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Adsorption of lanthanides(III) from aqueous solutions by fullerene black modified with di(2-ethylhexyl)phosphoric acid

Research Article

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Abstract: Fullerene black (FB) - a product of electric arc graphite vaporization after extraction of fullerenes - was modified with the di(2-ethylhexyl)phosphoric acid (D2EHPA). The distribution of D2EHPA between FB and aqueous HNO_3 solutions has been studied. The effect of HNO_3 concentration in the aqueous phase and that of D2EHPA concentration in the sorbent phase on the adsorption of microquantities of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y nitrates from HNO_3 solutions by D2EHPA-modified FB are considered. The stoichiometry of the sorbed complexes has been determined by the slope analysis method. The efficiency of lanthanides' adsorption increases with an increase in the element atomic number. A considerable synergistic effect has been observed upon the addition of the neutral bidentate tetraphenylmethylenediphosphine dioxide ligand to D2EHPA in the sorbent phase.

Keywords: *Fullerene black • Modification • Adsorption • Di(2-ethylhexyl)phosphoric acid • Tetraphenylmethylenediphosphine dioxide • Lanthanides.*

1. Introduction

It is now widely accepted that the use of adsorbents in metal recovery offers many advantages over the use of liquid-liquid extraction. The most important of these advantages are the simplicity of equipment and operation, and the possibility of using a solid adsorbent for many extraction cycles without losses in the metal extraction capacity. Unfortunately, the preparation of ion exchangers containing chelating groups connected to a solid matrix by chemical bonds is usually very complicated, expensive, and time consuming. Therefore, the concept of using solvent impregnated sorbents was put forward and developed in [1-3]. This is a very simple and in many cases the only way to prepare ion exchange sorbents containing reactive groups with special properties, which cannot be immobilized by chemical bonding. The method includes the incorporation of an extractant by a physical impregnation technique into a solid matrix. The use macroporous polymeric sorbents [1-3] and hydrophobized silica gels [4] impregnated with extractants of various nature for the extraction of metal ions from aqueous solutions was earlier described. One of the requirements imposed on the solid matrix is that it should possess a fairly large capacity with respect to an extractant, which, in turn, determines the capacity of an adsorbent with respect to the metal ion to be extracted. This requirement is usually fulfilled when materials with a high specific surface area are used as solid matrixes. In this respect, the fullerene black (FB) is a good candidate for the preparation of impregnated sorbents, because this material has a comparatively high specific surface area [5].

FB, a new member in the carbon family, is an amorphous product of electric arc graphite vaporization after extraction of fullerenes. Unlike graphite and glassy carbon, FB is readily oxidized by dioxygen, brominated and hydrogenolyzed [5]. FB is a promising catalyst for dehydrocyclization of alkanes [5,6] and activation of methane [7]. The high-temperature behavior of FB [8] and ESR study of the product [9] were described. Recently, FB has been found to be an efficient adsorbent for organic solvents (crude petroleum, oils, and

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chlorobenzene) from aqueous emulsions [5]. Impregnated with 1-phenyl-3-methyl-4-benzoylpyrazol-5-one, FB also showed a high adsorption efficiency for U(VI), Th(IV), Zr(IV), Sc(III), and lanthanides(III) recovery from aqueous solutions [10].

The aim of this work was to study the adsorption ability of FB towards phosphororganic acidic extractant, di(2-ethylhexyl)phosphoric acid (D2EHPA), and to estimate the feasibility of D2EHPA-modified FB for the adsorption of lanthanides(III) from nitric acid solutions.

2. Experimental Procedures

FB was prepared as described in [5]. The specific surface area of FB determined by the BET method was 274 $m^2\ g^{-1}$. Analytical grade D2EHPA was purified according to [11]. Tetraphenylmethylenediphosphine dioxide (TPMDPDO) was synthesized by the known method [12] and purified by crystallization.

The FB-D2EHPA sorbents were prepared according to the principles of the dry impregnation method [2]. An appropriate amount of FB (2 - 3 g) was placed in a round-bottomed flask and dichloromethane containing D2EHPA of different concentrations was added. The mixture was equilibrated for 12 hours on a rotary evaporator without applying a vacuum. Then dichloromethane was removed by applying a controlled vacuum and the sorbent was further dried to constant weight. The concentrations of D2EHPA in the sorbent were varied from 0.1 to 1.5 mmol g^{-1}. The same procedure was followed to prepare FB impregnated with TPMDPDO and with a mixture of D2EHPA and TPMDPDO.

In order to investigate the retention of D2EHPA on FB and its distribution between the sorbent phase and the aqueous phase as a function of HNO_3 concentration in the aqueous phase and that of D2EHPA in the sorbent phase, batch experiments were carried out at 20 ± 2°C. In these experiments 0.1 g of dry FB-D2EHPA and 10 mL of the aqueous phase were stirred in stoppered glass tubes for 2 h. The concentration of HNO_3 in the aqueous phase was varied between 0.003 and 1 M. The suspensions were then filtered through membrane filters and the total concentration of D2EHPA in the aqueous phase was determined by inductively coupled atomic emission spectrometry (ICP-AES) on an ICAP-61 spectrometer (Thermo Jarrell Ash, USA). The content of D2EHPA in the sorbent phase was evaluated from the material balance between the initial extractant concentration in the sorbent phase and that found in the aqueous phase after equilibration. The distribution ratio (D) was calculated as the ratio of concentrations in the equilibrium solid and aqueous phases.

Aqueous solutions of lanthanide nitrates were prepared by dissolving the corresponding oxides in high purity nitric acid. The distribution of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y in the adsorption systems was studied in model solutions of nitric acid of variable concentrations at the initial metal concentration (2 ± 0.1) × 10^{-5} M for each element.

The experiments on the adsorption of metal ions were performed in the static mode at 20 ± 2°C. A weighed sample (0.1 g) of the sorbent was mixed with an Ln aqueous solution (10 mL) for 1 h; this was time found earlier to be sufficient for the system to reach equilibrium. Preliminary experiments showed that the adsorbtion of lanthanides(III) onto FB from HNO_3 solutions in the absence of D2EHPA is negligible.

Isotherms of Eu(III) adsorption were studied by adding 0.1 g of the FB-D2EHPA sorbent to 10 ml solutions with initial concentrations of Eu(III) from 2 × 10^{-5} to 1 × 10^{-3} M at varied D2EHPA concentrations (0.3, 0.5 and 1.0 M) in the sorbent phase.

Lanthanide concentrations in the initial and equilibrium aqueous solutions were determined by inductively coupled plasma mass-spectrometry (ICP-MS) on a PlasmaQuad (VG Elemental, GB) following the procedure described in [13]. The concentration of lanthanides in the sorbent phase was found by the material balance equation. The distribution ratios lanthanides (D_{Ln}) were calculated as the ratio of concentrations in the equilibrium solid and aqueous phases. Duplicate experiments showed the reproducibility of the D_{Ln} measurements was generally within 10%. HNO_3 concentration in the equilibrium aqueous solutions was determined by potentiometric titration with KOH solution and pH was measured on a pH meter (pH-150, Russia) equipped with a combined glass electrode.

3. Results and discussion

The distribution of D2EHPA (HA) between the loaded FB and the aqueous solution was investigated for different loading amounts of the extractant in the sorbent phase at different HNO_3 concentrations in the aqueous phase. The distribution ratio of HA (D_{HA}) rises with an increase of HNO_3 concentration in the equilibrium aqueous phase (Fig. 1), because HA is largely sorbed in a nondissociated form. Far from the saturation concentration of HA in the sorbent, the variation of D_{HA} with H^+ ions concentration in the aqueous phase can be described by the equation

$$D_{HA} = K_{HA}(1 + K_a[H^+]^{-1})^{-1}, \quad (1)$$

where K_{HA} is the distribution constant of HA and K_a is the ionization constant of HA (pK_a = 1.3 [14]).

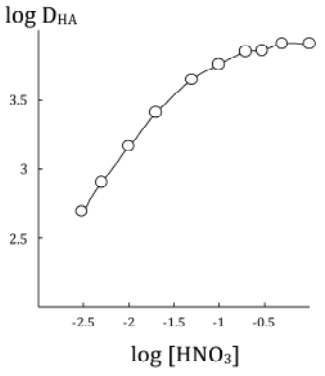

Figure 1. Influence of HNO_3 concentration in the aqueous phase on the distribution of D2EHPA between the FB-D2EHPA sorbent and the aqueous phase. CHA = 1.0 mmol g^{-1}. The sizes of the points represent error bars.

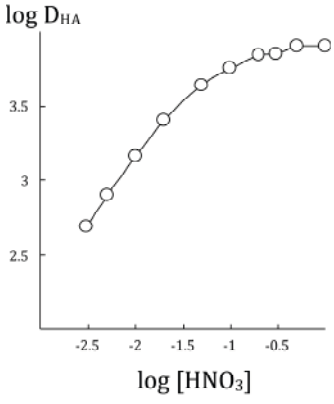

Figure 2. The distribution of D2EHPA between the FB-D2EHPA sorbent and the aqueous 1M HNO_3 solutions. The sizes of the points represent error bars.

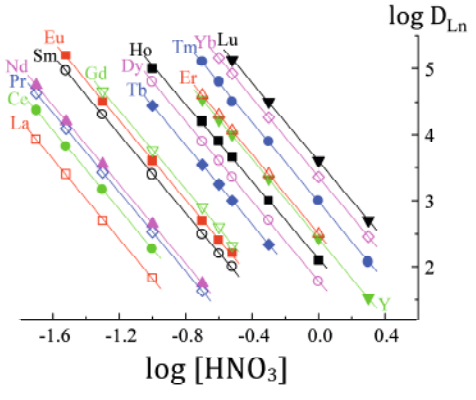

Figure 3. The effect of HNO_3 concentration in the aqueous phase on the adsorption of Ln(III) by the FB-D2EHPA sorbent. CHA = 1.0 mmol g^{-1}. The sizes of the points represent error bars. Slope: -3.01 ± 0.12 (Y), -3.0 ± 0.12 (La), -2.98 ± 0.13 (Ce), -2.98 ± 0.13 (Pr), -3.03 ± 0.15 (Nd), -2.97 ± 0.14 (Sm), -2.98 ± 0.15 (Eu), -3.03 ± 0.16 (Gd), -3.0 ± 0.15 (Tb), -3.02 ± 0.17 (Dy), -2.91 ± 0.19 (Ho), -2.97 ± 0.16 (Er), -3.03 ± 0.17 (Tm), -2.98 ± 0.15 (Yb), and -2.94 ± 0.18 (Lu).

The interphase distribution of HA at $[H^+] >> K_a$, when HA in the aqueous phase is nondissociated, can be described by the Langmuir equation

$$\overline{[HA]} = K_{HA}\overline{[HA]}_{max}[HA](1 + K_{HA}[HA])^{-1} \quad (2)$$

where [HA] and $\overline{[HA]}$ are the equilibrium HA concentrations in the aqueous and solid phases and $\overline{[HA]}_{max}$ is the maximum HA concentration in the sorbent for monolayer adsorption. From the experimental data presented in Fig. 2, through linearizing Eq. (2) as $1/D_{HA}$ versus [HA], we derived $\overline{[HA]}_{max}$ = 2.15 mmol g^{-1} and log K_{HA} = 3.88. The value of the distribution constant for D2EHPA on FB is higher than the corresponding value for D2EHPA in hexane (log K_{HA} = 3.48 [14]). This indicates that the interphase equilibrium of D2EHPA is considerably shifted to the sorbent phase, and it seems that the interaction of D2EHPA with FB acts to further drive the displacement of D2EHPA molecules from the aqueous solution towards the sorbent phase.
It follows from Eq. (2) that

$$D_{HA} = K_{HA}(\overline{[HA]}_{max} - \overline{[HA]}) \quad (3)$$

that is, HA transfer into the aqueous phase is enhanced when the HA concentration in the sorbent phase increases or, accordingly, as the free surface area of the FB matrix becomes smaller.
The adsorption of lanthanides(III) by the FB-D2EHPA sorbent decreases with an increase of aqueous HNO_3 concentration (Fig. 3).
The dependence $\log D_{Ln} = f(\log[H^+])$ is linear with a slope of -3. Therefore, the adsorption of the metal ion is accompanied by a release of free protons. Considering that the resulting Ln(III) complex may be solvated by nondissociated HA [15], the adsorption of lanthanide ions can be described by the following general expression:

$$Ln^{3+} + m\overline{HA} = \overline{LnA_3(HA)}_{m-3} + 3H^+ \quad (4)$$

where the overboarded formulas refer to the sorbent phase. The equilibrium constant of the above reaction is

$$K_{Ln} = [\overline{LnA_3(HA)}_{m-3}][H^+]^3[Ln^{3+}]^{-1}[\overline{HA}]^{-m} = D_{Ln}[H^+]^3[\overline{HA}]^{-m} \quad (5)$$

From Eq. (5), the following relationship can be obtained

$$\log D_{Ln} = \log K_{Ln} + m\log[\overline{HA}] - 3\log[H^+] \quad (6)$$

This relationship was used to determine the stoichiometry of the adsorbed complexes.

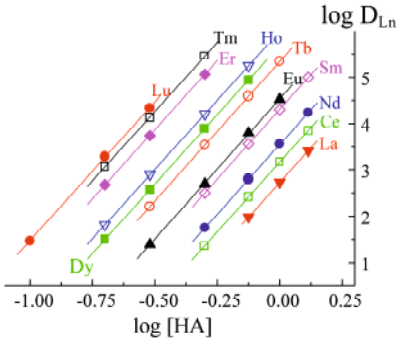

Figure 4. The effect of D2EHPA concentration in the sorbent phase on the adsorption of Ln(III) from 0.05 M HNO_3 solutions. The sizes of the points represent error bars. Slope: 5.95 ± 0.25 (La), 6.01 ± 0.26 (Ce), 6.02 ± 0.21 (Nd), 6.04 ± 0.21 (Sm), 6.02 ± 0.23 (Eu), 6.02 ± 0.20 (Tb), 5.97 ± 0.0.26 (Dy), 5.96 ± 0.25 (Ho), 5.96 ± 0.24 (Er), 5.96 ± 0.22 (Tm), and 5.98 ± 0.21 (Lu).

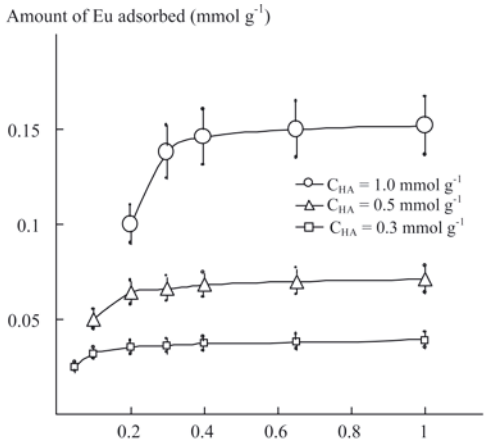

Figure 5. Adsorption isotherms of Eu(III) adsorbed by the FB-D2EHPA sorbent. (FB-D2EHPA dosage: 0.02 g per 10 mL; initial HNO_3 concentration: 0.002 M).

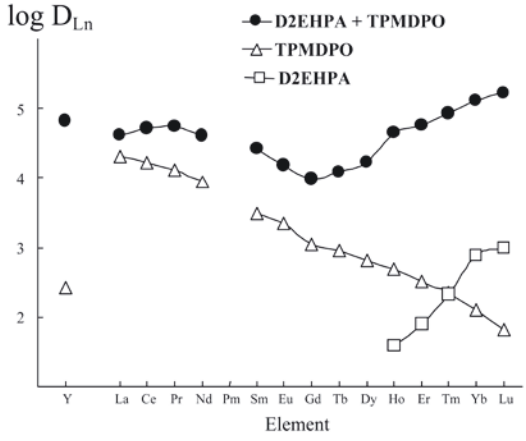

Figure 6. The adsorption of lanthanides and yttrium from 0.1 M HNO_3 by FB impregnated with D2EHPA, TPMDPO, and a mixture of D2EHPA and TPMDPO (sorbent dosage: 0.1 g per 10 mL; concentration of D2EHPA and TPMDPO: 0.35 mmol g^{-1}). The sizes of the points represent error bars.

The dependence $\log D_{Ln} = f(\log[\overline{HA}])$ is linear with a slope of 6 (Fig. 4). Hence, the $LnA_3(HA)_3$ species can be assumed to be present in the sorbent phase. The data on loading the FB-D2EHPA sorbent by europium(III)suggest the same stoichiometric ratio in the sorbed Eu(III) complex (Fig. 5).The D_{Ln} value at the given HNO_3 concentration grows in going from La to Lu (Fig. 3) with an increasing charge density on the Ln^{3+} ion, in analogy with the trends observed for the solvent extraction system with D2EHPA [15]. The difference in D_{Ln} values between Lu(III) and La(III) is fairly large (about 4.7 log units), showing the potential usefulness of the FB-D2EHPA sorbent as a stationary phase in the chromatographic system.

We expected that the replacement of HA solvated molecules in the $LnA_3(HA)_3$ complex by a neutral ligand (L) with a greater basicity and lipophilicity than those of HA would raise D_{Ln} if fullerene black impregnated with a mixture of HA and L is used. The stability of the resulting complexes would be governed by the acceptor properties of the LnA_3 chelates and the donor power of a neutral ligand, L [16]. In fact, introducing TPMDPO into the sorbent causes a nonadditive increase in D_{Ln} (Fig. 6). The synergistic effect, $S = D_{mix}/(D_{HA} + D_L)$ (where D_{HA}, D_L, and D_{mix} are the lanthanide distribution ratio for FB impregnated with HA, TPMDPO and their mixtures), grows in going from La to Lu, reaching S = 170 for Lu. The high complexing power of TPMDPO is apparently due to its bidentate coordination in the resulting complexes [17]. Earlier, a similar synergistic effect was observed in the solvent extraction of Eu(III) and Am(III) with a mixture of octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) and bis(2,4,4-trimethylpentyl)dithiophosphinic acid (HR) [18] or di(chlorophenyl)dithiophosphinic acid [19]. It was shown that Eu(III) passes into the organic phase as an $Eu(NO_3)R_2(CMPO)_{3-x}(H_2O)_x$ complex [18]. Complexes of similar composition would probably result when Ln ions are adsorbed from nitric acid solutions by the FB sorbent impregnated with a mixture of HA and TPMDPO.

4. Conclusions

Fullerene black is a convenient matrix for the impregnated sorbent preparation. The results of HNO_3 concentration effect on the distribution ratio of D2EHPA show that an increase of HNO_3 concentration in the aqueous phase leads to the minimization of the extractant loss. The efficiency of lanthanide ions adsorption increases when the concentration of D2EHPA in the sorbent phase increases or when the concentration of HNO_3 in the aqueous phase decreases. The distribution ratio of lanthanides increases with an increase in the atomic number of an element.

A considerable synergistic effect has been observed upon addition of the neutral bidentate TPMDPO ligand to D2EHPA in the sorbent phase.

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