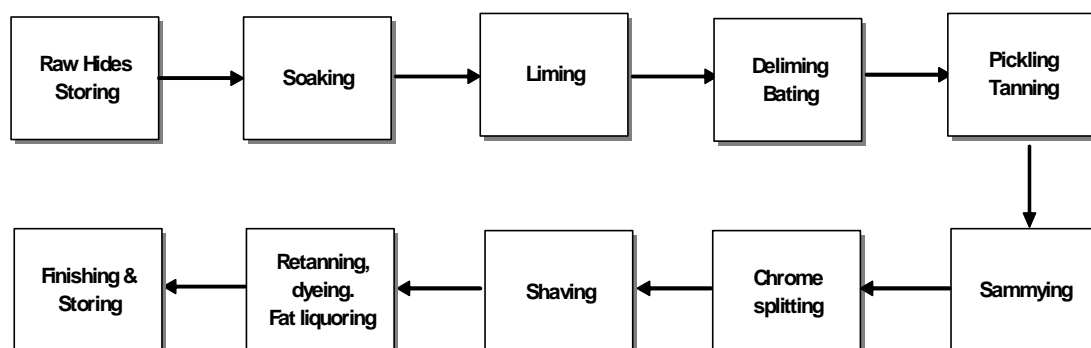| Raw Hides Storing | → | Soaking | → | Liming | → | Deliming Bating | → | Pickling Tanning |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |

| Finishing & Storing | ← | Retanning, dyeing. Fat liquoring | ← | Shaving | ← | Chrome splitting | ← | Sammying |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |

*Figure 1: Indicative Processes in leather industry*

Table 1: Added chemicals (kg·t$^{-1}$ of the wet salted hide) in the leather processing system, corresponding waste, and indicative pollution load per parameter in the effluent; parameters are not actually independent to each other (Cl$^-$ & SO$_4^{2-}$ are included in TDS, BOD$_5$ & COD are inter-related)

| Substance | Input (kg·t$^{-1}$) (addition) | Waste % of input | Parameters | Pollution load (mg·L$^{-1}$) |
|---|---|---|---|---|
| Chrome oxide, Cr$_2$O$_3$ | 20-29 | 60-48.2 | Cr$^{+3}$ | 135-170 |
| Acids, bases, salts | 173-204 | 98.2-98 | pH | 5.5-9.5 |
| Dyestuffs | 4-6 | 12.5-25 | BOD$_5$ | 1,750-2,200 |
| Enzymes | 4.5-7 | 88.8-92.8 | COD | 3,800-2,150 |
| Fat liquors | 17-26 | 23.5-23 | Suspended solids (SS) | 1,850-2,100 |
| Finishing products | 95-108 | 84.2-85.1 | S$^{2-}$ | 150-175 |
| Organic tanning | 18-27 | 25-20.3 | Total nitrogen (TKN) | 145-180 |
| Tensides | 2.5-3.5 | 80-85.7 | Cl$^-$ | 4,580-5,390 |
| | | | SO$_4^{2-}$ | 1,270-1,540 |
| | | | Oil and grease | 125-140 |
| | | | TDS | 9,000-11,500 |

The most common method for Cr$^{3+}$ removal (and subsequent recycle) is precipitation with alkaline agents, like Na$_2$CO$_3$, Ca(OH)$_2$, NaOH. Alternative methods proposed so far are the following (for References, see Wionczyk et al., 2006): (a) liquid-liquid extraction with partially ammoniated di(2-ethylhexyl) phosphoric acid (D2EHPA) and di(2,4,4trimethylpentyl) phosphinic acid (Cyanex 272); (b) four-stage extraction/re-extraction with (D2EHPA) or mono(2-ethylhexyl) phosphoric acid (M2EHPA); (c) ion exchange with cation-exchange resins; (d) partial freezing; (e) application of high temperature and pressure; (f) membrane technologies; (g) absorption on kaolinite; (h) flotation process using active charcoal and oleic acid surfactant. Since all these methods are continually improved while other techniques are also invented, there are certain difficulties in choosing the combination of processes that constitute the best method. These difficulties are stronger in case of tanneries co-operation as regards treatment of their wastes (usually in an industrial region, where several such plants have been established in order to take advantage of external economies) because of the very wide concentration range of (i) the chemicals used as input and (ii) the corresponding polluting effluents, as shown in Table 1.

## 2. Methodology

We have developed the following methodology, under the form of an algorithmic procedure (including 22 activities stages and 8 decision nodes, described subsequently and inter-related as shown in Figure 2) to cope with the difficulties mentioned above.

1. Analysis of tannery liquid wastes and determination of corresponding simulated solutions to be used in laboratory measurements, according to respective standards or recommended practices.
2. Selection of Cr-removal/recovery methods by using cation exchange resins (CER) and ontological mapping of the relevant concepts/relations by defining/structuring a controlled vocabulary.
3. Experimental design to obtain the supplementary data required to describe each Cr-removal/recovery method.
4. Performance of the designed measurements.
5. Collection of economic data.
6. Multicriteria choice of the method to be used for Cr-removal/recovery.
7. Decomposition of the chosen method into unit operations/processes.
8. Modeling of the removal/recovery process to be thoroughly examined, under the form of a quantitative expression suitable for parameters identification and their values estimation through statistical regression.
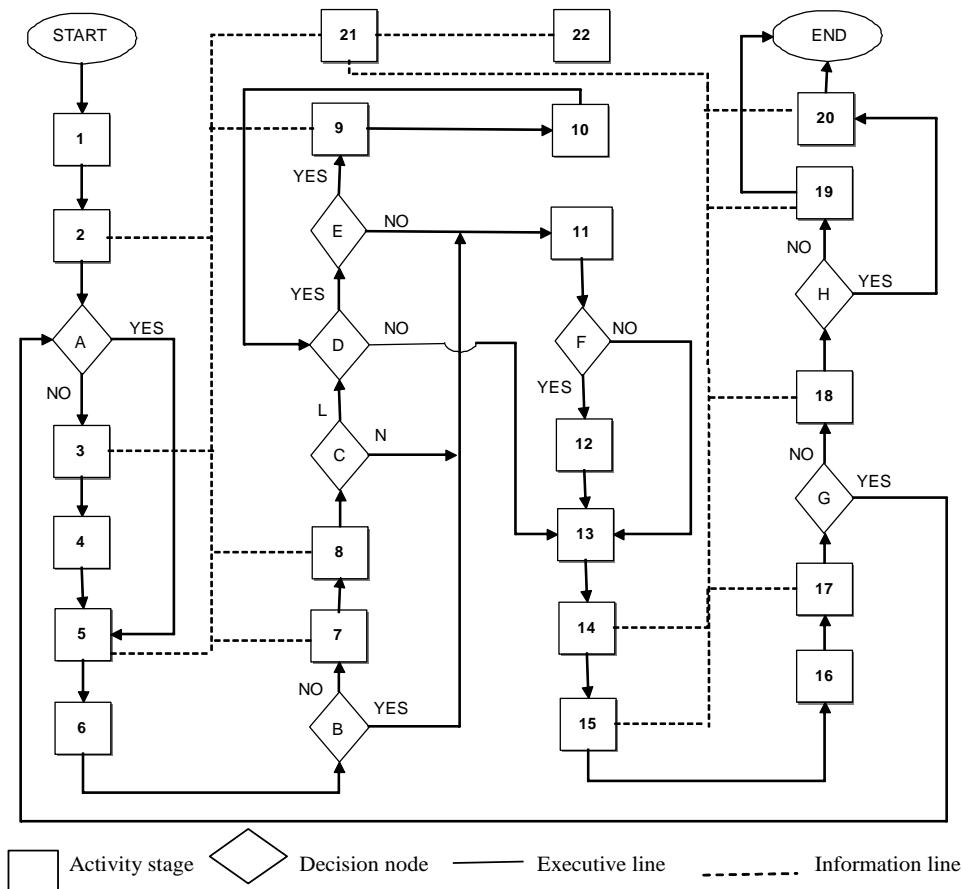
*Figure 2: The algorithmic procedure developed for chromium removal/recovery/recycle*

9. Experimental design.
10. Performance of measurements.
11. Standardization by mean-centering the independent variables values and normalization within a unique range.
12. In corporation of this relation into the regression model.
13. Regression Analysis.
14. Optimization of the process under consideration.
15. Estimation of materials- energy input-output value for the rest processes, best on the corresponding magnitude of the Cr- removal process.
16. Recomposition of all processes to obtain the initial method.
17. Total optimization.
18. Feasibility Study of Cr-recyclability, based on techno-economic and environmental criteria-data.
19. Technoeconomic Study, including environmental impact assessment, for disposal.
20. Break Even Analysis taking into account the 'environmental benefit' as a substitute for 'revenue'.
21. Development/operation/updating of an internal Knowledge Base (KB).
22. Searching in external KBs for data mining by means of an Intelligent Agent, according to Batzias and Markoulaki (2002).
A. Are the available data adequate, as regards quality and quantity?
B. Has this method a unique main process?

C.  Is the regression model linear or non-linear (denoted by *L* or *N*, respectively, in Figure 2)?
D.  Is the Condition Number (defined as the square root of the maximum eigenvalue divided by the minim eigenvalue) above 30, thus indicating significant multicollinearity?
E.  Is it possible to obtain more input data?
F.  Is there a quantitative relation, extracted through scientific knowledge, between certain explanatory (considered a priori as 'independent') variables?
G.  Is a subsequent stage necessary for scaling up?
H.  Is it feasible?

## 3. Implementation

The methodology described above has been implemented in several cases among which the redox-adsorption method that is presented subsequently as a paradigm, since it includes two stages (of a total of four) of cation exchange. The medium used was Amberlite IR 120-H (CAS: 39389-20-3, MSDS), a strongly acidic exchange resin of gel type, with sulphuric acid as functional group and styrene-divinylbenzene as matrix. The fist stage is oxidation of $Cr^{3+}$ to $Cr^{6+}$, the second is removal of sodium ions (which are competitors to chromium adsorption on and cation exchange with Amberlite), the third is reduction to $Cr^{3+}$ and the forth is similar to the second one. The later process of $Cr^{3+}$ adsorption on Amperlite is actually the one to be thoroughly examined, as quoted in stage 8 of the algorithmic procedure presented in the Diagram of Figure 2. The simulation solutions were $CrCl_3$/NaCl at 20 $^oC$ and the measurements in the samples were performed by means of Atomic Absorption and UV-VIS Spectrophotometry. Although this resin is a representative one of its category, the relevant technical literature is very poor to support the design of a batch-type processor and an adsorption/ion-exchange column, according to a methodology developed in Batzias et al. (2009) and Sidiras et al. (2011) for batch and continuous adsorption of other kinds of wastewater. For this purpose, we have chosen the best (with the minimum SEE criterion, as shown in Tables 2, 3) isotherm type and kinetic model, based on statistical processing (mainly through non-linear regression) of experimental results obtained in our Laboratory *ad hoc* in both modes, with synthetic and industrial wastewater. The final results are discussed in comparison with the conclusions we have reached recently, when using modified biomass for chromium removal within a framework of Industrial Ecology and sustainable development (Batzias et al., 2011; Sidiras and Politi, 2011).

For the batch adsorption experiments, the Freundlich (1906), the Langmuir (1916) the Sips (1948), the Radke–Prausnitz (1972), the Modified Radke – Prausnitz, the Tóth (2000) and the UNILAN isotherm equations were applied (Figure 3a) and their parameters are presented in Table 2. Moreover, the Lagergren (first order) (1898), second order (Ho et al., 2000) and a *κ*-order kinetic models were used (Figure 3b) and their parameters are given in Table 3. For the adsorption column experiments the 'bed depth service' model proposed by Bohart and Adams (1920), the Clark (1987) 'logistic' equation, the Thomas (1994) model, the Yoon–Nelson (1984) model and the Modified Dose–Response (MDR) model proposed by Yan et al. (2001) were used.
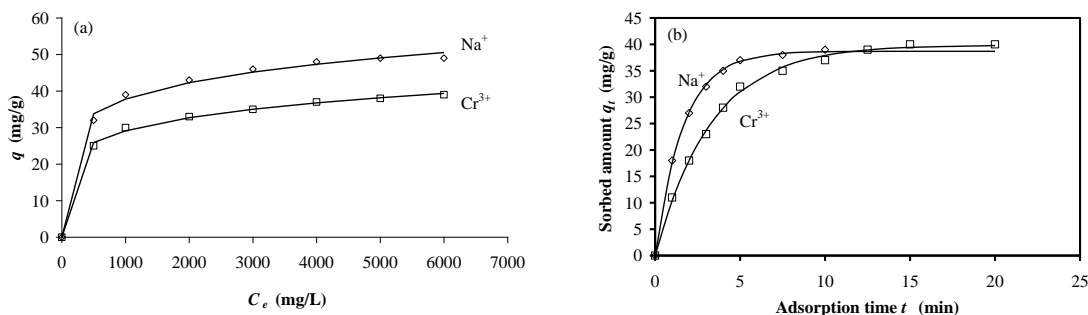


Figure 3: (a) Freundlich isotherms and (b) Lagergren kinetics of $Na^+$ and $Cr^{3+}$ adsorption on Amberlite

Table 2: *Estimated values for parameters and the Standard Error of Estimate (SEE), when least squares are used, for the alternative isotherm models considered herein ($K_F$ = Freundlich capacity; $K_L$ = Langmuir intensity; $q_m$ = Langmuir capacity; n = intensity coefficient; s = UNILAN constant; the determination coefficient $R^2$ corresponds to linearized forms)*

| | $K_F$ | $K_L$ | $q_m$ | n | s | $R^2$ | SEE |
|---|---|---|---|---|---|---|---|
| *Na$^+$ on resin* | | | | | | | |
| Freundlich | 12.34 | | | 6.170 | | 0.9633 | 1.1998 |
| Langmuir | | 0.003171 | 51.34 | | | 0.9915 | 0.7083 |
| Sips | | 0.003144 | 55.50 | 1.408 | | | 0.4928 |
| Radke-Prausnitz | | 0.006958 | 32.15 | 1.057 | | | 0.4821 |
| Modified Radke-Prausnitz | | 0.005153 | 41.17 | 1.066 | | | 0.4800 |
| Toth | | 0.04119 | 56.18 | 1.545 | | | 0.4882 |
| UNILAN | | 0.003484 | 53.75 | | 2.252 | | 0.4987 |
| *Cr$^{3+}$ on resin* | | | | | | | |
| Freundlich | 9.113 | | | 5.947 | | 0.9845 | 0.5636 |
| Langmuir | | 0.003101 | 39.87 | | | 0.9770 | 0.9170 |
| Sips | | 0.001546 | 53.58 | 2.298 | | | 0.4030 |
| Radke-Prausnitz | | 0.02048 | 15.09 | 1.125 | | | 0.3465 |
| Modified Radke-Prausnitz | | 0.003101 | 39.87 | 1.001 | | | 1.0021 |
| Toth | | 0.003012 | 39.91 | 0.9969 | | | 1.0085 |
| UNILAN | | 0.002419 | 48.45 | | 4.048 | | 0.3997 |

Table 3: *Kinetics of adsorption/removal (without and with a fixed kernel); all parameter values have been estimated by means of non-linear regression (k = adsorption/removal rate constant; q = saturation capacity; κ = reaction order)*

| | 1st order kinetics | | 2nd order kinetics | | κ-order kinetics | |
|---|---|---|---|---|---|---|
| | No kernel | Kernel | No kernel | Kernel | No kernel | Kernel |
| *Na$^+$ on resin* | | | | | | |
| SEE | 0.33982 | 0.36489 | 1.00618 | 1.09527 | 0.26999 | 0.30151 |
| kernel | | 0.16 | | -0.27 | | 0.029 |
| k | 0.60258 | 0.59960 | 0.01596 | 0.01609 | 0.42520 | 0.42670 |
| q | 38.69 | 38.71 | 45.67 | 45.62 | 39.21 | 39.21 |
| n | 1 | 1 | 2 | 2 | 1.1061 | 1.1048 |
| *Cr$^{3+}$ on resin* | | | | | | |
| SEE | 0.62912 | 0.65910 | 1.12349 | 1.16739 | 0.62308 | 0.66573 |
| kernel | | 0.26 | | -0.63 | | 0.06 |
| k | 0.30073 | 0.29783 | 0.00693 | 0.00712 | 0.20898 | 0.21125 |
| q | 39.86 | 39.90 | 47.95 | 47.77 | 40.47 | 40.45 |
| n | | | 2 | 2 | 1.1063 | 1.1026 |

## 4. Concluding Remarks

The methodology we have presented herein may apply to tannery waste water treatment for chromium removal/recycle. Its functionality has been proved by using a case example concerning the adsorption of $Cr^{3}+$ on and cation exchange with Amberlite IR 120-H. The thermodynamic equilibrium of this process has been studied through adsorption isotherms and the kinetics has been examined by applying several models of various order under batch conditions while for the continuous flow regime the Bohart Adams model and its relevant modifications were used. It is worthwhile noting that a complete methodology for tannery waste water treatment might contribute to successful reengineering in the leather processing industry, especially when tanneries examine the possibility of relocation from urban to industrial regions under the pressure of stricter environmental standards (influencing also the relevant legislation), as reported in Batzias and Batzias (2003).

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