New Hybrid TiO_2 Nano-structured Materials for Lanthanides Separation

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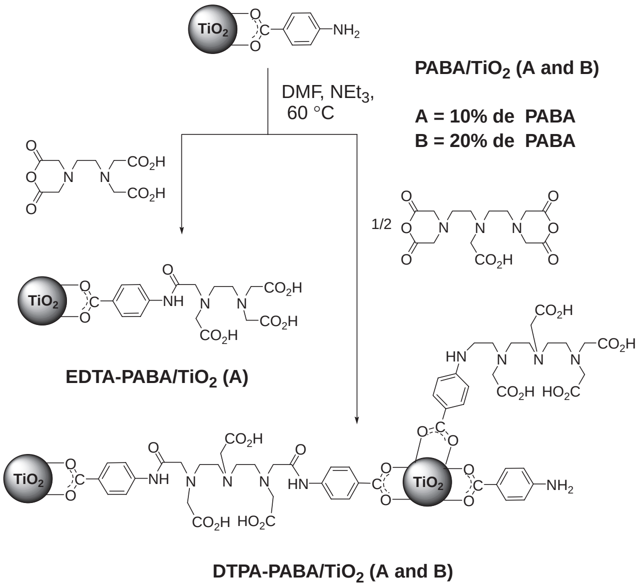
New nano-structured hybrid EDTA- or DTPA/TiO_2 materials were synthesized and were applied to the selective lanthanum(III)/gadolinium(III) separation in aqueous solutions.

A great deal of research is devoted to the separation of rare earths (RE) since these elements are increasingly used in the field of chemical engineering, metallurgy, luminescence, nuclear energy, high-temperature superconductors, and catalysis among others. While their separation is usually accomplished by solvent extraction;[1] nanofiltration-complexation,[2] chelating organic resin,[3] or ion-imprinted polymers[4] have been developed due to their greater efficiency and environmental friendliness. Solid hybrid adsorbents such as silica-based materials, prepared by sol–gel hydrolysis, containing malonamide,[5] CMPO,[6] or polyamine[7] were surprisingly less studied for the removal and the recovery of RE which will be associated with the development of reliable functionalization routes.[8] For titania-based materials, only Pb^{2+} and Eu^{3+} kinetic sorption studies in the presence of different complexing agents were described in the literature.[9] Herein, we present, to the best of our knowledge, the first example of hybrid TiO_2 nano-structured materials exhibiting high ionic RE separation performances. Recently, a new aqueous one-pot process for hybrid *para*-aminobenzoic acid (PABA)/TiO_2 mesoporous nano-structured materials has been developed in our laboratory.[10] It appeared to be an efficient and reliable method for controlling organic loadings (up to 20% in weight) and for adjusting the combined organic/inorganic properties. PABA molecules were found to be chemisorbed as a carboxylate onto TiO_2 nano-particles (5–6 nm in size), leading to the formation of strong interaction between the amino acid and the TiO_2 nanoparticles and good stability of these hybrids. It is worth noting that such hybrid nano-materials revealed to be stable (no total leaching of the organic part as confirmed by FT-IR experiments) between ca. pH 2 (HNO_3) and pH 10 (NaOH) for at least 12 months. In an attempt to use NH_2– functions as surface sites for further organic reactions, we studied the chemical reactivity of our PABA/TiO_2 nano-structured material (with 10 or 20% in weight of PABA) through coupling reactions with EDTA monoanhydride and DTPA dianhydride in dry DMF as depicted in Scheme 1.[11] ^{13}C solid-state CP-MAS NMR spectra of all samples [denoted EDTA-PABA/TiO_2(A) and DTPA-PABA/TiO_2(A or B)] featured broad resonance signals at 169.1 ppm and at 54.6 ppm corresponding to the *C*O and the *C*H_2N groups of EDTA and DTPA moieties, confirming the coupling of such molecules during the process.



Scheme 1. Syntheses of EDTA-PABA/TiO_2 and DTPA-PABA/TiO_2 samples.

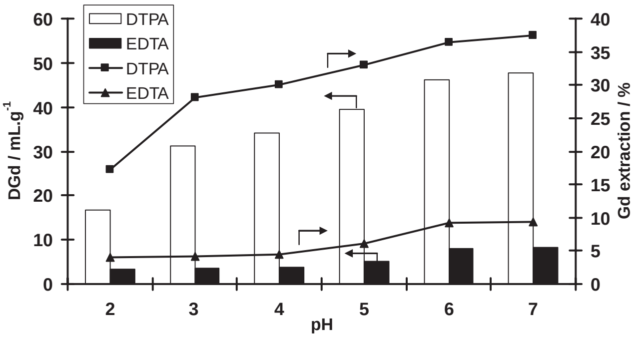


Figure 1. Gd^{3+} complexation by EDTA-PABA/TiO_2(A) and DTPA-PABA/TiO_2(A) nano-materials versus pH. Conditions: $Gd(NO_3)_3 \cdot 6H_2O$; $[Gd^{3+}] = 4.5 \times 10^{-3}\,mol\,L^{-1}$; HNO_3; 20 °C; H_2O (4 mL), 24 h.

While EDTA molecules would only be linked by one aromatic carboxylate group, DTPA molecules could be grafted by the two ones (Scheme 1). Lanthanum and gadolinium nitrates were chosen in order to check the efficiency of these hybrid nano-structured materials toward the selective separation of lanthanides in acidic aqueous solution. Amounts of lanthanides (La and Gd) in aqueous solutions were determined by ICP-AES spectrometry with a Spectro D (Spectro). Figure 1 shows distribution coefficients and percentages extraction towards Gd^{3+} of 50 mg of EDTA-PABA/TiO_2(A) and of DTPA-PABA/TiO_2(A) nano-materials as a function of the pH.[12] For both samples, several measurements were performed. These results showed that

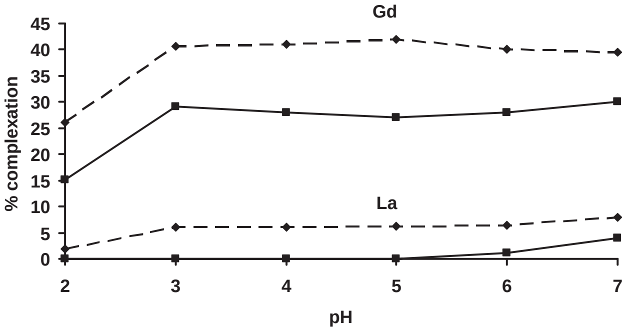


Figure 2. Percentages extraction of La^{3+} and Gd^{3+} by DTPA-PABA/TiO_2(A) (—) and DTPA-PABA/TiO_2(B) (- - -) materials versus pH. Conditions: $La(NO_3)_3{\cdot}6H_2O$, $Gd(NO_3)_3{\cdot}6H_2O$; $[La^{3+}] = [Gd^{3+}] = 4.5 \times 10^{-3}\,mol\,L^{-1}$; HNO_3; 20 °C; H_2O (4 mL), 24 h.

DTPA-PABA/TiO_2(A) sample ($D_{Gd} = 31.3$–$47.8\,mL\,g^{-1}$) was in average seven times more efficient than EDTA-PABA/TiO_2(A) one ($D_{Gd} = 3.6$–$8.3\,mL\,g^{-1}$) for the Gd^{3+} complexation in the pH range 3–7. With no increase of D_{Gd} from pH 6 to 7, we assumed that maximum extraction levels were reached (37.4 and 9.4%) corresponding to capacities of 0.126 and 0.025 $mmol\,g^{-1}$ for DTPA-PABA/TiO_2(A) and for EDTA-PABA/TiO_2(A), respectively. DTPA-PABA/TiO_2 (A and B) samples were thus applied to the Gd^{3+}/La^{3+} separation under the same experimental conditions.

Figure 2 illustrated the Gd^{3+} and La^{3+} complexations efficiencies of 50 mg of each DTPA-PABA/TiO_2(A) and -(B) nano-materials as a function of pH. Interestingly, DTPA-PABA/TiO_2(A) sample exhibited a high selectivity towards Gd^{3+} in the pH range of 2–5. With a D_{Gd} of 19.0 $mL\,g^{-1}$ and a $D_{La} < 0.25\,mL\,g^{-1}$ at pH 4 (taking into account the uncertainty of the experimental data), a selectivity $S_{Gd/La} > 76$ was obtained.[13] By increasing the organic content using DTPA-PABA/TiO_2(B) (Scheme 1), the maximum capacity increased strongly but the selectivity $S_{Gd/La}$ decreased to 12.6 from pH 3. The reasons are not still well understood but we thought that the increase of the ratio (mono-coordinated DTPA)/(di-coordinated DTPA) due to sterical hindrance might be implied. These data showed that the chemical organization in such hybrid nano-structured materials can deeply influence their physicochemical properties.

Recycling of DTPA-PABA/TiO_2(A) was also studied towards the possibility of organic ligand leaching into solution. After completing the first run at pH 7, the powder was isolated by centrifugation and washed with distilled water (16 mL) in order to remove Gd^{3+} cations potentially adsorbed onto nanoparticules surface.[14] Solution titration demonstrated that 30.3% of the Gd was extracted. Finally, all Gd^{3+} ions were released by washing the solid with a DTPA solution (16 mL) at pH 4. On reuse, we observed a rather constant efficiency with 23.5% of Gd^{3+} complexation in Run 2 indicating no significant organic leaching in our experimental conditions. Taking into account the very small particle size of DTPA-PABA/TiO_2(A) we can not exclude the presence (and loss) of the smallest hybrid particles in solutions after centrifugations.

In conclusion, we have described a simple synthetic methodology for hybrid TiO_2 nano-material which successfully formed ionic recognition devices to enable selective lanthanides separation. They provide a better understanding of the requirements in self-assembled (-organized) material design for further elaboration of functional nano-structured materials.

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11 Synthesis of DTPA-PABA/TiO_2(A): 2.04 mmol (4.64 g) of PABA/TiO_2(A), 20 mL of DMF and 4.12 mmol (0.57 mL) of NEt_3 were mixed, and were added to a mixture of 1.03 mmol (0.37 g) DTPA dianhydride and 10 mL of DMF. After heating at 60 °C during 24 h, centrifugation and ethanol washings, a yellow powder (5.13 g) was obtained after drying at 70 °C during 20 h.

12 Distribution coefficient D_M $(mL\,g^{-1}) = ([M]_i - [M]_f/[M]_f) \times V/m$ where V is the volume (mL) of the extracted solution and m the mass (g) of the material.

13 Selectivity $S_{Gd/La} = D_{Gd}/D_{La}$.

14 200 mg of DTPA-PABA/TiO_2(A) were stirred in 16 mL of gadolinium solution ($[Gd^{3+}] = 4.5 \times 10^{-3}\,mol\,L^{-1}$, pH 7, 20 °C) for 24 h.