Lead and zinc removal from aqueous solutions by aminotriphosphonate-modified converted natural phosphates

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HIGHLIGHTS

- Aminotriphosphonate–apatite nanoparticles were prepared from phosphate rocks.
- Adsorption kinetics and isotherms were studied for aqueous Pb2+ and Zn2+.
- Organics decrease access to apatite surface but provide additional binding sites.

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ABSTRACT

Apatite particles prepared from natural phosphate rock and grafted with nitrilotris(methylene)triphosphonate (NTP) were evaluated for Pb2+ and Zn2+ sorption from aqueous solutions. Sorption capacities as high as 640 mg g⁻¹ and 300 mg g⁻¹ could be obtained for the highest organic content (10 wt.%). Analysis of the sorption isotherms using Langmuir, Freundlich and Dubinin–Kaganer–Radushkevich models revealed that Pb2+ ions have a larger affinity for apatite (sorption energy = 8 kJ mol⁻¹) than for NTP so that organo-modified surfaces led to a heterogeneous adsorption process. In contrast, Zn2+ interacts weakly (sorption energy ≈ 1 kJ mol⁻¹) and similarly with the mineral surface and the organic moieties following a homogenous sorption process. Such an association of organic metal ligands with reactive apatite surfaces within porous materials appears as a promising strategy to obtain efficient adsorbents at low cost and limited environmental impact.

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1. Introduction

Heavy metals are of special environmental concern because they are non-degradable and therefore persistent [1]. They are toxic in both their elemental form and within mineral structures, even at low concentrations [2]. Among available heavy metal remediation methods, chemical precipitation has long been favoured [3]. Although other techniques such as ion exchange [4], membrane systems [5], and electrodeposition [6] have been widely developed over the last few decades, adsorption processes is considered as the most attractive alternative to chemical precipitation [7], not only because it is well-adapted to the treatment of wastewaters containing high concentrations of metals [8] but also because a wide variety of adsorbents such as activated carbon [9], clays [10], silica [11] as well as natural and synthetic apatites [12–16] are available.

Among these adsorbents, natural phosphate rock combines the advantages of very low cost, low environmental impact and great abundance, with well-known affinity of hydroxyl and phosphate groups for metallic cations [17]. However, they exhibit a limited porosity that limits their use as such for metal sorption applications [18,19]. Moreover, apatite surfaces exhibit a positively charged surface in acidic conditions that decreases their affinity for metal cations in polluted waters [20]. To address these points, we recently developed a novel procedure for the preparation of mesoporous organo-apatite materials derived from natural phosphate (modified natural phosphate, MNP), by incorporation of nitrilotris(methylene)triphosphonic acid (NTP) exhibiting amine and phosphonate surface moieties (Fig. 1) [21,22]. The introduction of amine groups was based on previous reports showing that apatite materials grafted with aminosilanes exhibit enhanced retention properties towards Cu2+ and Co2+, due to complexion between –NH₂ and metal ions [23,24]. Indeed, Pb2+ ions represent a specific case when considering apatite-based adsorbents because they are known to interact with apatite surface via dissolution and