

Phenol degradation in heterogeneous system generating singlet oxygen employing light activated electropolymerized phenothiazines



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ABSTRACT

Five selected amine-derivatives of phenothiazine were electropolymerized on an ITO/glass substrate and then used in the daylight-activated process to produce in situ singlet oxygen which degrades phenol in a solution. The phenothiazines were immobilized in a simple electrochemical procedure in an acidic solution which led to the formation of an ultrathin transparent polymeric film. All films obtained on the ITO substrate including azure A (AA), azure C (AC), methylene blue (MB), toluidine blue (TBO), and thionine (Th) had a comparable surface coverage at the level of picomoles/cm². The activity of these materials was then compared and presented in terms of an efficiency of the phenol degradation process in an aqueous solution by photogenerated singlet oxygen. That efficiency was determined by the UV-vis spectroscopy employing a phenol/4-aminoantipyrine complex. All the phenothiazine ultrathin polymeric films were capable of generating the singlet oxygen in the aqueous solution under daylight activation, which was used in the consecutive process of phenol degradation. The highest efficiency at a level of 51.4% and 45.4% was found for the AC/ITO and MB/ITO layers, respectively.

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1. Introduction

Photogeneration of singlet oxygen from atmospheric oxygen in a presence of specific compounds, organic or inorganic, is part of the strategy of green technology, which employs daylight energy to make many industrial and life processes more efficient. Singlet oxygen is a form of molecular oxygen with one of π -antibonding orbitals in its electronic structure occupied by two electrons with antiparallel spins [1], which has exceptionally high oxidation potential. However, due to the millisecond (or shorter) level of its lifetime, it has to be generated continuously in the environment of its use. The in situ photochemical generation of this active molecule has already found its applications in fine chemical synthesis [2], wastewater treatment [3], and medicine [4].

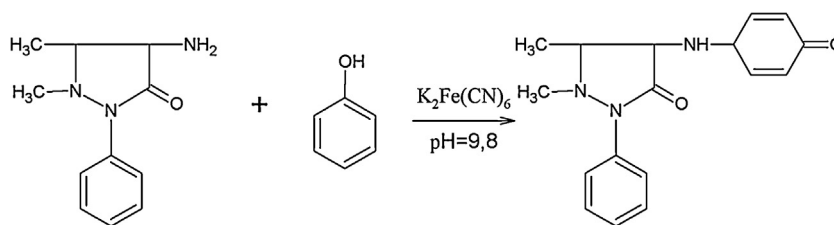
A ubiquitous presence of phenol and its derivatives in natural water systems [5,6] originates from various industrial processes including paper and plastic production [7] or bio- and pharmaceutical technologies [8,9]. Various treatment methods have been previously applied for the degradation of phenol in wastewaters including chlorination, ozonation, adsorption, and photocatalysis [3,10–12]. Still, high attention is paid to developing effective removal methods of these persistent and toxic organic

pollutants, as well as other bioorganic contaminants from wastewater leakage, since the currently applied conventional water treatment technologies are not fully effective for the removal of many hardly biodegradable chemicals [13–15]. Among possible strategies, a novel economically interesting photooxidation technique employing singlet oxygen (¹O₂) as a primary oxidant appears to be a promising alternative. The main advantage of such a process is a widespread accessibility of the ¹O₂ form and the employment of visible light. Additionally, a variety of pollutants may be subjected to such an intensive oxidation in which different biodegradable photoproducts are formed in both gaseous and liquid phases [16–19]. It has been found previously that frequently present organic pollutants and microbial disinfectants can be effectively decomposed by applying the ¹O₂-strategy [20–22]. When considering phenols, their direct photolysis in natural water systems and wastewater can occur together with their oxidation by singlet oxygen [23].

An ideal photo-active material should combine a high efficiency of solar radiation absorption together with effective energy conversion, a high photostability and an ease of operation [24]. It has been already demonstrated that the phenothiazine derivatives, when immobilized, either by suspension/adsorption in cellulose acetate, aluminium oxide or silica matrix [25–27], or by covalent bonding with a polymer matrix like poly(ethylene glycol), poly(vinyl chloride), poly(dimethylsiloxane) (PDMS) [28–30], retain their ability to generate singlet oxygen under illumination. Also, phenothiazine

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Scheme 1. The general scheme of phenol reaction with 4-aminoantipyrene.

derivatives electropolymerized on solid conductive surfaces are able to generate this reactive oxygen species, as shown in our earlier work [31].

In this study, we demonstrate an ultrathin polymeric layer of photosensitizers bound to a solid surface by means of electrochemical polymerization, which can be applied for the oxidation of phenol in aqueous systems. Here, phenol was used as a model compound for singlet oxygen oxidations occurring in the aqueous environment, mainly due to its widespread presence in wastewater. Among various photoactive compounds, five selected phenothiazines were employed as effective $^1\text{O}_2$ generating agents. These compounds were immobilized in a simple electrochemical procedure onto ITO/glass transparent substrate, which was chosen for the most effective light utilization. The effectiveness of phenol degradation using phenothiazine-based materials activated by daylight was monitored using UV–vis spectroscopy, employing the 4-aminoantipyrene batchwise method.

2. Experimental

2.1. Chemicals

Five amine-derivatives of phenothiazine including azure A (AA), azure C (AC), methylene blue (MB), toluidine blue (TBO), and thionine (Th) were selected as monomers for the electropolymerization.

AA (purity >90%) and TBO (purity >88%) were obtained from Sigma Aldrich; AC (purity >90%) was purchased from Fluka; MB (purity >92%), Th (purity >90%) and phenol were acquired from Across Organics, while 4-aminoantipyrene and potassium hexacyanoferrate(III) (both of an analytical grade) were obtained from POCH.

The Britton–Robinson (BR) buffer solution of pH 4.45 was used as the electrolyte solution in the process of the ITO-substrate modification. Ammonia buffer solution at pH 9.8, employed in the phenol quantitative analysis, was prepared with the analytical grade ammonium chloride and ammonia solution (both purchased from POCH).

2.2. Apparatus

Electrochemical measurements were carried out using CHI 660C electrochemical workstation (CH Instruments Inc.) with a conventional three-electrode system. The ITO/glass electrode (DELTA Technologies Ltd., the exposed surface area of 1.4 cm^2) was employed as a working electrode, Ag/AgCl (saturated KCl) was a reference electrode, and a glassy carbon (GC) rod was used as a counter electrode; all the electrodes were mounted in a Teflon holder.

The process of phenol photodegradation was carried out in a 50 ml glass beaker with the six modified ITO plates with a total active area equal to 8.4 cm^2 . These plates were simply attached around the beaker side walls by means of metal clips. The vessel containing the aqueous phenol solution was exposed to the daylight while stirring using a magnetic stirrer. The effectiveness of phenol degradation was determined by monitoring the decrease in the absorption of phenol complex (Scheme 1) using

Hewlett Packard 8452A UVVis spectrometer. The solution sample was placed in the standard $10\text{ mm} \times 2\text{ mm}$ quartz cuvette (Hellma Analytics).

2.3. Procedures

2.3.1. Electropolymerization of phenothiazines

Each phenothiazine derivative was polymerized electrochemically by means of cyclic voltammetry (CV), typically within the potential range of -0.3 V to $+1.2\text{ V}$, at the scan rate of 0.1 V/s . The process was carried out in 1 mM buffered phenothiazine solutions at pH 4.45. After the electropolymerization, a conditioning step i.e. holding the working electrode at a constant potential of 0.6 V for 2 min was employed, leading to a complete oxidation of the immobilized phenothiazine polymer. The modified electrodes were then tested in the pure electrolyte solution within the potential range of -0.3 V to $+0.7\text{ V}$.

2.3.2. The phenol photodegradation

The progress of phenol photodegradation was monitored by an indirect method based on its reaction with 4-aminoantipyrene in which a coloured complex is formed according to Scheme 1 [32].

The reaction vessel (as described above) was filled with 30 ml of 0.85 mM aqueous phenol solution and then exposed to daylight. A 0.5 ml sample was taken from the reacting system every 120 s. The sample was then diluted to 1 ml and 0.02 ml of ammonia buffer; 0.02 ml of 2% solution of 4-aminoantipyrene and 0.02 ml of 2% solution of potassium hexacyanoferrate(III) were added. The sample was mixed and left closed for 15 min prior to absorbance measurements. Blank ITO plates were used in the control experiment. Additionally, the phenol-complex calibration curve was established, which was then applied in the calculations of the actual phenol concentration.

3. Results and discussion

3.1. Materials preparation

The phenothiazine derivatives were immobilized on the ITO/glass electrode surface by means of electrochemical polymerization. That process has been widely discussed in the literature taking into account the effects of both the applied potential range [33] and pH of the buffer solution [34,35]. The typical course of the electropolymerization on the ITO electrode, recorded for the 1 mM aqueous solution of Th at an acidic pH, is shown in Fig. 1A. The redox pair observed in the potential range (-0.10 to 0.0 V) arises from the reversible oxidation–reduction process of phenothiazine monomer, while the irreversible anodic signal at 1.1 V arises from its irreversible oxidation assigned to the generation of radical forms of the molecule. These radical species are assumed to initiate the electropolymerization process. In the successive scans, both anodic and cathodic currents are gradually growing at around 0.1 V indicating a formation of the electroactive polymer on the electrode surface.

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