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EXAFS study of the phosphodiester bond cleavage by Mo-containing polyoxometallates

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The early transition metals (V, Nb, Ta, Mo, W) in their high oxidation states are able to form metal-oxygen clusters, commonly referred to as polyoxometallates (POMs) [1]. The diverse structures and compositions of polyoxometallates offer a wide versatility in terms of shape, polarity, redox potentials, surface charge distribution and acidity, and allow for numerous potential applications of POMs [2-3]. The first reports describing the antitumoral activity of POMs appeared about ten years ago, and they have revealed that the antitumoral activity of $[Mo_7O_{24}]^{6-}$ is even better than that of commercial drugs [4]. We have investigated the potential towards phosphodiester bond cleavage of the $[Mo_7O_{24}]^{6-}$ cluster. The reaction of $[Mo_7O_{24}]^{6-}$ with dinitrophenyl phosphate (DNPP) and nitrophenyl phosphate (NPP) has been monitored by UV-vis spectroscopy and NMR. DNPP and NPP serve as models for the phosphate bonds in DNA. Upon monitoring a mixture of NPP and $[Mo_7O_{24}]^{6-}$ at a temperature of 50°C, by recording the Mo K-edge EXAFS spectra as a function of time, a gradual conversion of the $[Mo_7O_{24}]^{6-}$ moiety into a $[P_2Mo_5O_{24}]^{4-}$ cluster is observed. This was evidenced by the gradual disappearance of the Mo-Mo distance at 3.2 Å, whereas the Mo shell at 3.4 Å remained unaltered. These results provide new insights in the mechanism of this biologically relevant reaction.

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X-ray diffraction techniques applied to prospection of fluvial aggregates

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Jarama river deposits are the main source of fluvial aggregates in the Madrid province. The lower course concentrates the greater number of pits, production volume and aggregate reserves of Spain. Open pits beneficiate the lower terrace deposits, where the conglomerate thickness can surpass 40 m. The sands and gravels are usually interbedded with silts and clays of the Quaternary palaeo-floodplain, with a varying thickness of these argillaceous sediments between 1 and 7 m. On the other hand, Miocene age silts and clays are also recognized as terrace substrate. A clear distinction between both silty clay sediments is decisive, because it allows to the producers of aggregates to define whether there are more useful conglomerates under this units (Quaternary clays) or no more useful fluvial deposits underneath (Miocene clays). After analysing the global mineralogy, clay and silt mineralogy, grain size distribution, plasticity, texture, colour, organic matter and carbonate contain, a clear distinction between both types of sediments is only possible using a detailed X-ray diffraction study of the clay minerals. Samples from the Quaternary floodplain are rich in smectite (>60%), while samples from the Miocene substrate are illite-kaolinite clays. Thus, the X-ray diffraction analyses of the clay fraction allows a save of time and resources to the mining companies located in the lower course Jarama river, because it can be used as a powerful tool in the aggregates prospection.