

Use of modified silica gel for concentrating Pb (II) and Cd (II) occurring in form of complex anions.

*R. T. Déniz, M.Seijo, Z.Fernández, A.M.Peron, H.Varela.
Faculty of Chemistry, Camagüey University, Camagüey, Cuba

*ruben.deltoro@reduc.edu.cu

Abstract: The performance of silica gel, modified by the impregnation with a high molecular weight quaternary amine (triethyl octadecyl ammonium iodide), used for the concentration of heavy metals occurring in water is studied. The material under study captures Cd, Pb, which are capable of forming stable complexes with I⁻ ions. The results obtained about the metal capture, under dynamic conditions, are described and metal ions are removed by desorption with EDTA and quantified by AAS.

Keywords: concentration; heavy metal; sorption behaviour; silicagel.

Introduction

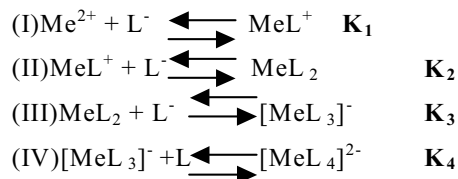
A large number of sorption methods have been proposed and used for the pre-concentration and removal of trace elements in the food and pharmaceutical industry, , water purification, etc. With the purpose of concentrating and removing traces of metal species occurring in aqueous solutions several adsorbents have been studied, there are included activated carbon, polymers, ion exchangers, chelating resins and many others [1-5].

The use of silica gel impregnated with various reagents utilised for pre-concentrating metal species such as Cs, Ag, Hg, Cu, Cd, etc., indistinctly occurring in the form of ions, has also been frequently practised [6,7,8].

The creation of an ion exchanger intended for the removal of only organic products is reported [6, 9,10]. Including in the silica gel particle lauryl-methacrylate polymer containing quaternary ammonium functional groups and having a capacity of 0.0012 meq/g makes such an ion exchanger.

The excellent capacity of high molecular weight quaternary ammonium salts for removing metals in the form of complex anions[11-15] and their selectivity with regards to such anions depending on the ligand accompanying the metal and its stability constant are also reported in

specialised literature. Such metals, i.e. Cd, Pb, can form, when combined with halides, complex anions as shown below:



K₁, K₂, K₃, K₄ are the equilibrium constants for complexation reactions.

Where Me²⁺ can be Pb²⁺, Cd²⁺ and the ligand L⁻, coming from halides, can be Cl⁻, Br⁻, I⁻, etc.

Literature reports [15] that the value of lg. K_{ext} for tri-iodides is within the range of 7 - 11 which enables liquid - liquid extraction and the removal of such metals from the aqueous medium where they occur.

In keeping with the above, the removal of PbI₃⁻ and CdI₃⁻ is achieved by applying solid-liquid extraction systems which are capable of capturing the lead occurring in solid phase in the liquid. For achieving maximal removal of lead and cadmium it is necessary to ensure a ligand concentration

such that enables the occurrence of a high percentage of lead in the form of complex anions. Assuming MeL_3^- , the value of the molar fraction, which ensured the occurrence of over 75 % of Pb^{2+} , Cd^{2+} in the form of anions was obtained at L^- concentrations higher than 0.01 mole/L.

$$\Phi MeL_3^- = \frac{c(MeL_3^-)}{c_T(Me)} = \frac{\beta_3 c^3(L^-)}{1 + \sum_{i=1}^3 \beta_i L^i} \geq 0,75 (V)$$

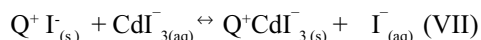
Where:

ΦMeL_3^- = Molar fraction of the complex anion (This value-0,75- permit the existence complex species MeL_3^-)

β = Stability constant ($\beta_3 = K_1 \times K_2 \times K_3$)

$c_T(Me)$ = total metal concentration

Thus the exchange in the matrix was achieved by using iodide as ligand as per the following equation where Q^+ represents the impregnated adsorbent:



In the present work, the sorption properties of silica gel are used to adsorption of an anion exchanger ($Q^+ I^-$) capable of capturing and concentrating toxic metals in aqueous

thus enhancing the factual possibility of determining the said metals by following their desorption and using conventional methods of chemical analysis.

Experimental details

Experiments were conducted at 298 ± 1 K, using Merck silica gel (diameter = 0.3 - 0.5 mm), which was impregnated with 96 % triheptyl octadecyl ammonium iodide dissolved in toluene. The impregnated adsorbent was put into a glass column of 7 mm in diameter and 22 cm in height and used to capture and remove the Pb^{2+} and Cd^{2+} occurring in water.

For so doing, the concentration of the potassium iodide solution was adjusted at 10^{-2} mol/L, this being the optimal condition for the formation of metal complexes.

The amount of impregnated silica gel and the flow rate used were 1g and 1 mL/min respectively. The various dilutions of the metals under study, at concentrations of 43 mg/L for Pb^{2+} and 47 mg/L for Cd^{2+} and pH 7, were filtered through such column.

The determination of such metal species was done, during filtration, by means of atomic absorption spectrophotometry at a wavelength of 283.3 nm for Pb and 228.3 nm for Cd in a Karl Zeiss AAS-3 spectrophotometer.

Desorption of Pb was subsequently carried out by filtering the 10^{-3} mole/L EDTA solution at a flow rate of 1 mL/min.

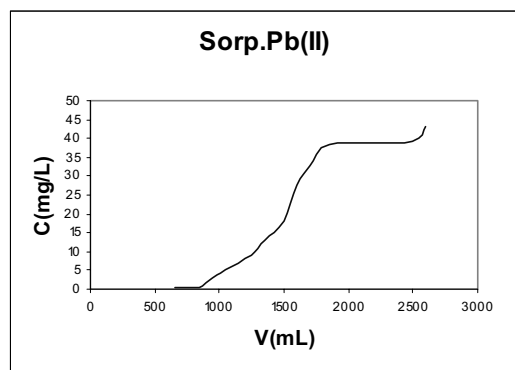


Fig. No 1. Sorption of Pb in dynamic conditions

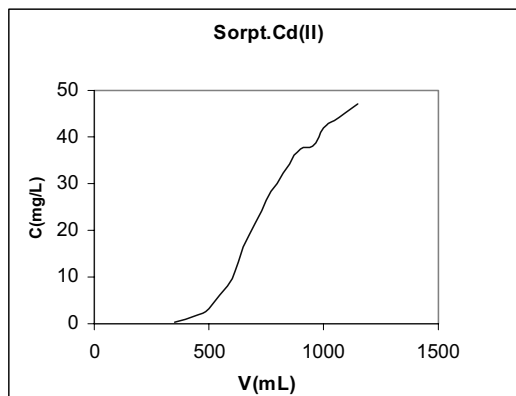
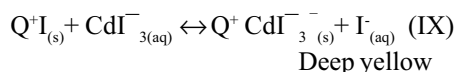
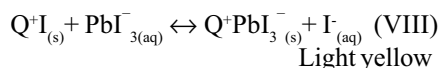


Fig. No 2. Sorption of Cadmium in dynamic conditions

Results and Discussion

The breakthrough curve of lead and cadmium in the form of a PbI_3^- and CdI_3^- complex anion is shown in Fig. 1, 2 which shows the excellent capabilities of the adsorbent for capturing the Pb and Cd occurring in water even at high concentrations.

The equation below shows that Pb^{2+} and Cd^{2+} in the form of MeI_3^- exchanges the ion occurring in the impregnated matrix with an effectiveness of 0,9 meq of Pb/g of adsorbent.



The calculations of the effective dynamic adsorption capacity (a_o) are carried out by using the following equation, starting from the data from the curves (fig. 1 and 2):

$$a_o = \frac{C_o V_f - \sum C_i V_i}{M(Me/2)m(ads)} \quad \text{(X)}$$

Where:

C_o : initial concentration of the metal Me^{2+}

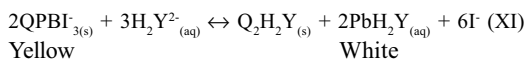
V_f : Final volume of saturation in Litres

C_i and V_i : Concentration and volume of the portions i , taken as sample.

$M(Me/2)$: equivalent mass of the metal, in g.

m : mass in gram of the adsorbent.

Fig. 3 shows the desorption of the Pb^{2+} exchanged by the impregnated silica gel, carried out with an EDTA disodium salt (H_2Y^{2-}) at 10^{-3} mole/L and pH 8 which provides for the breaking up of the Pb^{2+} complex with the iodide and its association with the EDTA as per the following equation:



Desorption takes place rapidly and the change in colour, from dark yellow to plain white, can be readily observed, the desorption capacity calculated being similar to the one actually observed.

The locking up, in silica gel, of a high molecular weight ion exchange matrix, corroborates the ion exchange equation.

The filtration of a Cd^{2+} dilution, under similar conditions, in the presence of a 10^{-2} mole/L iodide solution showed the lower affinity of the cadmium complex with respect to the matrix since the breakthrough curve shows saturation at lower volumes of treated water, this proving that the ion exchange affinity and capability depend, to a large extent, on the stability of the complex in a given medium, which, in this case, is higher for lead than for cadmium. The effective dynamic adsorption capacity established was 0,8 meq per gram of impregnated adsorbent.

Conclusions

The research conducted shows that it is possible to capture, by means of an exchange mechanism for complex ions of the metallic species, the Pb and Cd occurring in water by using silica gel impregnated with a quaternary amine as adsorbent; also demonstrate that the affinity for the anion exchanger is greater in PbI_3^- than in CdI_3^- .

The possibility of desorbing the metal by using disodium EDTA dilutions at pH 8 and of subsequently determining the amount of metal desorption by means of conventional analysis methods was also established.

Thus the effectiveness of the adsorbent enables the detection, concentration and removal of metal species and the utilisation of this adsorbent for the purpose of treating waters for various applications, also including highly-pure water free of Pb^{2+} , Cd^{2+} , and the purification of reactive.

Received 16 February 2007

Accepted 11 May 2007

References

- [1] K. Terada, Anal. Sci. 7 (1991)187.
- [2] M. Volkan, O. Yavuz and A. G. Howard, Analyst. (1987) 1409

- [3] A. I. Zouboulis, K. A. Kydros and K. A. Matis. *Wat. Sci. Tech.* 27(10) (1993) 83.
- [4] D. Petruzzelli, G. Tiravanti, M. Santori and R. Passino. *Wat. Sci. Tech.* 30(3) (1994) 225.
- [5] J. Rodriguez, Estudio de la Sorción de Pd, Pt, Au en Silica Gel modificada con Benzoil y Furoiltiureas, Ph.D. Thesis, Cuba (1997)
- [6] J. S. Fritz. *Ion Chromatography. Monography* 20 (1982)
- [7] F.V. Moraes, I.L. Alcantara, P.S. Roldan, G.R. Castro, M.A.L. Marcionte, P.M. Padilha, *Ecl. Quim.* 28(1) (2003) 9.
- [8] F.A. Silva, I.L. Alcantara, P.S. Roldan, C.C.F. Padilha, A.B. Araújo, J.P.S. Valente, A.O. Florentino, P.M. Padilha, *Ecl. Quim.* 30(3) (2005) 45.
- [9] P.M. Padilha, L.A. M. Gomes, C.C.F. Padilha, J.C. Moreira, N.L. Dias Filho, *Anal. Lett.* 32 (1999) 1807.
- [10] P.M. Padilha, J.C. Rocha, J.C. Moreira, J.T. S. Campos, C.C. Federici, *Talanta* 45 (1997) 317.
- [11] N. L. Lomako, *Izvestia (Belaruse)*, (1982)
- [12] Yu. Lurié, *Izvestia (Belaruse)*, (1989) 332
- [13] E. R. Mazovka, *Izvestia (Belaruse)*, (1981)
- [14] E. M. Rajmanko, *Zhurnal Anal. Chem. (Belaruse)*, 104 (1989) 335.
- [15] G. L. Starobinetz, *Zhurnal Fiz Jimii (Belaruse)* 2 (55) (1985) 2045.