



# Phosphomolybdic acid immobilized on graphite as an environmental photoelectrocatalyst



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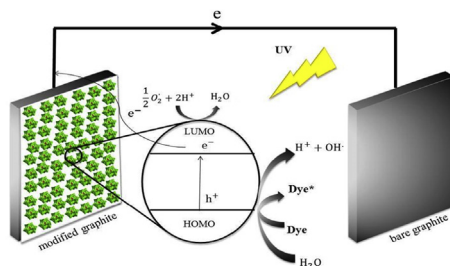
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## HIGHLIGHTS

- A PMA/Graphite surface was prepared on the graphite plate by phosphomolybdic acid.
- The PMA nano particles were well stabilized on the graphite surface.
- Applied potential was improved the photocatalytic activity of PMA.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A new phosphomolybdic acid (PMA)/Graphite surface was prepared based on electrostatic interactions between phosphomolybdic acid and graphite surface. The PMA/Graphite was characterized by cyclic voltammetry (CV) analysis and scanning electron microscope (SEM). SEM images showed that the phosphomolybdic acid particles were well stabilized on the graphite surface and they were evidenced the size of particles (approximately 10 nm). The CV results not only showed that the modified surface has good electrochemical activity toward the removal of the dyestuff, but also exhibits long term stability. The PMA/Graphite was used as a photoanode for decolorization of Reactive Yellow 39 by photoelectrocatalytic system under UV irradiation. The effects of parameters such as the amount of phosphomolybdic acid used in preparation of PMA/Graphite surface, applied potential on anode electrode and solution pH were studied by response surface methodology. The optimum conditions were obtained as follows: dye solution pH 3, 1.5 g of immobilized PMA on graphite surface and applied potential on anode electrode 1 V. Under optimum conditions after 90 min of reaction time, the decolorization efficiency was 95%.

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## 1. Introduction

By the development of textile industry, pollution of water caused by organic dyes has been raised environmental threats

dramatically (Mahdizadeh et al., 2014; Sheydaei et al., 2014). Photocatalysis has been extensively investigated for the environmental pollutants degradation (Ayoubi-Feiz et al., 2015). In recent years, polyoxometalates (POMs) have been used as efficient photocatalysts to remove organic dyes from wastewater (Dolbecq et al., 2012; Ghalebi et al., 2016). POMs have photocatalytic characteristics similar to semiconductors (Li et al., 2010; Xu et al., 2012; You et al., 2012). The photocatalytic performance of POM is based on

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electron transfer between HOMO and LUMO orbitals and creating hole in HOMO orbital. The hole has strong oxidative property which is basis of POM photocatalytic activity (Zhang et al., 2012; Yuan et al., 2014). Photocatalyst disfunction occurs if the excited electron returns to the hole. Every attempt to retard electron and hole recombination will improve the photocatalytic activity (Wang et al., 2013b, 2014). By applying a potential, electrons and holes are separated from each other and their recombination will be minimized (Wang et al., 2013a). Thus to compare with photocatalysis process, the photoelectrocatalytic process is more efficient in various catalytic processes like pollutants removal. For this reason, a comparative table (Table SM-1) has been provided that verify this description.

POMs that were compared with other photocatalytic system have some advantages that listed below:

- 1) POM have strong light absorption in UV/visible spectral range for the present of O→M (LMCT) absorption bands (Streb, 2012).
- 2) Compared with semiconductors and metal oxides, POMs exhibit fast reversible and multi-electron redox transformations due to the large number of metal centers exist in the structure of POMs (Song and Tsunashim, 2012).
- 3) Using POMs as photocatalyst is friendly to the environment by using the atmospheric O<sub>2</sub> as oxidant.

Among the different types of POMs used for surface modification, keggin-type POMs are the most extensive investigated ones (Cavaleiro et al., 2011; Derouich et al., 2014). However, POMs show high solubility in water that makes them difficult in recovering. Therefore it is desirable to develop a heterogeneous system to degrade organic dyes that for this purpose the silane agent can be added to a coating formulation and improved the bonding properties (Bigui et al., 2013; Thakur et al., 2014). Silane has both organic and inorganic properties and forms stable covalent bonds across the interface (Grinval et al., 2011; Maggini et al., 2013; Villanneau et al., 2013; Grinval et al., 2014; Kim et al., 2015). In this study we make a modified surface with phosphomolybdic acid (PMA, H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>) on the graphite plate and then the modified graphite surface are applied as photoanode in the photoelectrocatalytic system for decolorization of the dyestuff solution under UV light irradiation.

## 2. Experimental

### 2.1. Materials

The dye C.I Reactive Yellow 39 was provided by Ciba-GeigyCo (Switzerland). Its composition, structure and other characteristics are reported in Table SM-2. Phosphomolybdic acid (PMA, H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>) was obtained from Merck (Germany). All other chemical compounds were analytical grade from Merck and they were used without further purification. All dyestuff aqueous solutions were prepared with distilled water.

### 2.2. Apparatus

An autolab electrochemical analyzer PGstate 30 model (ECO chemie, Utrecht, the Netherlands) controlled by microcomputer with GPEs 4.9 software was used for voltammetric measurement. A three-electrode cell was applied, including graphite electrode modified with PMA as working electrode, an Ag/AgCl (saturated KCl) as reference electrode and another graphite electrode as counter electrode. A Eutech pH510 pH meter was used for pH measurements. Scanning electron micrographs (SEM) of the samples were taken using a MIRA FEG-SEM, Tescan microscope with

attached camera. To increase the resolution, samples were coated with gold vapor. SEM was operated at an accelerating voltage of 10.0 KV. Absorbance of each solution was determined spectrophotometrically by a double beam Perkin Elmer spectrophotometer (model 550 SE) at 419 nm.

### 2.3. Silane treatment of the graphite surface

Graphite surfaces were activated with NaOH 0.1 M (forming graphite-OH functions) for 10 min in an ultrasonic bath, followed by rinsing. External water was carefully removed by washing with dried *n*-hexane and then dried for 3 min at ambient temperature. The graphite plate was dipped in 1 vol% toluene solution of APS ((3-Aminopropyl)triethoxysilane) and then heated at 60 °C during 1 h. The silane-coated graphite plate was washed with dry *n*-hexane for 10 min in an ultrasonic bath and then dried at ambient temperature. Amine groups, separated from the silicon atoms by a propyl unit, were linked to the graphite surface via the reaction of OH groups on activated graphite surface with trimethoxysilane compound (Fig. 1). The amine function can be used to attach other molecular entities (Dong et al., 2014).

### 2.4. Preparation of PMA/Graphite surface

A solution of PMA (H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> = 1.5 g) in 30 mL distilled water was made and then the modified graphite plate was added to this solution and stirred for 12 h. Finally, the obtained product was separated and washed several times with distilled water and then dried at room temperature. The process of the preparation of the surface is sketched in Fig. 1. When graphite plate was added to the solution of PMA, amine groups were protonated and positively charged and then, electrostatically bonded to the produced heteropoly anions (Masteri-Farahani et al., 2012). The obtained product was insoluble in water. The excess of heteropoly acid was removed by washing the graphite plate with water. The attached heteropoly anions are stable on the surface of modified graphite plate and they are not leached into aqueous solution.

### 2.5. Experimental set-up

The experimental set-up was consisted of a round Pyrex reactor with the capacity of 150 mL, a magnetic stirrer, a potentiostat (Micro, PW-4053R, Iran), a UV lamp (UV-C, Philips, 30 W, Holland) on the top of the reactor. A modified graphite electrode as working electrode (4 cm × 5 cm × 0.5 cm), a graphite electrode without modification (4 cm × 5 cm × 0.5 cm) as counter electrode and a saturated calomel electrode (SCE) (+0.24 V vs. standard hydrogen electrode) as reference electrode. All three electrodes were put in the reactor containing 110 mL solution. The counter electrode was held horizontally parallel to the working electrode by a 1 cm gap. The solution pH was adjusted by H<sub>2</sub>SO<sub>4</sub> (1 M and 0.1 M) or NaOH (1 M and 0.1 M) solutions. The distance between the UV lamp and the surface of anode electrode was 10 cm.

The Reactive Yellow 39 solution coloration was monitored using UV/Vis spectrophotometer (Perkin-Elmer, 550SE, Germany) at 419 nm. The decolorization efficiency (%) was defined using the following equation (Eq. (1)):

$$\text{Decolorization efficiency}(\%) = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

where A<sub>0</sub> and A<sub>t</sub> are the initial solution absorbance and its absorbance at time t respectively.

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