APARATURA
BADAWCZA I DYDAKTYCZNA

Laboratory reactor for testing photocatalyst reactions in the liquid reagents – the solid catalyst system

PIOTR M. SŁOMKIEWICZ, BEATA SZCZEPANIK
JAN KOCHANOWSKI UNIVERSITY, KIELCE, POLAND, INSTITUTE OF CHEMISTRY

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ABSTRACT

The construction and the principle of operation of the laboratory reactor for testing photocatalyst reactions in the liquid reagents – the solid catalyst system have been described in the presented paper. Construction of reactor enables sampling of the reaction mixture and supplying to the reaction mixture of gases and inert gases too.

Laboratoryjny reaktor do badania reakcji fotokatalitycznych w układzie ciekłe reagenty – stały katalizator

Słowa kluczowe: fotoreaktor, reakcje fotokatalityczne, fotokatalizator

STRESZCZENIE

W pracy przedstawiono budowę i zasadę działania laboratoryjnego reaktora do badania reakcji fotokatalitycznych w układzie ciekłe reagenty – stały katalizator. Konstrukcja reaktora umożliwia pobieranie próbek z mieszaniny reakcyjnej oraz doprowadzanie do mieszaniny reakcyjnej gazów, w tym gazów obojętnych.

1. INTRODUCTION

Photochemical processes are widely used in practice, for example, during the air, water and sewage purification, in the production of self-cleaning surfaces, during the decomposition of water and photo conversion of CO_2 [1-6].
Advanced Oxidation Processes (AOP, Advanced Oxidation Technologies, AOT), where UV radiation is used, often in the presence of H_2O_2, O_3 and TiO_2, are used for disinfection and purification of water [7-17]. Most of the organic contaminants dissolved in natural waters (herbicides, pesticides, aliphatic and aromatic compounds, polymers and dyes) undergoes reactions with the participation of hydroxyl radicals $OH^{\cdot}$, which leads to complete degradation of these compounds to carbon dioxide, water, ammonia (or nitrogen) or simple organic compounds, such as acetic and formic acids [18]. The efficiency of AOP process increases with the amount of generated hydroxyl radicals. One way to obtain large quantities of these radicals is the use of high electromagnetic radiation from UV range in photochemical reactors. The reactors used for photochemical processes are modified depending on the conditions in which these processes are carried out. There are two basic types of reactors: the processes carried out in homogeneous liquid systems and processes in heterogeneous liquid-gas systems. The photo reactors operating in homogeneous systems can be periodic or continuous, which does not substantially affect their design. The diameter of the reactor (the thickness of the irradiated layer) is determined according to the absorbance value of the irradiated system for used wavelength. Due to the radiation source reactors can be divided into the reactors with an internal source of radiation or with an external source of radiation. As the radiation sources are commonly used low pressure mercury lamps (λ~254 nm), medium pressure and high pressure lamps (emitting a wide range of UV/Vis radiation). They require cooling, typically using a water jacket. Sodium lamps, xenon lamps, lasers (monochromatic radiation) and solar radiation are also used as radiation source [19, 20].
Prior to conducting a photochemical reaction in the laboratory scale several factors should be taken into account: the type of reactor, the type of radiation source, a solvent (for homogeneous reactions in solution), photo catalyst (in the case of heterogeneous catalyzed reactions), substrate concentration, exposure time, and the method of deoxidation [21].
Ace Glass Company [22] produces photochemical reactors of different designs. This company does not offer a solution of the reaction mixture circulation with simultaneous sampling. Another laboratory photochemical reactor is commercially available Heraeus reactor [23], which is a glass vessel with elements of quartz glass and pressure mercury UV lamp in its interior (low-pressure, air-cooled or water-cooled a medium pressure mercury lamp). In order to avoid heating of the reaction space by the working UV lamp Heraeus applied water cooling, and additionally applied standard glass connectors to connect with other laboratory equipment expanding research capabilities of the reactor. The disadvantage of this solution is the large volume of reactor caused standard size of glass connectors. In addition, the placement inside the reactor working UV lamp makes it difficult to control the temperature in the reaction space, which can cause significant measurement errors in the case of the catalytic reaction kinetics measurements. Also the problem is the mixing of liquid reagents with the suspension of the solid catalyst due to placing in the reaction space a UV lamp with a high volume.
A method of sampling during the measurement of the kinetics of the photo catalytic reactions is not solved in this reactor.
In this paper the design and principle of operation of the modified laboratory reactor for testing the photocatalytic reaction in the system liquid reagents – solid photo catalyst was described [24]. The modifications make it possible to avoid the difficulties regarding Heraeus laboratory reactor described above. This is achieved by constructing the reactor with possibility of temperature control in the reaction space and the possibility of the inert gas supply and mixing of the reagents with the catalyst suspension by a turbine agitator. An additional circulation of the reaction mixture was also used to obtain the additional flow through the reaction space, and a way of sampling the reagents for analysis was solved.

2. DESCRIPTION OF PHOTOREACTOR

Laboratory research reactor for the research of photo catalytic reactions in the system liquid reagents – solid photo catalyst is composed of a cylindrical reactor with a turbine mixer, of the

compartment of rotodynamic pump and compartment of reactants sampling, which consist of three way distribution valves, and three reactants sampling assemblies.

The principal components of the reactor (Fig. 1) are the lower base 1 in which is secured by a nut 2 with a gasket 3 the cylinder 4 made of quartz glass. From the top of the cylinder closes the upper head 5 is also mounted with a nut 6 with a gasket 7. A bottom base of the reactor block is mounted on the rotodynamic pump 8 and the compartment of reactants sampling 9. Between these blocks is the electromotor 10 rotates permanent magnet block 11 which by magnetic field drives the turbine mixer 12. By the top cover of the cylinder along its main axis inside the reactor, heat exchanger 13 is mounted by nut 14 with a gasket 15. The gas pipe 16 with connector 17 passes through heat exchanger. This pipe may be supplied inert gas into the reaction space of the reactor. The inlet 18 of valve 19 is used to fill the reactor with the reactants photo catalyst suspension.

It can also serve as an outlet in the case for the inert gas supply into the reaction space. Reagents with a suspension of the photo catalyst through the outlet 20 and inlet 21 flows into the rotary pump 22 driven by an electric motor 23, and then through the outlet 24 to the compartment of reactants sampling (unchecked combination of Figure 1, the inlet powered 45 by a pump is shown on Figure 4). The sampling unit of reactants consists the three-way distribution valves with conical rotor with two working positions and three groups for sampling via syringe. The three-way distribution valve 25 (in Figure 1 is one of the three valves) is connected to a channel 26 through the connector 27 with gasket 28 to the base of the reactor bottom in which there is a channel 29 leading to the nozzle 30 constituting a fixed axis turbine mixer. The three-way distribution valve through the channel 31 is connected to the reactants sampling assembly 32 by a syringe 33.

In the first working position three-way distribution valve 25 (Fig. 2 A) reactants flow through the valve and the channel 31 is disconnected. The sampling unit 32 provided a threaded spindle 34, within which is a channel filter 35. The threaded spindle is provided with a conical connector 36 to the syringe 33.

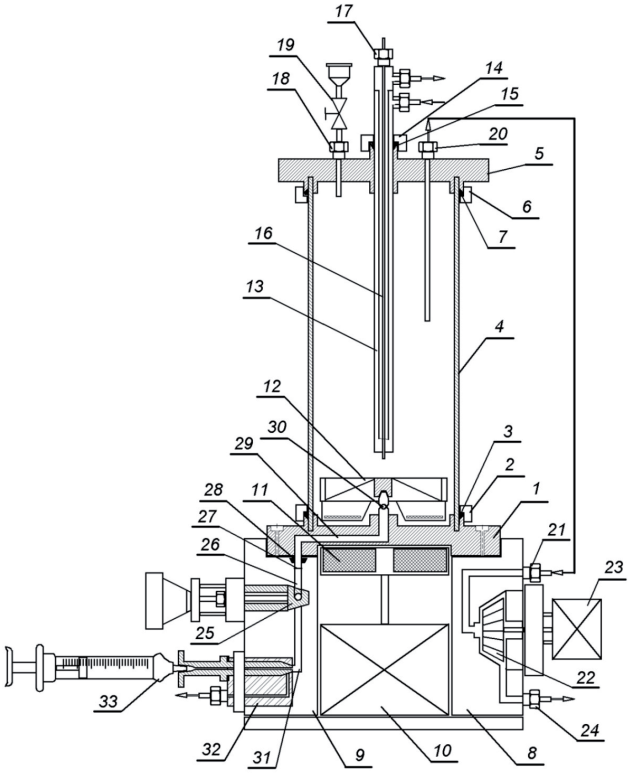

Figure 1 The diagram of reactor for investigations of photo catalytic reactions
1 – lower base, 2, 6, 14 – nut, 3, 7, 15, 28 – gasket, 4 – cylinder, 5 – upper head, 8 – compartment of rotodynamic pump, 9 – compartment of reactants sampling, 10, 23 – electromotor, 11 – block of permanent magnet, 12 – mixture turbine, 13 – heat exchanger, 16 – gas pipe, 17 – connector, 18, 21 – inlet, 19 – valve, 20, 24 – outlet, 22 – rotary pump, 25 – three-way distribution valve, 26, 29, 31 – channel, 27 – connector, 30 – nozzle, 32 – reactants sampling assembly, 33 – syringe

The other end of cone shape 37 of the threaded spindle is pressed against the conical socket 38 inside the sampling and closes the passage 39 leading to the outlet 40. In the second working position of three-way distribution valve 25 (Fig. 2 B), the channel 31 is connected to the channel 26 and the reagents are supplied to the sampling unit 32. Then the syringe 33 via the channel of the filter 35 can be sample reagents. Disconnection of the channel 31 and the channel 26 three-way distribution valve (Fig. 2 C) and partial loosening the spindle makes the conical end of the spindle 37 and conical seat 38 inside the sample block are spaced apart from each other. Then, the channel 39 is connected to the outlet guide 40 and the channel 31. Then it is possible to wash the sampling port 33 connected to a syringe port 36 of a conical seat.

Three three-way distribution valves 25, 41 and 42 of the sampling connectors 32, 43 and 44 have

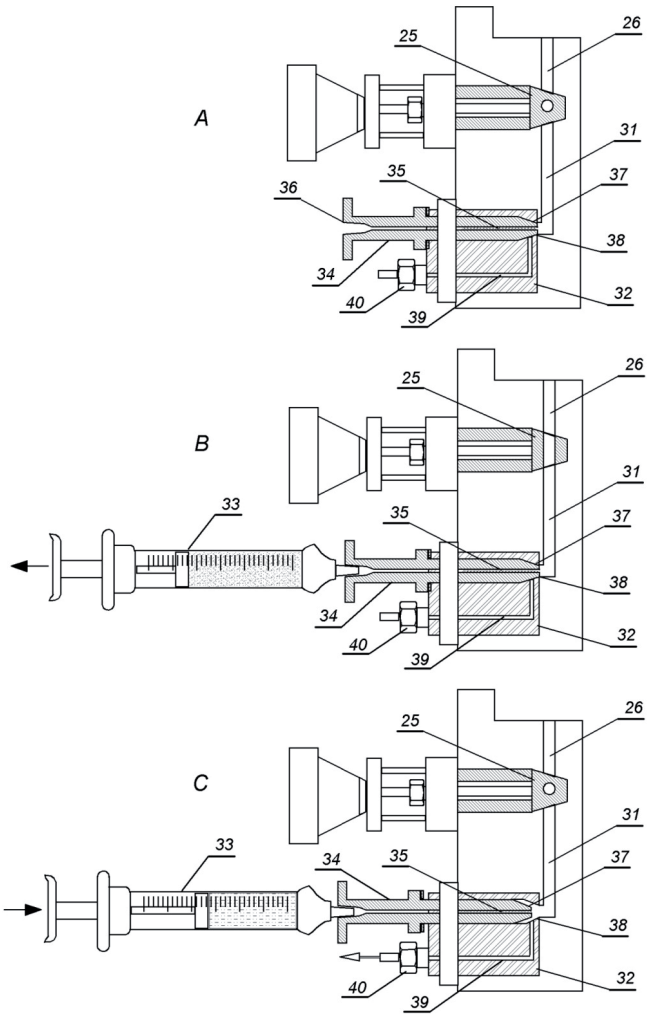

Figure 2 The diagram of syringe reactants sampling and interconnection diagram of two-position three-way valves with sampling connectors
Positions: A – reactants sampling off, B – reactants sampling on, C – the rinsing of reactants sampling connector
25 – three-way distribution valve, 26, 31, 39 – channel, 32 – reactants sampling assembly, 33 – syringe, 34 – threaded spindle, 35 – channel with filter, 36 – cone connection, 37 – conical end of spindle, 38 – cone seat, 40 – outlet

four operating positions (Fig. 3). The first one (Fig. 3 A) reactants from the inlet 45 fed by a pump, flow through the valves 41, 42 and 25 to the channel 26 and in this position all sampling connectors are disconnected.

In the second three-way valve 25 is connected to the sampling port 32 (Fig. 3 B), in the third three-way valve 42 is connected to the sampling port 44 (Fig. 3 C) and the fourth three-way valve 41 is connected to the sampling port 43 (Fig. 3 D).

Figure 4 shows a connection diagram of the reactor for the research of the photo catalytic reaction with the measuring devices. The electric motor 10 rotating permanent magnet block is powered by the speed adjuster 46, and the electric motor 23, the rotary pump 22 is powered by a speed adjuster 47 (Fig. 4). The thermostat 48 feeds heat exchanger 13 through an inlet 49 and an outlet 50. The gas flow in the gas line 16 through port 17 is controlled valve 51.

UV LED illuminator 52 powered by a power supply 53 is mounted on the side wall of the reactor.

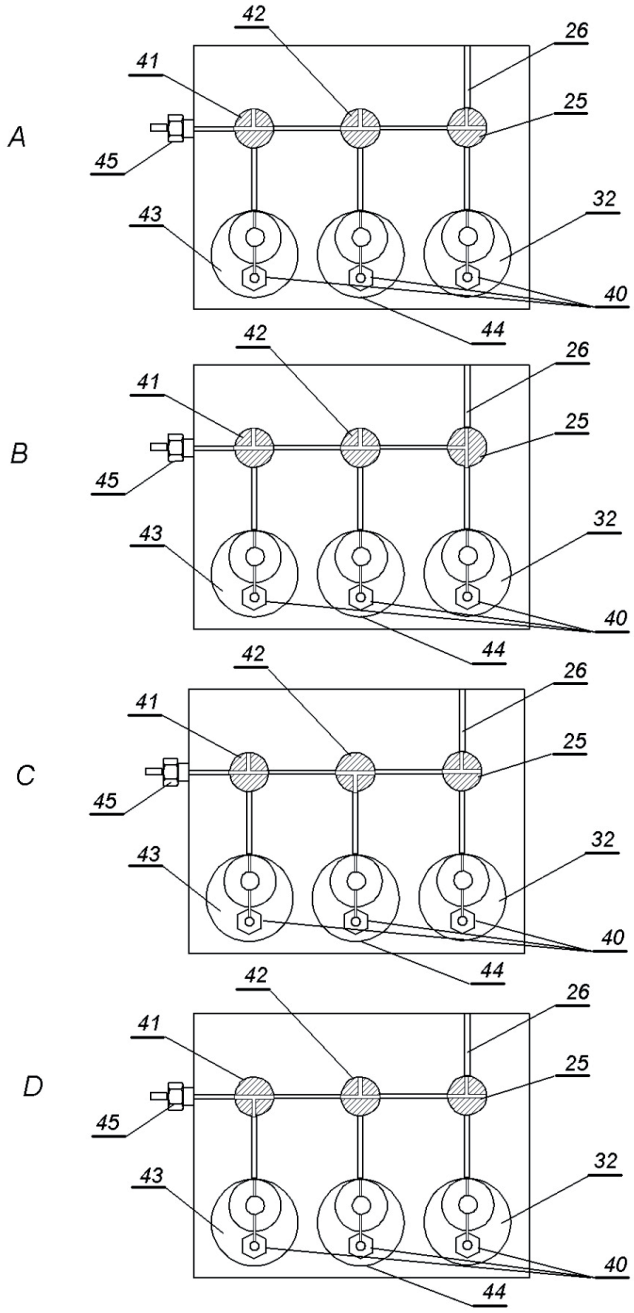

Figure 3 The interconnection diagram of two-position three-way valves with sampling connectors
Positions: A – reactants sampling off, B – reactants sampling with syringe by reactants sampling assembly 32, C – reactants sampling with syringe by reactants sampling assembly 44, D – reactants sampling with syringe by reactants sampling assembly 43
40 – outlet, 25, 41, 42 – three-way distribution valve, 26 – channel, 45 – inlet, 32, 43, 44 – reactants sampling assembly

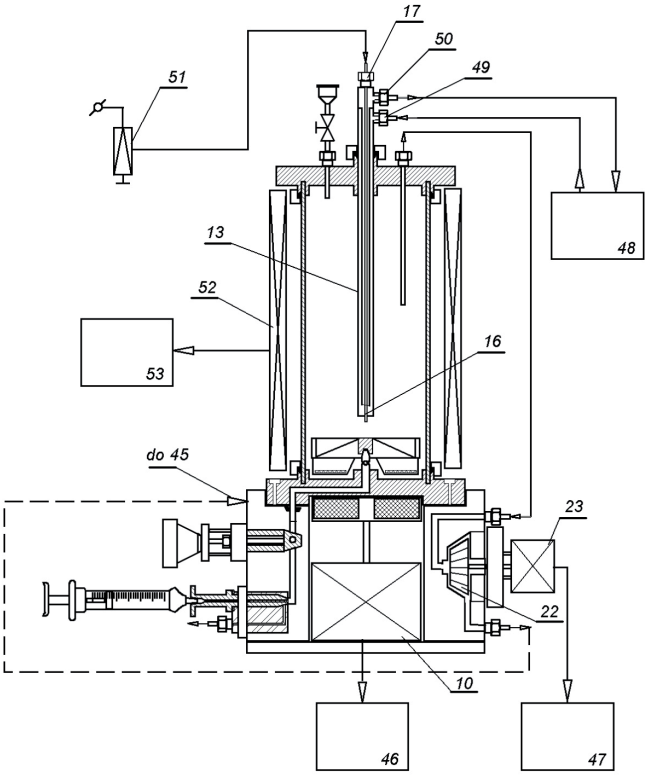

Figure 4 The diagram of reactor for investigations of photo catalytic reactions connection with measurement apparatus
10, 23 – electromotor, 13 – heat exchanger, 16 – gas pipe, 17 – connector, 22 – rotary pump, 45 – inlet supplied by pump, 46, 47 – speed adjuster, 48 – thermostat, 49 – inlet, 50 – outlet, 51 – valve, 52 – UV LED illuminator, 53 – power supply

3. CONCLUSIONS

Described in this article reactor for testing photo catalytic reactions on a laboratory scale reactor is one of the stationary reactor groups with stirrer.
A new solution is to minimize the effect of temperature and concentration gradients in the reaction space on the measuring results, by placing along the main axis of the cylindrical reactor heat exchanger and the use of dual system of photo catalyst reagent mixing using a mixer and a rotary pump, which forces an additional circulation of the reaction mixture.
The nozzle flow of the reaction mixture is placed in a turbine mixer near the lower base of the cylinder of the reactor.
This approach avoided the accumulation of the photo catalyst particles at the bottom of the reactor and really all photocatalyst participates in the reaction. The reaction mixture may be sampled to be analyzed from the additional circulation. In the study, the photo catalytic reaction three teams working independently sampling allow get sample of the reactants at any time, which is important for kinetic measurements.
The use of the plunger filter assemblies in each of the sampling allows sample of the reaction mixture after separation of the suspension of solid photo catalyst allowing the direct sampling into the liquid chromatograph. The solution of the sampling assemblies enables washing channels with a suitable solvent before taking the next sample. This avoids the analytical errors.
Also solved the inert gas supply method to the reaction chamber of the reactor by passing the gas line directly above the turbine mixer which causes the gas and the reaction mixture is efficiently mixed together.

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