

## Research Article

# Nickel(II) Selective PVC-Based Membrane Sensor Using a Schiff Base

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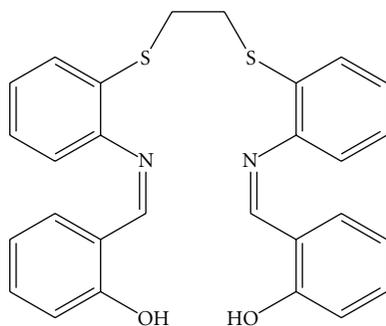
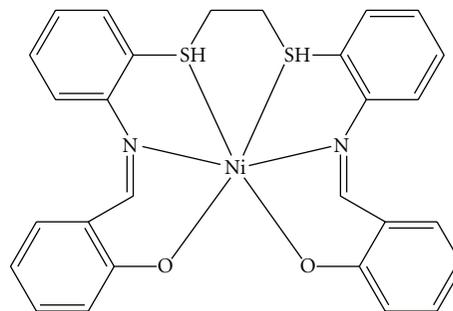
A polyvinylchloride (PVC) membrane optode was prepared by using 1,2-di(*o*-salicylaldiminophenylthio)ethane (H<sub>2</sub>DSALPTE) as a chelating reagent for selective determination of Ni(II) ions. The optimized membranes incorporating H<sub>2</sub>DSALPTE as an ionophore, sodium tetraphenylborate (NaTPB) as an anion excluder, and tributyl phosphate (TBP) as a solvent mediator were prepared and applied for determination of Ni(II) ions. The membrane responded to Ni(II) ion by changing the color from yellow to green in an acetate buffer solution at pH 6.0. The best performance was observed when the membrane having a composition of 3.17% ligand, 31.64% PVC, 63.29% TBP, and 1.90% NaTPB. The membrane can be worked well over a wide concentration range from  $1.0 \times 10^{-5}$  to  $5.0 \times 10^{-3}$  M. The membrane exhibited a detection limit of  $8.51 \times 10^{-6}$  M, and the response time of the membrane was within 7–12 min depending on the concentration of Ni(II) ions. The selectivity of the probe towards nickel determination was found to be very good. Experimental results showed that the probe could be used as an effective tool in analyzing the Ni(II) content of water samples.

## 1. Introduction

Over the years, nickel has been regarded as a potentially toxic metal. The main source of nickel in aquatic systems is decomposition or degradation of rocks and soil, biological cycles and especially industrial processes, and water disposal [1]. The maximum recommended concentration of Ni(II) ions in drinking water for livestock is 2.5 mg/mL [2]. Nickel is well known as a toxic metal that can cause cancer of nasal lungs, dermatitis, asthma, and disorders of central nervous system [3]. Thus, due to the urgent need for selective monitoring of Ni(II) in many industrial, environmental, and food samples, there have been a number of recent reports in the literature [4–8]. A number of methods, such as atomic absorption spectrometry (AAS), flame atomic absorption spectrometry-electrothermal atomization (AAS-ETA) [9–12], inductively coupled plasma-atomic emission spectroscopy (ICP-AES), and flame photometry [13], can be used for determination of nickel. However, these methods generally require sample pretreatment and infrastructure backup and are, therefore, not very convenient for routine analysis of large number of environmental samples. Thus, there is critical need for the

development of selective, portable, inexpensive diagnostic tool for the determination of nickel. Optical chemical sensors or optodes have become an important research area since their introduction two decades ago. Optical sensors are compact and ideally suited to miniaturization, while at the same time they are resisting to electrical interference and utilize the simplicity of photometric measurements. Many optical chemical sensors utilize colored complexes [14–16] or redox reagents [17, 18] immobilized in suitable matrix. Several methods have been used to immobilize reagents in optical sensors used for heavy metal ions, such as covalent binding [19, 20], electrostatic attraction to a resin [21, 22], incorporation into PVC membranes [23–28], and entrapment inside Nafion films [14, 17, 29]. Since polymer matrix, particularly PVC, can easily trap the ionophore-based liquid membrane system, a great deal of interesting has been focused on the PVC-based membranes [30–34].

In this paper, results on the PVC matrix membranes sensor incorporating 1,2-di(*o*-salicylaldiminophenylthio)ethane (H<sub>2</sub>DSALPTE) ionophore (Scheme 1) for the determination of Ni(II) in aqueous solutions have been presented and discussed.

SCHEME 1: Structure of Sal<sub>2</sub>dapte.SCHEME 2: Structure of complex Ni(Sal<sub>2</sub>dapte).

## 2. Experimental

**2.1. Reagents and Solutions.** All of the chemicals used were of analytical reagent grade (Merck). 1,2-Di(*o*-salicylaldiminophenylthio)ethane (H<sub>2</sub>DSALPTE) was synthesized according to the literature [35]. The Ni(II) stock solution (0.10 M) was prepared by dissolving of 1.4540 g Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in water and diluted to 50 mL in a standard flask. Sample solutions were prepared by appropriate dilution. Other reagents such as *ortho*-nitrophenyl octyl ether (*o*-NPOE), sodium dibutyl phthalate (Na-DBP), dioctyl sebacate (DOS), sodium tributyl phosphate (Na-TBP), high molecular weight PVC (HMW-PVC), and tetrahydrofuran (THF), all from Fluka or Merck chemical companies, were used as received. Other chemicals were of reagent grade and were used without further purification. Direct-Q water was used throughout the experiments.

**2.2. Apparatus.** UV-vis spectra were obtained with a UV/VIS/NIR JASCO spectrophotometer (model V-570) connected to a Pentium IV computer used for getting the absorption spectra and absorbance measurements. A Metrohm pH meter (model 780) with a combined double junction glass electrode, calibrated against two standard buffer solutions at pH 4.0 and 7.0, was used for monitoring pH values. All measurements were made in the absorbance mode. The pH of the solutions was kept constant by using 0.1 M acetate buffer at pH 6.0.

**2.3. Preparation of Optical Sensor.** The membrane solutions were prepared by mixing appropriate amounts of active components; 50 mg PVC, 100 mg TBP as plasticizer, 5.0 mg of H<sub>2</sub>DSALPTE, and 3.0 mg anionic additive in a glass vial and dissolving the components in 1.5 mL of THF. The solution was immediately shaken vigorously to achieve complete homogeneity. The glass plates by approximately dimensions of 0.9 cm × 3 cm were cleaned with pure THF to remove organic impurities and dust. Then, 25 μL of the above cocktail was injected with 100 μL glass syringe to the glass plate and spread evenly by using a capillary glass tube. Finally, the membrane was located in ambient air and allowed to dry for few minutes.

**2.4. Absorbance Measurements.** The prepared membranes were put in an acetate buffer solution of pH 6.0 for 10 min

to reach equilibrium, and after a conditioning time, its spectrum was recorded. A membrane without ionophore was used as reference for absorbance measurement. Then, the sensor was immersed into a Ni(II) solution in acetate buffer (pH 6.0) for 7 min. Finally, the sensor was washed with distilled water and dried in air. The absorbance of the membrane was measured over the wavelength range of 320–500 nm.

## 3. Results and Discussion

**3.1. Spectral Characteristic.** The key ingredient of such plasticized PVC membranes is the incorporated carrier that defines the selectivity of the sensor via selective complex formation with the certain cation. Due to sufficient insolubility of H<sub>2</sub>DSALPTE in water and the presence of six donor atoms (N<sub>2</sub>S<sub>2</sub>O<sub>2</sub>) in its structure, it was expected to act as a suitable ion carrier in the PVC membranes for complex formation with Ni(II) ions (Scheme 2). The chelate, H<sub>2</sub>DSALPTE, has two acidic phenolic protons and acts as dianionic hexadentate ligand. As can be seen in Scheme 2, coordination of DSALPTE<sup>2-</sup> to Ni(II) leads to the formation of five chelate rings (three five-membered rings and two six-membered rings). Thus, it is able to be a photometric reagent for Ni(II) ions at a suitable pH. Figure 1 shows the absorption spectra of the membrane which were obtained after being equilibrated in acetate buffer solution (pH 6.0) containing different concentrations of Ni(II) ion. The spectral change (decrease in absorption band at 350 nm and increase in the absorption band at 443 nm) is a result of an increase in Ni(II) ion concentration in the membrane which is due to the extraction of Ni(II) ion into the membrane. The formation of the complex causes a change in color of the reagent phase from yellow to green.

**3.2. Measuring Principle.** Measuring principle can be explained as follows. The membrane response may be defined as the ratio of the concentration of the free ligand [C] to the total amount present in the membrane [C<sub>T</sub>], that is,  $\alpha = [C]/[C_T]$ . Then, the  $\alpha$  value can be calculated by absorbance measurements at  $\lambda_{\max}$  of complexed ligand as  $\alpha = (A_C - A)/(A_C - A_L)$ , where  $A_C$  is the absorbance value of the membrane for complete complexation (i.e., at  $\alpha = 0$ ),  $A_L$  is the absorbance value of the membrane for the free

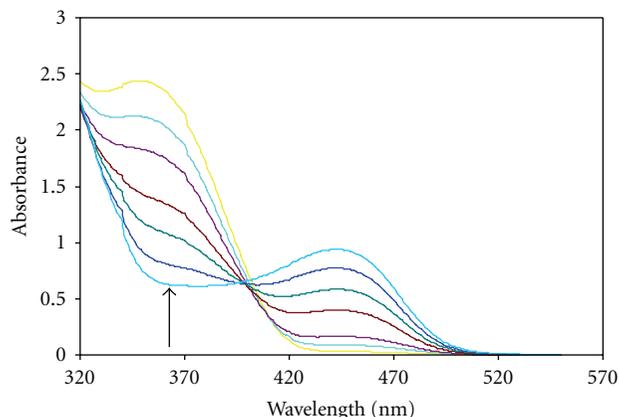


FIGURE 1: Absorption spectra for the immobilized Sal<sub>2</sub>dapte in the presence of  $0\text{--}5 \times 10^{-2}$  M of Ni<sup>2+</sup>. Arrow indicates increase in Nickel concentration.

ligand (i.e. at  $\alpha = 1$ ) [36], and  $A$  is absorbance measured at any time during the titration procedure.

### 3.3. Effect of pH and Buffer Type on Response of the Optode.

The equilibrium of the complexation reaction of H<sub>2</sub>DSALPTE with Ni(II) ion is affected by the solution pH. Figure 2 shows the effect of pH values on the absorbance intensity of the optode membrane. The absorbance measurements were made for 30  $\mu$ M Ni(II) ion with different pH values at 526 nm. The blank membrane (membrane without H<sub>2</sub>DSALPTE in buffer solution) was taken as the reference. All the absorbances were measured with respect to the conditioning solution, that is, as  $\Delta A = A - A_0$ , where  $A$  and  $A_0$  are the absorbance of the sensor in Ni(II) and buffer solutions, respectively, at 443 nm. The pH values were adjusted by the addition of dilute NaOH or HCl. As can be seen in Figure 2, as the pH increases from 1 to 9, the difference in absorbance reaches a maximum at pH 6.0, and then decreases. Because at low pH values (pH < 6.0), complexation is weak. The pH values > 8.5 were not examined because hydrolysis of Ni(II) complex may occur. Thus, the response was optimum at pH 6.0. Response studies of this membrane to various buffer solutions including acetate, phosphate, universal, and phthalate (pH 6.0 and 0.1 M) showed that it responded best to acetate buffer. In acetate buffer, the membrane optode showed better sensitivity and response time. Therefore, acetate buffer was selected as the optimum buffer for further studies.

### 3.4. Effect of Membrane Composition

**3.4.1. Choice of Solvent Mediator (Plasticizer).** The use of 61–65% plasticizer in the preparation of the PVC membranes resulted in optimum physical properties, as well as relatively high mobility of their constituents [37–40]. To select the best plasticizer, we conducted a preliminary study with different plasticizers (TBP, *o*-NPOE, DOS, DBP). The absorbance measurements were made for 50  $\mu$ M Ni(II) ion. The blank membrane (membrane in buffer solution without Ni(II) ion)

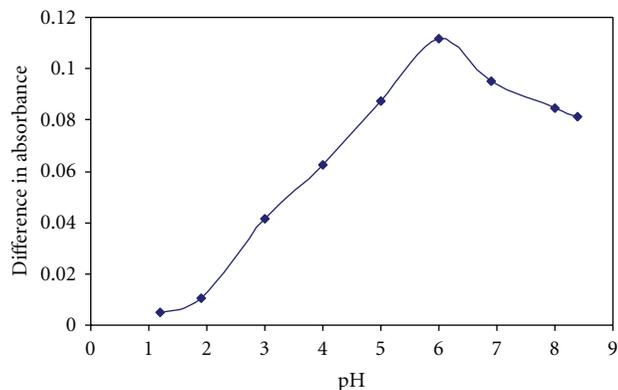


FIGURE 2: Effect of pH on the response of membrane in the presence of  $5 \times 10^{-5}$  M thorium at 443 nm.

was taken as the reference. The results are shown in Table 1. As can be seen for the case of TBP, the membrane response towards Ni(II) ions gives the widest working dynamic range and DOS does not give any response. The membranes containing TBP revealed the best physical properties. This is most probably due to the presence of phosphate group, which facilitates the extraction and complexation of the Ni(II) ions into the bulk of PVC-membranes. TBP was thus used as the plasticizer for all subsequent experiments.

### 3.4.2. Effect of the Amount of H<sub>2</sub>DSALPTE on the Optode Response.

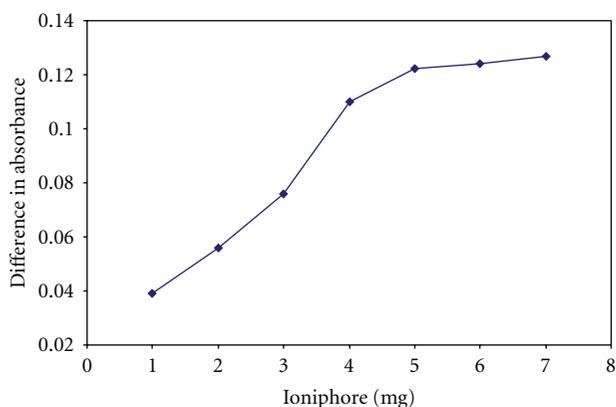
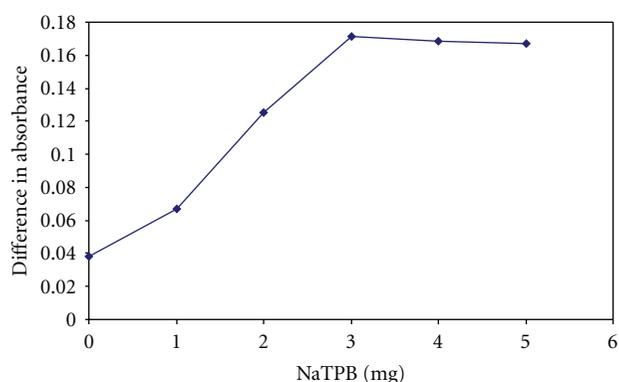
Different compositions (w/w) of the constituents of membrane were tried for the improvements of the response characteristics. To this purpose, seven membranes by different amount of H<sub>2</sub>DSALPTE were prepared to optimize the amount of ionophore. The total amounts of PVC, TBP, and NaTPB (anionic additive) were constant, and also the ratio TBP/PVC was 2.0 in each membrane. The effect of the amount of H<sub>2</sub>DSALPTE on the response of the membrane is illustrated in Figure 3. The absorbance measurements at 443 nm were made for 50  $\mu$ M Ni(II). The blank membrane (membrane without H<sub>2</sub>DSALPTE in the buffer solution) was taken as the reference. As can be seen from Figure 3, increase in the amount of H<sub>2</sub>DSALPTE results in an increase in difference in absorbance. It is important to mention that no considerable improvement was observed in any of these characteristics when the amount of H<sub>2</sub>DSALPTE was increased from 5.0 mg to 7.0 mg. Therefore, the membrane with 5.0 mg of ionophore with 3.17% w/w was chosen as the optimum.

### 3.4.3. Effect of the Amount of Anionic Additive (NaTPB) on the Optode Response.

Although neutral membranes may work properly even when they contain only a very small amount of ionic sites (e.g., as impurities), the addition of a salt of lipophilic ion is advisable and beneficial for various other reasons as well. In fact, it has been demonstrated that the negatively charged lipophilic additives can be improved the adsorption of Ni(II) ions by the membrane and prevented

TABLE 1: Effect of amount of the type of Plasticizer on dynamic range of membrane, pH = 6.0 at 443 nm.

Number membrane	Composition of membrane				Dynamic range (M)
	PVC (mg)	Plasticizer (100 mg)	Ionophore (Sal <sub>2</sub> dapte)	Anionic additive (NaTPB)	
1	50	DOS	5.0 mg	3.0 mg	—
2	50	DBP	5.0 mg	3.0 mg	$1.0 \times 10^{-2}$ – $1.0 \times 10^{-4}$
3	50	TBP	5.0 mg	3.0 mg	$5.0 \times 10^{-3}$ – $1.0 \times 10^{-5}$
4	50	o-NPOE	5.0 mg	3.0 mg	$5.0 \times 10^{-3}$ – $5.0 \times 10^{-5}$

FIGURE 3: Effect of amount of Ionophore (Sal<sub>2</sub>dapte) on the response of membrane in  $5.0 \times 10^{-5}$  M Ni(II), pH = 6.0 at 443 nm.FIGURE 4: Effect of amount of NaTPB on the response of membrane in  $5.0 \times 10^{-5}$  M Ni(II), pH = 6.0 at 443 nm.

from interference by the anions. Therefore, the selectivity increases significantly for determination of Ni(II). To optimize the amount of NaTPB, six membranes by different amount of NaTPB from 0 mg to 5.0 mg were prepared. The total amounts of PVC, TBP, and H<sub>2</sub>DSALPTE were constant. As shown in Figure 4, increase in the amount of NaTPB more than 3.0 mg results in an increase of interference of foreign ions. Also, the membrane with 1.90% w/w of NaTPB has the best sensitivity (3.0 mg of NaTPB to stead 50 mg of PVC) and was selected for further Studies.

Based on the results of the above-mentioned studies, the membrane obtained from a mixture of PVC (50 mg, 31.64%), TBP (100 mg, 63.29%), H<sub>2</sub>DSALPTE (5.0 mg, 3.17%), and NaTPB (3.0 mg, 1.90%) in THF (1.5 mL) gave the best results and was used as the membrane with optimized composition.

**3.5. Response Time.** An important analytical feature of any optode is its response time. The response time of the present optode is controlled by the time required for the analyte to diffuse from the bulk of the solution toward the membrane interface to associate with ligand. The response of the membrane was found to reach 95% of the total signal in 7–12 min depending on the concentration of Ni(II). In general, the response time is more rapid when proceeding from dilute to concentrated solution.

**3.6. Dynamic Range and Detection Limit.** The optical response of the proposed Ni(II)-selective absorbance sensor at different Ni(II) ion concentrations, under optimal experimental

conditions, is shown in Figure 1. The dynamic range response, which is an important characteristic for any ion-selective membrane sensor, was studied by plotting  $1-\alpha$  versus logarithm of Ni(II) ion concentration (M) (Figure 5). A concentration of  $5.0 \times 10^{-2}$  M was found as the concentration of Ni(II) ion that saturates the membrane optode. This curve can be suitably used as a calibration curve for the determination of Ni(II) ions in a concentration range from  $1.0 \times 10^{-5}$  to  $5.0 \times 10^{-3}$  M with equation of  $y = 0.2917 \log[\text{Ni}^{2+}] + 1.4799$  ( $R^2 = 0.9924$ ). The limit of detection (LOD) based on  $3\sigma$  of the blank was  $8.51 \times 10^{-6}$  M ( $n = 7$ ).

**3.7. Regeneration of Optode Membrane.** Some reagents including HCl, HNO<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, NaSCN, EDTA, NaF, and 5-sulfosalicylic acid dihydrate were studied as regenerating reagents. It was found that none of the above reagents or their mixtures could regenerate optode membrane completely and, thus, the membrane could be used as a probe for Ni(II) determination.

**3.8. Reproducibility, Short-Term Stability, and Lifetime.** The membrane reproducibility was obtained by preparing eight membranes using the same membrane solution and membrane preparations as described in Section 2.3. The R.S.D. value for these membranes was 6.5%, indicating that the procedure used for preparation of the membranes had an acceptable reproducibility.

The short-term stability of the optode membrane was investigated by its absorbance intensity measurements in

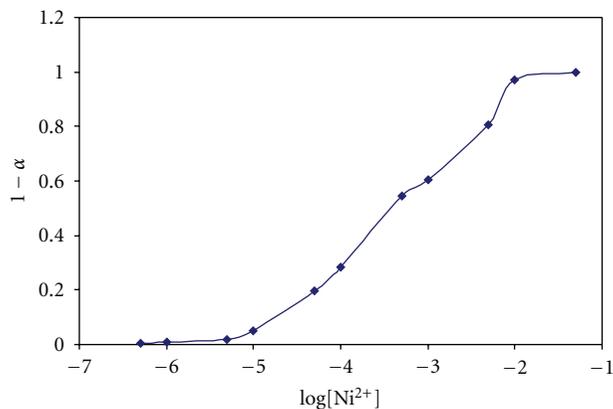


FIGURE 5: Calibration curve at 443 nm.

contact with a  $5.0 \times 10^{-5}$  M solution of Ni(II) buffered at pH 6.0 over a period of 5 h. During this period, there was no evidence of leakage of H<sub>2</sub>DSALPTE from the membrane.

The lifetime of the sensor was investigated, where the membranes were stored in laboratory ambient condition. The responses were measured daily, and the results were compared with those of the first day. Variation of the response was considered significant if it was different from the average  $\pm 3$  S.D. of the response measured in the first day. A significant change in its response was noticed after 9 days of continuous use.

**3.9. Selectivity.** The selectivity behavior is obviously one of the most important characteristics of an ion-selective optode, which reflects the relative response of the optode for primary ion over diverse ions present in solution determining whether a reliable measurement in the target sample is possible. Thus, the influence of a number of common metal ions on the response of the proposed Ni(II)-optical sensor was investigated. To determine the selectivity of the optode membrane, the membrane was tested for the determination of  $5.0 \times 10^{-5}$  M of Ni(II) ions in the presence of different metal ions. Table 2 summarizes the tolerance ratio for several cationic and anionic species. The tolerance limit was taken as the concentration of the interfering species causing an error of not more than  $\pm 3$  S.D. in the determination of nickel, where S.D. is the standard deviation obtained in the replicate measurements of  $5.0 \times 10^{-5}$  M Ni(II). The results of Table 2 indicate that several anionic and cationic species can be tolerated at much higher concentrations than Ni(II).

**3.10. Analytical Application.** To test the practical application of the present sensor, some drinking, river (Zayandehrod), and waste water samples, that is spiked with different amounts of Ni(II) ion, were measured by the proposed optode membrane. The pH of prepared water samples were adjusted by the addition of 5 mL of acetate buffer (pH 6.0) to 20 mL of them. Table 3 shows that by the use of the proposed optode very satisfactory recoveries are obtained for Ni(II) determination in real water samples.

TABLE 2: Effect of foreign ion on the determination of  $5.0 \times 10^{-5}$  Nickel ion.

Species	Tolerance limit ( $M_{\text{ion}}/M_{\text{Ni(II)}}$ )
$\text{Na}^+$ , $\text{K}^+$ , $\text{Ba}^{2+}$ , $\text{Cl}^-$ , $\text{BrO}_3^-$ , $\text{NO}_3^-$ , $\text{SO}_4^{2-}$	500
$\text{Zn}^{2+}$ , $\text{Hf}^+$ , $\text{Tl}^+$ , $\text{La}^{3+}$ , $\text{Zr}^{4+}$ , $\text{Cd}^{2+}$ , $\text{F}^-$	100
$\text{Mn}^{2+}$ , $\text{Mg}^{2+}$ , $\text{In}^{3+}$ , $\text{Pd}^{2+}$ , $\text{Fe}^{3+}$ , $\text{Ga}^{3+}$ , $\text{Rh}^{3+}$	50
$\text{Al}^{3+}$ , $\text{Ag}^+$ , $\text{Co}^{2+}$ , $\text{Fe}^{2+}$ , $\text{Cr}^{2+}$	10
$\text{Hg}^{2+}$ , $\text{Cu}^{2+}$	5

TABLE 3: Results of Nickel (II) ion determination in spiked water samples.

Sample	Added	Found ( $x \pm 3s$ )	Recovery
Drinking water	—	<DL*	—
Drinking water	$1.00 \times 10^{-5}$	$(1.06 \pm 0.09) \times 10^{-5}$	%106.0
Drinking water	$1.00 \times 10^{-4}$	$(9.80 \pm 0.15) \times 10^{-5}$	%98.0
River water	—	<DL*	—
River water	$1.00 \times 10^{-5}$	$(1.10 \pm 0.11) \times 10^{-5}$	%110.0
River water	$1.00 \times 10^{-4}$	$(1.09 \pm 0.10) \times 10^{-4}$	%109.0
Waste water	—	<DL*	—
Waste water	$1.00 \times 10^{-5}$	$(1.08 \pm 0.19) \times 10^{-5}$	%108.0
Waste water	$1.00 \times 10^{-4}$	$(1.03 \pm 0.18) \times 10^{-4}$	%103.0

\*DL; detection limit.

TABLE 4: Response characteristics of the proposed method are compared with reported methods.

Linear dynamic Range (M)	Detection limit (M)	Response time (min)	Interferences
$5.0 \times 10^{-6}$ – $1.0 \times 10^{-3}$ [41]	$5.2 \times 10^{-7}$	10	$\text{Pb}^{2+}$ , $\text{Fe}^{3+}$ , $\text{Al}^{3+}$ , $\text{Fe}^{2+}$ , $\text{Cu}^{2+}$
$8.52 \times 10^{-6}$ – $3.4 \times 10^{-4}$ [42]	$5.11 \times 10^{-6}$	3	$\text{Cd}^{2+}$ , $\text{Cu}^{2+}$ , $\text{Co}^{2+}$ , $\text{Zn}^{2+}$ , $\text{Hg}^{2+}$
$1.0 \times 10^{-5}$ to $5.0 \times 10^{-3}$ , this work	$8.51 \times 10^{-6}$	7	$\text{Hg}^{2+}$ , $\text{Cu}^{2+}$

**3.11. Response Characteristics.** The proposed sensor is a bulk optode, the increasing of ligand on film redound to the increasing of the sensitivity and used entrapment method for immobilization of indicator that elimination the agglomeration of indicator on the membrane and its leaching into the solutions. Agglomeration and leaching of indicator are a severe problem in physical adsorption immobilization. Covalent bonding that is covalent linkage of the dye to a suitable matrix appears to be efficient immobilization method since the resulting membranes do not leach, but most of time decrease activity of adsorption site.

In the Table 4, response characteristics of the proposed method are compared with two reported methods. In comparison with two methods [41, 42], our proposed method is more selective.

## 4. Conclusion

An optical sensor was designed for determination of Ni(II) ions. For this propose, plasticized PVC membrane with good optical and mechanical properties were used as a substrate for immobilization of reagents. The sensor responded to Ni(II) ion by changing the color from yellow to green. It was applied to determine the concentration of Ni(II) ions in real samples.

## Acknowledgment

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