Electrochemical behavior of methylene blue at self-doped TiO_2 nanotube electrode for environmental sensing application

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Voltammetric detection of organic pollutants requires sensitive, stable and low-cost electrodes. Self-doped TiO_2 nanotubes (SD-TiO_2NT) offer an alternative by combining high surface area with enhanced conductivity via electrochemical self-doping (induced by negative potential) [1]. This study investigated the interacting mechanisms between methylene blue (MB), a model textile pollutant, and SD-TiO_2NT for environmental sensing applications. Titanium sheets were anodised in (0.25 wt. % NaF and 10 vol. % water) glycerol solution at 20 V for 48 h. The material was calcined to convert the amorphous phase into crystalline anatase. The SD-TiO_2NT electrode (geometric area: 0.071 cm^2) was prepared by applying -1.5 V for 15 min in phosphate buffer solution (PBS pH 7.4), using a conventional three-electrode system. Scanning Electron Microscopy confirmed TiO_2 nanotubes (19-44 nm in diameter), and X-ray Diffraction identified the anatase phase. Cyclic voltammograms using negatively charged electrochemical probes revealed that, after self-doping, the surface was negatively charged, probably due to the phosphate adsorption from the PBS electrolyte. Furthermore, the voltammetric experiments showed a sharp reduction peak at pH 2.00, confirming strong electrostatic adsorption of the protonated MB form onto the negatively charged SD-TiO_2NT surface. MB redox kinetics exhibited clear dependence on scan rate (0.010 – 1.0 V s^{-1}). At scan rate ≤ 0.10 V s^{-1}, the slope of log I_{pc} *vs* log ν plots was 0.97, characteristic of an adsorptive process. A linear fit of E_{pc} *vs* log ν showed a slope of 31 mV dec^{-1}, confirming first-order chemical kinetics [2]. Tafel analysis (α = 1.5) indicated that the second electron transfer is rate-limiting. The Differential Pulse (MB) analytical curve performed at 0.1 M PBS presented a linear interval of (15 – 60 μM) with a detection limit of 0.2 μM.

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References:

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