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Application of Ion Exchange Techniques to Industrial Process of Metal Ions Removal From Wine

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Abstract. In this article, the application of selective ion exchange resins to the industrial metals removal of wine has been studied as an alternative to the "blue clarification" technique. In this sense, under the perspective of using this technology in the metals removal of sherry wines, a set of experiments at laboratory and pilot plant scale have been carried out. The study shows the behavior of several alkaline ions, metal ions and other parameters (pH, colour, protein index, etc.) during the process. Moreover, using the general theoretical model for continuous multistage processes, this study contemplates also the engineering design and the economic balance of the industrial process based on ion exchange columns. The experimental results demonstrates that ion exchange techniques are more effective and economic than "blue clarification" for metals removal of sherry wines. The proposed practice does not produce alterations in the qualities of the products; it achieves stability enough and also permits an important decrease of the contents of heavy metals.

Keywords: ion exchange, metal removal, iminodiacetic resin, wine oxidative stabilisation

1. Introduction

The oxidative degradation that can suffer the biologically aged wines of the Sherry zone (called "fino" or "manzanilla") constitutes one of the main enological problems that the area shows. This phenomenon can be observed some months after bottling depenend on the cases, and produces remarkable modifications in the organoleptic properties of wines (Navrotsky and Avakiants, 1986; Terry-Muñoz, 1973). This changes mainly consists to a continuous browning, a loss of aromatic freshness, and the appearance of precipitates of condensed phenolic material (Martínez et al., 1993, 1997). At last, this decaying process leads to a loss of quality that limits the commercialisation time.

At the moment, it is known that there are certain factors that intervene importantly in the redox stability of sherry wines. Among those it is necessary to highlight the presence of certain metal ions in the medium that can acts as process activators (Ribereau-Gayon et al., 1998). Fundamentally, the ferric cation (Fe^{3+}) is the main metallic element susceptible of producing alterations in wines, due to their majority presence, followed by the cupric cation (Cu^{2+}).

On the other hand, the health laws of most of the countries are reducing today the presence of metals in beverages; as it is the case of Pb^{2+}. The origin is the contact of liquids with diverse materials, as brass of pumps or machinery (De la Torre, 1997; Scollary, 1997; Desseigne, 1993). The resolution OENO/SCMA/96/25 of the Office Internationale de la Vigne et du Vin (OIV) has established the maximum content of lead in wine at 0.20 mg/L.

For those reasons, the separation of metals could constitute a stage of enormous importance in the

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industrial process of sherry wine making. Among all the methods or treatments described for the industrial metals removal of wine, the more used in the Sherry area is the "blue clarification" or potassium ferrocyanide method (Sánchez-Pineda and Martín-López, 1997; Spiess et al., 1984). The dosage of this compound constitutes an effective treatment of the ferric and cupric turbidity in wines, since the separation of metals usually obtained are of 65–80% for the case of iron and of 85–97% for the copper (Würdig and Woller, 1989). However, this technique has the inconvenience of having a limited effectiveness regarding the problem of the oxidative phenomena of sherry wines and of producing wastewater with difficult management.

A new possibility for demetalization of the wines is the application of the ion exchange techniques, but at the moment this is not a very widespread practice in the winemaking industry. In some countries, resins are used for the polyphenols or proteins adsorption and it have been demonstrated that they also have certain metals removal capacity (Díaz-Yubero, 1993; Willians and Hudron, 1991). In this sense, some studies show that the iminodiacetic acid presents a great selectivity on the metallic elements (Naden and Willey, 1976) and so, the first applications of metal ions exchange on wine were carried out on filters of cellulose-iminodiacetic acid, for the separation of lead and copper (Gennaro et al., 1983; Gennaro et al., 1985). Later, some other authors studied the main factors that affect to the metals removal of wines using chelating resins with iminodiacetic active groups. The application of these resins to the metals removal of wines shown an effective behaviour on the reduction of iron, copper and zinc levels (Kern and Wucherpfennig, 1996; Minguez et al., 1996). Lastly, a chelating resin have been developed (FEC-1, under patent), which manifests high selectivity on iron, reducing the Fe content more than 99,5% in grape musts (Minhua et al., 1997).

The aim of this study is the application of ion exchange resins of the chelating type for the metals removal of sherry wine and the analysis of the effects on some enological parameters of the product, like the pH, metal ions concentration, color, etc. Also, the modelization of the industrial operation is developed in the study, by application of the general theory of multistage processes. Finally, a comparative valuation of costs between ion exchange and "blue clarification" techniques is shown.

2. Material and Methods

2.1. Wine and Ion Exchange Resin

The composition of wines used in the metals removal experiments are detailed in Table 1, both at laboratory scale and plant scale. In all these experiments a strong-acid cationic resin has been used. This resin is constituted by a matrix of cross-linked polystyrene with divinylbencene (8%), presenting functional groups of the iminodiacetate type; i.e.: $-CH_2N(CH_2COOH)_2$, which have high selectivity for heavy and transition metals. The resin is provided in small beds (average diameter 1 mm) and the structure of the matrix is macroporous (average pore diameter 500 Å). The product fulfils the German law for the food industry, containing values of total soluble organic substances under the limit (<1 ppm).

The stability of complexes formed between the metal ions in solution and the functional group in the resin depends on the value of DpH (Decomplexing pH) for each cation. Therefore, the adsorption-desorption of a metal ion from the resin column depends on the proton concentration in the liquid at the tower inlet. The metal elements with a DpH value higher than the wine pH are normally not adsorbed by resin, due to the low stability of those complexes. The DpH values for different metal cations present in wines are indicated in Table 2 (Bayer, 1997; Weast, 1974).

The relative stability of complexes is associated with the acid character of metals cations (charge/radius

Table 1. Composition of wines used in the experiments at laboratory and pilot plant scales.

Parameter	Laboratory	Pilot plant
Alcohol grade (°GL)	15.5	15.5
Total acidity (gTH_2/L)	5.2	5.3
Volatile acidity (gAcH/L)	0.22	0.25
pH	3.35	3.32
Total sulfurous (mg/L)	94.3	96.0
K (ppm)	607	602
Na (ppm)	21	10
Ca (ppm)	66	63
Mg (ppm)	56	54
Fe (ppm)	4	4
Cu (ppm)	0.3	0.3
Optical density 470 nm (ua)	0.080	0.088
Protein index (ua)	0.65	0.69

Table 2. DpH value and ionic radii (R_i) of some metal cations present in wines.

Cation	DpH	R_i(Å)
K^+	7.0	1.33
Na^+	6.5	0.97
Mg^{2+}	4.6	0.66
Ca^{2+}	4.4	0.99
Fe^{2+}	3.0	0.74
Pb^{2+}	1.8	1.20
Cu^{2+}	1.0	0.72
Fe^{3+}	0.5	0.64

ratio), with the stereochemistry of the obtained molecules, and with the values of the formation entropy and force of the covalent bonds formed between metals and ligand (Hudson, 1986). Generally, as much as high is the charge/radius ratio of a metal, higher affinity for the resin will have and the value of the corresponding DpH will be lower.

2.2. Operation Conditions and Experiments

Two sets of metals removal experiments have been carried out, one at laboratory scale and the other at industrial scale. The laboratory columns was constituted of glass tubes with a height of 0.29 m and 350 mL of total capacity. In all the cases, the resin load was 200 ml. At industrial scale, the column was constituted of a tower of stainless steel with 1.37 m^3 of total capacity and 1.75 m height. In this case the resin load was 1 m^3. To control the feed flows a peristaltic pumps with speed selector was used. During the laboratory experiments, we took samples of 100 mL of the column effluent at short time intervals. In the industrial experiments the samples was of 1 L of liquid.

In a complete cycle of work of the metals removal column it is necessary to distinguish four different phases. The first one is the service-phase. During this operation the ion exchange phenomenon takes place among the metal cations dissolved in the wine and the protons fixed to resin. The second is the washing-phase. Once resin is completely loaded, it is necessary to wash the microchannels in the resin bed with water countercurrently, to eliminate remains of wine and retained particles. The third operation is the resin regeneration-phase. This is normally carried out with a HCl solution (10%) in co-current flow. During this operation, the dissolved protons in solution are exchanged with the fixed cations in the resin. The last operation is the clearing-phase. It is necessary to clear the rest of HCl solution retained into the resin bed, using distilled water in co-current flow. This operation is needed to start a new acidification cycle, avoiding acid additions to the product. Once this operation is finished, the resin is ready for a new service-phase.

Table 3. Work conditions for the different phases of the ion exchange operation.

Phase	Fluid	Flow*	Time (min)
Service	Wine	5	600
Washing	Water	10	30
Regenerating	HCl 10%	4	30
Clearing	Distilled water	10	10

*Flow as dilution rate ($L_{\text{liquid}}/L_{\text{resin}}h$).

The operation conditions used in the demetalization experiments are summarized in Table 3, both at laboratory and pilot plant scale. These conditions are within the recommended range by the supplier company of the resin.

2.3. Analytical Procedures

In all the experiments, the following analyses have been carried out to each sample.

- pH, by electronic pH-meter.
- concentration of K, Na, Ca, Mg, Cu and Fe cations, by atomic absorption spectrophotometry (O.I.V., 1973; Caputi et al., 1967).
- colour index (CI), by determination of the optical density at 470 nm (O.I.V., 1973).
- protein index (PI), by the Lowry method modified (Bensadoun and Weinstein, 1976).

3. Results and Discussion

3.1. Laboratory Experiments

3.1.1. Effect on Metal Cations Concentration. The variation of total Fe and total Cu concentrations in the column outlet during the metals removal experiments at laboratory scale, are presented in Fig. 1. It can be observed first of all, that the ion exchange treatment highly reduces the iron and copper levels in wine

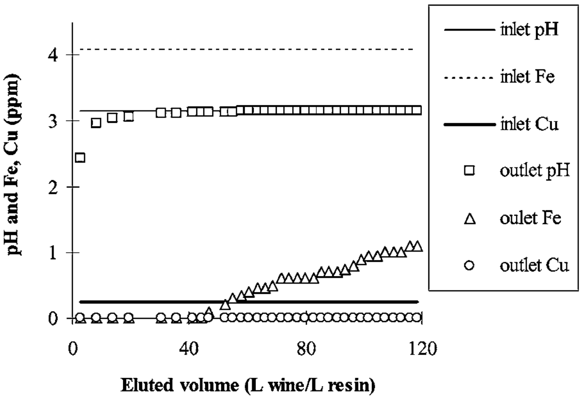

Figure 1. Variation of metal cations concentration (Fe and Cu) and pH at the column outlet, during the laboratory experiments.

(99%). However, the behaviour of each element is different during the process, since differences in the DpH values and in the column inlet concentrations exist.

On the other hand, the dissolved iron can be present in wine in two different oxidation states: Fe^{2+} and Fe^{3+}, so that the concentrations ratio will depend on the concentration of dissolved oxygen and, more concretely, on the redox potential of the medium. Since the DpH values of Fe^{2+} and Fe^{3+} differ sensibly (3.0 and 0.5 respectively), the effectiveness of the ionic iron removal will depend importantly of the aeration history of the wine. Moreover, because of the standard reduction potential of the Cu^{2+}/Cu^{+} pair (0.158 volts) is much lower than the one for the Fe^{3+}/Fe^{2+} pair (0.770 volts), the major Cu present in solution in wines is in the oxidized form (Cu^{2+}). So the redox state of the media does not influence normally on the effectiveness of the ionic copper removal.

3.1.2. Effect on pH. The variation curve of the eluted wine pH, during the metals removal experiments at laboratory scale, is also plotted in Fig. 1. As it can be observed, the pH does not suffer significant variations during the process, excepting a small decrease in the first fractions eluted. This fact is consequence of the respective ion exchanges between protons in resin and all the cations presents in solution, so the pH reduction reflects the first reaction fronts developed in the column. Later, when cations with very low affinity (like K^{+}) reach the ionic equilibrium concentration in the resin, the protons elution rate decreases and the outlet pH progressively recovers the column inlet value.

The general behaviour observed in pH during the second half of the service-phase indicates that there is not important exchange between protons in resin and the major cations in wine (alkali metals), because resin complexes are formed fundamentally with metals (Fe^{3+} and Cu^{2+}), which can be found only in small concentration. Therefore, the outlet pH is not modified practically once the process is stabilized.

3.1.3. Effect on Alkaline Cation Concentrations. As it can be observed in Fig. 2, the variation of the concentration of K^{+} and Na^{+} during the process is similar to the one shown by pH. Initially, those cations are partially retained by resin, but later the outlet value coincides with the inlet value. The reason resides essentially in the fast advance to the equilibrium concentrations mentioned above, which is reached during the first part of this service phase. So, in only 20 bed volumes the resin is saturated with alkaline cations as a consequence of their very high DpH value.

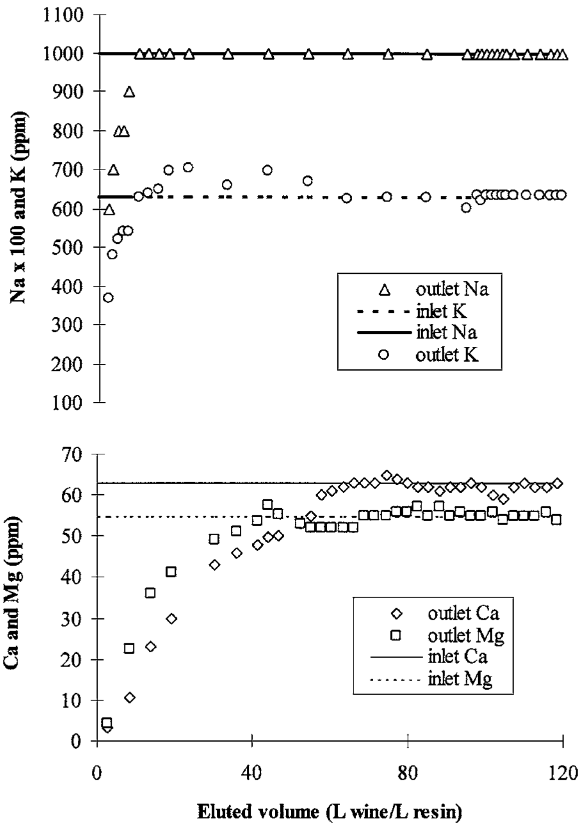

Figure 2. Variation of alkali metals concentration (K^{+} and Na^{+}) and alkali earth metals concentration (Ca^{2+} and Mg^{2+}) at the column outlet, during the laboratory experiments.

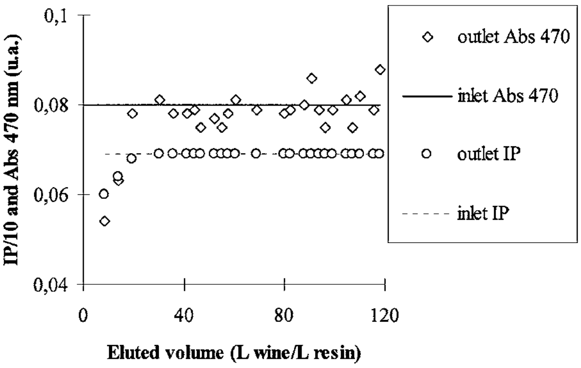

Figure 3. Variation of the protein index (PI) and color index (CI) in the outlet wine, during the laboratory experiments.

The variation of the concentration of Ca^{2+} and Mg^{2+} (Fig. 2) is also very similar to the pH evolution and the curves denote analogous behaviour of this alkali earth metals than the other alkali metals. However, due to their smaller DpH value the resin saturation is reached later in the first half of the service phase; i.e. 60 bed volumes.

3.1.4. Effect on Other Parameters. The colour index determination (CI) is carried out to establish the possible loss of organoleptic qualities of the wine during the process. The results, exposed in Fig. 3, reveal that this metals removal technique does not affects significantly the CI of the treated samples. The curve indicates a fast evolution to the equilibrium concentration (20 bed volumes). So, substances responsible of the colour of wines (polyphenols) are retained by resin in a similar way to the alkali metals and must to show very high DpH value too.

Moreover, in order to determine the organoleptic quality losses during the ionic metals removal, the effect of the ion exchange technique on the protein index of wine (PI) has been studied. The results are also shown in Fig. 3. The curve indicates that this operation does practically not reduce the PI of wine at all. As in the previous cases, the equilibrium concentration of the wine proteins is reached in the resin during the first part of the service phase, as it is normal for high DpH values.

3.1.5. Standard Model for the Industrial Operation. The industrial ion exchange process in a resin column can be approached to the general model for multistage processes, classically applied to unit operations of mass transfer. For the modellization of this operation (stationary solid bed and continuous liquid flow) it should be necessary to suppose that multiple theoretical equilibrium stages occur between resin and solution. So, the modellization contemplates, in the first place, the obtaining of the equilibrium curves and the operating lines and, in second place, the calculation of the heights equivalent to a theoretical stage or plate (HETP) for each cation involved in the exchange.

These calculations can be applied to the normal industrial operation of the column during the first phase of the work cycle: the service phase. During this phase the ion concentrations remain approximately constant at the column inlet and the column outlet and we can consider stationary process. The other phases (washing, regenerating and clearing) are not suitable for modellization in this way.

The equilibrium equation for the ion exchange multistage process relates the molar concentration of an ion in solution with the concentration of the ion in the resin, in an equilibrium stage. The form of this equation will depend on the type of the interchange produced between resin and solution. This equilibrium equation can be obtained from the data equilibria by using several theoretical models. However, the simplest one and so the recommended for the resin manufacturer due to its high specificity, assumes that the presence of other cations does not affect the ionic equilibria of the principal metal cations in the media (Bayer, 1997). In our particular case, due to there is a low concentration of each cation in the wine, this assumption is applied as a first approximation. So the equilibrium equation would derive from the the following chemical equation for each cation:

$$\mathrm{RH_2} + \mathrm{M}^{2+} \leftrightarrow \mathrm{R_2M} + 2\mathrm{H}^+$$

Where $\mathrm{RH_2}$ represents the initial form of a ligand in the resin (protonated) and $\mathrm{R_2M}$ is the final state of that ligand in the resin. M^{2+} is the metal cation in solution. Acording to the mass action law, the equilibrium equation for this process would be the following:

$$X_{\mathrm{RM}} = \frac{\left(\frac{X_{\mathrm{M}}}{1-X_{\mathrm{M}}}\right)}{\frac{\mathrm{H}^+}{\mathrm{K_M}} + \left(\frac{X_{\mathrm{M}}}{1-X_{\mathrm{M}}}\right)} \qquad (1)$$

Where X_{RM} and X_{M} are respectively the molar fraction of metal M^{2+} in the resin and in solution, H^+ is the concentration of protons in solution and $\mathrm{K_M}$ is the selectivity coefficient for the interchange $\mathrm{M}^{2+}/\mathrm{H}^+$. This coefficient can be calculated directly from the definition of DpH that indicates the pH from which the decomplexing of a metal begins (Bayer, 1997).

Under these conditions, when the pH of a medium is equal to the DpH, we have that X_{M} is equals to X_{RM}. Substituting in the previous equation, we have the equilibrium equation in the following form:

$$X_{\mathrm{RM}} = \frac{\left(\frac{X_{\mathrm{M}}}{1-X_{\mathrm{M}}}\right)}{[10^{\mathrm{DpH-pH}}] + \left(\frac{X_{\mathrm{M}}}{1-X_{\mathrm{M}}}\right)} \tag{2}$$

The cation balance between resin and solution will depend on the difference between the DpH of that cation and the actual pH of solution. As much as high is this difference largest is the fraction of metal adsorbed in the resin.

In second place, the equation of the operating line for the ion exchange multistage process relates the molar concentration of an ion in solution with the molar concentration of that ion in the resin, at a point between two consecutive equilibrium stages. So, the operation line equation would be the following:

$$\frac{X^{i}_{\mathrm{RM}} - X^{n}_{\mathrm{RM}}}{X^{o}_{\mathrm{RM}} - X^{n}_{\mathrm{RM}}} = \frac{X^{n}_{\mathrm{M}} - X^{i}_{\mathrm{M}}}{X^{n}_{\mathrm{M}} - X^{o}_{\mathrm{M}}} \tag{3}$$

Where the index "i" indicates the X values after the equilibrium stage number i and before the equilibrium $i+1$. The index "n" indicates the X values at the bottom of the column (after last stage n) and the index "o" indicates values at the top of the column (before the first stage 1).

In consequence, using the equilibrium equation and the operating line equation, the number of theoretical equilibrium stages (NTES) to carry out a required separation can be estimated. Later, the value of the heights equivalent to a theoretical stage or plate (HETP) can be calculated dividing the total linear height of the resin column by the number of theoretical stages obtained. So, the separation efficiency for each cation can be compared by mean of this parameter.

Analyzing the experimental data obtained, it can be observed that the reduction of the cation concentration in the feed stream is 99.7% for Fe^{2+} and 97.0% for Cu^{2+}, with less than 0.01 ppm of each cation in the outlet stream. Moreover, the final charge of the resin is only 0.64% for Fe^{2+} and 0.04 for Cu^{2+}. Thus, based on these data and calculating the HETP parameters as we indicate above, it can be obtained a HETP for Fe^{2+} of 13.0 cm and a HETP for Cu^{2+} of 29.2 cm. This shows that it is necessary double high of this resin to obtain the same removal of Cu than the one of Fe.

The HETP obtained in each real column for each metal will fundamentally depend on the affinity of the resin for that metal and on its concentrations in the wine. Independently of the differences among cations, the HETP, and therefore the separation efficiency, is influenced by the inlet pH of the wine. Thus, if the inlet pH diminishes, the equilibrium curves of cations move toward the operation line, being increased the number of calculated theoretical stages for a particular separation, and diminishing the effectiveness of the real column.

In consequence, both the pH and the redox potential of wine highly influence on the practice of this technique, because of its influence on the stability of the metal complexes formed. Those two operating conditions must be very well controlled in order to obtain the optimum efficiency of the industrial unit operation.

3.2. *Pilot Plant Experiments*

Generally, the obtained results in the pilot plant experiments corroborate all the concepts above exposed (Fig. 4). Thus, the behaviour of the different analysed variables does not differ significantly of the one shown at laboratory scale. The only experimental difference is that the average volume of wine eluted is lightly bigger at the industrial scale (52 to 46 L/L resin). The effects of hydrodynamic phenomena, like preferential channels, dispersion processes or back mixing, are more important at laboratoty scale than in the industrial columns.

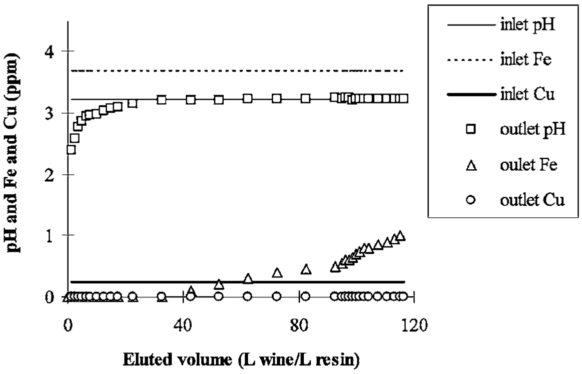

Figure 4. Variation of metal cations concentration (Fe and Cu) and pH at the column outlet, during the pilot plant experiments.

Moreover, in the pilot plant experiments it have been possible to notice a significant reduction effect on the concentration of other heavy metals, whose presence is very limited in wines, as Hg^{2+} and Pb^{2+}. Due to their low DpH value (1.7 and 1.8 respectively), those cations show a very high affinity by resin at the work pH. In the case of Pb^{2+}, the observed global reduction is from 30 ppb, at the column inlet, to 4 ppb at the column outlet. Currently, this fact attains great importance due to the observed tendency in several national regulations to decreases the maximum content permitted of these metals in wine.

Finally, a comparison of the operating costs between this ionic metals removal technique and the "blue clarification" technique has been carried out. The results are exposed in Table 4.

The obtained results clearly show that ionic metals removal reduces the operating costs to less than 10% with regard to the classic "blue clarification" technique. Moreover, this ionic procedure reduces the heavy metals content in wine more efficiently than the batch clarification. Finally, the complexing resin exhibit interesting capabilities in the way of modern environmental regulations, since the wastes of an ion exchange column have very easy management, contrary to the precipitates of ferric ferrocianide.

Table 4. Estimated calculations of metals removal costs.

Supplies*	Expense (Kg/m^3)	Unit cost (US$/Kg)	Total cost (US$/m^3)
Classic Blue Clarification			
$Fe(CN)_6K_4$	0.02	2.7	0.054
Bentonite	1.00	0.5	0.500
Gelatins	0.16	2.5	0.400
Filtration perlite	1.50	0.4	0.600
Inert nitrogen	1.20	3.0	3.600
Manpower			2.770
Wastes management			2.720
Raw material losses			1.610
Total			12.254
Ion Exchange Metals Removal			
Mineral regenerants	9.67	0.09	0.870
Cleaning water	7000	5.10^{-5}	0.350
Column amortization			0.620
Manpower			0.280
Total			2.120

*Supplies and total cost per one m^3 of demetalized wine.

4. Conclusions

The technology of ion exchange resins is an effective procedure for the metals removal of sherry wines, without producing significant alterations of the product quality. This technique contributes to the general improvement of the industrial process with a sensitive economic reduction in the operating costs.

The metals removal by this technique allows an important decrease in the content of heavy metals of wine, which are currently very restricted by regulations. Also this procedure presents an improvement in the effectiveness of the total metals removal, with regard to the traditional technique ("blue clarification"). As a consequence, the product acquires a higher stability, fundamentally with respect of oxidative degradations.

Moreover, the ionic operations avoid the production of cyanide-containing residuals originated in the traditional operations and with very difficult management. The application of ionic techniques in the elaboration of sherry wine allows a global improvement of the process, since this unit operation shows a great operability, high flexibility and good adaptability to the current demands of the sector companies.

Nomenclature

gAcH/L	grams of acetic acid per liter.
gTH_2/L	grams of tartaric acid per liter.
°GL	Gay-Lussac degree.
R_i	ionic radius of cation i, Å.
vvh	volume of liquid per volume of resin and per hour.

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