Development and characterization sensitivity of optical fibre pH sensor for industrial application

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Abstract. Optical fibre sensor (optrode) depending on a transmittance was presented as a valuable sensitive sensor for several applications. Thus, the development of a wide-area detection system for continuously monitoring structural changes, together with a capability for non-destructive evaluation and early warning, is an important task the sensitive fibre was preparing by removing the cladding from several places and modified by different chemical solutions. The transmittance spectrum used to measure the pH of distilled water that contains HCL and NaOH in a range between 2 to 12. The special design of this sensor made it a perfect for laboratory and industrial usage, only 25 cm of modified fibre was enough to measure the pH in real time with a sensitivity 0.015-0.2 1/pH. The results showed this sensor can work in different solutions and it gives accurate results at any conditions.

1. Introduction
Detecting of a chemical changing in environment is a central issue nowadays due to increase the pollutions in last decades. There is very important to monitor contaminations for using in variety of applications like environment, food quality and biomedical [1-4]. So it is useful to invent simple, efficient and faster devices that work at any conditions. The pH is most important for numerous applications and there are several ways to find it in solutions. To date the optical way is the simplest[5]. Fibre optic or “optrode” using for pH and other chemical sensing depending on the variation light intensity are presented as a new device recently[6, 7]. It is coated with several sensitive surface like metal oxide, polymers and cellulose[8, 9]. The configurations of the optical fibre sensor can be made in several different aspects like the light source or the detector position (transmission vs. reflection), or may depends on the nature of the sensing mechanism such as evanescent field, gratings, interferometers. [10]. Sensor structure basically is composed from a source and receiver fibre which connected to the sensing fibre by a special connector as shown in Figure 1. To achieve sensing capability, the tip of the sensing fibre is usually coated with a sensing material[11] by several coating procedures as illustrates in Figure(1a). Several disadvantages associated with the coating layer like cracking, inhomogeneity and which led to low sensitivity [12].

However, using fibre optic without any coating is fast and durable to make direct reaction between light and active groups in solution or air due to the absorption of light as presented in Fig. 1b and c. Among the several types of optic fibres, the glass fibres are the best for the chemical sensing because it can pass visible light and near infrared. However, for the UV region quartz fibre is needed.

The absorption and changing the refractive index of the optrode are the processes which make conclude the changes in the concentration of active chemical groups by sending light through the optrode to the sample. The amount of light absorbed by the target is determined by measuring the light coupled out via a second optical fibre.

The present work proposed a new pH sensing system associated with laser which overcomes the many disadvantages of other sensors mentioned above. The dissociation of the acid group allows for determination of the pH in certain chemical reactors as well as the measurement of pH in the different solutions by the varying light intensity, comparable to the method reported before. This device is very useful and work to determine the variation of pH in water produced by the reverse osmosis system (RO) in different steps from the production and continuous pH monitoring is critical for the process control and final quality of water.
2. Experimental

The chemicals materials and solutions purchased from Sigma-Aldrich and that used without purification. Figure 2 shows the experimental setup for a new pH probe (optrode) is designed for industrial applications with all components that used. Transmission measurement of the solutions was carried out on a spectrophotometer type (Brolight) and used the laptop to register the results as present in figure 2. The optrode (the circled part in figure 2) was made in the multi steps. First, 25 cm of multimode fibre was covered by a wax then removed from chosen places, each one 2.5 cm. Second the fibre was cleaned by a serous of solutions with acetone then immersed in HF (50%) for 15 min then in double distilled water (DDW) for 10 min. then in KOH (5%) and in isopropanol alcohol for 10 min finally rinsing in DDW. Third the sensitivity of the fibre increase by the following procedure, the fibre treated in a mixture of H$_2$O$_2$ and H$_2$SO$_4$ for 30 min then rinsed in distilled water for 10 min and dried in nitrogen for 5 min. The ends of the fibre were polished carefully to ensure the good coupling behaviour of the launched light into the fibre during the detection measurement. This technique made the surface of the fibre more sensitive by adding active bonds to the surface of core.

Figure 1: The shapes of probes for pH sensing (a) end closed probe, (b) reflectance probe and (c) end to end probe[12, 13].

Figure 2: Scheme of the experiment measurement set up.
3. Results and discussion
To determine the transmission spectrum for the experiment before using optrode, a series of solutions are prepared at different pH values then tested by spectrophotometer. The transmission spectra of the solutions is shown in Figure 3, which present normal bands that attributed to alkaline and acidic forms[14]. The spectrum clearly shows decrease intensity with increasing pH values from the centre of the peak between 519-523nm.

![Figure 3: Transmission spectra of the solutions at different pH value without optrode](image)

The reason behind of that is come from the nature of interaction (absorption and scattering) of light with active groups in solution by the effect of light (electric field) on the ions and groups. The mechanism of interaction presents in Figure 4. For more understanding of the light (electric field) interact with the solution and effect on the transmission. Inside the water, there is an electric field created due to dissolving the acid or base. They are dissolving in water to positive and negative ions as show in figure 4, the HCl dissolve to (H\textsubscript{3}O\textsuperscript{+} eq.) and (Cl\textsuperscript{-} eq.) causes the polar water molecules to orient themselves in response to the electric field of light, and would cause an agglomerate of negatively charged ion (Cl\textsuperscript{-} eq.))[15, 16]. The water molecule tends to decrease this agglomeration and create the internal electric field which caused to more scattering by that ions and water molecules. Similarly, the same dissociation is proper for alkaline when dissolved in water.
The optrode element is immersed in solutions with different pH values and then washed in DDW after each test. Figure 5 shows the output power collected from the optrode; the main changes in spectral occur in a range from 500 to 700 nm. This is due to the changing of refractive index of optrode because of the solution and/or maybe explained by interaction of active groups of the optrode surface with the solutions. The refractive index variation effects on the intensity of light in the optrode [5]. The results are calibrated by plotting the maximum power with the standard pH which measured electrochemically at 590 nm. The best pH values detected by this method are between 2 to 10 as shown in the calibration curve inset Figure 5 with sensitivity at 0.015-0.2 1/pH. Comparing this result using transparent solution with those used methyl (red to orange) as indicator shows a substance different because the methyl solution has color which affects the light transmission through it [3, 17]. Furthermore, this method is suitable for a wide range of solutions.

4. Conclusions
The optrode is developed to direct responses for pH without any coating. It is treated with malty types of solutions to be further improved for pH detection, in a pH range from about 3 to 9 in aqueous solutions. The interaction of light with solutions and refractive index of optrode are explained. However, the light transmission is used to pH detection and calibrated with electronic equipment. It was found possible to determine the pH value of the sample, by comparing the transmittance of light with the calibration pH curve. Such optrode is expected to fit for pH measurements on small and huge volumes of aqueous samples in industry.

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