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Mechanically adjustable chemostats based on stimuli-responsive polymers

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Abstract

A method for a mechanical operating point adjustment of hydrogel-based devices performing closed loop control has been developed. These so-called chemostats automatically control certain chemical and energy-based conditions of a liquid. The adjustment of the controlled condition is provided by a defined change of the triggering point by the activation unit of the device and the hydrogel actuator determining the basic functional relationship. The antagonistic principles of automatic valve chemostats were introduced, which can alternatively realize a normally open or a normally closed function. Using the hydrogel poly(*N*-isopropylacrylamide) the chemostat's switching concentration of ethanol in aqueous solution can be adjusted in the range of 5 and 20 wt.% with a practically relevant precision of 1 wt.%. The controllability of an energy-based condition by the chemostat was investigated on the process temperature control. We found that this temperature can be mechanically adjusted in a range of 25 and 35 °C with a standard deviation below 0.75 K.

Keywords: Chemostat; Hydrogel; Poly(*N*-isopropylacrylamide); Automatic flow control

1. Introduction

Concentration control of certain chemical substances is a key problem in liquid phase based processes. Devices able to regulate a chemical or physical condition of a liquid automatically are therefore of common interest. In microbiology a concept of such a device is known as chemostat maintaining the concentration of special chemical nutrient components in a bioreactor [1,2]. This device acts as an open loop control continuously supplying these chemical compounds, the so-called growth factors, which causes a defined growth rate of a bacterial population. Due to the high cost closed loop chemical control, consisting of sensors, data processing and actuator units, is rarely realized.

However, stimuli-responsive polymers and hydrogels respectively provide the probably simplest realization of closed loop chemostats applying both, actuator and chemical sensor properties. The material-based concept is based on a reversible change of volume in response to small alterations of the chemical [3–7] and energy-based [8–11] conditions of liquids. Valves that automatically control the ion and solvent concentration in aqueous solutions have been demonstrated on the example of various alcohols [12,13] and on the pH value [12,14,15]. Devices responsible to energy-based values were described for temperature [12,16,17] and light of a specific wavelength [18]. Also automatic pH [19] and temperature [20] controlled pumps are known. Devices able to regulate biochemical substances such as that of the pancreas [21] could be realized and are of particular interest because of substitution of body functions.

However, the disadvantage of hydrogel-based devices is the difficult adaptation to the application's requirements. In fact each application would require a stimuli-responsive polymer with an adapted phase transition behavior, usually realized by special polymer synthesis. This inhibits the broad practical use of hydrogel-based chemostats. A first adjustment method of chemostats without need to change the actuator material is described for hydrogels with a special double-sensitivity [22].

Herein, we describe a mechanical adjustment method of the chemostat's operating condition, which does not require special hydrogel properties. Using the hydrogel poly(*N*-isopropylacrylamide) (PNIPAAm) the antagonistic principles of automatic chemostats acting as valve are introduced, which

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realize alternatively either normally open or normally closed function. Furthermore, the closed loop control of chemical and energy-based conditions of liquids is investigated and demonstrated.

2. Experimental

2.1. Synthesis of hydrogel

PNIPAAm hydrogel was prepared as follows. Monomer *N*-isopropylacrylamide was recrystallized from *n*-hexane solution. Crosslinking agent was *N*,*N*′-methylenebisacrylamide. Initiator and accelerator for the polymerization reaction were potassium peroxidisulfate and *N*,*N*,*N*′,*N*′-tetramethyl-ethylenediamine (all from Aldrich Chemical Co.). *N*-Isopropylacrylamide and 4 mol% *N*,*N*′-methylenebisacrylamide were dissolved in deionized water. The total monomer concentration was 0.53 mol/l. To initiate the polymerization reaction 0.3 mol% of potassium peroxidisulfate and *N*,*N*,*N*′,*N*′-tetramethyl-ethylenediamine, respectively, were added to the oxygen free solution (bubbled with N_2). After polymerization (ca. 12 h at room temperature) the PNIPAAm gel was immersed in deionized water for about 1 week to wash out non-reacted reagents. After drying the PNIPAAm gel the particles were obtained by milling and subsequent fractionating into different particle sizes using test sieves. Particles possess an irregular shape. Particle size fraction used for experiments is (300 ± 100) μm.

2.2. Design and fabrication of the normally closed chemostat

The device shown in Fig. 1a involves two parts (1,2) forming a hydrogel chamber (5). Both parts are made of brass. Metal gauzes (mesh size 53 μm, wire diameter 24 μm) used as semi-permeable chamber walls (3) were adhered to inner and outer part using an epoxy based adhesive. The inner part can be screwed into the outer part using a metric fine thread (4). The chamber diameter is 5 mm. The length of chamber can be varied between 0 and 12 mm. To avoid a leakage flow between both parts the fit has a sealing ring (not shown in Fig. 1a). The chamber was filled with 24.4 mg dry hydrogel particles which correlates with a filling degree of about 30% of the chamber volume.

2.3. Design and fabrication of the normally open chemostat

This valve (see Fig. 1b) involves also two main parts (1,2). The valve body (1) (made from stainless steel) involves a conical valve seat (9) and a membrane (8) separating the two media circuits. Furthermore, the valve body possesses a metric fine thread (4). In this thread the position member (6) can be screwed in. This part consisting of the hydrogel, a flexible diaphragm (7) (polyurethane foil Walopur 4201, 25 μm thickness, from Epurex Films GmbH), and a metal gauze (mesh size 53 μm, wire diameter 24 μm) used as semi-permeable chamber wall (3). Gauze and elastic film were adhered to position member (6) using epoxy based adhesive. Before closing into the chamber 53.7 mg dry PNIPAAm particles were filled (equal to 60% of the chamber volume).

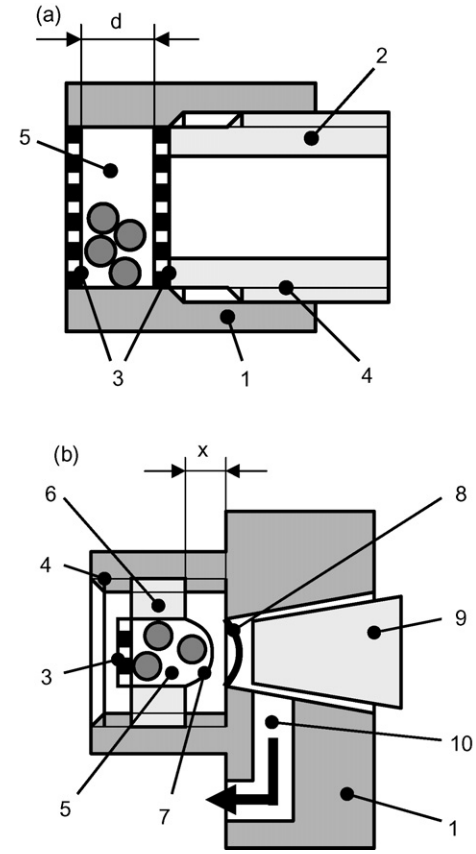

Fig. 1. Schematic designs of the mechanically adjustable chemostats. (a) Normally closed chemostat. (b) Normally open chemostat. 1, outer part; 2, inner part; 3, metal gauze; 4, fine thread; 5, actuator chamber filled with hydrogel; 6, position member; 7, flexible membrane of the actuator chamber; 8, flexible membrane separating the liquid circuits; 9, conic valve seat; 10, outlet; *d*, adjustable chamber length; *x*, adjustable distance.

3. Results and discussion

3.1. Hydrogel behavior

PNIPAAm shows sensitivities towards special organic solvents. Contents of alcohols in the aqueous solution cause a drastic change of hydrogel volume. As shown in Fig. 2a two phase transition concentrations of PNIPAAm at room temperature can be observed. Small amounts of alcohols cause a collapse of the gel. With increasing the length of the alcohol chain the lower phase transition concentration decreases. This lower critical alcohol concentration is 17.5 wt.% for methanol, 14 wt.% for ethanol and 6 wt.% for 1-propanol at 21 °C (see Fig. 2b). If the alcohol content is higher than 25 wt.% the hydrogel is completely shrunken in each case. In the range of the upper phase transition concentration the PNIPAAm shows an inverse behavior, that means, the hydrogel swells by increasing alcohol content. In pure alcohol the gel exhibits a swelling degree, which is comparable with that in pure water.

PNIPAAm is also a well-known temperature sensitive hydrogel exhibiting lower critical solution temperature behavior. As