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Comparative Study on Metal Extraction Properties of Empore SDB-XC and Amberlite XAD-4 Grafted by Salicylic Acid and its Derivatives via Different Bridges

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Abstract: Among commercially available sorbents, aromatic organic crosslinked copolymers allow to consider numerous ways of linking ligands. In this way, the grafting of salicylic acid and of its derivatives (methylene disalicylic acid and aurintricarboxylic acid) via the ketone, amide and diazo bridges on Amberlite® XAD-4 resin and Empore$^{\mathrm{TM}}$ SDB-XC membrane have been carried out. The modified sorbents thus obtained have been appraised according to their grafing rate and their efficiency to selectively retain different metallic ions versus pH. The grafting of the sorbents permits to obtain pretty good yields. Extraction yield studies have revealed that the supports have the same behavior whatever the ligand grafted via a diazo or an amide bridge. Thus, increase of salicylic acid entity number does not improve the performance of the supports. However, bridge used during grafting seems to have an influence upon the extraction yields observed.

Keywords: Solid-phase extraction, poly(styrene-*co*-divinylbenzene), membrane, resin, salicylic acid

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INTRODUCTION

There are now many analytical methods for trace metal ions determination, including inductively coupled plasma-mass spectrometry or atomic emission spectroscopy (ICP-MS or ICP-AES) or various spectrophotometry or spectrofluorimetry based on specific ligands reactions. However difficulties often arise as a result of interferences by coexisting elements or lack of sensitivity. A system coupling a separation/enrichment technique and detection module can overcome this problem. In this way, solid phase extraction (SPE) has been extensively used in the past 15 years for metal extraction avoiding the inconvenience of liquid–liquid extractions (1).

Commonly used SPE sorbents consist of specific functional groups immobilized on a solid support, improving the efficiency of metal extraction by providing better contact area with the samples (2). The most used sorbents are chemically modified resins based on styrene-divinylbenzene co-polymers (3, 4) and among these, commercially available resin from Amberlite® series (XAD-2, XAD-4) are often used as SPE supports (5).

More recently, new sorbents have been developed, namely extraction disks. These membranes consist of small polymer beads included in a polytetrafluoroethylene (PTFE) (6) or a glass fiber matrix. The smaller diameter of the polymer beads in the membrane than in the resin provides improving extraction rates of analytes (7). Moreover membranes offer a greater exchange area with the samples and reduce filling problems thus allowing working with higher sample flow (8, 9). Only few authors have worked with organic polymer membranes as SPE support. Fritz et al. have used Empore™ SDB-XC membranes but only impregnated by various ligands for copper, iron, nickel, or silver determination by diffuse reflexion spectroscopy (10, 11).

Our research group has recently covalent linked salicylic acid (SA) on Amberlite® XAD-4 resin (12) and Empore™ SDB-XC membrane via a ketone bridge, an amide bridge, and a diazo bridge. The graftings of a dimer and a trimer form of SA (respectively methylene disalicylic acid—MDSA—and aurintricarboxylic acid—ATA) were also performed (13). This paper presents the application of these grafted supports for the removal of metallic ions in aqueous samples. The influence of grafting bridge and number of SA entities on the extraction properties was studied. A comparative study of grafted resins and membranes complexing properties and capacities was also performed versus pH and metals.

EXPERIMENTAL

Materials

Amberlite® XAD-4 resin was obtained from Acros Organics (Noisy-le-Grand, France). Empore™ SDB-XC membrane was produced by 3M and purchased from Varian (Les Ulis, France). Both sorbents were previously cleaned out in methanol for 24 h, rinsed with diethyl oxide, and dried at 80°C for 48 h before use.

Salicylic acid (SA) and aurintricarboxylic acid (ATA) were purchased from Sigma (St Quentin Fallavier, France), and methylene disalicylic acid (MDSA) from Acros Organics. All other chemical reagents were purchased from Acros Organics and used without further purification. Commercial stock standard solutions of metals ($1\,g \cdot L^{-1}$) were purchased from Aldrich. Further dilutions were prepared daily as required in ultra high quality deionised water (resistivity $> 18\,m\Omega \cdot cm^{-1}$; Milli-Q Water System, Millipore, St Quentin en Yvelines, France).

Instrumentation

Metal concentrations were determined by inductively coupled plasma–atomic emission spectrometry (ICP-AES) (Jobin Yvon JY2000 Ultrace spectrometer, equiped with a CMA spray chamber and a Meinhard TR50-C1 glass nebulizer). Determinations were performed with following parameters: power 1000 W, pump speed $20\,mL \cdot min^{-1}$, plasma flow rate $12\,L \cdot min^{-1}$, coating gas flow rate $0.2\,L \cdot min^{-1}$, nebulisator flow rate 0.83 and nebulisator pressure 3.1 bar. Wavelengths were 394.401 nm for aluminium, 226.502 nm for cadmium, 283.263 nm for chromium, 228.616 nm for cobalt, 324.754 nm for copper, 259.240 nm for iron, 220.353 nm for lead, 257.610 nm for manganese, 231.604 nm for nickel, and 213.856 nm for zinc.

pH measurements of metallic solutions were performed with a digital pH meter model HI 92240 (Hanna Instruments, Lingolsheim, France).

Solid Phase Extraction runs were carried out by means of an Ismatec peristaltic pump model IPC (Glattberg, Switzerland).

SA and its Derivatives Complexation Constants

SA is a commercial ligand with a carboxylic and a phenolic function which can act as electron pair donnors reacting with most of hard and intermediates cations (Table 1). It has already been used, for example, for the spectrophotometric determination of copper (14), aluminum (15, 16), iron (17). Moreover, SA can be grafted via different bridges (12, 13) when submitted to electrophilic substitution reactions.

Dimer (MDSA) and trimer (ATA) derived forms of SA have also been grafted to study the influence of the number of salicylic acid entities on the complexation properties of the modified supports. Complexation constants of ATA and MDSA, found in the literature, are given in Table 1. MDSA has been poorly studied and only dissociation constnats with Fe(III), Ti(IV), Pd(II), and Zr(II) have been found in Capitan et al. publication (18).

Table 1. Complexation constants of salicylic acid (SA), methylene disalicylic acid (MDSA) and aurintricarboxylic acid (ATA) with metallic ions in water, expressed as Log β

	Metal									
Ligand	AI(III)	Cu(II)	Ni(II)	Zn(II)	Mg(II)	Fe(III)	Cd(II)	Co(II)	Mn(II)	Ref.
SA		12.03	8.41	9.20	3.30					(30)
	12.9	10.80	6.95	6.85		16.36	5.55	6.72	5.9	(31, 32)
MDSA						6.3				(18)
ATA	16.6	3.5								(30)
		4.1				4.68				(31, 32)

ATA, whose common name is Aluminon, has already been used for the photometric determination of Al (19, 20), Fe (21), Cr (22) and rare earth elements (23).

Grafting Rate

Direct determination by titration of salicylic entities grafted on supports could not be carried out because of diffusion problems when working in heterogenous phasis: equilibration time is superior to 4 hours. This problem has been overcome by a back titration leading to the quantification of carboxylic functions grafted. This "surface" titration is derived from Boehm method (24, 25). The sorbents (50 mg) were put in contact with 50 mL of a sodium hydroxide solution ($0.01\,\mathrm{mmol}\cdot\mathrm{L}^{-1}$). 25 mL of each solution were then titrated with hydrochloric acid solution ($0.033\,\mathrm{mmol}\cdot\mathrm{L}^{-1}$). This titration allowed the quantification of the number of carboxylic functions grafted, and as a consequence, of the grafting rate (α) by the following relation (26).

$$\frac{\alpha \mathrm{Mg}}{\alpha \mathrm{Mg} + \beta \mathrm{Mu}} = \frac{\mathrm{n\ Mg}}{\mathrm{x_c}} \tag{1}$$

This equation (1) can be simplified by using the fact that ($\alpha + \beta = 1$)

$$1 + \frac{(1-\alpha)\mathrm{Mu}}{\alpha \mathrm{Mg}} = \frac{\mathrm{x_c}}{\mathrm{n\ Mg}} \tag{2}$$

The grafting rate α can thus be expressed after recombination of equation (2)

$$\alpha = \frac{1}{1 + 1/\mathrm{Mu}(\mathrm{x_C}/\mathrm{n} - \mathrm{Mg})} \tag{3}$$

where n is the number of carboxylic acid functions grafted (moles of acid functions grafted per gramm of sorbent, determined by back titration), Mg is the molecular weight of the graft fixed on the aromatic ring, Mu is the molecular weight of the unmodified sorbent, x_c is the mass fraction of sorbent available for the grafting (x_c values are 1 for the resin and 0.9 for the membrane), α the grafting rate of support and β the rate of the unmodified support ($\alpha + \beta = 1$). M_u, the molecular weight of the unmodified sorbent, minus an hydrogen to permit the grafting, is equal to $129.4\,\mathrm{g{\cdot}mol^{-1}}$.

Metal Extraction Experiments

A disk of 13 mm diameter (20 mg) is cut from the dried membrane and set in a specific filter holder (Swinnex® from Millipore). A column (Supelco) is filled with 50 ±0.1 mg of dry resin, immobilized between two polyethylene frits of 0.2 μm porosity. These equipments permit the percolation of the metallic solutions through the supports with a peristaltic pump. In order to determine the metal extraction rate, solutions containing 50 $\mu g \cdot L^{-1}$ of the different metallic ions were prepared. For each pH value (from 2 to 10), 50 mL were passed throught the samples. Complexing capacities of modified supports were obtained by passing 200 mL of a monometallic solution at 5 $mg \cdot L^{-1}$ through the sample. The flow rate was 1 $mL \cdot min^{-1}$ and after each experiment, the metal(s) were eluted from the supports using few milliliters of hydrochloric acid (0.5 N) and the sorbents were rinsed with large amounts UHQ water. In both cases (complexing capacity and extraction rate determinations), eluates were analysed by ICP-AES.

RESULTS AND DISCUSSION

Grafting Rate

The quantification of carboxylic functions grafted per gramm of dried sorbents are summarized in Table 2, with grafting rates obtained thanks to Equation (3). The grafting rate of SA via the ketone and diazo bridges are quite close together, between 22 and 25% for the resin and between 33 and 38% for the membrane.

Concerning SA and its derivative grafting via the diazo bridge, the more the ligand contains salicylic entities the more the grafting rate decreases. Finally, the number of SA entities grafted seems similar whatever the ligand considered; number of –COOH entities grafted (expressed in mmoles per gramm of support) varies from 1.8 (ATA and SA) to 2.1 (MDSA). This phenomenon can be explained by steric hindrance induced by MDSA and ATA molecule sizes.

Grafting rates of SA and its derivatives onto resin and membrane via the amide bridge can not be determined by this titration method. Efficiency of this bridge will be only evaluated during metal extraction experiments.

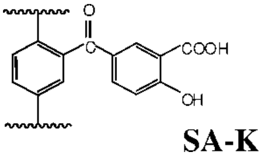
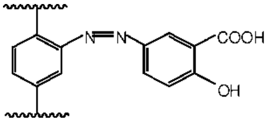
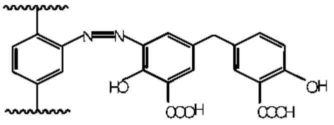
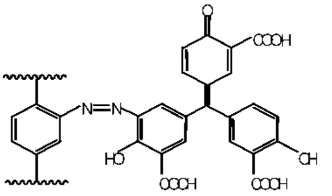
Metal Extraction Experiments

Influence of the Nature of Metals

Experiments described here have been carried out with membranes where SA have been grafted with the three bridges above-mentioned. The role of supports and ligands grafted will be approached in the following sections.

Metallic elements can be divided into three classes: soft (Cd(II), Pb(II), Zn(II)), intermediate (Cu(II), Mn(II), Co(II), Ni(II)) and hard cations (Al(III), Fe(III), Cr(VI)).

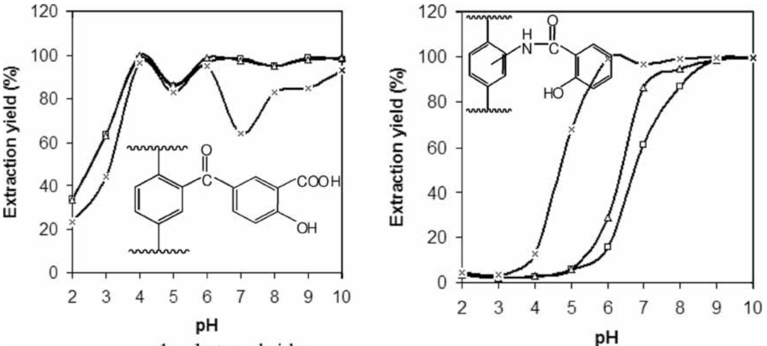
Table 2. Grafting rates of the different modified sorbents

		Resin	Membrane
 **SA-Ketone**	n_{COOH} (mmoles $\cdot$ g^{-1})	1.8	2.2
	Grafting rate (%)	23	33
 **SA-Diazo**	n_{COOH} (mmoles $\cdot$ g^{-1})	1.9	2.5
	Grafting rate (%)	25	38
 **MDSA-Diazo**	n_{COOH} (mmoles $\cdot$ g^{-1})	2.1	1.8
	Grafting rate (%)	17	16
 **ATA-Diazo**	n_{COOH} (mmoles $\cdot$ g^{-1})	1.8	1.6
	Grafting rate (%)	9	9

As can be seen from Figs. 1 to 3, these classes of metals adopt the same behaviour when comparing their extraction yields as a function of bridge used for grafting SA.

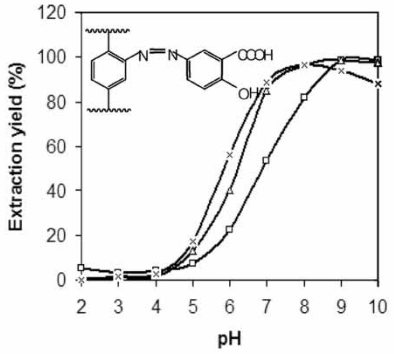
Figure 1 represents retention of intermediate cations by SA grafted by ketone (1.a), amide (1.b.), and diazo bridges (1.c.). Behavior of Ni(II) is some different from the two other metals with a retention on the amide bridge obtained at a more acid pH (pH 5.0 for Ni(II) and pH 7.0 for the Mn(II) and Co(II)). Co(II) will be chosen as representative of behavior of intermediate cations in the following sections.

In Fig. 2, extraction yields of hard cations are presented. Fe(III) and Al(III) adopt the same behaviors whatever the bridge used during grafting of SA onto membranes. In the following section, Fe(III) has be chosen to be representative of hard cations.



1.a. ketone bridge

1.b. amide

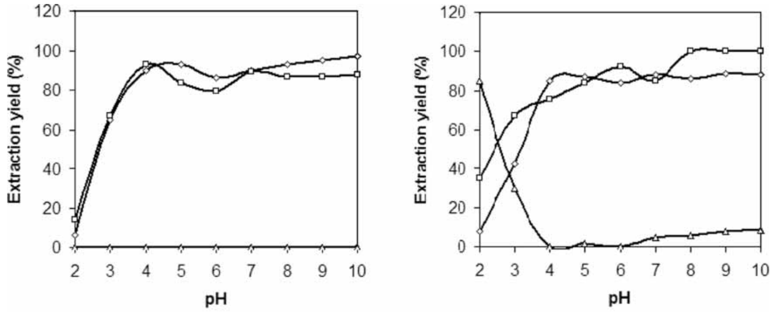


1.c. diazo bridge

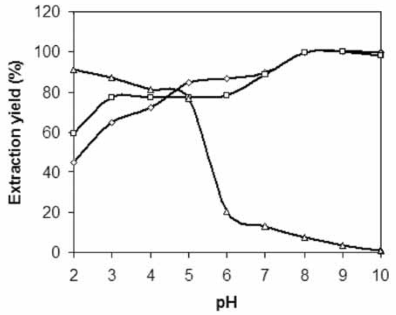
Figure 1. Extraction yields of intermediate cations versus pH onto membranes grafted with SA through different bridges (–□– Mn(II)/–△– Co(II)/–×– Ni(II)).

Behavior of chromium is very singular: Cr(VI) is absolutely not extracted by the membrane grafted via a ketone bridge; and, at the opposite of all the metals tested, it is selectively retained on membranes grafted via a diazo bridge at very low pH values. This is probably due to the fact that chromium(VI) is mainly present as an oxyanion ($HCrO_4^-/CrO_4^{2-}$ according to pH) and thus not retained by carboxylic groups. A recent study carried out on supports grafted by aminodiacetic acid has also highlighted this behavior (26). The presence of residual amine groups or diazo bridge could explain the retention of Cr(VI) by the protonation in acidic medium of these various functions [27]. Nevertheless the grafting of SA via a ketone bridge could be of a particular analytical interest by its capacity to specifically separate Cr(VI) from other metallic elements in aqueous samples.

Figure 3 shows evolution of extraction yields of soft metals as a function of bridge used during grafting of SA onto membranes. The three metals tested (Pb(II), Zn(II), and Cd(II)) handle equally on the three modified supports.



2.a. ketone bridge 2.b. amide bridge



2.c. diazo bridge

Figure 2. Extraction yields of hard cations versus pH onto membranes grafted with SA through different bridges (–□– Fe(III)/–△– Al(III)/–◇– Cr(VI)).

A light shift of pH is still observed for Pb(II) on the amide and diazo bridges. Due to the intermediate behavior of Cd(II), this one will act as a representative of soft cations in the following sections.

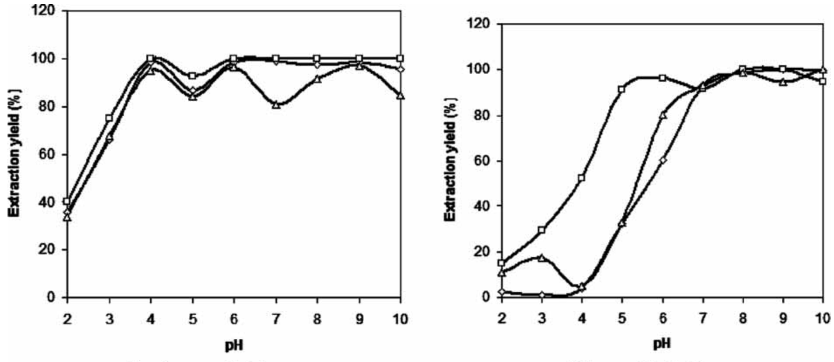
Influence of the Nature of Bridge on the Extraction of Metals

Figure 4 represents retention yield of only one metal of each classes, defined above, obtained onto membranes grafted by SA.

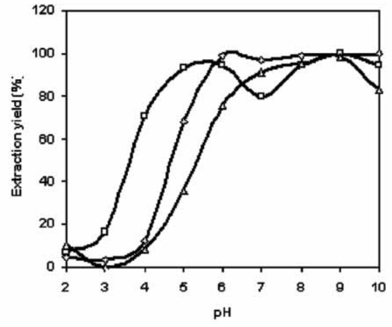
Cd(II), representative of soft cations, is more retained on membranes where SA has been grafted by a ketone bridge from pH 4.0 to pH 12.0 with an extraction yield around 100%.

Amide and diazo bridges begin to be competitive with ketone bridge from pH 8.0.

Retention of Fe(III), representative of hard cations, is strongly pH-dependent: at pH 4.0, it is more retained on membranes grafted with SA by a ketone bridge then, from pH 6.0, it is more retained on membranes where SA has been grafted through amide and diazo bridges. Extraction of Co(II),



3.a. ketone bridge 3.b. amide bridge



3.c. diazo bridge

Figure 3. Extraction yields of soft cations versus pH onto membranes grafted with SA through different bridges (–□–Pb (II)/–△–Zn(II)/–◇–Cd(II))

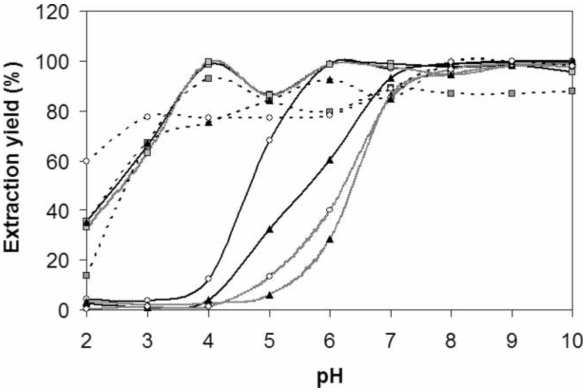


Figure 4. Extraction yields of metallic ions versus pH onto membranes grafted by SA with different bridges (■ ketone bridge, ▲ amide bridge, ○ diazo bridge /▬▬ Cd(II) ▬▬ Co(II) ▬ ▬ Fe(III)).

representative of intermediate cations, is efficiently retained on membranes where SA has been grafted with a ketone bridge from pH 4.0. The other bridges seem to have a positive effect only from pH 7.5. These cations are known to preferentially react with hard ligands (28) and it is thus not surprising to establish a correlation between affinity of these intermediate cations and the ketone bridge. This one is thus supposed to have a contribution to the extraction of these ions due to the presence of oxygen (29).

Influence of the Ligand

As seen above, although the number of SA entities increases according to SA<MDSA<ATA, the grafting rate evolves in opposite direction and finally, the number of complexing functions is quite closed (from 1.8 to 2.1 mmoles $\cdot$ g^{-1} of –COOH groups- Table 3).

The extraction rate of Co(II), Fe(III) and Cd(II) obtained on membranes grafted by SA, MDSA, and ATA via a diazo bridge is presented in Fig. 5. Retention of these metals by the different ligands seems to be pH-correlated: between pH 2.0 and pH 4.0, only Fe(III) is significantly retained and more specifically on membranes grafted by SA; between pH 4.0 and pH 7.0, Fe(III) is more retained by MDSA, Co(II) by ATA and Cd(II) by SA; above pH 7.0, influence of salicylic derivatives seems to be negligible, except for Fe(III) which is less retained on ATA membranes.

From these results, no positive correlation can be done between the number of salicylic acid units grafted and the extraction yields of metals. In this way, it seemed to be more interesting to graft SA instead of MDSA or ATA, if considering the full domain of pH.

Influence of the Sorbent

The preceding results have shown that SA grafted via a ketone bridge gives the best extraction yields for the different metals tested. In this experiment,

Table 3. Complexing capacities of the different modified supports, expressed in mg of metal per gram of support, and saturation rate of complexing sites (determined at pH 4.0 for Fe(III))

	Resin	Saturation rate (%)	Membrane	Saturation rate (%)
SA-Ketone	11.3 ± 0.6	11.2	19.2 ± 1.0	15.9
SA-Diazo	11.6 ± 0.6	10.8	13.4 ± 0.7	9.7
MDSA-Diazo	12.9 ± 0.6	11.1	14.0 ± 0.7	14.1
ATA-Diazo	10.2 ± 0.5	10.3	13.0 ± 0.6	14.8

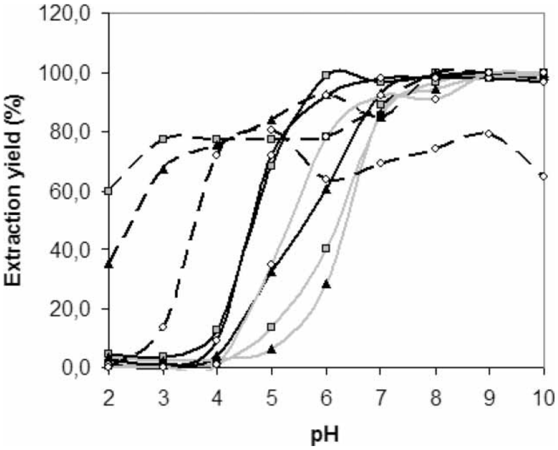


Figure 5. Extraction yields of representative cations versus pH onto membranes grafted with SA, MDSA and ATA via a diazo bridge (▬ ▬ Fe(III) ▬▬▬ Co(II) ▬▬▬ Cd(II)/ ■ SA, ▲ MDSA ○ATA).

influence of the support nature has been studied. Extraction rates of representative metallic ions versus pH are presented in Fig. 6 for grafted resin and membrane.

The results show that the resins and membranes present quite similar retention behavior whatever pH values, with a better extraction yield for membrane supports. This observation can be correlated to the grafting rates obtained for this two supports: 33% for membranes and 23% for resins (Table 2).

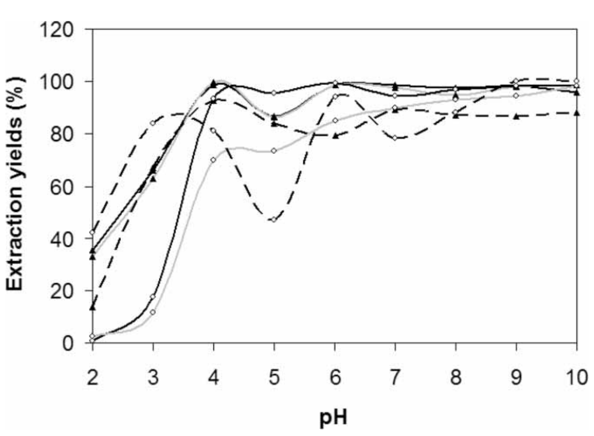


Figure 6. Extraction yields of metallic ions versus pH onto membrane and resin grafted with SA via a diazo bridge (▬ ▬ Fe(III) ▬▬▬ Co(II) ▬▬▬ Cd(II)/▲ membrane ○|resin)

This behavior has been confirmed by the determination of complexing capacities of the different supports elaborated, according to pH and metals. Table 3 presents these complexing capacities towards Fe(III) at pH 4.0. Whatever the ligand and the bridge used during grafting, membranes extract more amount of metal than resins, with the best yield obtained for membranes grafted with SA via a ketone bridge.

From these complexing capacities (CC, expressed in milligramm of metal per gramm of support) and from the grafting rate (GR, expressed in mmoles of $-$COOH per gramm of support), extracted from Table 2, a pseudo value of complexing site saturation rate (SR) can be calculated as follows:

$$\frac{\mathrm{CC}}{\mathrm{M} \times \mathrm{GR}} \times 100 = \mathrm{SR}$$

where M is the molar weight of considered metal, expressed in milligramm per mmole.

Results obtained for Fe(III) at pH 4.0 are given Table 3.

The capacities compared to the grafting rate of the modified supports permit to conclude that less than 16% of the complexing sites are accessible to metallic ions; best results being obtained onto membranes. It is important to remember that these results have been obtained during flow experiments (flow rate of $1\,\mathrm{mL \cdot min^{-1}}$). These values might be increased by two methods. The first one deals with a decrease of hydrophobicity of membranes due to PTFE matrix. It could be achieved by wetting the sorbents with an appropriate solvent, as methanol, before passing the metallic solutions through the support. The second one could be carried out by decreasing the flow rate of the peristaltic pump, allowing thus a longer contact time between metals and supports.

CONCLUSIONS

The grafting of two supports (XAD-4 resin and SDB-XC membrane) by different salicylic acid derivatives via three bridges, made it possible to undertake a comparative study of the chelating properties of these modified supports during flow experiments. The extraction rates and complexing properties of numerous cations were studied according to pH. The similarity of behavior between SA and MDSA grafted on the same type of support was shown, and it was highlighted that ATA did not improve significantly the performances of the grafted supports. The bridge used during grafting seemed moreover to play an important part in the metals extraction according to pH: ketone bridge gave the best extraction yields for all the metals, especially at acid pH values. Amide and diazo bridges began to be competitive from pH 6.0. Interesting results have also been obtained with Cr(VI): this metal has absolutely not been retained onto membranes grafted with SA via a ketone bridge whatever pH, and is specifically retained at acid pH on membranes grafted with SA via a diazo or an amide bridge. Lastly, determination of the chelating capacities of the modified supports showed that all the grafted sites were not accessible. This drawback could be overcome by decreasing hydrophobicity of membranes used, and above all, by decreasing flow rate of extraction step. To our knowledge, ligands were covalently linked to the membrane Empore^{TM} SDB-XC for the first time and not only sorbed, as it was done until today. In this way, it was shown that the membrane could be grafted by ligands with success and be used effectively for solid phase extraction, by judicious choices of extraction pH and of modified supports. Further studies will concern validation of these new sorbents with real samples. In particular, our current work concerns the selective determination of chromium (Cr(VI)) from tannery wastewater samples.

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