

Phosphate adsorption on thin films made of transition metal oxides, as measured by Electrochemical Impedance Spectroscopy

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Phosphorus is both an essential nutrient and a major pollutant in natural and engineered waters. Real-time phosphorus measurements, however, are far from being commercially available. Phosphate species are amongst the most bioavailable forms of phosphorus; hence, developing sensors for their detection would have a tremendous impact in monitoring water quality.

It is known that phosphate readily adsorbs to transition metal oxides (or to their hydrated forms). In order to make this adsorption detectable by electrochemical means, the oxide layer must be of high surface area as well as very thin, due to its inherent low electric conductivity. In this work, films made of these materials using sol-gel techniques were deposited on a metallic substrate. The resulting electrodes were placed in phosphate-containing solutions in concentrations ranging from  $10^{-9}$  to  $10^{-4}$  M, in order to determine the ability of these electrodes to detect phosphate adsorption. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) analyses were performed for this purpose.

The results showed that EIS may be a suitable tool to further develop a phosphate sensor, using electrodes made of titanium or iron (hydr)oxides. As pH is critical on determining the speciation of dissolved and adsorbed phosphates, we evaluated its effects on the EIS response over a circumneutral range. Equivalent circuit models were postulated to interpret the adsorption processes, whereas statistical analyses using partial least squares were performed to fit the impedance spectra as ‘fingerprints’ of phosphate concentrations as well as pH levels. Response in the range of 100 to 0.05 Hz was the most sensitive to phosphate. In order to evaluate the practicality of these sensors, current experiments involve their immersion in wastewater lab-sized reactors.