

Euro Green Chemistry 2019-TiO₂-Based Hybrid Nanocomposites Modified by Phosphonate Molecules as Selective PAH Adsorbents-Nadine Bou Orm- Abu Dhabi University

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Introduction:

Polycyclic aromatic hydrocarbons are a nonpolar neutral chemical compounds ensuing from the condensation of numerous benzene rings ranging from two to three, to four and five and up to seven (heavy molecular weight PAHs, HMW PAHs). The existence of PAHs in surface water comes normally from the deposition of airborne particles formed via incomplete oil combustion, from the leaching releases from coal storage areas, from products of wood treatment plants and other industries and from the use of composts and fertilizers. The number of PAHs recognized is in the order of 130, including PAHs containing sulfur, nitrogen or oxygen atoms. The U.S. Environmental Protection Agency has compiled a list with 16 PAHs pretense major environmental problems due to their determination, their poisonous causes on human health and are associated with a wide variety of effects: degradation of the immune system, causes on the reproduction and development as endocrine disrupter and carcinogenic properties. PAHs are constant pollutants in the environment since they are frequently resistant to biodegradation. Their deletion using conventional physical and chemical technologies available for remediation of wastewater pollutants such as oxidation with ozone/hydrogen peroxide, photocatalytic degradation. Hybrid (organic-inorganic) nanostructured materials of class II combine large surface-to-volume ratio and convenient surface functionalization can provide an influential potential to update traditional adsorption treatment process. One of the targets of nanotechnology for the pollutant elimination from wastewater is to develop proficient and selective nanosorbents that can eliminate low concentration contaminants in the presence of competing ones. A current study on the deletion selectivity of PAHs from a wastewater treatment plant (WWTP) located in an urban area in China shows that LMW PAHs such as naphthalene can be detached at a level of 80%, while HMW ones became even additional

Concentrated with treatment in both the dissolve phase and the without water sludge. Given the nature of PAHs, usage of supported aromatic derivatives to form "stacking" charge transfer complexes has already been report since these interactions are successful in an aqueous medium, non-degrading and reversible. Preceding studies have reported the removal of PAHs from aqueous solutions using a huge variety of supports such as clay, resins, activated carbon, periodic modified mesoporous organosilane (POMs), metalorganic frameworks (MOFs). In this study, we noticed the synthesis, characterization and properties of novel hybrid (in this case

organic-inorganic) nanotitania supports functionalized with a series of a wide variety of organophosphorus molecules (R-OPO₂H₂) holding diverse unsaturated groups.

The performances of such stacking complication sites will be compared in terms of selectivity, capacity and kinetic of adsorption in an aqueous mixture of 16 PAH molecules. There is an plentiful literature Reporting the use of organophosphorus molecules for surface alteration of metal oxides (MO_x) because they allow to manage mono-layer functionalization of metal oxide surfaces resulting from the noncompetition between hetero and homocondensation but also but also because this ionocovalent anchoring is enormously constant through multiple M-O-P bonds. In exactly, the Titanium oxide will be our nano-support of choice, because of the easy "soft chemistry" preparation routes of crystallized nanoparticles of titanium oxide extensively studied in the literature and in our laboratory.

Product Characterizations:

¹H liquid and ¹³C solid state MAS NMR spectra were noticed on an AM-250 spectrometer Bruker. ³¹P solid state MAS NMR were recorded on a Bruker DSX400 spectrometer spectra with a 4 mm probe and rotation various speeds of 5 to 10 Kz. Analytical data were obtained from the Institut des Sciences Analytique by ICP. FT-IR spectra were recorded as Nujol suspension (for air sensitive derivatives) or as KBr pellets (for hydrolyzed powders) on a Bruker Vector 22 FT-IR spectrometer at room temperature and registered from 4000 to 400 cm. DRIFT experiments were done out on a Nicolet 6700 FTIR spectrophotometer (Thermo Fischer, Waltham, MA, USA) equipped with a MCT detector. The recording mode was dispersing reflectance and the optical unit, Praying Mantis (Harrick). TGA/TDA data were Collected with a model 92 system in air with a thermal ramp of 10 C min⁻¹. Powder X-ray diffraction results were obtain with a D5005 diffractometer (Siemens, Munich, Germany) by using Cu-K radiation at the scan rate of 0.022q s⁻¹ with step times of 1 and 16 s for routine or for expanded region spectra, correspondingly. BET experiments were done with an ASAP 2010 system after the samples were desorbed at 100°C for 6 h.

Conclusions:

In conclusion, a robust sol-gel process, starting from new heteroleptic titane phosphonate-alkoxides precursors, was developed in order to tune delicately the surface functionalization of nanocrystallites of titania with phosphonate ligand (PA). Series of hybrid nanomaterials department various amount and nature of unsaturated groups (vinyl, phenyl,

naphtyl) were elaborate and thoroughly characterized. Their performance as nano-adsorbents through stacking Demonstrated remarkable removal efficiencies of 100% over a mixture of 16 PAHs. The adsorption kinetics consequences have shown that systems with a ratio $TiO_2/PA = 100$ reached the equilibrium after 24 h and high adsorption capacities of around 1 mg/g per PAH were found. The selectivity of PAH sorption procedure depended on the nature of the unsaturated-based phosphonate ligands, on the self-agglomeration of the surface-functionalized nano-particles and on the textures of the nanomaterials. Hence, mesoporous vinyl-based titania nanomaterials have confirmed high affinity for light PAHs while macro-, mesoporous phenyl-based one had high affinity for heavy PAHs. Such findings would be very supportive in identifying factors affecting selective PAHs remediation from aqueous media in the presence of challenging species (PCB, diclofenac) or PAH mixtures.