Removal of Metal Ions from Aqueous Solutions by Complexation – Ultrafiltration Hybrid Process: A Bibliographical Overview

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Abstract: Water pollution by metal ions contaminants is a worldwide alarming problem. Clean and safe water is becoming in the same time an increasing scare resource. Thus, to keep this fundamental resource available and suitable for use, water treatment methods are investigated by means of numerous research studies since the purification of water and its re-use and, in a larger scale, the environmental protection will be essential henceforth in any strategy of development.

Membrane processes, in general, and ultrafiltration, in particular, develop, without stopping, since the beginning of the sixties to meet the vital need for environmental safety which justifies the policies of durable development adopted today all over the world. Thanks to its growing, ultrafiltration becomes an irreplaceable weapon in the control of pollution. It is classified as a soft and clean technology since it needs low energy consumption and ensures a notable reduction in pollution production during the treatment step.

Ultrafiltration is a pressure driven membrane process with the ability to separate molecules in solution on the basis of size. A microporous ultfafiltration membrane retains species with molecular weight higher than its cut off, while small molecules as solvents and microsolutes can pass freely through it. Thus, metal ions aren't rejected by ultrafiters. However, ultrafiltration can be used to remove metal ions from aqueous solutions by coupling the process with complexation. Indeed, the complexation of metal ions using water soluble polymers as substrates is able to expand artificially the size of the metallic species so as to make possible their rejection by the microporous ultrafilters.

The complexation –ultrafiltration hybrid process was first suggested at the end of the sixties by A. S. Michaels. Since then, many studies have shown its effectiveness in the treatment of aqueous solutions containing metal ions.

This paper gives an overview of academic studies that illustrate and demonstrate the efficiency and the promising of the hybrid process in the purification of water from metal ions contaminants beforehand sequestered by adequate water – soluble macromolecular substrates.

Keywords: Ultrafiltration, complexation, hydrosoluble polymers, metal ions, macromolecular complex.

INTRODUCTION

The purification and the re-use of water constitute a priority today on a worldwide scale and the environmental protection becomes a main challenge of the 21Th century, a challenge that will be crucial henceforth in any development strategy.

Rejection standards become severely hard to reach the objective of zero reject recommended in the programs of preventive fight against pollution developed in many countries all over the world [1-3].

Thus, the processes of treatment and purification of water will be henceforth selected not only for their economical interest, but more and more for their ecological interest. The techniques implemented will have to satisfy the condition of effectiveness in term of environmental protection and they must, also, not to be themselves source of pollution. Moreover, the techniques implemented will have to satisfy increasingly rigorous conditions of selectivity, because of the growth and the diversification of the industrial activities which generate increasingly new pollution, and, also because of the occurrence of inopportune incidents of pollution, generally accidental, but sometimes malevolent and even criminal.

All these concerns are able to spur significant growth in the market of water and wastewater treatment technologies for the foreseeable future [4]. Researchers in all fields of water treatment will be hence intensively solicited and the quality of their studies could become irreplaceable guides to find the more appropriate solutions for many of complex water problems that are area of severe concern for all.

One of these issues and not the least is water pollution by metal ions contaminants which becomes one of the worldwide alarming problems today. The purification of wastes containing metallic species that are valuable or particularly toxic and the prospective re-use of the obtained cleaned water present evident economical and environmental advantages.

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Metals are present in a multitude of industrial effluents in very variable proportions. Metals most usually mentioned are copper, chromium, nickel and zinc because of the diversity of their industrial applications. The industries that are concerning by these metal rejects need high specific methods to remove these contaminants from an otherwise useful or recyclable stream. The very toxic elements, such as mercury and cadmium, are also the subject of many research tasks aiming to find the means of removing them from streams before their reject in the environment. Besides, the chemical commodity industry produces effluent streams containing low levels of valuable metal ions, such as copper, silver, gold, palladium, and platinum, and in this case the separation process must be able to detoxify effluent streams containing low levels of these valuable metals and, at the same time, the metals must be recovered.

In general case, the functions of separation processes include the removal of impurities from raw materials, products, and by-products, the separation of recycle streams, and the removal of contaminants from waste streams. In the treatment of industrial effluent containing metal ions, the objective of the separation process is the recovery of valuable components or the removal of contaminants from a stream. In fact, ideally, the effluent stream would be detoxified and the metals recovered simultaneously.

Ultrafiltration is a pressure-driven membrane process capable of separating solution components on the basis of molecular size and shape. Under an applied pressure difference across the membrane, the smaller molecules pass through the membrane and are collected as permeate while the larger molecules are retained by the membrane and are concentrated in the retentate. Membrane processes, and ultrafiltration in particular, typically do not involve a phase change and therefore do not involve a specific heat of vaporization, contrarily to distillation for example, or a specific heat of crystallization, contrarily to crystallization for example. Because there is no phase change, highly selective membranes can, in a number of circumstances, accomplish separations with considerably less energy than other methods. As environmental regulations become increasingly stringent, the costs associated with waste management are expected to rise. By reducing these costs, ultrafiltration is a soft separation technology that can contribute to the competitiveness of several industries. Coupled to complexation, ultrafiltration can be employed for the treatment of dilute effluent streams containing metal waste products that must be separate, either for their recovery and their recycling or for their removal.

Bibliographical overview of the complexation – ultrafiltration hybrid process and several application fields of the process applied to remove metal ions from aqueous solutions are given in the following pages.

I. PRINCIPLE OF THE PROCESS

In ultrafiltration process, the membrane retains species that have molecular weight higher than its cut off, whereas the small molecules, as the solvent and the micro solutes, pass freely through it [5-11]. Indeed, the molecular sieving through the ultrafilters is primarily governed by the surface porosity of the membrane imposed by the microstructure of the skin. It is important to note that the diameters of the pores are, at best, of 5 nm for the most selective ultrafilters. The

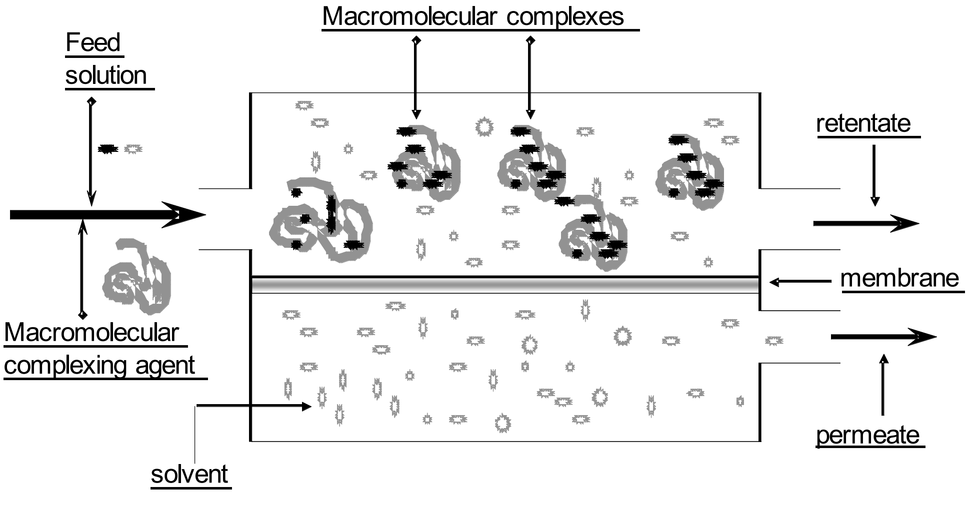

Figure 1: The principle of complexation –ultrafiltration process.

metal ions in solution are of lower size and thus cross without resistance the microporous membrane. Their retention by the ultrafilters is nevertheless possible if their size is increased artificially by complexing them on adequate macromolecular substrates as illustrated in the Figure **1** above.

This is the principle basis of the process associating complexation and ultrafiltration, introduced for the first time by A.S. Michaels, in *Advances in Separation and Purification* [12], at the end of the Sixties, when ultrafiltration was initiating its first industrial challenges, shortly after the advent of the asymmetric membranes [13].

The purification of the solution containing the metal ion to be extracted consists in complexing the ion by an adequate hydrosoluble macromolecular sequestering agent which binds it selectively.

The solution is then ultrafiltered through a suitable membrane, selected to ensure a good rejection of the formed macrocomplexe, so that the filtrate obtained would contain neither macromolecular species, nor free ions in solution. This objective can be achieved thanks to a judicious choice of the implemented membrane that should have a sharp molecular weight cut-off. If the membrane has moreover a high flux, this would give it an additional advantage.

However, when choosing to proceed using a high flux membrane it must be taken account of the intensification of the phenomenon of polarization concentration for the high cut-off membranes which can be explained by the fact that a relatively high-molecular-weight cut-off membrane, even though it may have a higher flux, is more susceptible to internal fouling than a membrane with a lower molecular weight cut-off which have lower pure water flux, but often provides a more sustained flux because less internal fouling occurs [14]. Thus, to gather the best operating conditions, the microstructure of the ultrafiltration membrane must be taken into account as well as the hydrodynamic behaviour of the treated solutions insofar as the interactions membrane/solution have a dominating effect in the effectiveness of separation by ultrafiltration.

The metal species can moreover be released if an acid is introduced in solution. This allows the regeneration and the re-use of the macrocomplexant and makes the process economically competitive [15-16]. Indeed, complex formation is a reversible process, this is the reason why it is possible to regenerate the retentate in order to recover the metal species and the complexing agent by shifting the equilibrium. Namely, breaking down the macromolecular complex into metal ions and regenerated polymer is carried out in acidic medium. The adjustment of pH is in fact simply done by adding to the retentate stream the appropriate amounts of selected strong acids such as HCl or HNO_3. Then, the introducing of successive ultrafiltration stages permits to the regenerated polymer of being able to be used again in the separation process.

Furthermore, the choice of the polymeric complexing agent depends on numerous criteria. It should have a high selectivity and a high binding capacity so as to permit proceeding in dilute macromolecular solutions in order to reduce the effects of the phenomenon of polarization of concentration and also in order to delay the fouling of the membrane. This feature would also permit that the maximum enrichment could be achieved [17]. In addition, the polymeric complexing agent should have a narrow molecular weight distribution to obtain the greatest rejection of the macromolecular species by the membrane. Besides, both the macrocomplexant and the macrocomplex should have a high water solubility so as to proceed in good operating conditions and to avoid the fouling of the membrane during process.

In academic studies as well as in industrial applications the polymers that were particularly used are those with carboxylic groups and amine groups [17-20].

II. THEORETICAL STUDY OF THE PROCESS

II.1. Introduction

Complex refers to the atomic build formed of a positive or neutral centre fixed to a finished number of molecules or ions. The metal ions can form stable complexes with many organic or inorganic compounds.

Indeed, whenever any metal salt and any Brönsted base come into contact, coordination is likely to occur to give a complex compound [21].

When the sequestering agent is of macromolecular size and when it is water-soluble, the formation of macromolecular complexes of metal ions in aqueous solution is then possible and the concentration of the sequestered metal ions becomes feasible by ultrafiltration.

Several theoretical models were developed to study the rejection by ultrafiltration of beforehand complexed metal ions [17, 20, 22-27]. These models permit the evaluation or the prediction of the effectiveness of the separation process; and some of these models even permit the determination of parameters suitable for the formed macrocomplexe, namely the chemical equilibrium constants and the coordination number [25, 28, 29].

It is worth to note that the most studied and reported case in literature is the binding of divalent transition metal ions to water-soluble macromolecular complexing agents. It is presented below a review about the formation of metal macromolecular complexes and about the selective removal of metal ions by the complexation-ultrafiltration hybrid process through data reported in various papers.

II.2. Metal Macromolecular Complexes

When a macromolecular complexing agent LH exhibits an acid comportment, the occurring reactions to be taken into account to describe the binding of the macromolecules to the M^{m+} metal ions, include the dissociation of the acid species LH, the different successive steps of the complex formation that permit to obtain the desired stable macromolecular complex $ML_n^{(m-n)+}$ and the formation of soluble and insoluble hydroxide complexes $M(OH)_p^{(p-m)-}$ that disadvantage the complex formation.

II.2.1. The Dissociation of the Acid Species LH

The dissociation of the acid species LH may be written:

$$LH \rightleftharpoons L^- + H^+; \quad K_a = \frac{[H^+][L^-]}{LH} \qquad (1)$$

II.2.2. The Macrocomplex Formation

If the macromolecule is a synthetic polymer, containing functional groups that are able to act as ligands in complex formation reactions, the functional groups of the polymer chain, which can been considered as independent each others, are added to the central metal ions, successively [30] or simultaneously [31, 32].

When the general case of stepwise complex formation is assumed to be occurring according to successive additions of several functional groups, the stepwise equilibrium stability constants of the reactions, beginning by the fixation of the metal ion M^{m+} to the ligand group L^-, may be written:

$$M^{m+} + L^- \rightleftharpoons ML^{(m-1)+} \quad K_{11} = \frac{[ML^{(m-1)+}]}{[M^{m+}][L^-]} \qquad (2)$$

$$M^{(m-1)+} + L^- \rightleftharpoons ML_2^{(m-2)+} \quad K_{12} = \frac{[ML_2^{(m-2)+}]}{[M^{(m-1)+}][L^-]} \qquad (3)$$

$$\vdots \qquad\qquad \vdots$$

$$M_{n-1}^{(m-(n-1))+} + L^- \rightleftharpoons ML_n^{(m-n)+} \quad K_{1n} = \frac{[ML_n^{(m-n)+}]}{[M_{n-1}^{(m-(n-1))+}][L^-]} \qquad (4)$$

It is worth to note that the stepwise formation equilibrium constants K_{1j} of the macromolecular complex $ML_n^{(m-n)+}$ decrease. Indeed, the first stepwise complexation involves the neutralization, by mutual Coulombic attraction, of the full n+ charge of the metal ion by the single negative charge of L^-. For the second step and the following steps, the Coulombic interaction is smaller, because of being between the same single negative charge on L^- and a less intensely charged (ML) species, with only (n−m) charge. In the final steps of stepwise coordination, the negatively charged anionic ligand is being added to an already negatively charged metal species. Thus, the order $K_{11} > K_{12} > K_{13} > \cdot\cdot\cdot K_{1n}$ is expected and even if irregularities are observed for some metal-ligand complex systems that reveal departure from this order or a sharp, such discontinuity occurs rarely and the above order is almost always observed [21].

The equations 2-4 are obtained for the general case of stepwise complex formation; however, numerous papers assume that for number of metal-polymer systems complex formation does not proceed by a series of steps but in a single step. Thus, the equilibrium binding reaction and the corresponding stability constant may then be expressed according to the following reactions and equations respectively:

$$M^{m+} + nL^- \rightleftharpoons ML_n^{(m-n)+} \quad K_n = \frac{[ML_n^{(m-n)+}]}{[ML^{m+}][L^-]^n} \qquad (5)$$

$$M^{m+} + nHL \rightleftharpoons ML_n^{(m-n)+} + nH^+ \quad B_n = \frac{[ML_n^{(m-n)+}][H^+]^n}{[ML^{m+}][LH]^n} \qquad (6)$$

The complex formation between the metal ion and the macromolecule proceeds in this case by a no step-by-step mechanism; in fact, the solution contains only the species $ML_n^{(m-n)+}$ and the free ions M^{n+}. The stability constant obtained by this model is an effective parameter because it depends on the conformational state of the macromolecule and the polymer composition [31].

K_n and B_n are dependant to each other by the relationship $B_n = K_n \times K_a^n$ where K_a is the observed dissociation constant of LH and K_n is the overall stability constant of the complex $ML_n^{(m-n)+}$ and it is easy to see that $K_n = K_{11} \times K_{12} \times \ldots \times K_{1n}$.

On the basis of this model, the calculation of the stability constant and the average number of polymer units bound with metal ions is now more and more based on modern computing techniques [33]. However, the modified Bjerrum's method is still of use. Indeed, the modified Bjerrum's method is a well-developed technique which takes into account the difference observed during the pH titration of a polymer in the presence of a metal salt and in a free metal salt solution. Namely, the titration curve for a polymer in presence of metal ions is lower than that of a free polymer.

Despite its large use, the major limitation of this method is the assumption that the acidity of the unbound polymer units in the macromolecules is equal to the acidity of the unbound polymer units in the correspondent macrocomplexes. In other words, this method assumes that the properties of the ligand units are independent of the degree of complexation. Thus this assumption restricts the applicability of the method since the conformation of the macromolecule changes doubtless during complexation, it becomes more compact, and the acid-base properties of the unbound groups are then affected [34].

The example of the variation with pH of the viscosity of aqueous solutions of Poly(vinylalcohol) and Cu^{2+} -Poly(vinylalcohol) macrocomplex and the marked difference between the viscosity-pH curves of Poly(vinylalcohol) and Cu^{2+}-Poly(vinylalcohol) macrocomplex which has been explained by the fact that the polymer takes up a tightly packed conformation due to the complex formation when the pH medium is in the pH field of the complex formation, reported in several works [35, 36], illustrates in clear the occurrence of the conformation change of the macromolecular chain during complexation.

In spite of its principal advantage which is incontestably its simplicity, the stepwise complex formation model describing the interaction of the polymer with the metal ions that proceeds either by a series of steps or in a single step fails to take into account the changes in macromolecular conformation during complexation. Indeed, the validity of the model is limited by the assumption about the independence of the reactivity of the polymer's functional groups bounded to the metal ion. In fact, groups combined with the polymer chain may not behave independently, which is, for example, illustrated by the difference between the local concentration of polymer units and the mean concentration in solution [37]. In fact, the macromolecular charge is changed during complexation, consequently, a reorganization of the macromolecular conformation occurs, indicated by a change in viscosity of the system [31, 35]. Simultaneously, the acid-base properties of the polymer are changed [32, 37] and therefore the properties of the macromolecular ligand are changed as a whole.

The model described above is one of the two principal different models applied in the study of polymeric features of the complexing process. Its limitation explains the use of the other important model in numerous works reported in the literature [37, 38]. In this other model, the macromolecule is considered as a matrix with a certain number of perfectly defined binding sites. The model is principally based on the assumption that binding is not accompanied by a change in the free energy of the matrix and that the macromolecular coils have the same molecular weight. The polymer-metal complex formation in solution is described in this model by the following set of equilibria:

$$PM_{n-1} + M \rightleftharpoons PM_n,\ n = 1,2,3\ldots,N \quad K_n = \frac{[PM_n]}{[PM_{n-1}][M]} \qquad (7)$$

Where P is the macromolecular complexing agent and N is the maximum number of metal ions which can be bound with a single chain. The simplification given by this scheme is that the equation relates, in the maximal associated form, the associated coils to the number of the metal ions complexed by one single coil.

This model is applicable to strongly crosslinked synthetic polymers having a rigid matrix. In fact, it satisfactorily describes the complexation of metal ions with proteins. Nevertheless, it is inapplicable for linear flexible polymers. Indeed, for flexible polymer chains, the chain free energy changes during the binding of a metal because of the crosslinking of different macromolecular sections or the changes in the charge density on them. This fact makes the principal assumption of the model that says that binding is not accompanied by a change in the free energy of the matrix becoming erroneous. Besides, the concept of a "binding site" has not been defined in the model since a metal ion coordinates with arbitrarily located functional groups.

In fact, the binding of metal ions to a polymer chain restricts the mobility, not only of the functional groups, but also of neighbouring groups in the chain. The larger the group bound in the complex by a single metal atom, the stronger the steric limitation developed and therefore, the less applicable is the given model. Thus, neither one nor the other of the two models considered will permit a strict description of complexing with linear synthetic polyligands. Indeed, the applicability of the first or the second model depends on the degree of conformity of the assumptions to reality [37] and each of the two models will have, for long time, their fervent believers and also their not less fervent detractors.

II.2.3. The Formation of the Hydroxy Complexes

In addition to the principal reactions that permit the dissociation of the species LH and the formation of the macrocomplex $ML_n^{(m-n)+}$, the possible formation of soluble and insoluble hydroxy complexes $M(OH)_p^{(p-m)-}$ must be taken into account and the occurrence of these secondary reactions may be written:

$$M^{m+} + pOH^- \rightleftharpoons M(OH)_p^{(p-m)-}$$

Worth to note that the uncharged hydroxy complex $M(OH)_m$, formed of one metal ion M^{m+} linked to m (OH^-), is almost always insoluble [39]. The formation of this species may be written:

$$M^{m+} + mOH^- \rightleftharpoons M(OH)_{m(S)}$$

II.3. Selective Removal of Metal Ions by the Complexation-Ultrafiltration Hybrid Process

The users of the complexation-ultrafiltration hybrid process have preferentially adopted the first model mentioned above to describe the macromolecular complex formation, since the macromolecular complexing agents used in this specific application are commonly flexible synthetic polymers.

In addition, it is generally considered that the complex formation proceeds in a single step by the complexation-ultrafiltration process users [23, 24], even if the literature has also reported studies taking into account the stepwise complex formation model [20]. Thus, only the equilibrium reaction and the corresponding stability constant reported in the equation (5) have been considered below.

In the case of only one metal ion reacting with the polymeric complexing agent in solution, the reaction (5) may be written as it is. Nevertheless, in the case of a multicomponent solution containing several metal ions, as it is the case when the target metal is to be removed from real wastewaters, the metal to be considered is indicated by the subscript i in the equation. Thus, the reaction of each i-th metal with the ligand group L^- may be written:

$$M_i^{mi+} + n_i L^- \rightleftharpoons M_i L_{ni}^{(mi-ni)+} \qquad K_{ni} = \frac{[M_i L_{ni}^{(mi-ni)+}]}{[M_i^{mi+}][L^-]^{ni}} \tag{8}$$

Moreover, the formation of the hydroxy complexes of the i-th metal may be written:

$$M_i^{mi+} + p_i OH^- \rightleftharpoons M_i(OH)_{pi}^{(pi-mi)-} \qquad \beta_{pi} = \frac{[M_i(OH)_{pi}^{(pi-mi)-}]}{[M_i^{mi+}][OH^-]^{pi}} \tag{9}$$

Written like that, the reactions and equations can be used as well to describe single component systems and multicomponent systems.

The rejection R_i for the each i-th metal ion may then be written:

$$R_i = 1 - \frac{[M_i]_p}{[M_i]_0} \tag{10}$$

Where $[M_i]_0$ and $[M_i]_P$ are the i-th metal concentration in the feed solution and in the permeate respectively.

And the rejection R_L of the macroligand may be written:

$$R_L = 1 - \frac{[L]_p}{[L]_0} \tag{11}$$

Where $[L]_0$ and $[L]_P$ are the total macroligand concentration in the feed solution and in the permeate respectively.

To state mass-balance relations that are really able to describe accurately the studied system, and in order to simplify the calculation, the users of the complexation-ultrafiltration hybrid process considered many assumptions. A concise recapitulation of the most generally assumptions that are made is given below [20, 23, 24]:

(1) The complexing groups on a polymer chain behave as independent complexing groups, i.e. the complexing groups are thermodynamically independent.

(2) The protonated form LH is excluded from the balance of complexation and the metals in soluble or insoluble hydroxide forms cannot form complexes.

(3) The equilibrium constants are independent of the pH and the species in solution

(4) The membrane rejects the macrocomplexe similarly to the free macroligand and it interacts neither with free metals, nor with the soluble hydroxides.

In the most general case, the overall concentrations of the metal ions and the macroligand in the feed solution, which could be considered as the initial solution, may be written:

$$[M_i^{mi+}]_{feed} = [M_i]_0 = [M_i^{mi+}] + [M_iL_{ni}^{(mi-ni)+}] + \Sigma[M_i(OH)_{pi}^{(pi-mi)-}] \quad (12)$$

$$[L]_{feed} = [L]_0 = [L^-] + [LH] + n_i[M_iL_{ni}^{(mi-ni)+}] \quad (13)$$

Volchek *et al*. [20] suggested that the separation of the metals may or may not be accompanied by the formation of insoluble hydroxides. The choice of the possible proceeding in presence of insoluble hydroxide salts was directed in this study by the fact that the process was applied for the treatment of complex mixtures as seawater and a real waste obtained from a fertilizer plant effluent. In these cases, the overall concentrations of the metal ions in the feed solution may be written:

$$\begin{aligned}[M_i^{mi+}]_{feed} = [M_i]_0 = [M_i^{mi+}] + [M_iL_{ni}^{(mi-ni)+}] + \\ \Sigma[M_i(OH)_{pi}^{(pi-mi)-}] + [M_i(OH)_{mi}]\end{aligned} \quad (14)$$

Contrarily to this approach, several studies in the eighteens [25-27] were based on theoretical models that ignored the formation of both the insoluble and the soluble hydroxides and it was reported that the experimental data obtained gave satisfactorily correlation with the developed models.

The applicability of these models is undeniably limited since the hydrolysis effects must be taken into account particularly when highly hydrolysed metals are considered [20], however, a judicious choice of the operating conditions may permit to avoid the insoluble hydroxide salts formation and to proceed in adequate ultrafiltration operating conditions, i.e. to treat a feed solution containing only hydrosoluble species. Thus, the latest term in the equation (14) could be neglected, and the equation (12) is then preferentially used to calculate the overall concentrations of the metal ions in the feed solution.

Based on the assumptions given above, the overall concentration of the i-th metal in the permeate seems to bee the sum of:

(1) the metal M_i in free ion form and in the hydroxyl complex forms that are able to cross the membrane without resistance;

(2) the fraction of the macromolecular complex form that has not been retained by the membrane, if the reject of the macromolecular complexing agent isn't complete.

Thus, the mass balance concerning the concentration of metal in the permeate may be written:

$$[M_i]_p = [M_i^{mi+}] + [M_iL_{ni}^{(mi-ni)+}](1 - R_L) + \Sigma[M_i(OH)_{pi}^{(pi-mi)-}] \quad (15)$$

The rejection R_i for the each i-th metal ion may then be written:

$$R_i = \frac{[M_iL_{ni}^{(mi-ni)+}]}{[M_i]_0} R_L \quad (16)$$

In this expression, $[M_i]_0$ and R_L are experimentally known, the determination of R_i is possible if the unknown term $[M_iL_{ni}^{(mi-ni)+}]$ can be calculated. So that, the rewriting of the above equation by combining it with the equations (8), (9) and (12), permits to express R_i in the following form:

$$R_i = \frac{[L^-]^{ni}K_{ni}}{1 + [L^-]^{ni}K_{ni} + \Sigma[OH^-]^{pi}\beta_{pi}} R_L \quad (17)$$

Rewritten like that it is easy to see that the only unknown on which R_i depends is $[L^-]$.

Elsewhere, by combining the equations (12), (13) and (8), the mass balance of the macroligand may be written:

$$[L]_0 = [L^-] + [L^-]\frac{[H^+]}{K_a} + n_i \frac{[M_i]_0[L^-]^{ni}K_{ni}}{1 + [L^-]^{ni}K_{ni} + \Sigma[OH^-]^{pi}\beta_{pi}} \quad (18)$$

Therefore, under given operating conditions, the value of $[L^-]$ can be calculated iteratively using the equation (18) and then substituted into the equation (17) to determine the rejection R_i for the each i-th metal ion in solution. In other words, this theoretical approach allows to study the efficiency of the retention of the macromolecular complex, when the stability constants and the number of coordination are known.

III. APPLICATIONS OF THE PROCESS

Metal water pollution is often caused by the presence in undue concentrations of species such as arsenic, cadmium, iron, cobalt, chromium, copper, manganese, mercury, molybdenum, nickel, lead, selenium, vanadium and zinc. Besides, some more specific polluting species like radionuclides could be present. The danger of the so called heavy metals even in very small amount is explained by their bio-accumulative property on living organisms and by their interfering with chemical and biochemical processes because of poisoning chemical catalysts and disturbing enzyme action for example. Thus with the obvious toxicity at high concentrations which harmful impacts are well known on medical and environmental scale, traces of metal ions cause an alarming insidious pollution that must be taken into account so as to be prevented. In fact, it is this particular field where membrane processes are most efficient and where the hybrid process of complexation –ultrafiltration does the challenge to win a leader position.

Indeed, enhanced with complexation, ultrafiltration becomes a selective process that is able to be used to concentrate metal ions beforehand sequestered by water-soluble polymers and the process befalls, besides, a separation technique that is not exclusively suitable for fractionation of the only macromolecular solutions. In fact, complex formation is based on equilibrium reactions. Their feasibility is favored by high stability constants. Thus, higher is the stability constant stronger is the linking between the metal ions and the polymer ligands and better is the rejection of the metal species by the ultrafilter membrane. If several metal species are present in the feed solution, the macromolecular complex the most stable allows to remove selectively a metal species instead of another by means of compexation-ultrafiltration process. Thus, ultrafiltration membranes which reject unselectively every macromolecular species that have molecular sizes greater than their membrane cut off are able to become selective to metal species bonded to specific macomacromolecular complexing species.

Several authors have studied the process and revealed the originality, the effectiveness and the simplicity of its implementation [11,15-20, 23-24, 36, 40-60]. Thus, although the complexation –ultrafiltration has not been applied on a large industrial scale yet, the hybrid process promises to be a technique suitable for the purification of polluted wastes containing metals ions, since the principal advantages of ultrafiltration are the treatment in liquid homogeneous phase at ambient temperature and the low energy requirement involved.

The industrial application of the process was considered, in studies reported in literature, for the purification of industrial effluents [61, 62], for the concentration of pollution [63] and for the removal of toxic elements [64]. However, the greatest number of works that is reported in literature concerns academic studies. These studies can be classed on the basis of the macromolecular complexing agents used or on the basis of the metal to be removed, and since the metal predicts the industrial application, it is in fact the metal to be removed that edicts all the other experimental conditions enclosing the choice of the macroligand. That said, so as to ensure the complexation – ultrafiltration process efficiency, the choice of the macromolecular complexing species must be judicious. Indeed, it should have a high selectivity for the target metal ion, a high binding capacity, a narrow molecular weight distribution and a high water solubility [17]. Both synthetic hydrosoluble polymers and biopolymers have been used. In the range of synthetic water-soluble polymeric macroligands, poly(ethyleneimine) [32, 47] and poly(acrylic acid) seem to be the most employed polymers [23, 24, 56], followed by poly(vinyl alcohol) [59, 60, 65], poly-4-vinylpyridine [31], poly[acrylamide-co-1-(2-hydroxyethyl)aziridine] [51] and poly(allylamine) [53]. The most employed biopolymers are chitosan and chitosan derivatives. These abundant biodegradable biopolymers have been widely used for the removal of particularly toxic species as cadmium [54], Mercury [66] and arsenic [67]. Besides, literature reports the use of alginic acid [68] and sodium alginate [69] which are natural polysaccharides derived from brown algae. Regarding to the metal ions removed by the hybrid process of complexation –ultrafiltration, a large range of metal species have been studied. Copper, one of the most widely used heavy metals which is mainly employed in electrical and electroplating industries is certainly the most studied, especially at the laboratory scale. Alone, or in presence of other more or less toxic species, removal, concentration or recovery of cupric ions takes a central place in numerous studies [70-76]. As well, zinc, nickel and chromium are not left in the academic studies and several studies are reported [16, 77-80]. Besides, the process finds an important area of applications in the removal of particularly toxic metal species as lead which is one of the most dangerous metal species contaminants, cadmium [81, 82], one of the most toxic heavy metals with its negative effect on the environment where it accumulates throughout all the food chain [83] and mercury which is collectively known as one of the most toxic metal species pollutants [66, 84-86]. Numerous other metal species have found in complexation –ultrafiltration a relevant alternative to classical processes of separation [87-91], the above cited research studies are some samples of the rich fields of application of this promising hybrid process.

CONCLUSION

A chaos of uncertainties, of illusions and of errors for Duclaux [92] in the forties, adolescent technology with a promising future for Michaels [93] in the eighties, the process that Bechhold named ultrafiltration in 1906 [94], is described today as a clean and soft technology. The knowledge of the continuous development of ultrafiltration during the last century informs us about all the importance this process will inevitably take in the industrial landscape of the 21th century [95, 96]. Indeed, the simplicity and the low need of energy that are the principal industrial assets of ultrafiltration make that the process will become finally indispensable in any treatment of industrial liquid effluent.

For the removal of metallic ions from aqueous effluents, the most commonly used process, at industrial scale, is chemical precipitation. This technique is however not efficient when it is applied to effluents with low metallic concentrations and afterward treatments are always necessary in order to reach the legal discarding policies of these wastes. Besides, precipitation processes are accompanied by the formation of large amounts of solids containing metal species. To counter these disadvantages, numerous processes have been investigated to be alternative methods for chemical precipitation. Electrolytic methods, adsorption onto activated carbon, liquid–liquid extraction and ion exchange resins have been studied and implemented amongst others [68, 80, 97, 98]. Although these alternative processes are used in several specific applications, they are often unsatisfactory because of interface transfer, long contact time problems of multiphase separation and production of large volume of wastes [81]. That is, thanks to the fact that ultrafiltration is a continuous molecular separation process which do not involve change or interphase mass transfer, one of the most important advantage of the hybrid process of complexation-ultrafiltration respect to the above cited techniques to remove metal species pollutants is in fact the invaluable quality to proceed in liquid homogeneous phase without phase change. This is the best argument of the adepts of the process to continue its study and its promotion and it is the purpose of this overview.

Without being exhaustive this report takes care to be systematic. Thus, we hope that this study permits to highlight the importance of all the cited bibliographic references and the work of their respective authors who allowed, with other emeritus researchers, the emergence, the development and the industrial challenges of the hybrid process of complexation – ultrafiltration.

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