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Full Length Research Paper

Chemical Selective Sensors for Zinc Detection in Water

R. Kihal [1,2], M. Benounis [1]*
[1] Laboratory of Sensors, Instrumentations and Process (LCIP), University Abbas Laghrour, Khenchela (Algeria)
[2] Laboratory of Industrial Analysis and Materials Engineering (LAIGM), University 08 Mai, Guelma (Algeria)

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ABSTRACT

The aim of this work is to elaborate two selective chemical sensors for zinc detection applied to the control of water. In order to optimize the work pH of sensor, a Zeolite-self-assembled monolayer sensor was elaborated and studied by using voltametry cyclic in several solutions and at different pH. The zone of pH detection was located between pH 4 and 6. The cathodic limits of zinc deposition were identified and its electrode position was revealing in working sensor zone. Once the zone of working pH was located, a second type of Zeolite-PVC-membrane sensor was elaborated and studied by potentiomeric method for zinc detection. We show that the choice of plasticizer for membrane preparation was important. Optimal selectivity and better response of sensor can be obtained for a membrane composition: 80 mg of PVC, 160 mg of DOS and 5 mg of Zeolite. Sensor based on this membrane shows that Nernstian response to zinc ions over a wide concentration range (10^{-5}-10^{-2} M) with a slope of 24.2 mV / decade in pH work zone with a short response time (<20 s) and a good reproducibility. A detection limit of sensor reached is for about 10^{-5} M. We show that two chemical sensors can be elaborated in order to detect and control heavy metals in water.

Key words: Chemical sensors, selectivity, self-assembled monolayer, PVC membrane, potentiometry, voltammetry, heavy metal, zinc, zeolite

1. INTRODUCTION

The field of ion-selective electrodes has been growing fast since the past two decades. These have been the subject of interest for analytical chemists as they provide accurate, rapid and low cost method of analysis.

This technique is nondestructive, adaptable to very small sample volume and online monitoring is also possible by these devices. Some commercialized sensors for alkali and alkaline earth metals, halides, etc. are available; however, more efforts are required to develop ion-selective electrodes of commercial standards for heavy metal ions, which are toxic beyond a certain concentration level.

The determination of zinc is important as it is widely used in electroplating, fine chemicals, pharmaceuticals, paint industries and thus occurs widely in the environment. Also some biomedical and a number of wash steams process contain less activity of this metal and a zinc-selective electrode is specially needed to analyze them. Besides, zinc is also

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*Corresponding author: benounis@yahoo.fr

present in high protein foods and its large doses can cause fever, chills, pulmonary manifestation, gastro enteritis, vomiting, nausea, anemia and renal failure [V.K. Gupta et al. 2001, V.K. Gupta et al. 2005, A. M. Bond 1999, P. Kumar, N. Bachheti 2006, H. R. Pouretedal, M. Shamsipur 1998, H. A. Zamani et al. 2006, E. M. Rakhmanko et al. 2003, M. Shamsipur et al. 1999, V. K. Gupt et al. 2006].

Zeolites are crystalline aluminosilicates displaying in a single material both ion exchange capacity and size selectivity properties. This attractive feature was exploited in electrochemistry by designing a variety of zeolite-modified electrodes with, mediated electrocatalysis and electroanalysis [M. Giahi et al. 2005, M.L. Hamlaoui et al. 2002, S. Zougar et al. 2008].

In the present work, we have used Zeolite $Na_{12}(AlO_4)_{12}(SiO_2).27H_2O$ as an ionophore in polymeric membrane for the selective detection of zinc trace amounts in water.

2. EXPERIMENTAL

2.1 Reagents

All the reagents used for the preparation of metal salt solutions and the membranes, were of analytical reagent grade. Zeolite Na(A) was obtained from SOMEZ (Society Mediterranean of the Zeolites), O-Nitrophenyloctyl ether (O-NPOE) and Dodecyle sebacate (DOS) from Fluka Switzerland, high molecular weight polyvinyl chloride (PVC) and tetra hydro furan (THF) were from Aldrich. The solutions of metal salts were prepared in doubly distilled water and standardized by appropriate methods.

2.2 Apparatus

Potentiometric and Voltammetric measurements were carried out in a Potentiostat/ Galvanostat 273 A EG&G PAR, coupled to a personal computer with power suite software for data acquisition and potential control. These measurements are carried out using an electrochemical cell consisting of three electrodes; the reference electrode was a saturated calomel electrode (ECS); a platinum wire of 1 mm diameter as the auxiliary electrode and a graphite rod 30 mm long and 6 mm in diameter as the working electrode (Fig. 1). The experiments were performed in darkness and in a faraday box in order to eliminate electrical interferences.

Figure 1: Experimental device

2.3 Graphite electrodes pre-treatment

The graphite electrodes were previously treated with metallurgical papers at various ranks. The aim of this cleaning is to eliminate the impurities from the working graphite surface. This last is cleaned with acetone during 5 minutes under sonication, rinsed with distilled water and dried [J. Zhang et al. 1995].

2.4 Elaboration of Zeolite-SAM sensor

Once the cleaning of the electrode of graphite ended, a part of electrode is immersed in a solution of sulphuric acid 1M during 10 minutes, rinsed with distilled water and then dried. After then, the dried activated surface is immersed in a concentrated solution of sulphuric acid and appropriate amounts of Zeolite Na(A). After some hours, a molecular monolayer of Zeolite is formed on the surface of the graphite activated [A. Shabani et al., 2008].

2.5. Elaboration of Zeolite-membrane sensor

The PVC-based membrane was prepared by dissolving appropriate amounts of ionophore (Zeolite Na(A)), plasticizers DOS or o-NPOE and PVC in THF (5 mL). The homogeneous mixture was obtained during 5 minutes after complete dissolution of all the components by sonication in the ultrasounds. The polished graphite electrode was dipped into the membrane solutions (Dip-coating) and the solvent was evaporated. A membrane was formed on the graphite surface, and the electrode was allowed to stabilize overnight. The electrode was finally conditioned by soaking in a solution 10-2 M of zinc sulfate for 12 h [S. Sadeghi et al. 2006, S. Rouhani et al. 2009].

3. RESULTS AND DISCUSSION

3.1 Behavior of Zeolite-SAM sensor in zinc electrolyte

Fig. 2 presents the comparison between two voltammograms obtained from the behavior of the Zeolite-SAM sensor, in various solutions (a pure solvent (0.1M H3BO3 + 0.1M NaCl) and in zinc supporting electrolyte (0.1M Zn(SO4).7H2O + 0.1M H3BO3 + 0.1M NaCl)), covering the domain of potential between 500 mV / ECS and -1400 mV / ECS.

So, the cyclic voltammogram of the Zeolite-SAM sensor in zinc supporting electrolyte shows the reduction of the zinc from the potential -1000 mV / ECS. This last one followed by a very fine peak until reach a maximum about - 1300 mV / ECS according to the reaction of the following reduction: [K. D. Song et al. 2004, S. S. gamani, M. Pushpavanam 2009, Hsin-Yi et al., 2003]. But, the cyclic voltammogram of the same sensor in a pure solvent presents only the release of hydrogen. This comparison has shown that the reduction of the zinc appears clearly as an inhibitive effect to the release of hydrogen.

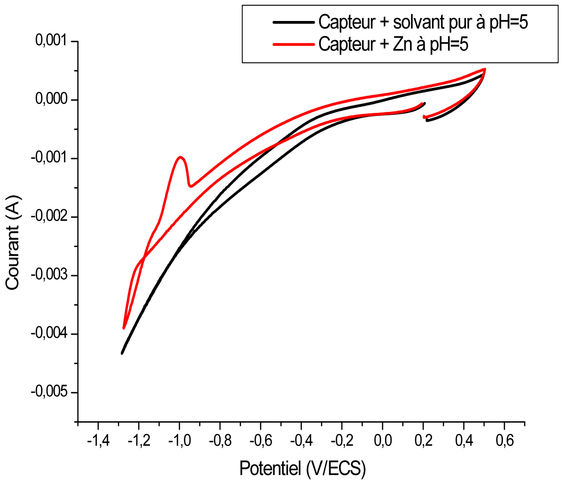

Figure 2: Voltammograms of Zeolite-SAM sensor in the absence and the presence of zinc supporting electrolyte, Scan rate 50 mV/S.

3.2 Effect of the pH on the reduction of the zinc

To study the influence of the pH on the reduction of the zinc and optimize the working pH of sensor, the pH of the solution of electrolysis was varied by 1.00 until 6.43. Then, Fig. 3 shows that only a release of hydrogen is observed in pH = 1, 2 and 3.

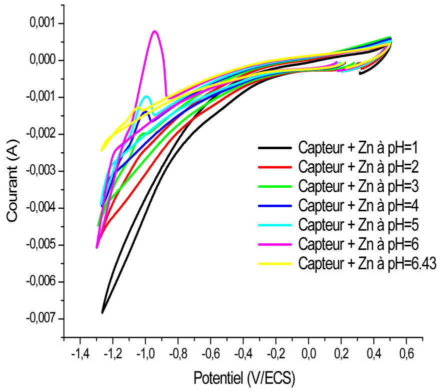

Figure 3: Voltammograms of Zeolite-SAM sensor at different pH of zinc supporting electrolyte, Scan rate 50 mV/S.

In the case of pH 4, 5 and 6 we observe that the obtained voltammograms are identical. Thus, the reduction of the zinc is favor in this zone of pH [Hsin-Yi et al. 2003]. However, the cyclic voltammogram of sensor in pH 6.43 presents only the formation of the zinc hydroxide [$Zn(OH)_2$].

The obtained results show that in the zone of pH between 4 and 6, the electrolyte exercises an important role in the reduction of the zinc. Thus, it is very important to play on the pH of electrolyte to bring to light this phenomenon.

3.3 Influence of the composition of membrane on the characteristics of the selective zinc sensors

It is well understood that the sensitivity, linearity and selectivity obtained for a given ionophore depends significantly on the membrane composition [Y. A. Naik et al. 2002, A. Soleymanpour et al. 2008, M. R. Hassanzadeh et al. 2006, M. K. Amini et al. 2003, A. K. Sing et al. 2009, I. Isildak 2000, D. Nanda, et al. 2007, M. H. Arbab-Zavar et al. 2009, A. K. Singh et al. 2008] and nature of the plasticizer used. So, variations of potentiometric responses were measured at the concentration range 10^{-2}-10^{-6} M of buffer solutions of zinc. Thus, four membranes of varying plasticizer/PVC/ionophore were tested. Then, the results are summarized in Table 1.

It is obvious that a membrane N°1 composition of 80 mg, 160 mg O-NPOE and 5 mg Zeolite Na(A) gave a narrow working concentration range of 10^{-5}-10^{-3} M with a slope of 16 mV/decade. While, the membrane N°3 and N°4 without ionophore, did not show much improved response characteristics (range of concentration or slope).

It can be seen from Table 1, the best performance was exhibited by membrane N°2 containing DOS as solvent mediator with the composition I: DOS: PVC (5: 160: 80) (w/w; mg). This sensor N°2 (Fig. 4) displayed the widest working concentration range of 10^{-5}-10^{-2} M with a slope of 24 mV/decade.

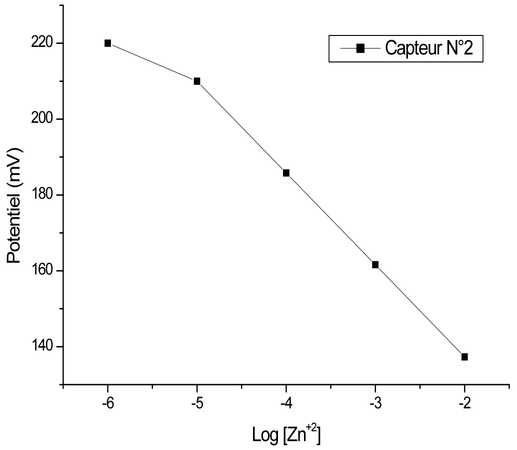

Figure.4: Calibration curve of the sensor N°2 with the optimum composition (80 mg PVC, 160 mg DOS and 5 mg Zeolite).

However, the limit of detection as determined 10^{-5} M from the intersection of two extrapolated segments of the calibration curve.

3.4. Effect of the pH on the response of selective sensor N°2 of the zinc

The pH dependence of the electrode potential for 10^{-4} M zinc ion was tested over the pH range 1.0–8.0 (adjusted with 0.1M HCl or 0.1M NaOH), the results are shown in Fig. 5.

Table. 1: Optimization of the membrane ingredients

Membrane	PVC (mg)	Plasticizer (mg)		Zeolite Na(A) (mg)	Concentration (M)	Slope (mV/decade)
		DOS	O-NPOE			
N°1	80		160	5	10^{-5}-10^{-3}	16
N°2	80	160		5	10^{-5}-10^{-2}	24.2
N°3	80		160		10^{-5}-10^{-3}	13.5
N°4	80	160			10^{-5}-10^{-3}	15

As can be seen, that the potentials are independent of pH in the range 4.0–6.0 and the same can be taken as the working pH range of the sensor N°2 of the zinc. Above and below these pH values, the sharp change in potential may be due to the hydrolysis of Zn^{2+} and H^+ co-transport respectively.

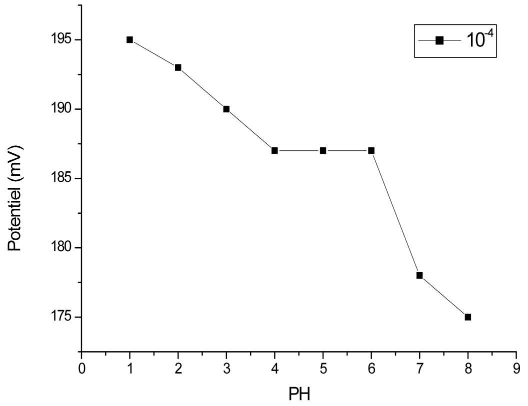

Figure 5: Potential response of the sensor N°2 at different pH of 10^{-4} M zinc ion.

3.5. Dynamic response of zinc selective sensor N°2

The study of the response of zinc selective sensor N°2 is realized by measuring the potential (mV) according to the time (s), in two levels of buffer solutions of zinc 10-4 M and 10-5 M. then, the results are shown in Fig. 6.

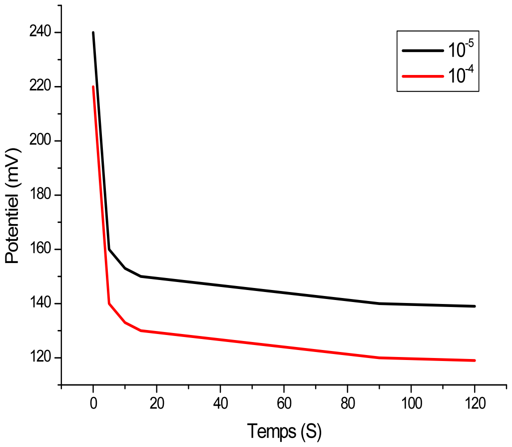

Figure 6: Dynamic response time of the sensor N°2.

As can be seen, the dynamic response time of sensor N°2 selective zinc in two levels (10^{-4} M and 10^{-5} M) is observed lower than 20 seconds.

4. CONCLUSION

In this work two chemical sensors can be elaborated in order to detect and control heavy metals in water.

We show that the optimum selectivity and responses of the sensor were obtained only for a membrane incorporing the mixture of PVC, DOS and Zéolite.

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