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Influence of the phosphonate coupling molecules of TiO₂ hybrid nano-composites on PAH adsorption performances

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The ever-growing worldwide demand of safe water and rapid population growth of improving life standards are facing tough challenges associated to emerging pollutants such as pharmaceuticals and personal care products in the aquatic environment. As a solution, hybrid (organic-inorganic) nanostructured materials combining large surface-to-volume ratio and rational surface functionalization possess a powerful potential to update traditional adsorption treatment process. Our project aims at the development of highly efficient and selective nano-adsorbents that can remove contaminants in trace concentrations in the presence of competing ones. The study is focused on hydrophobic polycyclic aromatic hydrocarbons (PAHs) adsorptions through experimental and modeling pi-pi interaction experiments. What distinguishes this work from others available for water treatment is the adoption of an eco-friendly approach, where the nanomaterials are prepared by soft green chemistry, and the pollutants are removed by physical adsorption that does not generate harmful by-products. A robust sol-gel process was developed for the synthesis of surface-functionalized titania nanocrystallites bearing unsaturated groups starting from molecular heteroleptic single-source precursors. Molecules and nanomaterials were thoroughly characterized by multinuclear liquid and solid-state nuclear magnetic resonance (NMR), infra-red (FT-IR, DRIFT) spectroscopies. Nitrogen adsorption-desorption (BET), thermogravimetric (TG) and elemental analyses demonstrated the reliability and the fine tuning of the surface functionalization in terms of ratio TiO₂:ligand. The as-prepared materials were used as nano-adsorbents to remove mixture of 16 polycyclic aromatic hydrocarbons (PAHs) from aqueous solutions. Adsorption kinetic experiments were carried out for 24 hours in solutions of one PAH [benzo(a)pyrene, 220 ppb] and of a mixture of sixteen ones [220 ppb for each PAH]. Most kinetic data best fitted the pseudo-second order model. However, in PAHs mixture, a competition process took place during the first hours leading to a remarkable high selectivity between light and heavy PAHs. This selectivity could be fine-tuned depending on the nature of the unsaturated group of the phosphonate framework and on the nanomaterial textures.