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Photoelectrocatalytic and Photocatalytic Oxidation of Azodye at High Oxygen Pressure

Abdulgalim B. Isaev, Naida K. Tajibova,
Farid F. Orudjev, Patimat M. Salikhova,
Ruslan V. Ilkanaev and Marat N. Medjidov*
Dagestan State University,
43a M. Gadjieva Str., Makhachkala, 367001 Russia

Influence of dissolved oxygen at different pressure to photocatalytic and photoelectrocatalytic azodye C.I. direct black 22 (DB) oxidation is investigated. It is shown, that at the presence of dissolved oxygen photocatalytic and photoelectrocatalytic DB oxidation rate on TiO_2 increases. The azodye decolouration higher than 98 % by photoelectrocatalytic oxidation at oxygen pressure was 0.42 MPa.

Keywords: photocatalytic, photoelectrocatalytic, azodye, oxygen pressure, oxidation, C.I. direct black 22.

Introduction

The textile activities have a high potential environmental impact, principally due to the release of large volumes of wastewaters that contain high organic charge and strong coloration. Many dyes used in textile processes show toxicity to the aquatic biota (or can be biologically transformed to toxic species) and could cause interference in natural photosynthetic processes.

The problem of colour in textile dyehouse effluent and the possible problems associated with the discharge of dyes and dye degradation products are of concern. Traditional methods for dealing with this kind of wastewater are usually the biological, physical and chemical techniques as well as the various combinations of theses. It has been widely reported that many dye chemicals are difficult to degrade using conventional biological treatment processes. It is more important to reuse this kind of wastewater than to discharge it after treatment in that the costs of chemicals, energy and water continually increase.

Heterogeneous photocatalytic processes, especially with use of titanium dioxide, have been extensively applied in the treatment of wastewater [1]. Numerous studies have shown that the application of this method can lead to complete color removal, detoxification and mineralization of

* Corresponding author E-mail address: abdul-77@yandex.ru

textile dyes wastewater [2-5]. In the last decade, advanced oxidation processes (AOPs) were used widely in the treatment of wastewater since they were able to handle the problem of organic pollutants destruction in aqueous solution [6, 7]. Among AOPs, there was a great interest in the development of photocatalytic and photoelectrochemical methods for degrade pollutants [8-10]. Several pollutants, such as azo dyes [11, 12], have been degraded by advanced oxidative processes that produce hydroxyl radicals as the primary oxidant. Hydroxyl radicals are very efficient oxidizers; the oxidation potential of OH· is as high as 2.80V. Therefore, photoelectrocatalytic degradation has been widely established as an alternative electrochemical process for environmental remediation [13, 14]. The use of UV-light and semiconductor photocatalysts such as TiO_2 immobilized films [15, 16] can degrade and even mineralize these dyes. In this work, photocatalytic and photoelectrocatalytic oxidation of azodye C.I. Direct Black 22 (DB) in 0,1M Na_2SO_4 solution at high oxygen pressure are described.

Experimental

Photocatalytic and photoelectrocatalytic oxidation of azodye was carried out in a avtoclave-electrolyser (Fig. 1) in which there is a teflon cylindrical vessel cell with a quartz glass window and volume 250 ml ahd to electrodes (Pt – cathode, Ti/TiO2 – semiconductor anode) lowered in a solution. The autoclave is equipped with gates for input and output of gas, the manometer for measuring of pressure and lead wires for current supply [17, 18].

Ti sheet were first cleaned in alcohol and acetone solutions, respectively, and then mechanically polished with different abrasive papers followed by washing with distilled water. The cleaned Ti sheet was submerged in the mixed solution (HF/HNO_3 is 1:4 in volume) for 10 min to polish its surface chemically. The Ti/TiO_2 prepared in a oxygen low-pressure system within 0.74 Pa and current 160 mA technique at the temperatures 600-660 °C. Cooling of a Ti sheet up to a room temperature was made
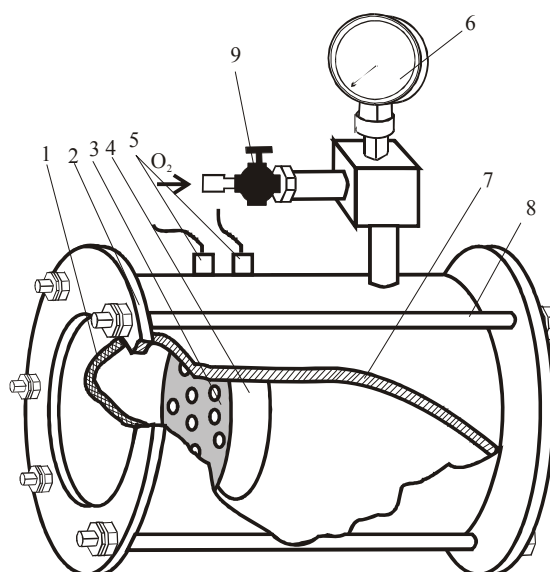

Fig.1 Schematic representation of the autoclave-electrolyser: 1 – quartz glass window; 2 – washer; 3 – Ti/TiO_2 anode; 4 – Pt cathode; 5 – lead wires; 6 – manometer; 7 – teflon case; 8 – bolts; 9 – gate

in vacuum ~10^{-3} Pa. The low pressure system for preparation of metal oxide thin films are described [19].

For the determination of concentration of dye Spekord UV VIS spectrophotometer was used. Aliquot of the reaction mixture was withdrawn and concentration of azo dye diluted from with a distillation water so that concentration made 20 mg·l^{-1} in recalculation on initial compounds.

Results and discussion

In a photocatalytic process, oxygen is necessary to form superoxide radical anions that will further generate other active radicals to promote the degradation reaction [20].

Furthermore, the distribution of the intermediates is different in the presence and absence of oxygen [21]. Although the use of anodic bias obviates the need of oxygen as an electron acceptor in photoelectrochemical catalysis, the presence of molecular oxygen affects both the degradation rate and the degradation pathways of organic pollutants [22]. As stated above, the compressed oxygen was sparged into the reactor from the gate. Thus, the photocatalytic and photoelectrocatalytic oxidation of C.I. direct black 22 was conducted at different oxygen pressure.

Obviously, the oxygen have an important role in the photocatalytic process [23]. When oxygen was submited at pressure 0.18 MPa, the reaction rate was relatively slow.

However, the reaction rate increased significantly with the increase the oxygen pressure. Fig. 2 presents the azodye removal with different oxygen pressure under UV-light illumination.

From the Figure 2, we can see that, when the oxygen pressure to increase from 0.32 to 0.42 MPa, the photocatalytic reaction rate changed slightly. This is because further increasing the pressure the
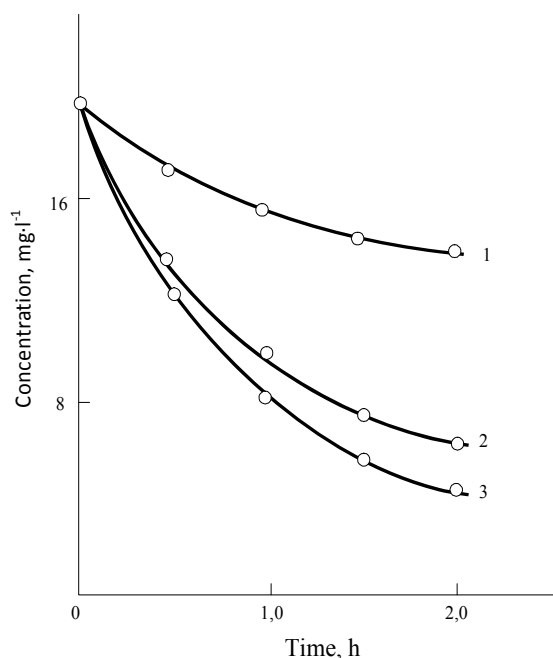

Fig. 2. DB removal with different oxygen pressure at photocatalytic oxidation under UV-light illumination: 1 – 0.18 MPa; 2 – 0.32 MPa; 3 – 0.42 MPa
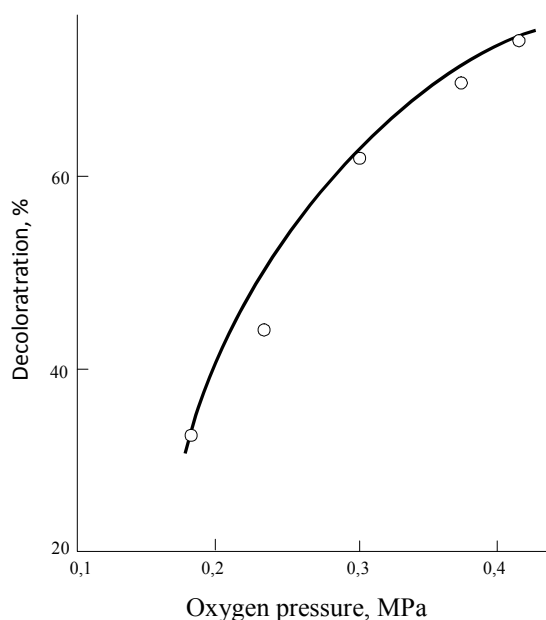
Fig. 3. Effect of oxygen pressure on the decoloration of azodye solution at photocatalytic oxidation under UV-light illumination. $[DB]_0$=20 mg·l^{-1}, t = 2 h, V=250 ml

dissolving oxygen will reach an equilibrium, resulting in a slight change of reaction rate. The effect of oxygen pressure on the decoloration of azodye solution at photocatalytic oxidation are shown in Fig. 3.

It can be seen that the degree of DB degradation varied with the oxygen pressure. In the photocatalytic oxidation reaction, the efficiency of DB degradation increased with the increase of oxygen pressure significantly, since the oxygen served as an electron acceptor in photocatalysis with generation active particles. Above oxygen pressure 0.4 MPa, the degree of DB degradation only further increased slightly.

The DB degradation in the photoelectrocatalytic reaction was also investigated using TiO_2/Ti electrode. In the photoelectrocatalytic reaction, the TiO_2/Ti electrode was used as the anode and the Pt electrode was used as the cathode. Aqueous DB solution was prepared with an initial concentration of 20 mg·l^{-1} and 0.1 M Na_2SO_4.

The photoelectrolysis reaction tests were carried out for DB degradation when oxygen pressure was 0.1 MPa and 0.42 MPa. The experimental results are presented in Fig. 4 as curves "1" and "2", respectively. It can be seen that the overall removals of DB after 30 min at oxygen pressure 0.1 MPa were 85 % and 98 % when oxygen pressure 0.42 MPa. These experiments demonstrated the significant enhancement of DB photoelectrocatalytic degradation under UV illumination.

The increases removal of DB at photoelectrocatalytic process is due to dissolved oxygen reduction up to hydrogen peroxide or active particles on the Pt-cathod and oxygen reduction could be utilized to exercise indirect oxidation and to improve photoelectrocatalytic efficiency.

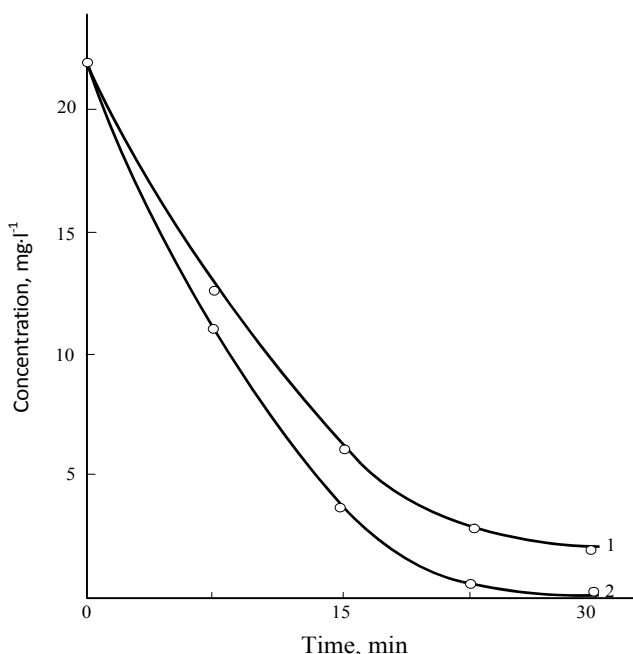Dissolved oxygen can be reduction with the formation of superoxide, hydroperoxide radicals and hydrogen peroxide:
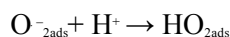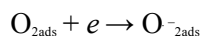
Fig. 4. DB removal with different oxygen pressure at photoelectrocatalytic oxidation under UV-light illumination:
1 – 0.10 MPa; 2 – 0.40 MPa

$$O_{2ads} + e \rightarrow O^-_{2ads}$$

$$O^-_{2ads} + H^+ \rightarrow HO_{2ads}$$

$$O^-_{2ads} + e + 2H^+ \rightarrow H_2O_{2ads}$$

The concentration of hydrogen peroxide or active particles increased due to the cathodic reduction of dissolved oxygen at 0.42 MPa and these active particles were consumed in the oxidative degradation of azodye in the volume of solutions. The peroxide hydrogen existing in solution is consumed for oxidation of azodye.

The reaction mechanism of the photocatalytic and photoelectrocatalytic degradation of organic pollutants was discussed in literatures [24-26], and the degradation mechanism is believed to involve many oxidation ways, such as anodic oxidation, oxidation of electrogenerated H_2O_2, oxidation of photogenerated hole and $OH^.$, and the photoelectrocatalytic synergetic effect, etc.

The UV-visible spectra of the initial, photocatalytic and photoelectrocatalytic treatment of DB solution are presented in Fig. 5. Two absorbance peaks were observed during the scanning of DB solution at 540 and 680 nm which was due to green and blue color of the chromophore. At photocatalytic treatment of DB solution with oxygen pressure of 0.42 MPa in the UV region at 280 nm appears new peak was due to the aromatic fragments of degraded DB molecule, and in the visible region – at 370 nm.

Conclusions

A new way to photocatalytic and photoelectrocatalytic oxidation of azodye was investigated. Photoelectrocatalytic degradation of DB at high oxygen pressure is faster and more efficient than
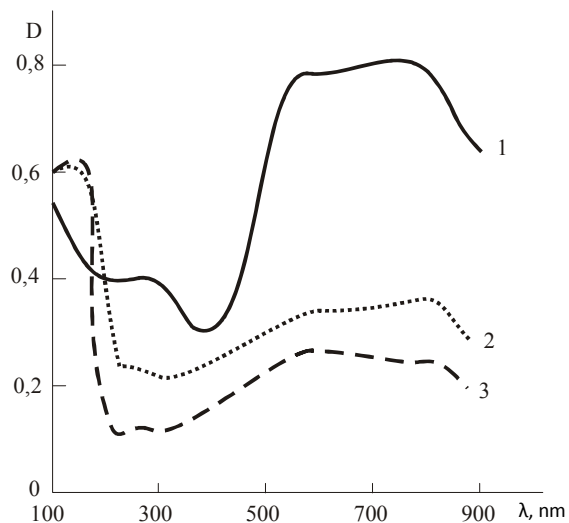
Fig. 5. UV-visible spectra during different treatment of DB: 1 – initial; 2 – photocatalytic (t = 2 h); 3 – photoelectrocatalytic (t = 30 min)

photocatalytic degradation. Increasing the oxidation rate at high oxygen pressure is due to dissolved oxygen reduction up to hydrogen peroxide or active particles, and oxygen reduction could be utilized to exercise indirect electrochemical oxidation and to improve photoelectrocatalytic efficiency.

It is clear that both the colour removal (75 %) and the degradation of aromatic structure is achieved at photoelectrocatalytic treatment of DB solution with oxygen pressure of 0.42 MPa. However, new peak was observed at 220 nm, which were due to the absorbance the lowmolecular organic compounds.

Acknowledgment

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Фотоэлектрокаталитическое и фотокаталитическое окисление азокрасителей при повышенных давлениях кислорода

А.Б. Исаев, Н.К. Тажибова, Ф.Ф. Оруджев,
П.М. Салихова, Р.В. Ильканаев, М.Н. Меджидов
Дагестанский государственный университет
Россия 367001, Республика Дагестан,
Махачкала, ул. М. Гаджиева, 43а

Исследовано влияние давления кислорода на фотокаталитическое и фотоэлектрокаталитическое окисление красителя прямого черного 22 (ПЧ). Показано, что повышение давления кислорода приводит к росту скорости фотоэлектрокаталитического и фотокаталитического окисления ПЧ на диоксиде титана. Степень обесцвечивания раствора азокрасителя при фотоэлектрокаталитическом окислении при давлении 0,42 МПа достигает 98 %.

Ключевые слова: фотокаталитическое, фотоэлектрокаталитическое, азокраситель, давление кислорода, окисление, прямой черный 22.