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APPLİCATİON OF PORPHYRİNE MODİFİED SORBENTS FOR METAL PRECONCENTRATİON

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ABSTRACT

The preconcentration of some divalent metal ions by complexation with carboxylphenylporphyrine (TCPP) and retention on conventional anion-exchange resins and nonionic sorbent was examined. Two different procedures - ligand in solution or immobilised on the solid sorbents - were evaluated as a function of pH. The selectivity order for TCPP-loaded resins was established as: Pb(II) > Ni(II) > Cd(II) > Cu(II) > Mg(II).

Introduction

Porphyrins naturally occurred macrocyclic compounds are widely applied for numerous analytical applications [1]. Their unique properties have been already utilised for design of electrochemical and optical sensors [2,3], catalytic determinations [4] and modification of voltammetric electrodes [5,6]. Recently published works, opening new field in porphyrin applications, describe new chiral catalysts for asymmetric synthesis [7] and the stationery phases in HPLC [8-10].

Mentioned above applications of porphyrins ligand are the result of their specific structure and properties. The porphyrin molecule with the four nitrogen atoms of the pyrrole rings toward the centre of its large aromatic system form strong complexes with transition metal ions. This feature caused attempts of application of porphyrins as a chelating agents and spectrophotometric reagents [11-14]. To enhance the rate of metal ion incorporation into porphyrine ring several procedures have been employed [15]. The strong affinity of metal ions towards porphyrin ligands leads to ideas of application of these compounds for metal preconcentration.

The complexing agents that have been mostly used for preconcentration of metals are sodium diethyldithiocarbamate (DDTC) [16], ammonium pyrrolidinedithiocarbamate [17-18] and 1,10-phenantroline [19,20]. The stability and selectivity of phenantroline is better than DDTC, however, this complexing reagent is sparingly soluble in water.

The main aim of this work was to check the potentiality of carboxyphenylporphyrine (TCPP) as a complexing agent for preconcentration of some divalent metal ions. As a support for TCPP and its metal complexes the microporous and macroporous conventional anion-exchange resins, Amberlite IRA-401 and Amberlite IRA-904 respectively, as well as nonionic sorbent Amberlite XAD-2 were examined. Atomic absorption spectrometry with flame and electrothermal atomisation was used as the detection method.

Experimental

Reagents and apparatus

The chemicals used were of analytical grade and all solutions were prepared with deionised water obtained from a Milli-Q system.

The metal standard solutions were prepared by appropriate dilution of 1000 mg l^{-1} stock solutions from Merck.

Tetracarboxyphenylporphyrine (meso-tetrakis(4-carboxyphenyl)porphyrin, TCPP) from Fluka was used without further purification.

The following solid sorbents were used: Amberlite IRA-401, macroporous anion-exchange resin (Bio Rad), 50-100 mesh; Amberlite IRA-904, microporous basic anion exchanger from BDH and Amberlite XAD-2, nonionic polymeric sorbent from Aldrich, 20-60 mesh.

Concentration measurements were performed by atomic absorption spectrometry using a Perkin Elmer 3110 apparatus with flame (air-acetylene) atomisation and Zeiss AAS-30 spectrometer equipped with pyrolytic graphite furnace and deuterium background correction. The instrumental settings of the manufacturers were followed.

The pH adjustment was performed with Radelkis OP-211/1 pHmeter and a combined glass electrode from Orion.

Determination of the adsorption isotherms of TCPP

The sorption of TCPP on the sorbents under study was measured by static method. A 0.10 g portions of sorbents were shaken with 10 ml of ligand solutions of various concentrations at pH 9 (borate buffer) for 2 h. After this time the concentrations of TCPP in the external solutions were measured spectrophotometrically at 411 nm.

Preparation of modified sorbents

The sorbents were preliminary washed with 6 mol l^{-1} HCl, water, then with 2 mol l^{-1} NaOH and water again. Washed sorbents were shaken with 10^{-4} mol^{-1} TCPP solution at pH 9 for 24 h until the supernatant solution become colourless. The sorbents were then filtered off, washed with water and alcohol. The modified sorbents contain 0.1 mmol of TCPP per gram of the appropriate sorbent.

Retention of metal ions as a function of pH

100 mg of dry sorbents (modified and unmodified respectively) was gently shaken for 60 min with 10 ml of 1μg ml^{-1} solutions of metal ions alone or with TCCP at concentration of 10^{-5} mol l^{-1} at appropriate pH value (adjusted with HNO_3 or NaOH). The concentration of metals were then determined in the filtrate by AAS method.

Results and discussion

It was established that some organic complexing reagents are sorbed on the hydrophobic surface of conventional anion-exchange resins and nonionic sorbents. Such a procedure leads for preparation of so-called „modified resins” or „ligand-immobilised resins” which can react with a large variety of metal ions by complex formation. In the immobilisation of organic ligands on a polymeric matrix, generally, the mechanism of ion exchange and/or adsorption is involved [21]. Dealing with anion exchangers, retention according to the mechanism of ion exchange would occur by means of the exchange of Cl^-, NO_3^- or Ac^- ions attached to quaternary ammonium groups of the resin and the negatively charged groups of the ligand (not hindering in the chelation) such as sulfonate or carboxylate. In addition the retention of organic reagents may be due the physical attraction, namely π-π dispersion forces arising the aromatic structures of the resin and ligand.

Fig. 1 shows the adsorption isotherms of carboxyphenylporphyrine on the studied sorbents. The capacity of TCPP sorbed on Amberlite IRA-401, Amberlite IRA-904 and Amberlite XAD-2 were 0.0028, 0.0023 and 0.0014 mmol g^{-1}, respectively. In all cases the obtained curves fit the equation of Langmuir well. The time necessary for equilibrium to be reached was about 60 min. As expected the lowest capacity was obtained for nonionic sorbent where only π-π interaction occurs.

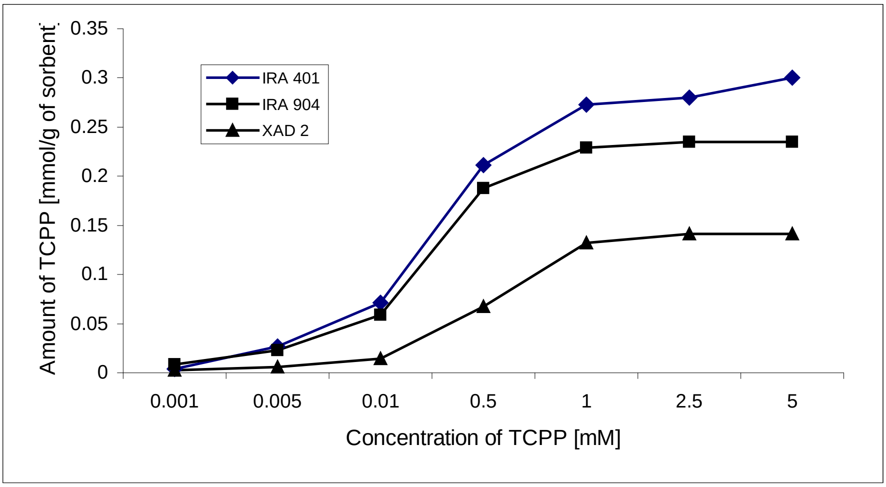

Figure I: Adsorption isotherms for TCPP loaded on different sorbents.

The resistance of TCPP-loaded sorbents to mineral acids and base solutions was also investigated. It is important to know the conditions for total elution or release of ligand from sorbent in order to predict its potential application for preconcentration and separation of metal ions. The portions (25 ml) of appropriate electrolytes at 0.1 mol l^{-1} concentration level were passed through the columns containing 0.25 g of each modified sorbent at a flow rate of 1 ml min^{-1}. The concentration of TCPP was measured spectrophotometrically. As it can be seen from Fig. 2 the resistance of TCPP-loaded sorbents to hydrochloric acid solution is the lowest. However, an increase in acid concentration did not affect so drastic release of ligand; for 1 mol l^{-1} HCl solution only 25% of TCPP elution was observed.

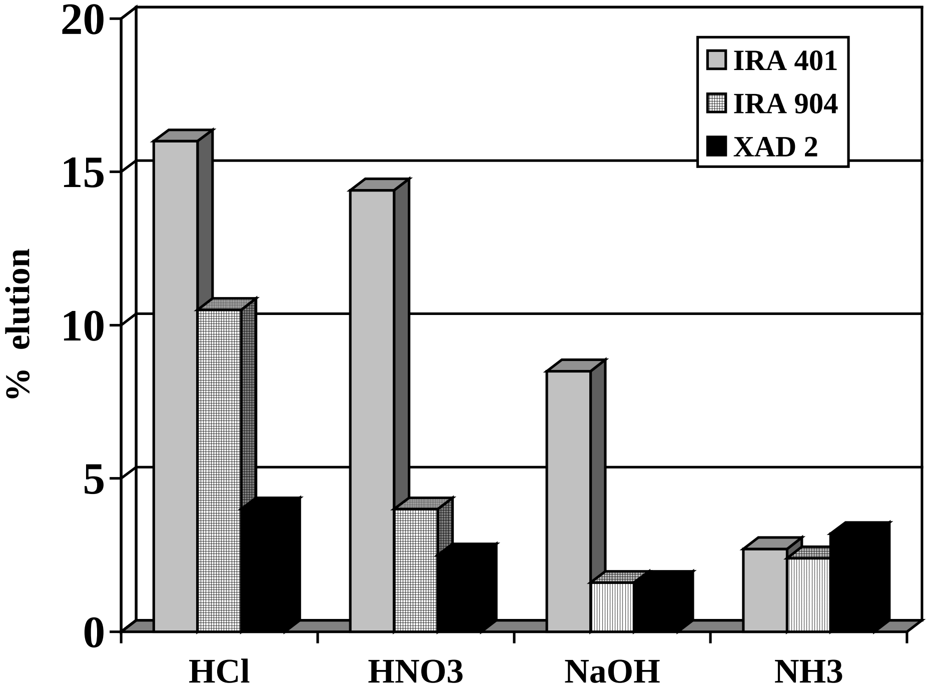

Figure II: Release of TCPP from modified sorbents by electrolytes at their concentration 0.1 mol 1^{-1}

The selective retention of metal ions could be obtained by two different procedures. (*i*) A ligand which interacts with the analytes is added to the sample and the resulting complex species are retained on a given sorbent. (*ii*) The complexing ligand is immobilised on the stationery phase, which then retains the metal ions as the sample is in the contact with solid sorbents. Both of these procedures were evaluated in this work. The reaction of complexation and also metal ions retention should depend on the protonation of chelating agent which is presented in a solution or immobilised on a resin. The sorption of metal ions at their concentration of 1 μg ml^{-1} on the sorbents under study by the batch method was examined for three pH values in the range of 5-9. This range covers the natural acidity of environmental samples, so enrichment procedure could be done without any pH adjustment.

The obtained results for pH 5,7 and 9 are presented in Table 1 (for unmodified sorbents) and Table 2 (for TCPP-loaded sorbents).

Generally, investigated metal ions show higher retention at higher pH values. The influence of acidity of the sample is at least apparent for Pb(II) when modified resins were used for enrichment. Sorption of Pb(II) is almost quantitative, even at pH 5, when TCPP was present onto the stationery phase. At this pH value for unmodified sorbents only 22-39% retention of this metal ion was observed. Similar, the sorption behaviour of Ni(II) not so much depends on pH. Retention of Ni(II) is much higher compared to SiO_2-TPP sorbent (5-p-carboxyphenyl)-10,15,20-triphenyl porphyrin covalently attached to aminopropyl silica gel) [22]. The observed low retention of Cd(II) could be explained by the large size of this ion. Such ions react with porphyrins forming mononuclear activated complex, which distorts the symmetry of the ligand nucles. In this conditions another metal ion (medium-size or small) can attack from the lower side of the molecule. The reaction of large metal ions with porphyrin ligands is relatively fast but the complexes formed are not stable. Due to their ability for deforming the symmetry of ligand molecule, however, they could catalyse the incorporation of other metal ions into the porphyrin nucles. A low uptake of Mg(II) is the advantage in the view of application for enrichment and separation procedure in analysis of natural water samples.

Table 1. Effectiveness of sorption of metal-TCPP complexes at different pH values.

	SORPTION OF METAL IONS, %, (n=2)								
	IRA 904			**IRA 401**			**XAD 2**		
Metal	pH 5	pH 7	pH 9	pH 5	pH 7	pH 9	pH 5	pH 7	pH 9
Pb	39.1	87.9	96.6	38.5	91.8	96.9	22.1	68.3	79.9
Cd	53.5	83.8	93.0	47.3	68.5	91.5	36.3	56.4	72.5
Cu	67.5	77.0	94.5	58.0	72.8	79.5	45.8	57.0	58.0
Ni	79.3	87.8	93.0	82.8	86.0	87.0	80.5	88.5	96.9
Mg	5.0	11.9	18.8	2.4	13.1	19.0	0	0.5	11.0

Table 2. Effectiveness of metal sorption on modified with TCPP sorbents at different pH values.

	SORPTION OF METAL IONS, % , (n=2)								
	IRA 904			**IRA 401**			**XAD 2**		
Metal	pH 5	pH 7	pH 9	pH 5	pH 7	pH 9	pH 5	pH 7	pH 9
Pb	98.6	99.9	99.5	99.9	99.9	94.9	83.5	84.8	81.1
Cd	15.0	30.0	45.0	12.5	30.0	52.5	11.0	17.5	37.5
Cu	37.8	54.5	85.0	40.0	67.5	92.7	71.8	92.8	100
Ni	74.3	79.1	87.2	68.8	81.5	83.1	59.7	82.9	87.4
Mg	3.1	9.8	15.3	1.0	9.8	15.1	0	0	9.7

The following selectivity order for metal ions on the TCPP-loaded sorbents could be establish: Pb(II) > Ni(II > Cd(II) > Cu(II) > Mg(II).

The affinity of metal complexes with TCPP towards examined sorbents decreases in the order: Pb(II) > Ni(II) > Cu(II) > Cd(II) > Mg(II).

Generally, lower retention of investigated metal ions was obtained for nonionic sorbent Amberlite XAD-2, where only π-π interaction between aromatic structures of polymeric matrix and chelating agent occurs.

The difference in the retention of metal ions under study indicate that some of them, such as Pb(II) or Ni(II), should be separable from the less strongly sorbed metal ions. The TCCP-modified sorbents can be used not only for separation, but also for the removal of some trace metals from aqueous solutions as well as for purification of reagents. As the column technique is widely applied in trace metal preconcentration from large volume sample solution, the experiments concerning the conditions for elution of metal ions from investigated sorbents will be undertaken in the future.

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