

# Highly Sensitive Fluorescence Optode Based on Polymer Inclusion Membranes for Determination of Al(III) Ions

F. B. M. Suah · M. Ahmad · L. Y. Heng

Received: 6 March 2014 / Accepted: 19 May 2014 / Published online: 29 May 2014  
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**Abstract** This paper reports the use of a polymer inclusion membranes (PIMs) for direct determination of Al(III) ions in natural water by using a fluorescence based optode. The best composition of the PIMs consisted of 60 wt.% (m/m) poly (vinyl chloride) (PVC) as the base polymer, 20 wt.% (m/m) triton X-100 as an extractant, 20 wt.% (m/m) dioctyl phthalate (DOP) as plasticizer and morin as the reagent, was used in this study. The inclusion of triton X-100 was used for enhancing the sorption of Al(III) ions from liquid phase into the membrane phase, thus increasing the optode fluorescence intensity. The optimized optode was characterized by a linear calibration curve in the range from  $7.41 \times 10^{-7}$  to  $1.00 \times 10^{-4}$  molL<sup>-1</sup> of Al(III), with a detection limit of  $5.19 \times 10^{-7}$  molL<sup>-1</sup>. The response of the optode was 4 min and reproducible results were obtained for eight different membranes demonstrated good membrane stability. The optode was applied to the determination of Al(III) in natural water samples. The result obtained is comparable to atomic absorption spectrometry method.

**Keywords** Aluminium(III) determination · Optode · Natural waters · Polymer inclusion membrane

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## Introduction

In recent years, the creation of more firm environmental control and monitoring is producing a need for simple and sensitive portable detection kits for monitoring the presence of the environmental contaminants. In that sense, the optical fibre chemical sensors or optodes have attracted growing attention due to their essential qualities such as capable for real time monitoring and remote sensing, immunity to electrical interference and ease of miniaturization [1–4]. It is well known that heavy metal ions denote the main environmental problem and their monitoring especially in water is essential. Al(III) in certain, is found in waste waters from metal processing industries and construction industries as well as water supply systems due to the use of Al(III) salt as coagulants in the water treatment plants.

The construction of optodes based on organic polymeric membranes or films have been carried out extensively for the last two decades [5–7]. These membranes not only act as the supports which reagents are immobilized, but also provide permeation for certain species. In this type of optode, the immobilization technique and the organic reagents used play massive roles in the construction of the optode. Generally, the immobilization of the reagent into the support materials is accomplished by chemical retention, covalent bonding or physical entrapment methods. But, in some cases the immobilized reagent which is responsible for the chemical reaction is often inaccessible to the target analyte which shall affect the optode performances such as response time, sensitivity, reversibility and lifetime.

In order to overcome this problem, a couple of methodologies have been proposed. The introduction of novel reagents and schemes [8], lipophilization of the dye molecules [9], use of sol-gel [10, 11] and use of ion-exchanger [12] are the examples of the approaches that have been carried out. Although these approaches have been proven successful, yet

some of these optodes are still lack of information on the optimization parameters such as sensitivity, lifetime and reversibility.

In this work, an improved fluorescence technique has been employed for the construction of an optode for the determination of Al(III) ion in water samples. By using the fluorescence technique rather than other techniques, the constructed optode has produced greater sensitivity and selectivity for the determination of Al(III) ion [13]. In terms of reagent dye, this work focused on the use of morin, neutral reagent from flavonol group, which is one of the most sensitive dyes for fluorimetric determination of Al(III) ion [14]. A plasticized poly (vinyl chloride) (PVC) optode based on polymer inclusion membranes (PIMs) technique has been prepared and characterized in order to evaluate its potential application for Al(III) ion sensing. A tremendous improvement of the reagent sensitivity is achieved after its immobilization into the membrane matrix thus made this novel system very encouraging for Al(III) sensing.

## Experimental

### Materials

All chemicals used were analytical grade unless stated otherwise. All solutions were prepared by using MilliQue distilled deionized water. Reagents used in the study were aluminium potassium sulphate dodecahydrate (Merck); morin (Fluka), polyoxyethylene(9.5)-*t*-octyl-phenol (triton X-100), (Fluka), poly(vinyl chloride) (PVC) (high molecular weight 200,000) (Sigma-Aldrich), dioctyl phthalate (DOP) (Fluka), ethanol 95 % (Hmbg Chemical), Nitric acid (HNO<sub>3</sub>) (BDH) and tetrahydrofuran (THF) (BDH). Other reagents such as sodium fluoride, disodium EDTA, zinc sulphate, mercury chloride, cobalt chloride, ferrous(II) chloride, iron(III) sulphate, beryllium chloride, mercuric chloride, magnesium sulphate, barium nitrate, lead nitrate, cadmium sulphate were obtained from Merck.

### Preparation of the Solutions

The Al(III) stock solution (10 mgL<sup>-1</sup>) was prepared daily by dissolving 0.1758 g of aluminium potassium sulphate dodecahydrate in water and diluting to 1 L with water. The stock solution of morin (5.0 × 10<sup>-3</sup> molL<sup>-1</sup>) was prepared by dissolving 0.1691 g of morin in 85 mL of 95 % ethanol and diluting to 100 mL with water. Triton X-100 was used without further purification. Triton X-100 was prepared by diluting the surfactant to the percent required with ethanol. An acetic acid buffer containing 1.0 mol L<sup>-1</sup> CH<sub>3</sub>COOH (BDH) and sodium acetate (Analar) containing 1.0 molL<sup>-1</sup> were prepared too. All of the standard solutions for Al(III), ethanolic morin solution,

triton X-100 solution and buffer solutions of pH 3–7 (acetic acid-sodium acetate buffer system) were prepared at room temperature of 25 °C.

### Apparatus

The pH was measured to a pH of ±0.01 with a Hanna Instrument model HI 2211 pH Meter. The pH meter was calibrated using pH=4, pH=7 and pH=10 standard buffer solutions (Hamilton). The thickness of the membrane samples was measured using a digital microscope (Rax Vision Y 103) equipped with JVC digital colour video camera (model TK-C751EG) with an accuracy of ±0.001 mm. The fluorescence measurement of each optode was carried out by placing the membrane on the tip of fiber optic which attached to the fluorescence spectrometer. The spectra were recorded using fluorescence spectrometer fitted with optical fiber sensor accessories model LS55 from Perkin-Elmer and operated with 5.0 nm slits for excitation and emission measurements.

### Membrane Preparation

Solution of PVC was prepared by dissolving 300 mg of PVC in 10 mL of THF. A separate solution containing triton X-100 (100 mg) and DOP (100 mg) was prepared in 5 mL of THF. Then both of these solutions were mixed and stirred for two hours to form a homogenous casting solution. After that, the casting solution was spread on a 9 cm diameter flat bottom Petri dish, which kept on a levelled surface for uniform membrane formation. The lid of the Petri dish was covered with filter paper to allow gradual evaporation of THF from the casting solution. After leaving the THF to evaporate from the casting solution for two days, the transparent membrane was peeled off from the Petri dish. The membrane was then washed with deionized water for three times. Then the membrane was immersed and stirred in 20 mL morin (6.0 × 10<sup>-4</sup> molL<sup>-1</sup>) for four hours to form a uniform colour on it. The membrane was washed again with deionized water for three times to remove unbound reagent and soluble component and dried between fold of tissue paper. Finally, the membrane was kept into sealed airtight plastic bag. The area of the membrane was kept as 2 cm × 1 cm through the experiment.

### Fluorescence Measurement

The effect of pH on optode performance was studied by equilibrating the membrane with 25 mL aqueous solution of pH 3.0–7.5 containing 5.0 × 10<sup>-5</sup> molL<sup>-1</sup> of Al(III) for a period of 4 min and the emission was recorded at λ<sub>max</sub> = 495 nm, with the slit width of 5 nm. The influence of the concentration of triton X-100 on emission intensity was studied with fixed concentration of Al(III) and morin with variables concentrations of triton X-100 between 1 and 30 % (m/m), while the

influence of morin concentration was studied by varying the concentration of morin solution which was used in the preparation of the membrane. The stability of the optode was tested by monitoring the emission ( $\lambda_{\text{max}}=495$  nm) of the optode in contact with aqueous solution of Al(III) over a period of two weeks.

Fluorescence measurements of the optode samples were carried out to determine the intensity of Al(III)-morin-triton X-100 complex formed in optode samples. The intensity of the complex acts as a function of Al(III) concentration. Therefore, samples containing known amount of Al(III) (volume 25 mL) were prepared for this purpose. The pH of these samples solutions were adjusted to pH 6.0. Initially, a membrane of 2 cm×1 cm was immersed in known amount concentration of Al(III) and was well-stirred for 4 min. The membrane was washed again with deionized water and dried with folds of tissue paper. Next, the dried membrane was attached to the fiber optic tip and its emission intensity was taken. This procedure was repeated for other Al(III) samples. Freshly prepared membrane was used for every measurement. The emission measurements of these samples were carried out at 495 nm.

In order to study the kinetics, the optode was placed in a stirred known amount concentration of Al(III) (25 mL) at pH 6.0 for 12 min. The difference in emission intensity of the optode was measured occasionally by removing the optode from the Al(III) solution and attaching it to the fiber optic tip. The emission was quantified at  $\lambda_{\text{max}}=495$  nm.

#### Reversibility Studies

The reversibility of the optode was examined by immersing the optode in a well-stirred 15 mL aqueous solution of sodium fluoride ( $1.0 \text{ molL}^{-1}$ ) buffered at pH 6.0 for a specified time. The emission was measured at 495 nm.

#### Selectivity Studies

The degree of interference of ions such as EDTA,  $\text{F}^-$ ,  $\text{PO}_4^{2-}$ , Ba(II), Be(II), Ca(II), Cd(II), Co(II), Cu(II), Fe(II), Fe(III), Hg(II), Pb(II) and Zn(II) were studied too. This was examined by equilibrating the membrane optode with solution containing known amount of Al(III) ( $5.0 \times 10^{-5} \text{ molL}^{-1}$ ) and varying the amounts of interfering ions at pH 6.0.

#### Application to Real Samples

For the determination of Al(III) in real samples, Water from lakes and river were collected in 1 L polyethylene bottles. Upon collection, 2 ml of 69–70 %  $\text{HNO}_3$  was added to the water samples for preservation. Samples were analyzed less than 2 h after sampling. Water samples with visible suspended solids or the turbidities were filtered through 0.45  $\mu\text{m}$

(Whatman 45) membrane filter before being analysed. All water samples were used without any further dilution.

## Results and Discussion

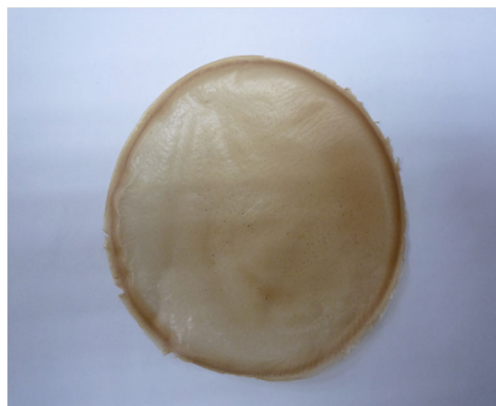
### Choice of Reagent and Membrane Composition

Morin is a fluorogenic reagent for various metal ions including Cd(II), Fe(III), Pb(II) and Zn(II). Its selectivity to certain ions can be achieved through appropriate combination with masking agents. Morin was chosen in this study because it is a reagent that is extensively used in the fluorimetric determination of Al(III) and studies show that it is the most sensitive and selective reagent [14–16]. An aqueous solution of morin is orange and its color changes due to reaction with Al(III) at specific pH as a result of proton dissociation [17]. In the present work, the creation of bright yellowish complex was observed when the PIMs optode was equilibrated with Al(III).

Parameters influencing membrane composition, such as the type of base polymer and plasticizer used, mass composition and thickness have been studied. The membrane produced in this study was homogenous, transparent and self-supporting (Fig. 1). Its average thickness was found to be  $20 \pm 5$   $\mu\text{m}$  making it suitable for use in stirred aqueous solution environment and has good mechanical strength.

Several combinations of the matrix-forming polymer (PVC), plasticizer (DOP), non-ionic surfactant (triton X-100) and the reagent (morin) were studied to optimize the Al(III) uptake in the membrane with pH of 6.0. Table 1 lists different membrane compositions and its emission at 495 nm. Unmistakably, all the membranes need a plasticizer (DOP) to form homogenous and transparent membranes. The role of plasticizer in the preparation of the membrane is to improve its chemical and mechanical stability by reducing intermolecular attractive forces among chains in the polymer systems. As for the type of base polymer used in this study, PVC has been chosen owing to its special abilities, for instance, provide permeation selectivity for certain species, its solid support, excellent suitability for plasticization and easy availability.

The proportions of the membranes were optimized to increase their emission, uniformity and mechanical strength. To determine the optimum composition, the membranes were prepared by fixing the mass to 500 mg and varying the mass composition of different components (PVC, triton X-100 and DOP). A comparison of emissions of different membranes after loading them with fixed amounts of Al(III) at pH 6.0 shows that membrane IV with the composition of PVC=60 wt.% (m/m), triton X-100=20 wt.% (m/m), DOP=20 wt.% (m/m) offers the highest emission intensity at 495 nm (Table 1). This membrane is also transparent and has no fracture confirming its distinctive optical and



**Fig. 1** A photo of optode's produced (before the reaction with Al(III) ions) in this study

mechanical properties. Therefore the membrane was chosen for further studies.

The optimum concentration of triton X-100 used in the preparation of the membrane was studied by varying its concentration. The maximum emission of the membrane after contact with Al(III) was achieved with 20 wt.% (m/m) of triton X-100. This is because the concentration of triton X-100 is above its critical micelles concentration (cmc) value, which indicates that this amount is sufficient to provide extra solubility for morin to contact with Al(III) at an optimum condition within the membrane. Further increase of triton X-100 concentration did not have any significant effect on membrane response.

The consequence of morin concentration on the membrane response was studied by evaluating numerous concentrations of morin during immobilization. Figure 2 shows the influence of morin concentration used in the preparation of the membrane with fixed concentration of Al(III) and membrane composition of PVC=60 wt.%, triton X-100=20 wt.%, DOP=20 wt.%. The emission of the membrane was optimal at  $6.0 \times 10^{-4} \text{ molL}^{-1}$ . This emission was achieved as morin's concentration achieved complete equilibration with Al(III). An

optimum concentration of morin was therefore employed for further studies.

### Spectral Characterization

Morin has been used previously in immobilized form for preconcentration purposes, e.g., for the quantitative determination of Al(III) [18, 19]. However, both sets of sensors have limited dynamic range, the reagent being prone to leaching, low selectivity and due to the irreversible nature of sensors. To overcome those problems, an innovative approach was followed. In this study, morin immobilized in the PIMs optode consists of PVC: triton X-100: DOP. Figure 3 presents the fluorescence spectra of the blank optode (PVC: triton X-100: DOP: morin), control optode (PVC: DOP: morin) upon contact with Al(III) and PIMs optode (PVC: triton X-100: DOP: morin) upon contact with Al(III). The maximum emissions ( $\lambda_{\text{max}}$ ) for the blank, control and PIMs optode are 482, 482 and 495 nm, respectively. Interestingly, there was a large bathochromic shift in the emission of the PIMs optode from the blank optode, which was from 482 to 495 nm. This unique phenomenon occurs largely owing to the presence of triton X-100 in the PIMs optode. The presence of triton X-100 in the PIMs optode can intensify the metal ion complex emission band as well as prominent bathochromic shift of the metal ion complex emission. According to Von Wandruszka [20], such consequences are due to the formation of complex of higher order (higher ligand: metal ratio) on the interfaces of triton X-100. Further, triton X-100 will provide a micro-environment between morin and Al(III), which enhances the solubility of the system. Thus, the reaction between morin and Al(III) will take place without outside interference. As a result of the continuous reaction between morin and Al(III), the deprotonation of an OH group of morin occurred extensively which actually contributed to the large red shift observed in this study. It is also noted that the emission at  $\lambda_{\text{max}}$  495 nm increased proportionally with increase in the amount of Al(III) upon contact with PIMs optode.

**Table 1** The membranes compositions

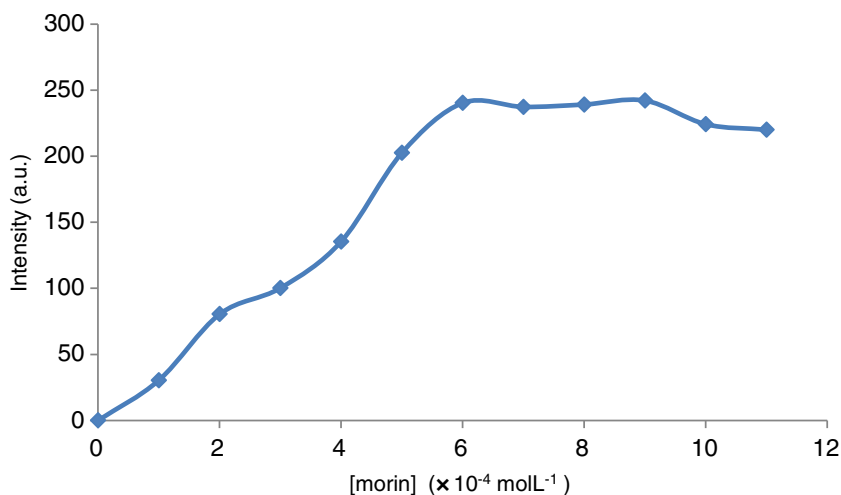
Membrane	PVC (mg) ( $\pm 0.2$ )	Triton X-100(mg) ( $\pm 2.0$ )	DOP (mg) ( $\pm 0.5$ )	Composition (wt.%)	Maximum emission (a.u) <sup>a</sup>
I	350	150	–	70:30:00	Non forming membrane
II	350	100	50	70:20:10	206.45
III	300	150	50	60:30:10	218.11
IV	300	100	100	60:20:20	240.25
V	300	50	150	60:10:30	185.44
VI	250	250	–	50:50:00	Non forming membrane
VII	250	150	100	50:30:20	214.92
VIII	250	100	150	50:20:30	162.19
IX	200	350	50	40:50:10	Non forming membrane
X <sup>b</sup>	300	–	200	60:00:40	61.82 <sup>c</sup>

<sup>a</sup> Emission measured at 495 nm, [Al(III)]= $5.0 \times 10^{-5} \text{ molL}^{-1}$ , pH=6.0

<sup>b</sup> Control optode (consist of PVC: DOP: morin)

<sup>c</sup> Emission measured at 482 nm, [Al(III)]= $5.0 \times 10^{-5} \text{ molL}^{-1}$ , pH=6.0

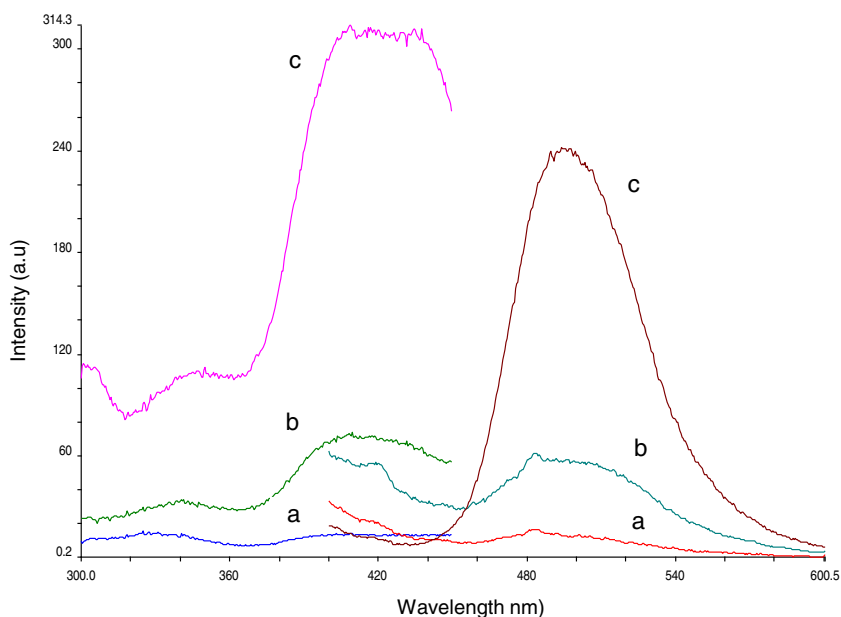
**Fig. 2** Concentration of morin used during preparation of the membrane. Conditions: [Al(III)]= $5.0 \times 10^{-5}$  molL<sup>-1</sup>, pH 6.0



From the spectra above, it is clear that the emission of the PIMs optode is also higher compared to the emission of the blank optode. This is the other significant result obtained from the present study. The enhancement of PIMs on contact with Al(III) increased about four fold compared to the control. The factors responsible for this increased emission have been credited to the triton X-100 abilities, which shield the optode from vibrational quenching of the hydrogen bond structure of water, increase in local viscosity of morin-Al(III) reaction (providing extra solubilization) and reduced access of other solvent-borne quenchers to actual contact with optode. The outcome is that triton X-100 provides protection to the excited single state so that the radiative process can compete completely with the quenching processes such as water and oxygen [17].

The sensitivity enhancement of the PIMs optode also depends on the type of extractants employed. In this study, triton X-100, a nonionic extractant, has been chosen. Triton X-100, which belongs to polyoxyethylene group, comprises two parts, the hydrocarbon tail (bounded to the interior core of the micelle) and polar head group (hydrated to the polyoxyethylene group at the outer sphere). Metal complexes that have large affinity power to the polyoxyethylene group may be incorporated into this area. Morin could be dissolved by this phenomenon, as this species has an OH group, which interacts with the ether oxygen of polyoxyethylene group by hydrogen bonding. The formation of the Al(III)-morin complex in the presence of triton X-100 medium could be explained by considering that the solubilization process is dynamic. It seems that morin dissolves in triton X-100, reacts

**Fig. 3** Excitation and emission spectra of **a** blank optode (PVC: triton X-100: DOP: morin) **b** control optode (PVC: DOP: morin) equilibrated with Al(III) and **c** PIMs optode (PVC: triton X-100: DOP: morin) equilibrated with Al(III). Conditions: [Al(III)]= $5.0 \times 10^{-5}$  molL<sup>-1</sup>; [morin]= $6.0 \times 10^{-4}$  molL<sup>-1</sup>; pH 6.0



with Al(III) ions to form a non-polar complex. In addition, the structure of triton X-100, which has a much shorter tail, also plays a major part in enhancing the emission of the optode. The short tail of triton X-100 is also capable of increasing the attractive force (including van der Waals attraction between hydrocarbon parts) between morin and Al(III). The emission obtained from the PIMs optode upon contact with Al(III) was found stable for a period of 48 h. No significant changes of the emission intensity were observed.

#### pH Effect

The sensitivity of the optode is largely influenced by the pH of equilibrating aqueous solution used in the study. Therefore it is necessary to maintain the hydrogen ion concentration of the sample. The optimum pH value of the optode was examined by loading Al(III) in the optode at different pHs and monitoring the emission change at 495 nm (Fig. 4). Maximum emission of the optode was achieved at pH 6.0. Emission at lower and higher pH values was very low. The former happened because of the changes in protonation of immobilized morin due to low  $pK_a$  value [21], while the latter happened due to the formation of  $Al(OH)_3$  in solid form, which effectively eliminates Al(III) from binding to the immobilized morin.

#### Response Time

Besides the chemical parameters of the membrane (e.g. composition of membrane and concentration of reagent used), the response time of the optode is also influenced by the physical parameters of the optode-sensing configuration. In this study, the influence of two physical parameters, namely, stirring effect and membrane thickness, were investigated.

By stirring the analyte solution (in this case Al(III)), a remarkable outcome on the response time of the optode has been observed. Figure 5 demonstrates that the emission

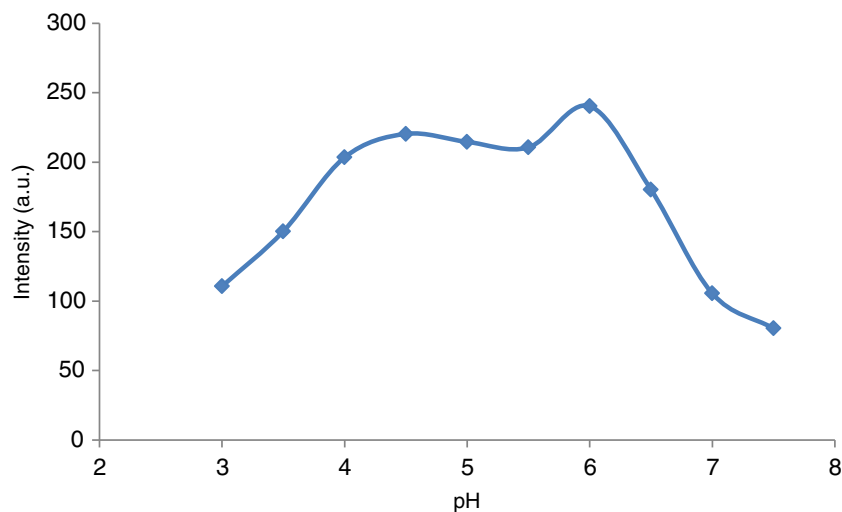
increases higher when the Al(III) solution is stirred compared to that without stirring. After 5 min of exposure, the response curve of the optode became linear as the optode reached saturation once the quantity of Al(III) exceeded the binding capacity of the optode. The increase in the emission reading could be attributed to the fact that stirring process could facilitate the diffusion of Al(III) ions across the membrane to the reagent (morin), which eventually speed up the reaction between Al(III) and morin. In contrast to the optode without stirring, the diffusion of Al(III) across the membrane depended solely on the concentration gradient factor [5]. Therefore, all the measurements were carried out after stirring the optode for 4 min in the Al(III) solution.

The average thickness of the membrane prepared in this study was found to be  $20 \pm 5 \mu\text{m}$ . The response time of this optode with complete mass transfer (co-extraction-based optode) is within an order of minutes indicating that the optode's thickness is sufficient to accelerate the complete mass transfer of Al(III) ions to go through the optode. Although it is desirable to have a thinner optode to increase emission, a further reduction in thickness would influence the mechanical strength of the optode and cannot be used in the stirred aqueous solution environment.

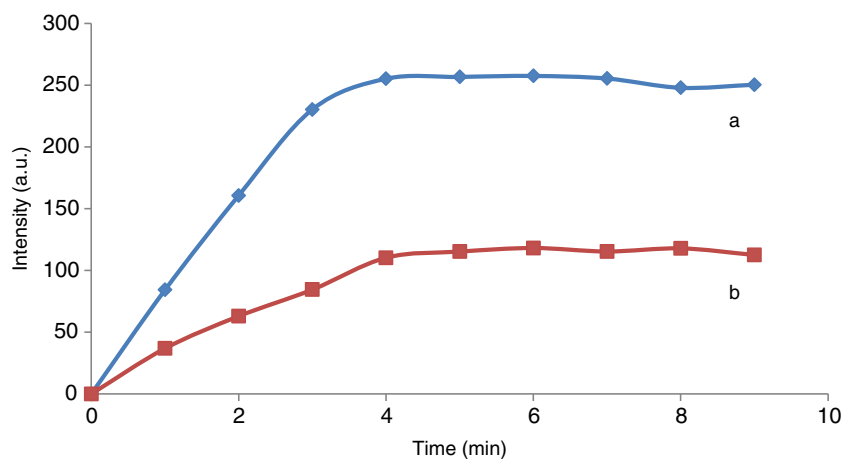
#### Kinetic Study

The dynamic response to Al(III) was monitored as a change in emission intensity at 495 nm. Characteristic response curves found for different concentrations of Al(III) are shown in Fig. 6. The optode displayed significant changes on exposure to different concentrations of Al(III) at pH 6.0 with the optode's steady response depending on the concentration of Al(III). After 6 min of exposure to Al(III), the optode's response was linear or unchanged because of the saturation of the reagent phase with the analyte. Thus, the time used for each measurement was fixed at 4 min since it provides a good

**Fig. 4** pH dependence of the emission intensity of the PIMs optode in aqueous buffer. Conditions:  $[Al(III)] = 5.0 \times 10^{-5} \text{ molL}^{-1}$ ;  $[morin] = 6.0 \times 10^{-4} \text{ molL}^{-1}$



**Fig. 5** The effect of **a** stirring and **b** non stirring on the optode's response. Conditions:  $[Al(III)]=5.0 \times 10^{-5} \text{ molL}^{-1}$ ;  $[morin]=6.0 \times 10^{-4} \text{ molL}^{-1}$



sensitivity and a wide dynamic range of determination of Al(III).

#### Stability of the Optode

The optode used in this study was found to be stable and produced constant emission reading up to 14 days. It was also noticed that morin did not leach out from the optode at pH 6.0 and up to pH 6.5. This is likely due to the nature of the optode which contains plasticizer in which its function is to bind the components within the optode thus providing additional chemical stability.

#### Dynamic Range and Reversibility

The working range of the optode was studied under optimum experimental conditions, with an average of three emission readings at each concentration. The readings are plotted against Al(III) concentrations. The dynamic range of the system after 4 min of reaction was determined to be linear from  $7.41 \times 10^{-7}$ – $1.00 \times 10^{-4} \text{ molL}^{-1}$  with a correlation coefficient ( $R^2$ ) of 0.996. In addition, the limit of detection (LOD) was

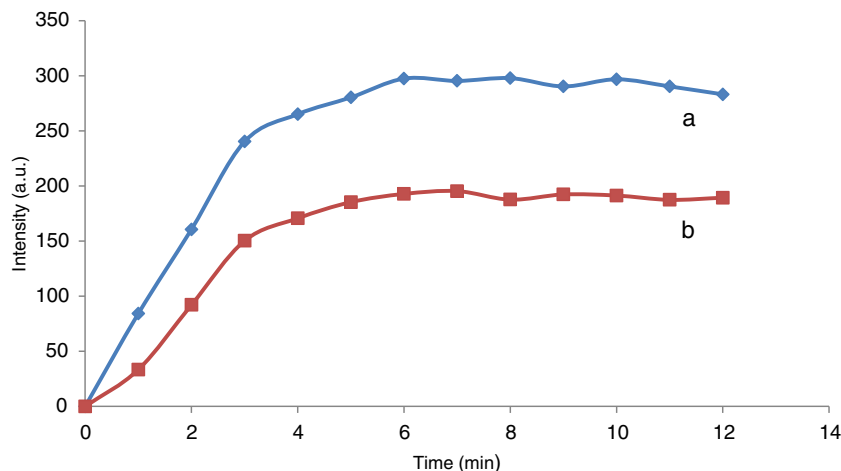
evaluated using  $3\sigma/s$ , where  $\sigma$  is the standard deviation of the blank signals and  $s$  is the slope of the linear calibration plot. The calculated LOD was found to be  $5.19 \times 10^{-7} \text{ molL}^{-1}$ .

The reversibility of the optode was studied by repeating three of its cycles with  $5.0 \times 10^{-5} \text{ molL}^{-1}$  Al(III) aqueous solution and regenerate the optode with  $1.0 \text{ molL}^{-1} \text{ F}^-$  aqueous solution at emission  $\lambda_{\text{max}}=495 \text{ nm}$  and pH 6.0. The results obtained from reversibility analysis are presented in Fig. 7. Apparently, the optode is fully reversible. Even though Al(III) could be displaced by  $\text{F}^-$  or  $\text{Cl}^-$  ions within a short period of time [22], it was observed that it took some moment for Al(III) to be removed from the optode, with a complete cycle between 8 and 10 min. This phenomenon could be contributed to the structure of morin itself. The existence of hydroxyl groups in the morin molecule is expected to repulse the approaching  $\text{F}^-$  ions during the regeneration process thus delaying the removal of Al(III) ions from the optode.

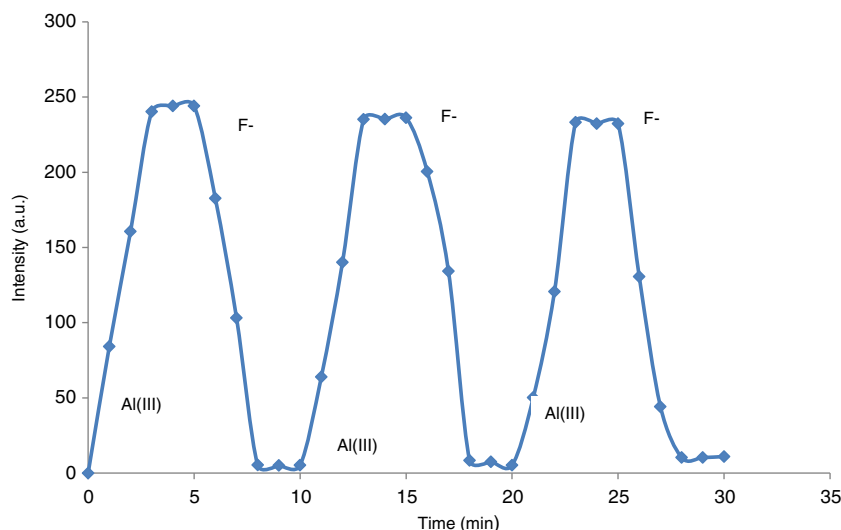
#### Repeatability and Reproducibility

In this study, the repeatability of the optode was studied by measuring the response of the same optode to the Al(III)

**Fig. 6** Response of the optode to **a**  $5.0 \times 10^{-5} \text{ molL}^{-1}$  and **b**  $7.41 \times 10^{-6} \text{ molL}^{-1}$  Al (III) ions



**Fig. 7** Reversibility of the optode when exposed to  $5.0 \times 10^{-5} \text{ molL}^{-1}$  Al(III) and  $1.0 \text{ molL}^{-1} \text{ F}^{-}$



**Table 2** Relative error for different interfering ion with  $[\text{Al(III)}]=5.0 \times 10^{-5} \text{ molL}^{-1}$

Ion	Mole ratio (Al(III): ion)	Intensity	Intensity error	Relative error (%)
EDTA	1:01	232.8	-7.45	-3.1
	1:05	223.87	-16.38	-6.81
$\text{F}^{-}$	1:01	220.14	-20.11	-8.37
	1:05	204.03	-36.22	-15.06
$\text{PO}_4^{-2}$	1:01	233.93	-6.32	-2.63
	1:05	229.04	-11.21	-4.67
Be(II)	1:01	248.9	8.65	3.6
	1:50	252.57	12.32	5.13
Ca(II)	1:01	240.25	n	n
	1:50	240.25	n	n
Cd(II)	1:01	245.37	5.12	2.13
	1:50	249.03	8.78	3.65
Co(III)	1:01	243.46	3.21	1.37
	1:50	243.97	3.72	1.55
Cu(II)	1:01	247.22	6.97	2.9
	1:50	253.46	13.21	5.5
Fe(II)	1:01	244.23	3.98	1.66
	1:50	245.9	5.65	2.35
Fe(III)	1:01	256.57	16.32	6.79
	1:50	291.36	51.11	21.27
Hg(II)	1:01	243.93	3.68	1.53
	1:50	245.31	5.06	2.11
Mg(II)	1:01	243.98	3.73	1.84
	1:50	244.21	3.96	1.65
Pb(II)	1:01	245.68	5.43	2.26
	1:50	247.81	7.56	3.15
Zn(II)	1:01	249.61	9.36	3.9
	1:50	254.9	14.65	6.1

n No interference

aqueous solution ( $5.0 \times 10^{-5} \text{ molL}^{-1}$ ) for eight times. On the other hand, the reproducibility of the optode was studied by measuring the response of eight different optodes, which were prepared separately. It was perceived that repeatability of the membrane was better than its reproducibility. The relative standard deviation (RSD) for repeatability and reproducibility of the optode were found to be 1.95 % and 5.02 %, respectively. These results prove that the optode is operational because the RSD value for both parameters is below or within the acceptable limit (<5.0 %) [23].

### Selectivity Studies

Results in Table 2 show that most ions have low interference or did not interfere at all with the measurement of the constructed optode, even when the interference concentration increased up to 5 or 50 times higher than the concentration of Al(III) ( $5.0 \times 10^{-5} \text{ molL}^{-1}$ ). These results also prove that these ions formed complexes with morin, but they were less stable compared to Al(III)-morin complex. The notable selectivity displayed by the optode is conceivably contributed by triton X-100, which plays a part in enhancing the sorption of

**Table 3** Determination of Al(III) in natural water samples using the PIMs optode

Sample	Spiked Al(III) ( $\mu\text{g mL}^{-1}$ )	Optode found ( $\mu\text{g mL}^{-1}$ ) (n=3)	Recovery (%) (n=3)
Putrajaya Presint 18 lake	0	0.105 <sup>a</sup>	–
	2	2.25	106.9
Putrajaya Presint 2 lake	0	0.182 <sup>a</sup>	–
	1.35	1.647	107.52
Semenyih river	0	0.420 <sup>a</sup>	–
	0.2	0.596	96.18

<sup>a</sup> The samples were determined by the AAS method



ions (especially metal cations) from liquid to membrane phase. Only  $F^-$  and  $Fe(III)$  were found to reduce the emission of the optode. As for  $F^-$ , the interference was expected since it was known to form a stable complex with  $Al(III)$  and consequently, decreased the analytical signal. However, interference of  $F^-$  with the determination of  $Al(III)$  could be eliminated with the addition of 150 mM  $Be(II)$ , whereas that of  $Fe(III)$  could be reduced by introducing 10 mM of 1,10-phenanthroline.

### Application to Real Samples

In order to examine the practical application of the method, some spiked lake water samples and spiked river water samples with different amounts of  $Al(III)$  were analyzed by using the optode. As seen in Table 3, the result of each optode recovery is satisfactory. Therefore, the proposed optode is considered sensitive, selective and could be applied for determination of  $Al(III)$  in real samples.

### Conclusion

The PIMs optode produced in this study was homogenous, transparent, has a good mechanical strength and relatively easy to prepare. The sensitive and selective determination of  $Al(III)$  was achieved by immobilizing morin reagent in a plasticized membrane containing triton X-100. Low interference at the working wavelength was noticed from other interferents. The PIMs optode reacts to  $Al(III)$  at emission maximum of 495 nm by changing colour from orange to bright yellowish orange. It is also sensitive to  $Al(III)$  within the range of  $7.41 \times 10^{-7}$ – $1.00 \times 10^{-4}$  molL<sup>-1</sup> for an equilibrium time of 4 min. The PIMs optode is also sensitive to pH, and the study must be carried out in buffered solution of pH 6.0.

**Acknowledgments** This work was supported by the Ministry of Higher Education of Malaysia within project FRGS 1/2011/ST/USIM/01/1 and by the Universiti Sains Islam Malaysia within project Grant PPP/FST-05-12711, which is gratefully acknowledged.

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