**Preparation and characterization of a novel optical chemical sensor for
determination of trace amounts of Praseodymium ion by UV/Vis
spectrophotometry**

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Abstract

In the present work, a novel optical chemical sensor (optode) was prepared based on impregnation of N, N'-bis (salicylidene)-1, 3-ethylenediamine (BESA) Schiff base into mesoporous SBA-15 paste for determination of trace amounts of Praseodymium (Pr) ion by UV/Vis spectrophotometry. The sensor was fabricated by dip-coating triacetylcellulose membrane into indicator solution. The proposed optical sensor was prepared through a routine procedure and characterized by various techniques such as ATR-FT-IR and SEM analyses. This optode exhibited a linear range of 10 to 190 ng mL⁻¹ for Pr(III) ion concentration with a detection limit of 5.0 ng mL⁻¹. The value of the response time for the newly synthesized optode was within 100 s while depending on the Pr(III) ion concentration. The proposed optode showed low detection limit, fast response time and high selectivity with respect to the group of transition metal ions (Ce³⁺, Nb³⁺, La³⁺, Cr³⁺, Zn²⁺, Hg²⁺, and Fe²⁺ ions). The optode was successfully regenerated with a mixture of thiourea and NaOH solution and the response was reversible with the relative standard deviation (R.S.D.) of 1.6%. The optode was stable and stored for at least 17 days without any considerable change in its sensitivity. Finally, the developed optode was applied to determine the Pr(III) ions in spiked samples.

Keywords: Optical sensor; UV/Vis spectrophotometry; Praseodymium; Mesoporous SBA-15 past; Dip-coating; Triacetyl cellulose

1. Introduction

Lanthanides are important elements from an industrial point of view. Praseodymium which is one of the most abundant rare earths, has attracted an extensive interest due to its application in atomic batteries [1], color televisions, fluorescent lamps, energy-saving lamps and glasses as well as a core material for carbon arc lights which are generally used in the motion picture industry. It is dumped through different places in the environment, and mainly can be produced at petroleum industries [2]. It can also penetrate into the environment by household stuffs which are thrown away. Praseodymium is being gradually accumulated by soils and water resources, and eventually would lead to increase the concentrations of Pr(III) in human body, animals and soil particles via the food chain [3]. Water soluble compounds of praseodymium are considered mildly toxic, while its insoluble compounds are non-toxic. According to the some experiments had been performed on animals, praseodymium and its compounds caused lung and liver damage [4, 5]. In rats, inhalation of praseodymium caused pulmonary edema and dyspnea and caused liver edema, pleural effusions, and pulmonary hyperemia. Exposure to praseodymium compounds in humans may cause lung disease [6]. Therefore, the monitoring of low and high level of Pr(III) ions in accurate, repeatable and reversible way is of high importance. Nowadays, many instrumental methods have been reported in order to determination of Pr(III) ion in real sample including absorption spectra of 4d electron transitions [7], derivative spectroscopy [8], flotation-spectrophotometric [9], polyvinylchloride (PVC)-membrane electrode [3], PVC-membrane sensor [10-11], resonance light scattering [12], fluorescence enhancement sensor [2], chemiluminescence [13] and some other spectroscopic methods [6, 14]. However, all of these techniques usually require proficiency and infrastructure backup. Moreover, their performance is expensive and nearly time consuming. Therefore, a simple and low cost method is needed to be developed for the analysis of Pr(III) ions while dealing with large number of environmental samples. In this cases, optical sensors can be used for this purposes with simple instrumentation and suitable for array fabrication. Among different factors affecting the outcome of optical sensors, type of polymer matrix has a significant effect [15, 16]. Many supporting materials such as PVC [17-19] or sol-gel [20, 21] can be employed to prepare the optical sensors. In this work, a mesoporous SBA-15 matrix was synthesized by hydrothermal method introduced by Tadjarodi et al. [22]. The mesoporous SBA-15 past was formed by the method proposed by Michael Gratzel and coworkers for TiO₂ nanoparticles powder where the difference is that the TiO₂ was used instead of mesoporous SBA-15 [23]. The current study presents a highly selective

Praseodymium sensor based on a novel technique and ionophore which corresponds to determination of Pr(III) ions with a wide concentration range and low detection limit.

2. Experimental

2.1. Reagents and Materials

Buffer solutions were prepared from boric acid/sodium acetate and phosphoric acid (0.04 mol L^{-1} each), and then pH adjustments were carried out by the addition of sodium hydroxide and hydrochloric acid solutions (1.0 mol L^{-1}). A stock solution of 1000 ppm Pr(III) solution was prepared by weighing 0.025 g of praseodymium nitrate hexahydrate (Fluka) and adjusting the volume to 25 mL. The standard solutions of lower concentrations were prepared by suitable dilutions of the stock solution with deionized water. Metal cations applied for evaluation of the effect of interferences were based on their nitrate salts.

2.2. Instrumentation

Spectroscopic measurements were performed using a PG Instruments T80+ UV/Vis spectrophotometer with 1.0 cm quartz cells. Also, the pH measurements were carried out with a Methrom double junction glass electrode and a Methrom 691 pH meter. The morphology of samples was studied by scanning electron microscopy (SEM: KYKY-EM3200) under an acceleration voltage of 26 KV. The FT-IR spectra of compounds were recorded on a shimadzu instrument in the range of $500\text{--}4500 \text{ cm}^{-1}$. X-ray diffraction (XRD) pattern was recorded by an automated Philips X'Pert X-ray diffractometer (40 kV and 30 mA) for 2θ values over $2\text{--}10^\circ$. The BET Surface area and BJH analysis were studied by Micromeritics Instrument. The ultrasonic homogenization was performed using an elmasonic S 60/ (H) sonicator.

2.3. Preparation of mesoporous SBA-15 paste

SBA-15 was synthesized by the hydrothermal method introduced by Zhao et al., using Pluronic P123 as a template, tetraethylortosilicat (TEOS) and HCl to cause the media acidic [22, 24]. To do this, 4.0 g Pluronic of P123 ($M_w = 5800$), 90 mL of 2.0 M hydrochloric acid and 21 mL deionized water was stirred for 5.0 hours at room temperature. Then, 6.8 mL of TEOS was slowly added to the above solution and stirred at the 40°C for 24 hours. The mixture was kept in an oven at 100°C for 24 hours in order to get sterilized. The synthesized

product was then filtered, washed, dried, and calcinated at 600 °C for 6.0 h in order to remove the residual templates.

Mesoporous SBA-15 paste was prepared using the method proposed by Michael Gratzel et al. The fabrication process for SBA-15 pastes in the ambient air at room was described in Fig. 1. At each step, liquids were added drop wise into an agate mortar. The diameter of the mortar was ca. 5.0 cm. The SBA-15 powders stuck inside of the mortar should be removed by a plastic spatula in order to grind large aggregates. The dispersed particles of SBA-15 were transferred into a tall beaker by using excess amounts of ethanol (100 ml) and stirred with a 2.0 cm long magnet tip at 300 rpm. Anhydrous terpineol (Fluka) and the mixture solution of two ethyl celluloses in ethanol were added, followed by stirring and sonication. The contents in dispersion were concentrated by evaporator at 40 °C into the oven.

Fig. 1

2.4. Ligand Preparation

N,N'-bis(salicylidene)-1,3-ethylenediamine (BSEA) is a tetradentate ligand without any amino group in the ring. The dye molecules can be linked to the cellulose acetate film by special treatment. BSEA was synthesized by refluxing a mixture of 3.28 g N-(2-aminoethyl)-salicylaldehyde (AESI, taken from our previous report (Ref. [25])), 2, 4-dihydroxy benzaldehyde (2.76 g) and ethanol (50 mL) in an oil bath at 75 °C for 3 h. Then, the reaction mixture was cooled to room temperature. The yellow crystals were filtered, and subsequently were washed with ethanol and dried at room temperature (Fig. 2) [25].

Fig. 2

2.5. Preparation of the sensing film

The immobilized indicator on triacetyl cellulose was prepared according to the following procedure: The transparent triacetyl cellulose membranes were produced from waste photographic film tapes that have been previously treated for a few minutes with commercial hypochlorite in order to remove the colored gelatinous layers. In order to increase the porosity of the membrane, the triacetyl cellulose film was hydrolyzed to de-esterify the acetyl groups. This was accomplished by treating the membrane with 1.0 mol L⁻¹ NaOH solution for 48 h. The film was then washed with distilled water before being used [26].

To prepare the coating solution, 0.1 g SBA-15 paste was dispersed in 6.0 mL ethylenediamine for 1.0 h. then, 0.1 mL (3-chloropropyl) triethoxysilane (CPTES) was added

to the resulting solution, and the reaction was continued for 1.0h. 10 mg BSEA was then added to the solution and the mixture was dispersed again for 2.0 h. The prepared solution was kept for 48 h at ambient temperature and then was dispersed for 1.0 h. The film was immersed into the indicator solution for 2.0 min at ambient temperature. Then, they were washed with water for removing excess ethylenediamine and the loosely trapped indicator. Prepared membranes were kept under 1.0 M NaOH solution when they were not being used (Fig. 2).

3. Results and discussions

3.1. Sample properties

The characterization of mesoporous SBA-15 was carried out by XRD, SEM, FT-IR, BET and BJH analysis. The FT-IR spectrum of SBA-15 (Fig. 3a) exhibits a large broad band at 3435 cm^{-1} and 1630 cm^{-1} , which belongs to the O–H bond stretching and bending of the surface silanol groups, respectively [27]. The vibrations of O–Si–O and Si–O of silanol groups were appeared at 1083 and 960 cm^{-1} , respectively [22]. The low-angle XRD patterns of SBA-15 has been exhibited two peaks (110, 200) and a single strong peak (100), which can be confirmed on hexagonal and order lattice (Fig. 3b) [28]. The transition electron microscopy (TEM) image of the SBA-15 was used for studying the specification morphology. TEM image indicates a rod and regular hexagonal structure for SBA-15 (Fig. 3c) [29]. Textural and physicochemical properties of SBA-15 such as the pore diameter (D_{BJH}), the BET surface area and total pore volume (V_{total}) are given in Table 1. Fig. 3d displays a typical type IV nitrogen sorption isotherm in accordance with the defined behavior of SBA-15 [30-36].

Fig. 3 & Table 1.

The characterization of hydrolyzed cellulose acetate and sensing film was carried out by SEM and ATR-FT-IR while immobilized BSEA on hydrolyzed cellulose acetate by proposed method for designing of novel optical sensor was derived. The ATR-FT-IR spectrum of hydrolyzed cellulose acetate (Fig. 4a) exhibits a small band at 3435 cm^{-1} , which belongs to the O–H bond stretching of the surface cellulose acetate groups [37], After the modification of triacetylcellulose with SBA-15-BSEA, the ATR-FT-IR spectrum (Fig. 4a) exhibits a large broad band at 3435 cm^{-1} , which belongs to the O–H bond stretching of the

surface silanol groups [22]. The vibrations of O-Si-O and Si-O of silanol groups were appeared at 1083 and 960 cm^{-1} , respectively, and also a new peak at 2931 cm^{-1} was displayed, which belongs to the stretching and bending vibrations of C-H bond in propyl group. The new peak appeared at 1639 cm^{-1} is related to C=N from BSEA, verifying the successful immobilization of N, N'-bis (salicylidene)-1,3-ethylenediamine [22]. Fig. 4b and c show SEM images of triacetylcellulose and mesoporous SBA-15-BSEA coating, respectively. It can be observed that SBA-15-BSEA was coated by triacetyl cellulose. The uncoated triacetyl cellulose was relatively smooth (Fig. 4b). However, the triacetyl cellulose fully covered by the SBA-15-BSEA coating revealed homogeneous dispersion over the large area (Fig. 4c).

Fig. 4

3.2. Spectral characteristics of BSEA immobilized on hydrolyzed cellulose acetate

After immobilization of BSEA on hydrolyzed cellulose acetate by proposed method and current method, the absorbance spectra of the two optodes were recorded against blank thin film (Fig. 5a). As seen, in comparison with the current method, the optical sensor prepared by the proposed process indicated a higher increase in adsorption intensity which is due to the high surface area and OH bonded of indicator with support. The absorbance spectra of the optode before and after reaction with different concentrations of Pr(III) ions at pH 5.0 (Fig. 5b) reveal that complex formation caused a change in absorbance spectra 420 nm. This observation could be attributed to the fact that the structured conformation of the immobilization indicators is more planar than that of its soluble analogue. A strong absorption maxima at 420 nm was also observed which was the favorite wavelength for further analytical measurements.

Fig. 5

3.3. pH effect

The influence of pH on the changes in absorbance of the optode was studied over a pH range between 2.0 and 5.0 by changing the pH of the solution for 90 ng mL^{-1} Pr(III) solutions at 420 nm. It can be concluded, over the pH 6.0, formation of hydroxyl complex of Pr(III) ions occurred. Therefore, the effect of pH on the optode was studied in the pH range of 2.0–5.0 by changing the universal buffer pH (Fig. 6). As seen, the maximum response of optode

was obtained at pH 5.0, because BSEA is not protonated and hydroxyl complex of Pr(III) ions are not formed, while formation of the complex between OH group and imines group on BSEA was easily observed. At pH<5.0 the response of the sensor membrane changed which is due to the proton binding by imines nitrogen or other ionophore functional group protonation. pH of 5.0 was selected for subsequent works in order to achieve high efficiency and good selectivity.

Fig. 6

3.4. Response time

Response time was defined as the time between the instant at which the optical sensor are dipped in the sample solution, and the first instant at which the absorbance of the optode becomes equal to its steady-state value (i.e. being reached to 90% of the final value). In this study, the practical response time was tested by recording the absorbance change from a pure buffer (pH = 5.0) to a buffered Pr(III) solution of 90 ng mL⁻¹ and results is shown in Fig. 7. As seen, the response time of the proposed optical sensor was 100 s. This is likely due to the fast exchange kinetics of complexation of Pr (III) ion with BSEA at the test solution-optode interface.

Fig. 7

3.5. Analytical figure of merit

All optimized parameters mentioned above are employed in order to develop a Pr(III) ion calibration curve. The calibration graphs for Pr(III) ion was derived by plotting absorbance change values as a function of the Pr(III) ions concentration during a time of 100 s after the contact between solution and sensing phase was being linear in the range 10 – 190 ng mL⁻¹. The following equation with the correlation coefficient (R^2) of 0.9923 was obtained:

$$\Delta\text{Abs} = 0.0012 [\text{Pr (III)}] + 0.0456 \quad (\text{Eq. 1})$$

where Pr(III) is concentration of Pr(III) in ng mL⁻¹ and ΔAbs is a absorbance difference (defined as the difference between the absorbance of the immobilized BSEA solely and the absorbance of Pr(III)–BSEA complex at 420 nm (Fig. 8). In this case, the limit of detection can be defined as the sample concentration that yielding was 5.0 ng mL⁻¹.

Fig. 8

3.6. Repeatability and reproducibility

The repeatability and reproducibility are two important properties of the chemical sensors for identification their applicability. The repeatability was studied using a single membrane by preparing five standard solution of Pr(III)ion in 90 ng mL^{-1} independently in similar conditions, followed by, measuring the absorbance of all sensors under optimum conditions at 420 nm. The coefficient of variation of sensor response found to be 1.6 %. In addition, reproducibility was tested by obtaining five optodes independently through similar conditions, and afterwards, measuring the absorbance of all optodes under optimum conditions for 90 ng mL^{-1} Pr(III)ion solution at 420 nm. The relative standard deviation (R.S.D.) for these determinations was 2.1%.

3.7. Effect of the foreign ions

One of the most important characteristics of an optical membrane sensor is its relative response towards the primary ion over other ions present in the solution. To determine the selectivity of the optode film, the film was examined in the presence of other metal ions in order to detect Pr(III) ions at the concentration of 90 ng mL^{-1} . Tolerance limit was taken as the concentration causing an error of $\pm 5.0\%$ in the Pr(III) assay. The results are summarized in Table 2. The high selectivity of the optode film for Pr(III) ions over other taken cations and anions most probably arises from the strong tendency of the complexation (BSEA) toward Pr(III) ions.

Table 2.

3.8. Life time stability of optode

The Life time stability of optode was determined by adding a buffer solution ($\text{pH} = 5.0$) into the cuvette containing the film. The change in the absorbance after keeping the optode in buffer solution ($\text{pH} = 5.0$) for 3.0 weeks was measured at 420 nm. The absorbance values of optode were decreased only about 2.9% over a period of 3.0 weeks. This result indicates that the sensor is surprisingly stable; therefore, the prepared membranes were kept under water, while not being used in order to prevent them from drying out. Additionally, stability of film response was investigated over 6.0 weeks under ambient conditions, which confirmed that the film was stable over this period of time.

3.9. Optode regeneration

For an optode membrane to perform suitably, absorbance change must be reversible. A good sensor should completely be regenerable at short time. Some tests were conducted with several number of reagents to reverse the absorbance of Pr(III) ions complex. Complexing agents such as EDTA, thiourea and sulfosalicylic acid have a partial reverse effect, and prolonged exposure to them showed no further improvement in reversibility of the optode [38, 39]. According to our results, the sensor can be regenerated and reused by exposure to the solution of thiourea (1.0 M) and NaOH (0.1 M). Furthermore, the solution of thiourea (1.0 M) and NaOH (0.1 M) revealed a short regeneration time (Fig. 9, about 60 s). After the second regeneration, a drift of about 1.7% was obtained in response of the sensor film.

Fig. 9

3.10. Praseodymium determinations in aqueous media and recovery tests

The proposed optical sensor was applied to determine the Pr(III) ion content in water samples through spiking method. The amounts of the Pr(III) ions added to the water samples could be efficiently determined by the sensor. In order to investigate the accuracy of the method, a comparison was carried out between the results obtained by the proposed method and those achieved by ICP-OES. This technique cannot be successfully applied for the determination of Pr(III) ions in this concentration range.

The recovery tests were performed using real samples by using spike method. The test for each sample was carried out in triplicate measurements. As it is obvious from Table 3, Pr(III) can be accurately recovered from the solutions with a remarkable recovery percentage between 97.88% and 104.77%.

Table 3.

4. Conclusion

In this work, a new procedure was introduced to fabricate a sensitive and selective optical sensor for Pr(III) ions determination based on covalent bound of N,N'-bis(salicylidene)-1,3-ethylenediamine (BSEA) with hydrolyzed cellulose acetate. The sensor was easily prepared, readily regenerated with a thiourea and NaOH solution and demonstrated a long lifetime. The developed sensor can be used for the determination of Pr(III) ions in the range of 10-190 ng mL⁻¹ with a good limit of detection (LOD = 5.0 ng

mL⁻¹) and short response time (~100 s). The fabricated optode elucidates high performance in terms of some important parameters such as reproducibility, reversibility, stability, response time and leaching characteristics. Moreover, this optode offers low limit of detection, fast response time and long-term stability in comparison with some sensors which are used for other supporting materials. The characteristics of the proposed Pr(III) optical sensor were also compared with other analytical methods for determination of Pr(III) reported in the literature (Table 4). The linear range, detection limit and relative standard deviation of the proposed optode is acceptable. However, to the best of our knowledge, no attempt has been made to report an optical sensor membrane with chip reagents applicable for Pr (III) ions determination in solution.

Table 4.

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Figure Captions:

Fig. 1, Fabrication scheme of mesoporous Sba-15 paste.

Fig. 2, Structure of N, N'-bis(salicylidene)-1,3-ethylenediamine (BSEA) and possible schemes of reaction between SBA-15-BSEA with membrane.

Fig. 3, FT-IR spectra (a), low-angle XRD pattern (b), TEM image (c) and diagram of pore size distribution and N₂ adsorption-desorption isotherms (d) of mesoporous SBA-15

Fig. 4, ATR-FT-IR spectra of triacetyl cellulose and triacetyl cellulose-SBA-15-BSEA (a), SEM image of triacetyl cellulose (b) and SEM image of triacetyl cellulose-SBA-15-BSEA (c)

Fig. 5, Comparison of absorbance spectra of optode film response by proposed method and current method (a) and absorbance spectra of optode film response to Pr(III) ions between 0.0 and 60 ng mL⁻¹ at pH 5.0 (b)

Fig. 6, pH effect on the optode film response

Fig. 7, Response time curve of the film optode at 420 nm when the film was exposed to 90 ng mL⁻¹ Pr(III) ion.

Fig. 8, the optode film response versus the Pr(III) ion concentration in the range of 10-190 ng mL⁻¹ at pH 5.0 and 420 nm.

Fig. 9, Absorbance variation of the membrane at 420 nm for repeatedly exposing in to 90 ppb Pr(III) solution, 1.0 M thiourea and NaOH solution.

Table Captions

Table 1. Summary report of SBA-15 properties.

Table 2. Influence of the foreign ions on the Pr(III) determination of 90 ng mL^{-1}

Table 3. Results of the recovery of Pr(III) ion in three samples by spike method.

Table 4. Comparison of analytical parameters of proposed Pr(III) optical sensor with other methods for determination of praseodymium.

Table 1.

Summary report of SBA-15 properties.

Surface Area	
BET Surface Area:	869.3 m ² g ⁻¹
Langmuir Surface Area	1079.9 m ² g ⁻¹
BJH Adsorption cumulative surface area of pores between 17.000 Å and 3000.000 Å width:	662.5 m ² g ⁻¹
Pore Volume	
BJH Adsorption cumulative volume of pores between 17.000 Å and 3000.000 Å width:	1.034 cm ³ g ⁻¹
t-Plot micropore volume	0.096 cm ³ g ⁻¹
Pore Size	
Adsorption average pore width (4V/A by BET):	85 Å

Table 2.

Influence of the foreign ions on the Pr (III) determination of 90 ng mL⁻¹.

Interferent	Tolerance limit ^a
Ce ³⁺ , La ³⁺ , Nb ³⁺ , Er ³⁺	150
Zn ²⁺ , Hg ²⁺ , Ni ²⁺ , Fe ²⁺ , Pb ²⁺	300
Cr ³⁺ , Cd ²⁺ , Cu ²⁺	700
K ⁺ , Ba ²⁺ , Ca ²⁺	1000
SO ₄ ²⁻ , NO ₃ ⁻ , CO ₃ ²⁻ , Cl ⁻	1600

^a Maximum ratio of the foreign ions to the lanthanum ions 90 ng mL⁻¹ giving an error of < 5%.

Table 3.

Results of the recovery of Pr (III) ion in three samples by spike method.

Sample	Pr(III) added (ng ml ⁻¹)	Pr(III) found (ng ml ⁻¹)	R.S.D. % (n=3)	Recovery (%)
Mineral water	0	ND ^a	-	-
	90	88.1	0.95	97.88
Tap water	0	ND	-	-
	90	90	1.00	100
Well water	0	ND	-	-
	90	94.4	1.21	104.77

^a Not detected.

Table 4.

Comparison of analytical parameters of proposed Pr (III) optical sensor with other methods for determination of praseodymium.

Ionophore	DL ^a (ng mL ⁻¹)	RL ^b (ng mL ⁻¹)	RSD	Sample	Measured signal	Ref.
NAFT	3.0	5.9-29500	1.1	Tap, minral and river water	Potential	[40]
BMT	38	59-590	-	Soils and Sediments	Potential	[3]
LMFX	850	3500-65000	1.8	Buffer solution	Absorbance	[8]
L	5.0	8.0-142	-	Tap and river water samples	Fluorescence	[2]
BSEA	5.0	10 to 90	1.6	Tap, minral and river water	Absorbance	This work

^a Detection limit.

^b Linear range.

Pr(III) ions