Materials Science and Engineering C 61 (2016) 333–337

Contents lists available at ScienceDirect

Materials Science and Engineering C

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

Preparation of a novel pH optical sensor using orange (II) based on agarose membrane as support

Rouhollah Heydari [a,*], Mohammad Hosseini [b,*], Ahmadreza Amraei [c], Ali Mohammadzadeh [b]

[a] Razi Herbal Medicines Research Center, Lorestan University of Medical Sciences, PO Box 68149-89468, Khorramabad, Iran
[b] Young Researchers and Elite Club, Arak Branch, Islamic Azad University, Arak, Iran
[c] Department of Chemistry, Faculty of Sciences, Islamic Azad University, Arak Branch, Arak, Iran

ARTICLE INFO

Article history:
Received 31 October 2015
Received in revised form 4 December 2015
Accepted 23 December 2015
Available online 29 December 2015

Keywords:
pH optical sensor
Agarose membrane
Orange (II)
Covalent immobilization

ABSTRACT

A novel and cost effective optical pH sensor was prepared using covalent immobilization of orange (II) indicator on the agarose membrane as solid support. The fabricated optical sensor was fixed into a sample holder of a spectrophotometer instrument for pH monitoring. Variables affecting sensor performance including pH of dye bonding to agarose membrane and dye concentration were optimized. The sensor responds to the pH changes in the range of 3.0–10.0 with a response time of 2.0 min and appropriate reproducibility (RSD ≤ 0.9%). No significant variation was observed on sensor response after increasing the ionic strength in the range of 0.0–0.5 M of sodium chloride. Determination of pH using the proposed optical sensor is quick, simple, inexpensive, selective and sensitive in the pH range of 3.0–10.0.

1. Introduction

Measurement of pH is one of the most important and common tests which is carried out in many laboratories. Chemical and biological properties of many substances are dependent on pH of their mediums. For example, pH influences the solubility of metals and toxicity of some substances such as ammonia, hydrogen sulfide and hydrogen cyanide in aqueous solutions [1]. Also, pH can be affecting the rate of chemical reactions. Therefore, pH monitoring is important in laboratory and industrial processes.

pH determination is carried out using several methods including indicator reagents, pH test paper strips, and electrochemical and photochemical sensors. Although the pH test paper strips are available and easy to use, they were not used in high accuracy cases. On the other hand, the range of response for indicator reagents is limited. Development of electrochemical and optical pH sensors has grown rapidly in the recent decade which indicates the importance of these devices in various disciplines [2–8].

Signal of optical sensors are based on the changes in absorption or luminescence of active reagents which are fixed in thin membranes. Due to their cost-effective and simple operation, pH optical sensors were evaluated during the recent decade [9–13]. These optical sensors have several advantages such as low-cost, high sensitivity, suitable selectivity, possibility of real samples analysis and remote sensing [14]. Often, pH optical sensors are prepared by immobilizing the acid or base indicators on a solid support. Usually, an indicator binding to solid support occurs via adsorption or covalent interactions [9,15,16]. Polymers which are used as solid support, e.g. cellulose [17], triacetylcellulose [18,19] and agarose [20,21], are capable of forming covalent bonds with indicators.

Orange (II) or acid orange 7 (Fig. 1) with –N═N– azo structure as a chromophore is an inexpensive azo dye that is used as a pH indicator in a relatively basic medium. Orange (II) is an anionic monoazo dye which is classified as an acidic dye. It is resistant to various environmental conditions such as light degradation, oxidation with O_2 and common acids or bases. Because of these properties, it is used in many industries including organic light-emitting diodes (OLEDs), inks, soaps, wood preservatives, textiles, hair dyes, leather materials, shoe polishes, cosmetics and wood stains [22].

In this study, orange (II) is used for the preparation of a new optical pH sensor with a suitable working range. The response change range of orange (II) indicator with pH was enhanced using covalent immobilization of this pH indicator on the agarose membrane. For the first time, immobilized orange (II) on agarose membrane was applied as a pH optical sensor. The behavior of this optical sensor was monitored at different pHs. Factors affecting the performance of the sensor, such as pH of

* Corresponding authors.
E-mail addresses: rouhollahheydari@yahoo.com (R. Heydari), smhosseini2007@gmail.com (M. Hosseini).

http://dx.doi.org/10.1016/j.msec.2015.12.051
0928-4931/

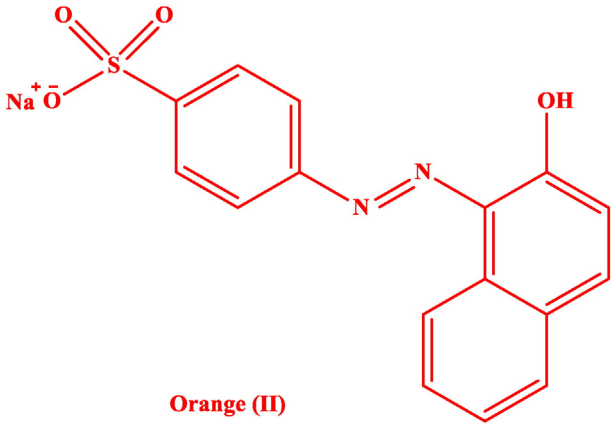


Fig. 1. Chemical structure of orange (II).

dye bonding to agarose membrane, dye concentration, ionic strength, reversibility, response time and storage time, have been investigated and optimized.

2. Material and methods

2.1. Chemicals and reagents

Orange (II) or sodium 4-[(2E)-2-(2-oxonaphthalen-1-ylidene) hydrazinyl] benzene sulfonate, agarose with the quality of medium electroendosmosis, epichlorohydrin and other chemicals were purchased from Merck Chemicals Company (Darmstadt, Germany). Double-distilled water was used for preparation of aqueous solutions. Test solutions were buffered in 0.02 mol L^{-1} solutions of sodium dihydrogen phosphate and pH adjusted with dropwise addition of 1 mol L^{-1} hydrochloric acid or sodium hydroxide solutions.

2.2. Instrumentation

Absorption measurements were carried out using a Shimadzu double-beam spectrophotometer (Model 1650 PC, Japan). A Jenway pH meter (model 3020, UK) with a combined glass electrode was used after calibration against standard Merck buffers for pH measurements. A homemade polyacrylamide holder was used for holding agarose membranes inside the cell of the spectrophotometer instrument [18].

2.3. Preparation and activation of the sensor membranes

Transparent agarose membranes were prepared according to previous report [20] with some modifications. Briefly, 0.8 g of agarose powder was mixed with 20 mL double-distilled water. The mixture was stirred at 90 °C until its volume decreased to 15 mL. Then the viscous mixture was heated at 70 °C in a water bath for 10 min. After complete removal of bubbles, the transparent-viscose solution was dispersed between two 20 cm × 20 cm clean glass plates and subjected to pressure. Borders of one of the glass plates were already lined with a 0.25 mm thickness tape to adjust the thickness of the membrane. After cooling, the solidified membrane was cut into appropriate pieces and stored in 50% ethanol solution at 4 °C. Membrane activation was performed by epichlorohydrin which is an epoxide [23]. For bonding of orange (II) on the surface of activated agarose membranes, the membranes were immersed in orange (II) solution (with concentration of 1×10^{-2} mol L^{-1} and pH 11 adjusted by phosphate buffer) for 24 h. The obtained orange color membranes were washed with double-distilled water and soaked in water overnight. Finally, membranes were washed with a large volume of double-distilled water to remove any non-bonded dye.

2.4. Measurement procedure

A piece (1 cm × 3 cm) of the prepared agarose optical membrane was fixed on a polyacrylamide holder and placed vertically inside the quartz cell containing buffer solutions with different pHs. The absorbance data were collected against a blank cell containing a non-activated agarose membrane in buffer solution with the appropriate pH. To study the influences of different parameters on the response of the optical membrane, absorbance measurements were carried out at 490 nm as a maximum wavelength.

3. Results and discussion

3.1. Optimization of orange (II) bonding to agarose membrane

The effect of pH on the immobilization of orange (II) on the agarose membranes was tested using dye solutions with various pHs in the range of 5–13. The results were illustrated in Fig. 2. As can be seen from Fig. 2, the amount of bonded dye to agarose membrane was increased with an increase of pH of up to 11. This behavior can be explained by the protonation of the sulfonyl group of orange (II) in acidic mediums which avoids more bonding. The results are compatible with the proposed mechanism for bonding orange (II) to an activated membrane (Scheme 1). Therefore, pH 11 was selected as the optimum pH for further experiments.

Concentration of bonded dye to the agarose membrane has significant effect on the performance of the optical sensor. For this reason, the prepared agarose membranes were treated with solutions containing different dye concentrations in the range of 10^{-5} to 10^{-2} mol L^{-1}. As shown in Fig. 3, the amount of immobilized dye on the membrane increases with an increase of orange (II) concentration. Hence, concentration of 10^{-2} mol L^{-1} with a maximum absorbance of about 0.94 AU was chosen as the optimum dye concentration.

3.2. Optical characteristics of the sensor membrane

Fig. 4 shows the absorbance spectra of immobilized orange (II) on the activated agarose film and aqueous solution of orange (II) at different pH values from 3.0 to 10.0. Interestingly, it is found that the absorbance of the immobilized dye decreases with increasing pH of a solution within a broad pH range, in contrast to the optical behavior of the free dye in the solution. As it can be seen from Fig. 4, the sensor membrane shows a maximum at 490 nm in the visible region. Therefore, 490 nm was selected as an appropriate wavelength for pH monitoring. It is clear from Fig. 4 that with the increase of solution, pH absorbance of optical sensor and orange (II) solution were decreased. Fig. 4a shows that the resolution of the sensor in the acidic pH region is higher than the basic region. In higher pHs (>10), absorption spectra

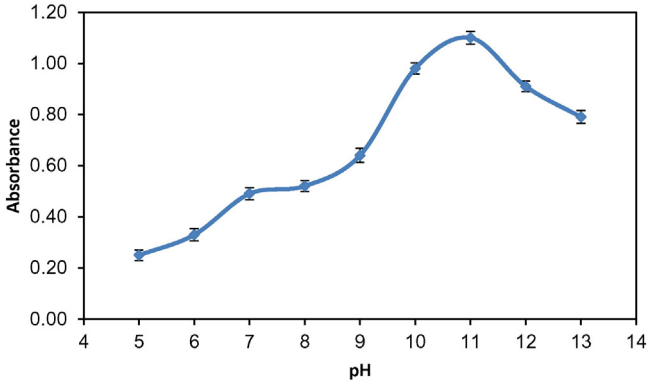
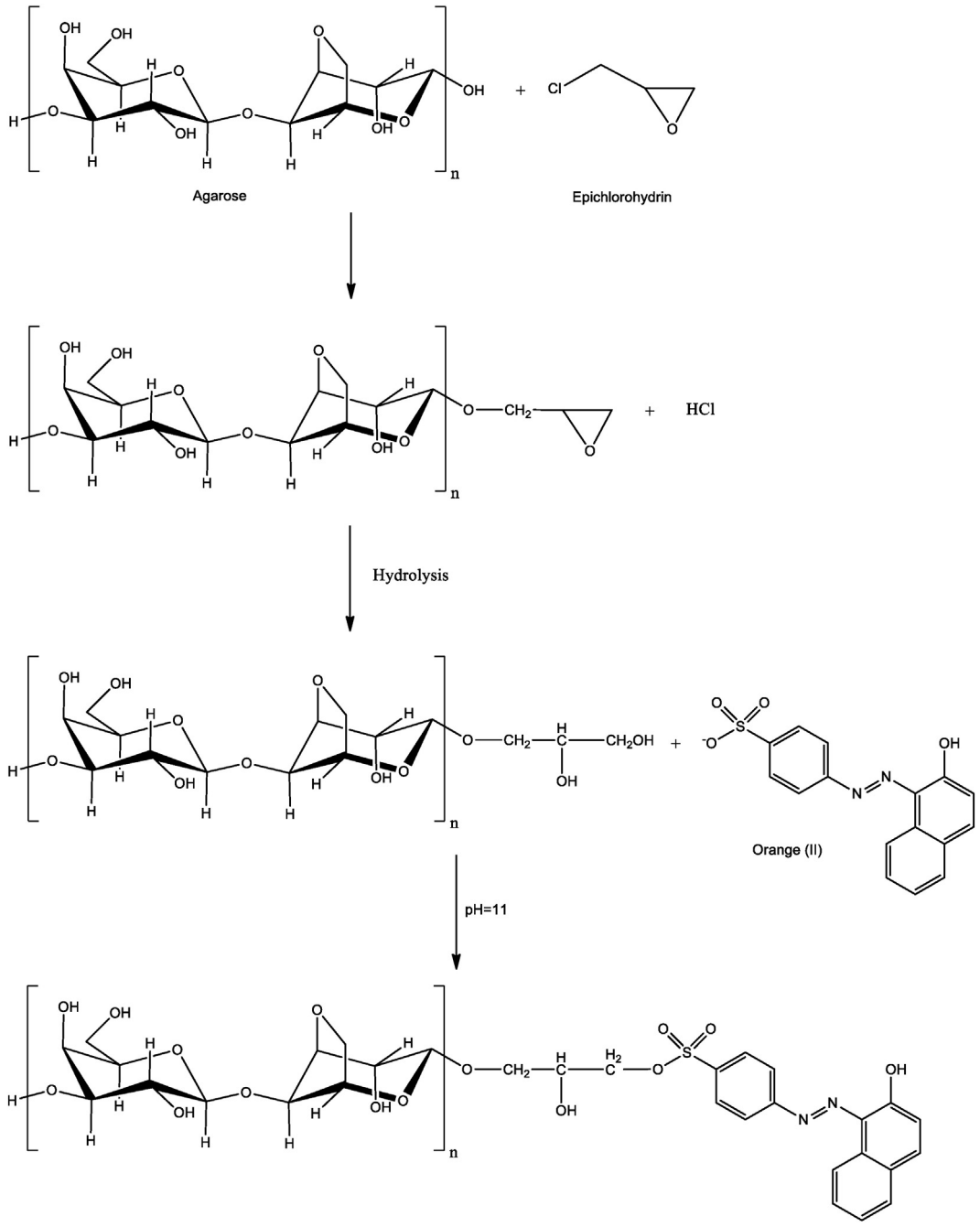


Fig. 2. Absorbance of the optical sensor as a function of the immobilization pH at 490 nm. The dye concentrations, 10^{-2} mol L^{-1}. Error bars are expressed as standard deviation.



Scheme 1. The proposed mechanism of activation and dye bonding to agarose membrane.

of the optical sensor completely overlapped and destroyed sensor resolution. Similarly, absorption spectra of orange (II) solution in higher pHs completely overlapped and are not distinguishable. However, the absorbance changes of the immobilized orange (II) against pH variations in the range of 3.0–10.0 were greater than the soluble form of orange (II). This behavior increases the sensitivity of the optical pH sensor. On the other hand, pK_a of orange (II) is 11.4 and its solution can be used as pH indicator in basic medium while the immobilized orange (II) can be used in a broad pH range from 3.0 to 10.0 [24].

3.3. Effect of ionic strength

Effect of salt concentration on the sensor response was examined at three pH levels (4.0, 7.0 and 10.0) by using various sodium chloride concentrations in the range of 0.0–0.5 mol L^{-1}. The results in Table 1 indicate that the sensor response is approximately constant with increasing the ionic strength in the range of 0.0–0.5 mol L^{-1} of sodium chloride. Therefore, the proposed optical sensor can be used for pH monitoring of samples containing salt in the range of 0.0–0.5 mol L^{-1}.

3.4. Response time

The response time of the optical sensor was determined using record of absorption data at pH 4 against time in the range of 0–5 min at 490 nm. The response time of the pH sensor was calculated from this absorption profile. As shown in Fig. 5, the absorbance of the optical sensor reaches to a steady state after about 2 min. The absorbance signal of optical sensor levels off after equilibrium and no signal drift is observed under the experimental conditions. Therefore, 2 min was selected as the optimum response time for the prepared sensor.

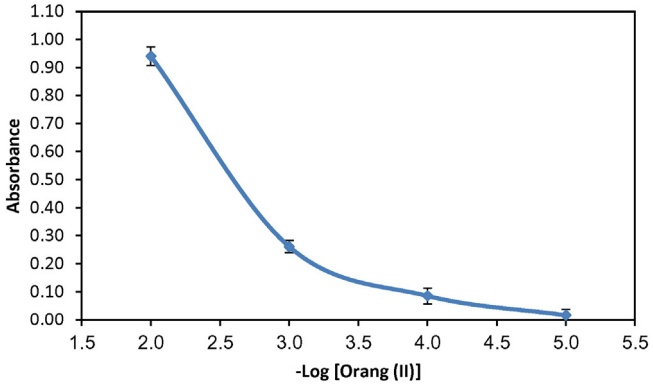


Fig. 3. Absorbance of the immobilized agarose membrane as a function of orange (II) concentration at 490 nm. Error bars are expressed as standard deviation.

3.5. Calibration curve

The calibration curve of the prepared optical sensor was constructed using buffer solutions with different pHs in the range of 3.0–10.0. Fig. 6 shows a typical calibration curve which was derived from absorbance measurements of the optical sensor in the pH range of 3.0–10.0 at 490 nm. The obtained data was fitted using an empirical second order polynomial graph with a R^2 value of 0.9985 and equation: Absorbance = $0.0188pH^2 - 0.3679pH + 2.0792$. Repeatability of the sensor membrane at individual pHs was demonstrated using repeated measurements. Relative standard deviation (RSD) values were less than 0.3%. Error bars in Fig. 6 are expressed as percentage of relative standard deviation.

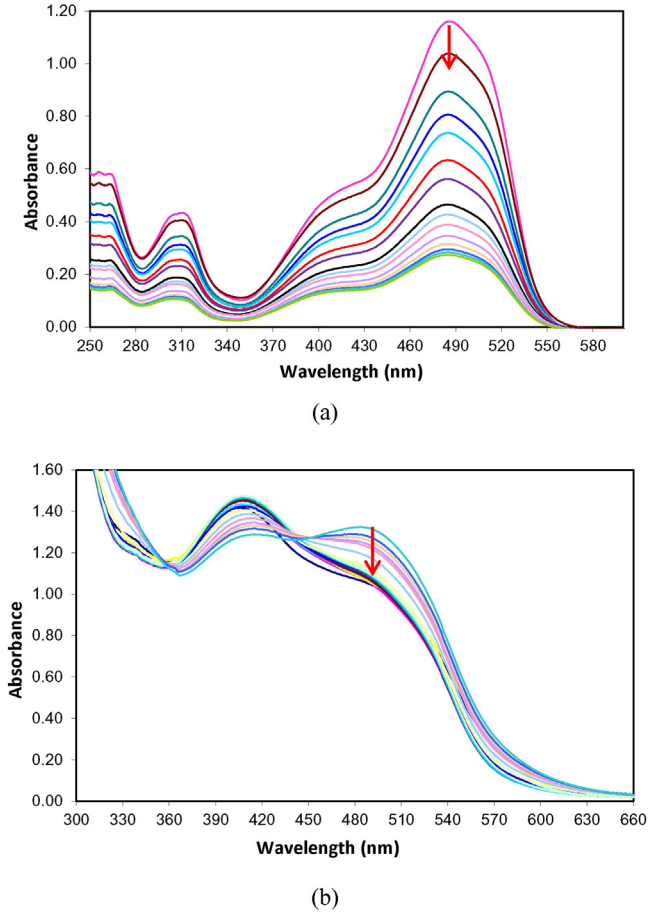


Fig. 4. Absorption spectra of immobilized orange (II) on agarose membrane (a) and orange (II) aqueous solution (b) at different pHs (3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7, 7.5, 8, 8.5, 9, 9.5 and 10). Concentration of orange (II) in aqueous solution was 10^{-3} mol L^{-1}.

Table 1
The results of ionic strength on sensor response at various pHs.

pH	NaCl concentration (mol L^{-1})					RSD (%)
	0.0	0.1	0.2	0.4	0.5	
4.0	0.884	0.886	0.881	0.879	0.878	0.38
7.0	0.422	0.423	0.420	0.419	0.423	0.43
10.0	0.271	0.270	0.269	0.273	0.269	0.62

3.6. Reproducibility, repeatability, reversibility and stability of sensor membrane

Sensor membrane reproducibility at several pHs was examined using three prepared membranes. RSD values for three membranes at various pHs were less than 0.9% (Table 2). To demonstrate the repeatability and reversibility of the sensor membrane, buffered solutions with different pHs (3.0, 5.0 and 8.0) as test solutions were subsequently delivered to spectrophotometer cell containing sensor membrane. Fig. 7 indicates the obtained results for a period of 105 min. RSD values of results are less than 0.3%. The results showed that the response of the sensor is repeatable and reversible. In order to investigate the life time of the sensor membranes, they were maintained in water/ethanol (50:50, *v*/*v*) solution for 4 months at 3–5 °C. No significant variation in sensor response was observed during this period. However, since the pH indicator is immobilized covalently to the agarose membrane, there was no color leakage during use [20].

4. Conclusions

A suitable optical pH sensor using orange (II) based on agarose membrane for pH determination in the range of 3.0–10.0 has been developed. Orange (II) indicator was immobilized on the agarose support by covalent bond. The advantages of the proposed pH sensor are as follows: wide range, suitable response time, repeatable response, reversible response, low-cost and easy to prepare. Stability results showed that the sensor is stable after 4 months of storage in water/ethanol (50:50, *v*/*v*) solution at 3–5 °C. Investigation of several aspects of prepared optical sensor including reproducibility, repeatability, reversibility, response time and stability demonstrated the potential of the proposed optical sensor for applications as an optical pH sensor.

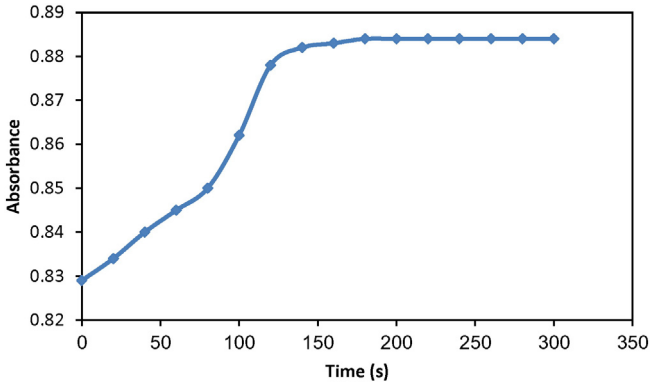


Fig. 5. Response time graph of the sensor as a function of time at 490 nm. Test conditions: sample pH, 4; immobilized orange (II) concentration, 1×10^{-2} mol L^{-1}; immobilization pH, 11.

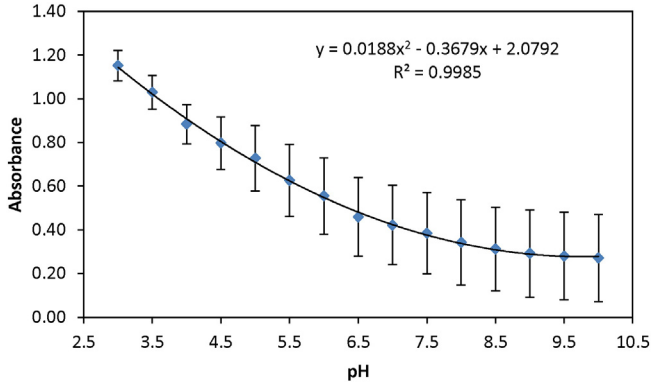


Fig. 6. Calibration curve of the optical sensor at 490 nm. Error bars are expressed as percentage of relative standard deviation.

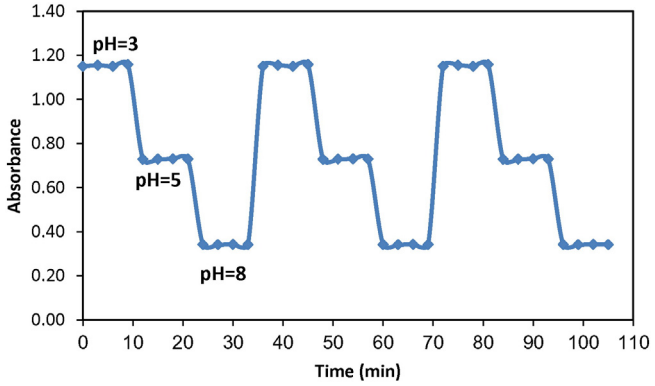


Fig. 7. Reversibility results of the optical sensor by changing the solution pH.

Table 2
The results of reproducibility test for three membranes.

pH	Membrane 1	Membrane 2	Membrane 3	RSD (%)
3	1.152	1.145	1.157	0.52
6	0.554	0.546	0.550	0.73
8	0.340	0.344	0.338	0.90

Acknowledgments

The authors are gratefully acknowledging the support of Islamic Azad University, Arak Branch and Razi Herbal Medicines Research Center, Lorestan University of Medical Sciences.

References

[1] E.R. Weiner, Applications of Environmental Chemistry: A Practical Guide for Environmental Professionals, CRC Press, Boca Raton, Florida 33431, USA, 2000.
[2] A. Moutsiopoulou, A.K. Andreopoulou, G. Lainioti, G. Bokiasa, G. Voyiatzis, J.K. Kallitsis, Quinoline-functionalized cross-linked poly(vinyl acetate) and poly(vinyl alcohol) nanoparticles as potential pH-responsive luminescent sensors, Sensors Actuators B 211 (2015) 235–244.
[3] S. Zaman, M.H. Asif, A. Zainelabdin, G. Amin, O. Nur, M. Willander, CuO nanoflowers as an electrochemical pH sensor and the effect of pH on the growth, J. Electroanal. Chem. 662 (2011) 421–425.
[4] S. Trupp, M. Alberti, T. Carofiglio, E. Lubian, H. Lehmann, R. Heuermann, E. Yacoub-George, K. Bock, G.J. Mohra, Development of pH-sensitive indicator dyes for the preparation of micro-patterned optical sensor layers, Sensors Actuators B 150 (2010) 206–210.
[5] H.X. Chena, X.D. Wanga, X.H. Songa, T.Y. Zhoua, Y.Q. Jianga, X. Chen, Colorimetric optical pH sensor production using a dual-color system, Sensors Actuators B 146 (2010) 278–282.
[6] N. Raoufi, F. Surre, T. Sun, M. Rajarajan, K.T.V. Grattan, Wavelength dependent pH optical sensor using the layer-by-layer technique, Sensors Actuators B 169 (2012) 374–381.
[7] C.R. Zamarreño, M. Hernáez, I. Del Villar, I.R. Matías, F.J. Arregui, Optical fiber pH sensor based on lossy-mode resonances by means of thin polymeric coatings, Sensors Actuators B 155 (2011) 290–297.
[8] A. Safavi, M. Sadeghi, Development of an optode membrane for high pH values, Spectrochim. Acta A 66 (2007) 575–577.
[9] S.J. Glenn, B.M. Cullum, R.B. Nair, D.A. Nivens, C.J. Murphy, S.M. Angel, Lifetime-based fiber-optic water sensor using a luminescent complex in a lithium-treated Nafion membrane, Anal. Chim. Acta 448 (2001) 1–8.
[10] A. Safavi, M. Bagheri, Novel optical pH sensor for high and low pH values, Sensors Actuators B 90 (2003) 143–150.
[11] E. Teknikel, C. Unaleroglu, Colorimetric and fluorometric pH sensor based on bis(methoxycarbonyl)ethenyl functionalized BODIPY, Dyes Pigments 120 (2015) 239–244.
[12] D. Staneva, P. Bosch, A.M. Asiri, L.A. Taib, I. Grabchev, Studying pH dependence of the photophysical properties of a blue emitting fluorescent PAMAM dendrimer and evaluation of its sensor potential, Dyes Pigments 105 (2014) 114–120.
[13] M. Tian, X. Peng, J. Fan, J. Wang, S. Sun, A fluorescent sensor for pH based on rhodamine fluorophore, Dyes Pigments 95 (2012) 112–115.
[14] K. Alizadeh, B. Rezaei, E. Khazaeli, A new triazene-1-oxide derivative, immobilized on the triacetyl cellulose membrane as an optical Ni^{2+} sensor, Sensors Actuators B 193 (2014) 272–276.
[15] U. Krause, I. Klimant, T. Werner, O.S. Wolfbeis, Luminescence decay time-based determination of potassium ions, Anal. Chem. 70 (1998) 3983–3985.
[16] S. Motellier, P. Toulhoat, Modified acid–base behaviour of resin-bound pH indicators, Anal. Chim. Acta 271 (1993) 323–329.
[17] T. Carofiglio, C. Fregonese, G.J. Mohr, F. Rastrelli, U. Tonellato, Optical sensor arrays: one-pot, multiparallel synthesis and cellulose immobilization of pH and metal ion sensitive azo-dyes, Tetrahedron 62 (2006) 1502–1507.
[18] M. Hosseini, R. Heydari, M. Alimoradi, A novel pH optical sensor using methyl orange based on triacetylcellulose membranes as support, Spectrochim. Acta A 128 (2014) 864–867.
[19] S. Khodadoust, N. Cham Kouri, M.S. Talebiyanpoor, J. Deris, A.A. Pebdani, Design of an optically stable pH sensor based on immobilization of Giemsa on triacetylcellulose membrane, Mater. Sci. Eng. C 57 (2015) 304–308.
[20] P. Hashemi, M. Hosseini, K. Zargoosh, K. Alizadeh, High sensitive optode for selective determination of Ni^{2+} based on the covalently immobilized thionine in agarose membrane, Sensors Actuators B 153 (2011) 24–28.
[21] P. Hashemi, M.M. Abolghasemi, Preparation of a novel optical sensor for low pH values using agarose membranes as support, Sensors Actuators B 115 (2006) 49–53.
[22] T. Gan, J. Sun, Z. Lin, Y. Li, Highly sensitive determination of orange II based on the dual amplified electrochemical signal of grapheme and mesoporous TiO_2, Anal. Methods 5 (2013) 2964–2970.
[23] I. Matsumoto, Y. Mizuno, N. Seno, Activation of sepharose with epichiorohydrin and subsequent immobilization of ligand for affinity adsorbent, J. Biochem. 85 (1979) 1091–1098.
[24] M. Hou, F. Li, X. Liu, X. Wang, H. Wan, The effect of substituent groups on the reductive degradation of azo dyes by zerovalent iron, J. Hazard. Mater. 145 (2007) 305–314.