Catalysis Today 268 (2016) 150–155

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Removal of trichloroethylene from water in the catalytic membrane reactor

Inna V. Petrova*, Tatyana S. Anokhina, Roman S. Borisov, Vladimir V. Volkov, Andrey B. Yaroslavtsev

A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, 29 Leninsky Prosp., Moscow 115408, Russia

ARTICLE INFO

Article history:
Received 19 September 2015
Received in revised form 24 February 2016
Accepted 25 February 2016
Available online 25 March 2016

Keywords:
Trichloroethylene
Hydrodechlorination
Palladium adlayers
Polymeric catalytic membrane
Three-phase hydrogenation
Membrane reactor

ABSTRACT

This work describes a single-stage method for the removal of chlorine-containing species from water using a catalytic membrane reactor based on Pd-loaded porous polypropylene hollow fiber membranes. The kinetics of this process is characterized. The degree of water purification is shown to be not less than 98%.

1. Introduction

Chlorinated hydrocarbons are widely used as solvents and degreasing formulations for technical and agricultural needs. Trichloroethylene (TCE) and tetrachloroethylene serve as key components in the solutions for dry cleaning of apparel, metalware, etc. Global production volume of trichloroethylene only is rated at the level of hundreds of kilotons [1]. However, due to high stability and low degradation rates, chlorine-containing compounds are classified as environmentally hazardous components [2,3]. Moreover, these compounds are also known to be highly toxic and exert an adverse effect on human health. Due to their high solubility in lipids, they can easily penetrate various human organs. The induced intoxication can have serious and even lethal consequences [4].

In common practice, chlorine-containing organics are removed by alkaline hydrolysis and via high-temperature vapor treatment. However, after the removal procedure, the contaminated substances also require additional purification [5]. Evidently, this challenging problem calls for the development of innovative methods providing deactivation of chlorine-containing products [6–9]. Catalytic hydrodechlorination is known to be a promising and effective tool for purification of organochlorine-containing groundwater and waste waters [10–14]. Among traditional catalysts used for hydrogenation, metals belonging to so-called platinum group (Pt, Pd, Ni) proved to be most efficient. For the purposes of selective hydrogenation, of special value are palladium catalysts. Palladium and its alloys are characterized by unique ability to dissolve appreciable amounts of hydrogen. Due to their highly selective hydrogen permeability, palladium and its alloys can be used as a partition in catalytic reactors [15]. One of the methods used for the removal of trichloroethylene is concerned with the two-stage process of reduction by hydrogen on the Pd/Al_2O_3 catalyst. The experimental evidence showed that, in the presence of oxygen, hydrodechlorination rate decreases by 55% from 0.034 down to 0.0007 for the batch reactors [16]. This process proceeds without any formation of by-products and the degree of conversion of trichloroethylene to ethane achieves 97% [17]. After several hours of operation, the catalyst becomes deactivated [18]. This problem can be solved by the thermal treatment of the catalyst [19] or by using catalysts doped with Fe, Ni, Ti, etc. [20–22].

A comparatively new approach is related to the use of hollow fiber membranes providing direct contact between a gas and a liquid. In particular, these “membrane contactors” prove to be efficient for the removal of dissolved oxygen from water and production of ultrapure water [23–25]. The advantages of hollow fibers are related to their exceptionally high working surface per volume unit of the contactor (up to 13,000 m^2/m^3). The benefits of this approach were validated by the effective removal of dissolved oxygen from

* Corresponding author.
E-mail address: ivpetrova@ips.ac.ru (I.V. Petrova).

http://dx.doi.org/10.1016/j.cattod.2016.02.023

water using porous polypropylene hollow fiber membranes with the surface-deposited metallic palladium [25–28]. In Ref. [29], the method providing removal of azo dyes with porous polypropylene membranes containing palladium nanoparticles deposited onto the inner membrane surface is described. In this case, the hydrogen flux is supplied into the lumen of hollow fibers. Additionally, the membranes should be washed for, at least, 30 min, after each experimental run.

The objective of this work is targeted on the development of a single-stage procedure for the removal of chlorine-containing compounds from water using a catalytic membrane reactor based on Pd-loaded porous polypropylene hollow fiber membranes. As an example of a contaminating species, trichloroethylene is selected.

2. Experimental

2.1. Preparation of catalytic membranes

In this work, we used Celgard X50 hydrophobic porous polypropylene hollow fiber membranes (lumen diameter is 220 μm, wall thickness is 40 μm, porosity is 40%, pore size is 0.03 μm). Celgard X50 membranes are produced (Membrane, Germany) as a sheet assembled as an array of parallel hollow fibers stitched by polymeric yarns. Metallic palladium was deposited onto an outer surface of polymeric membranes by the reduction of palladium salts by aliphatic alcohols according to the procedure described elsewhere [30].

Surface of initial and modified membranes was studied by scanning electron microscopy with the use of JSM-7600F microscope (Japan Electron Optics Laboratory, Japan) in the secondary electron emission regime with accelerating voltage 10 keV.

The X-ray phase analysis of the Pd-loaded membranes was performed on a Rigaku D/Max-2200 diffractometer (CuKα1 irradiation).

Catalytic lab-scale modules were assembled by in-gluing of Pd-loaded porous polypropylene hollow fiber membranes by epoxy resin into a glass housing. Hydrogen and water were supplied into lumen side and shell side, respectively. The effective membrane surface area was 500 cm^2.

2.2. The principle of a single-stage purification of water from trichloroethylene

The proposed approach for the purification of water from trichloroethylene using the above Pd-loaded catalytic membranes can be described as follows (Fig. 1): water contaminated with TCE sweeps the Pd-loaded membrane and hydrogen is supplied into the hollow fiber membrane lumen side and penetrates through membrane pores towards the Pd-loaded surface. Palladium catalyst for hydrogentation is involved in the delivery of hydrogen from gas or liquid mixtures via absorption of hydrogen molecules and their transformation into the most active atomic form. Interaction of hydrogen with metallic catalysts involves several processes, including chemical absorption of hydrogen on the surface, its dissolution in the metal and transformation into the atomic form as well as catalytic reactions with the participation of hydrogen [15]. Catalytic hydrodechlorination by hydrogen absorption on the palladium surface proceeds through the following scenario:

$$Cl_2C{=}CHCl + H_2 \rightarrow ClCH{=}CHCl + HCl \quad (1)$$

$$ClCH{=}CHCl + H_2 \rightarrow CH_2{=}CHCl + HCl \quad (2)$$

$$CH_2{=}CHCl + H_2 \rightarrow CH_2{=}CH_2 + HCl \quad (3)$$

$$CH_2{=}CH_2 + H_2 \rightarrow CH_3{-}CH_3 \quad (4)$$

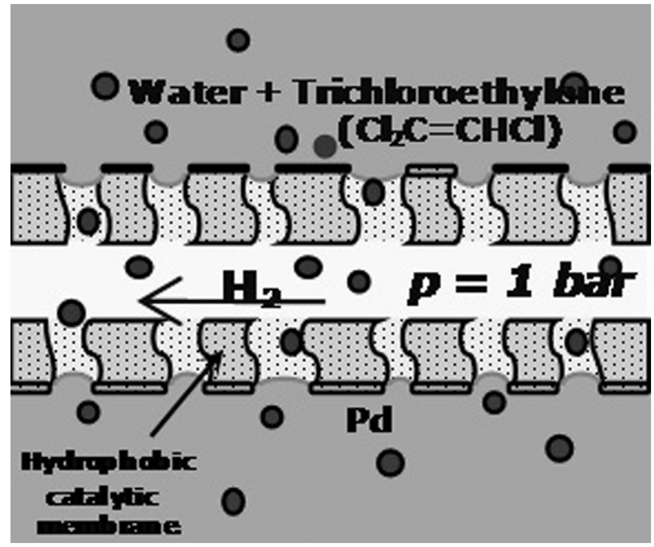

Fig. 1. The principle of a single-stage purification of water from trichloroethylene.

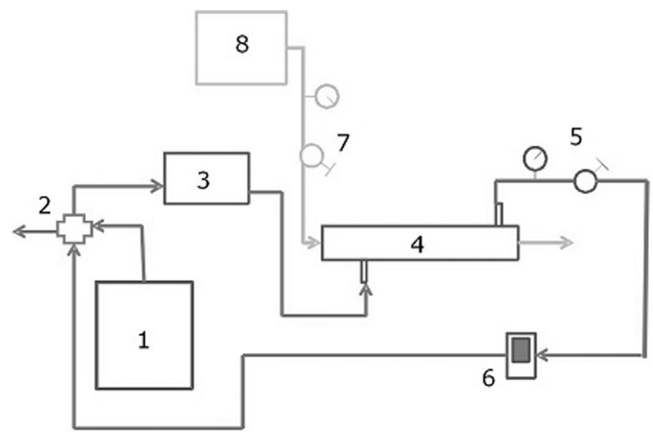

Fig. 2. The scheme illustrating the removal of dissolved TCE from water using a catalytic membrane reactor.
1—vessel for distilled water with TCE; 2—four-way valve; 3—regulated peristaltic pump; 4—catalytic membrane reactor; 5—water pressure control valve; 6—pH-meter; 7—gas pressure regulator; 8—hydrogen generator GVCh-6.

Fig. 2 depicts the general scheme illustrating the set-up for catalytic hydrodechlorination. Distilled water containing dissolved trichloroethylene is supplied from the vessel (1) using a regulated peristaltic pump (3) into a catalytic membrane reactor (4). At the exit of the membrane reactor, the pH-meter is installed (6). Hydrogen from a hydrogen generator (8) is supplied into the lumen side of hollow fiber membranes. To prevent bubbling of hydrogen in water and penetration of water into the pores of the hollow fiber membranes, excessive pressure of water (0.25 atm) and gas (0.2 atm) was maintained using a water pressure valve (5) and a gas pressure control valve (7). Using a four-way valve (2), the flow regime can be switched to the water recirculation in the system. As a result of hydrodechlorination of trichloroethylene, hydrogen chloride is formed, and its concentration is monitored by the pH-meter. The experiments were performed when water flow rate was varied from 10 to 50 l/h. The advantages of this process are related to the fact that the removal of trichloroethylene from water proceeds in a single stage at room temperature.

The content of trichloroethylene in water was quantitatively estimated using a Thermo Focus DSQ II GC/MS instrument (Varian VF-5 ms capillary column, length is 30 m, inner diameter is 0.25 mm, phase thickness is 0.25 μm, carrier gas is helium). The