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Mimicking new receptors based on molecular imprinting and their application to potentiometric assessment of 2,4-dichlorophenol as a food taint

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ABSTRACT

Innovative host-tailored polymers were prepared, characterized and used as recognition elements in potentiometric transducers for the selective quantification of 2,4-dichlorophenol (DCP).The polymer beads were synthesized using DCP as a template molecule, acrylamide (AM),methacrylic acid (MAA) and ethyl methacrylate (EMA) as functional monomers and divinylbenzene (DVB) and ethylene glycol dimethacrylate (EGDMA) as cross-linkers. The sensors were fabricated by the inclusion of MIPs in plasticized polyvinyl chloride (PVC) matrix. Response characteristics of the proposed sensors revealed anionic slopes of −59.2, −49.7 and −80.6 mV/decade with detection limits of 5.6×10^{-5},5.9×10^{-5} and 13.2×10^{-5} mol/L for MIP/AM/DVB, MIP/MAA/DVB and MIP/EMA/EGDMA membrane based sensors, respectively. Good selectivity was observed over common inorganic/organic anions. Validation of the assay method according to IUPAC recommendations was justified ensuring the synthesis of good reliable novel sensors for DCP determination. The method was successfully applied for routine analysis of food taint in fish and fish farms water samples.

1. Introduction

Chlorophenols are significantly harmful environmental pollutants due to their high toxicity and persistence in the environment(Galán-Cano, Lucena, Cárdenas, & Valcárcel, 2012). Among the 19 possible congeners of chlorophenols, 2,4-dichlorophenol (DCP) is listed in the Priority Pollutant List of the US EPA (ATSDR, 2013). It is used as pesticide and disinfectant (Lee, Yeh, Hsiang, & Hwang, 1998)and considered an important by-product of water chlorination(Czaplicka, 2004) causing disinfectant-like taint in habitat water, fish and shellfish (Shumaway & Palensky, 1973). Toxic reference values for DCP in surface waters and daphnia magna were reported to be 36.5 μg/L and 2.68 mg/L, respectively(Devillers & Chambon, 1986; Pera-Titus, García-Molina, Baños, Giménez, & Esplugas, 2004; Schatzow & Steven, 1980). Flavor-impairment studies showed that flesh tainting occurred at DCP concentrations varying depending on the species of fish tested and ranging from 0.4 μg/L to 10,000 μg/L in species like Crayfish (Telford, 1974). Therefore, the determination of DCP concentration is of crucial importance to environmental protection and human health. Several methods are reported for the determination of DCP, such as gas chromatography (GC) (Al-Janabi, Alazawi, Mohammed, Kadhum, & Mohamad, 2012), HPLC (Chao, Tu, Jian, Wang, & Huang, 2013; Feng, Zhao, Yan, Lin, & Zheng, 2009; Higashi, 2016) and voltammetry (Mohd Rasdi, Mohamad, Abdul Manan, & Nodeh, 2016; Peleyeju, Idris, Umukoro, Babalola, & Arotiba, 2017). All these reported methods are of high cost, not applicable for routine purposes and require complicated sample preparation and sample pretreatment.

Molecular recognition-based separation and sensing systems have been applied in various fields because of their high selectivity for target molecules(Takeuchi & Haginaka, 1999). Molecular imprinting is recognized as the most promising methodology for the preparation of synthetic tailor-made polymers with selective adsorption(Hall, Quaglia, Manesiotis, De Lorenzi, & Sellergren, 2006; Öpik, Menaker, Reut, & Syritski, 2009). Besides their antibody-like molecular selectivity, molecular imprinting polymers (MIPs) have several other attractive features including robustness, stability at elevated temperatures and pressures, resistance to many chemical environments, ability of using MIPs in both aqueous and non-aqueous media, low preparation cost, good shelf-lives and re-use without significant deterioration of their properties (Cormack, Haupt, & Mosbach, 2009; Svenson & Nicholls, 2001). In addition, MIPs are able to bind a variety of target hosts and thus have been used in many different fields. These areas include

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chromatographic separations(Lu & Chen, 2011; Zaidi, 2013), solid phase extraction(Ansari & Karimi, 2017; Sarafraz-Yazdi & Razavi, 2015; Speltini, Scalabrini, Maraschi, Sturini, & Profumo, 2017) voltammetry (Ashley et al., 2017; Peng, Wu, & Liu, 2014) and potentiometry (El-Naby & Kamel, 2015; Kamel & Galal, 2014).

Potentiometric sensors form one of the most important groups of electrochemical transducers and are one of the lowest cost analytical devices available today (Li, Ge, Piletsky, & Lunec, 2012). The integration of MIP materials in electrochemical sensors has the advantages of high selectivity, high sensitivity, low detection limit, ease of miniaturization and automation (Kamel, Moreira, Silva, & Sales, 2011; Li et al., 2012).

In the present work, DCP polymeric membrane sensors doped with the MIPs in PVC matrix were prepared, characterized, compared and used for the assessment of DCP as a food taint in fish and fish farms water samples. The novelty of the present work lies in the absence of potentiometric sensors for the determination of DCP, an important food tainting substance, so the main purpose was to develop highly selective electrodes for DCP with the implementation of the molecularly imprinting technology with its exquisite properties in addition to the application of these synthesized sensors to environmental samples including fish and water samples . The response characteristics of potentiometric sensors reported for other chlorophenols (Abbas, Mostafa, & Homoda, 2001; El-Kosasy, Riad, Abd El-Fattah, & Ahmad, 2003; Kormosh, Savchuk, & Bazel, 2013) are described in the supplementary materials [Table (S1)].

2. Material and methods

2.1. Apparatus

Potential measurements were recorded at ambient temperature with a digital pH/mV meter (Orion SA 720) using 2, 4-dichlorophenol membrane sensors in conjunction with a90-02 Orion Ag/AgCl double junction reference electrode filled in the outer compartment with 10%(m/v) KNO_3.When necessary, pH values were controlled by means of a combined glass pH electrode (Schott blue line 25, Germany). The EMF signals were recorded for stirred solutions using the following electrochemical cell: Ag/AgCl/KCl (10^{-2} mol/L)/10^{-2} mol/L DCP (buffered with 10^{-3} mol/L phosphate buffer, pH8)//sensor membrane//buffered sample test solution/Ag/AgCl double junction reference electrode.

2.2. Reagents and materials

All reagents were of analytical grade and doubly distilled water was used throughout. High molecular weight poly (vinyl chloride) (PVC), tetrahydrofuran (THF), dioctylphthalate (DOP), Azobis-isobutyronitrile (AIBN) and acetonitrile (Chromasolv grade) were obtained from Sigma-Aldrich (St. Louis, Mo, USA). methyltricapryl ammonium chloride (Aliquat 336S) and divinylbenzene (DVB) were obtained from Aldrich (Milwaukee, WI, USA). Methacrylic acid (MAA), acrylamide (AM), ethyleneglycoldimethacrylate (EGDMA), and Ethyl methacrylate (EMA) were obtained from Fluka (Ronkonoma, NY)0.2,4-dichlorophenol (DCP) was obtained from Alfa Aesar (Ward Hill, MA,USA).

A stock solution of DCP (1.0×10^{-2} mol/L) was prepared by dissolving the calculated weight of pure DCP in 100 mL1.0×10^{-3} mol/L phosphate buffer solution at pH 8.0 ± 0.05. Working solutions (1.0×10^{-2} – 1.0×10^{-5} mol/L) were daily prepared by accurate dilutions and stored in brown bottles.

2.3. General polymer synthesis

For preparing MIPs, 0.25 mmol of the template (DCP) was placed in 25 mL test tube with 1.0 mmol of the functional monomer (i.e. AM, MAA or EMA), 10.0 mmol of the cross–linker (i.e. EGDMA or DVB) and 0.15 mmol of the initiator(AIBN), all were dissolved in 5 mL acetonitrile. Degazing with nitrogen was done for 5 min, followed by sealing under nitrogen atmosphere. The mixture was then placed in thermostated water bath at 60 °C for 10 h. Non-imprinted polymer beads (NIPs) were prepared similarly but without the template. The resulting beads were ground and collected. Removal of non-reacting species and extraction of the template molecule were carried out by washing several times with methanol/acetic acid (9:1,v/v). All polymers (MIP/AM/DVB, NIP/AM/DVB, MIP/MAA/DVB, NIP/MAA/DVB, MIP/EMA/EGDMA and NIP/EMA/EGDMA) were left to dry at ambient temperature before their use as potentiometric transducers.

2.4. Sensors fabrication and mV measurements

Aliquots of 190 mg PVC powder, 350 mg of DOP as plasticizer and 30 mg of each polymer were used to prepare several polymeric membranes. The mixtures were separately stirred and dispersed till homogenity in 3.0 mL THF in a 5-cm glass Petri-dish covered with a filter paper and left to stand overnight at room temperature allowing the evaporation of the solvent. 9 mm-discs were cut with a cork borer and glued to the end of 10 mm tygon tubes using THF. The other end of the tygon tubes was fitted onto a micropipette tip which was filled with equal volumes of 1.0×10^{-2} mol/L DCP buffered with 10^{-3} mol/L phosphate buffer, pH8 and 1.0×10^{-2} mol/L KCl as an internal solution. Conditioning of these sensors was done by soaking in 1.0×10^{-2} mol/L DCP solutions buffered with 10^{-3} mol/L phosphate buffer, pH 8 for 24 h before use. Storage of sensors was done in the previous solutions when not in use but in distilled water in between measurements.

Different DCP concentrations ranging from 1.0×10^{-5} to 1.0×10^{-2} mol/L were prepared in 10^{-3} mol/L phosphate buffer (pH8). The emf of each sensor was measured for various concentrations after potential stabilization ± 2 mV, and a plot between the resulting emf and logarithm [DCP] concentration was obtained.

2.5. Binding experiments

Binding experiments were carried out by placing 20.0 mg of MIP and NIP washed particles in contact with 10.0 mL DCP aqueous solutions ranging from 10 to 70 μg/mL. The solutions were left to stand overnight at room temperature and the solid phase was then separated by centrifugation (3000 rpm, 15 min.). Free DCP concentrations in the supernatant were measured by UV spectrophotometry at 284 nm (Wu, Tian, & Wang, 2015) using calibration graph with DCP standard solutions. The concentration of free DCP was subtracted from the initial DCP concentration in order to obtain the amount of DCP bound to the polymers. The maximum binding capacity and dissociation constant for all synthesized polymers were calculated using scatchard equation.

2.6. Analytical applications

For DCP quantification in fish, catfish samples were purchased and procured dead from a local fish market after being freshly slaughtered by the fish seller. Aliquots (100 mg) of blank well ground catfish muscle samples were separately spiked with 10 mL aliquots of DCP solutions in the range from 1.0×10^{-4} to 1.0×10^{-3} mol/L buffered with 10^{-3} mol/L phosphate buffer (pH 8). Mixing was done in 15-mL screw capped falcon centrifuge tubes. Sonication was allowed for 5 min ensuring convenient extraction of the analyte. A supernatant liquid was obtained by centrifugation for 15 min at 1000 rpm, filtered then transferred into a 50-mL beaker. Potentiometric measurements were conducted over these solutions.

For the assessment of DCP in fish farms water samples, the samples were collected from local fish farms in North Sinai. Samples were stored at 4 °C in order to avoid any degradation or deterioration. In volumetric flasks 25 mL, 10-mL aliquots of water samples were spiked with DCP