Anal. Bioanal. Electrochem., Vol. 14, No. 2, 2022, 144-159

Analytical &
Bioanalytical
Electrochemistry

2022 by CEE
www.abechem.com

Review

Pb(II)-Imprinted Polymers for Construction of Lead-Selective Electrochemical Sensors

Morteza Rezapour*

IP Department, Research Institute of Petroleum Industry (RIPI), Tehran,
P.O. Box 14665-137, Iran

*Corresponding Author, Tel.: +982148252228

E-Mail: rezapourm@ripi.ir

Received: 28 June 2021 / Received in revised form: 26 November 2022 /
Accepted: 20 December 2021 / Published online: 28 February 2022

Abstract- Pb(II) is an important pollutant, known for seriously affecting humans and animals. The contemporary industrial activities and their emissions of various pollutants, lead ion included, have exacerbated such effects and have hence raised concern and attention on the implications on peoples' health. Subsequently, the quick, selective, and accurate detection of lead ions in different environmental samples is receiving marked attention. Among the various tools and techniques developed and used for such purposes, electrochemical sensors constitute a prominent class. Yet in many cases, developing effective sensors calls for developing selective ion receptors, and hence myriads of research projects have aimed at developing efficient selectophores for species like Pb(II) ions. The different ionophores developed have had their own pros and cons, and therefore different techniques have been used for designing more efficient alternative materials. An important approach in this regard has been the application of ion imprinting technology for developing highly selective materials for use in ion-selective sensors. This review tends to provide an outlook on the applications of ion imprinted polymers in developing Pb(II)-selective sensors, based on a review of the publications cited in the Scopus database, on the development of Pb(II) sensors.

Keywords- Electrochemical sensor; Ion imprinting polymer; Ion Recognition; Pb(II) ion; Modified electrode

1. INTRODUCTION

The widespread application and proliferation of technology and industry has greatly increased the emission of soluble metal compounds and the subsequent exposure of humans and animals to many toxic pollutants including heavy metals. This issue is worsened by direct and indirect discharge of such materials into the environment due to the non- or sub-standard mining, metallurgy, and electroplating procedures, as well as the widespread and incremental production and application of fertilizers and pesticides, batteries, and disposal of electronic waste. Once soluble compounds of heavy metal ions are released, they are here to stay, given that they do not biologically degrade n, and hence they permanently contaminate soil and water, and in some cases the air. These contaminants bioaccumulate in plant and animal tissues and find their way into the human body either directly or indirectly via food chain.

As an instance of heavy metal ions, lead(II) ions, are known for causing to the so-called plumbism of the vital organs in humans and animals causing conditions such as anemia, hepatopathy, kidney dysfunctions, damages to the brain and blood cells, etc. [1,2]. This, and other indicators, necessitate the development and application of precise and accurate methods and techniques for the analysis of this ion in various real samples as a preventive measure.

In this light, various techniques have been proposed for this end. The majority of such techniques have been based on various spectrometric methods, like different atomic absorption methods like electrothermal atomization atomic absorption spectrometry (ET-AAS) [3,4], sequential multi-element flame AAS [5], graphite furnace AAS [6], electrothermal AAS [7] inductively coupled plasma-mass spectrometry (ICP-MS) [8] hydride generation AAS [9], and flame AAS [10]. Advantages of spectroscopic techniques include considerable sensitivity, selectivity, and accuracy, yet the techniques are often costly, require high levels of expertise and require complicated instrumentation, and are time-consuming. Accordingly, different approaches include the application of various sensors, based on the optical [11,12], potentiometric [13-17], and voltammetric [18,19] properties of this analyte. Sensors can be highly adopted for the analysis of metal ions and enjoy advantages of considerable sensitivity, low cost, ease of use, and so on.

To customize sensors for specific analytes and/or enhance their sensitivity and selectivity for the determination of the analyte various modified materials have been tested as the basis for constructing electrodes during the past decades [20-32]. Some of the modifiers or modified materials used for constructing lead ion electrodes include bismuth [33,34] organic ligands [35,36] PAN-incorporated Nafion [37] zeolite [38], SiO_2–Al_2O_3 mixed-oxide [39] clay nanoparticles [40] and silica [41]. Yet the selectivity of the resulting sensors have has not been flawless and in some cases, serious interferences were observed in the presence of interfering species like Cu(II), Ag(I), etc. This, as well as other needs, have kept the need for developing proper modifiers, or modified materials for lead(II) in the spotlight.

A rivalling approach with various advantages is ion imprinting technology, which offers one-of-a-kind advantages including superb specificity and selectivity. Also, molecularly imprinted polymers (MIPs) are commonly known to have chemical and thermal stabilities [42-46]. Given that the approach is based on the application of the target species as the template in the preparation of the MIP, great target specificity behaviors are observed, which have turned the method as a major area for developing materials for separation, enrichment, and identification of various species in recent years.

An important development in the area of MIPs has been the development of Ion-Imprinted Polymers (IIPs), where an ion, and not a molecule is used as the template in the structure of the prepared molecules [47]. Similarly, IIPs reveal selective binding properties for the target ions and can be further modified using ligands via coordination reactions to stabilize forces of charge, coordination geometry, and size of the target cation. This text tends to provide an overview of the reports on the application of IIPS in the development of electrochemical sensors for lead ions.

2. Pb(II) ION-IMPRINTED POLYMERS

The Ion Imprinting Technology (IIT), is based on the so-called lock-and-key concept, and as described above, offers unique advantages including great specificity and selectivity in extracting/interacting with analytes in complex matrices, which eliminates various sources of uncertainties in results, and has hence attracted a great deal of attraction in the areas of separation, enrichment, and analysis of materials.

IIT involves the application of a selective binding agent (functionalized ligand) to induce specificity through creating tailored cavities in a polymeric body (Figure 1).

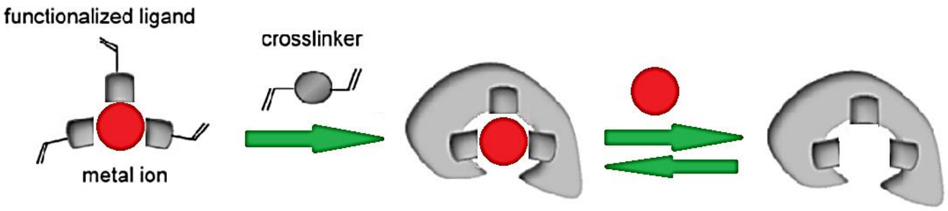

Figure 1. The overall steps of preparing IIPs

Generally, preparing Pb-IIP is performed through precipitation polymerization forming irregularly shaped colloidal particles or nanoparticles. It is noteworthy that the size of the IIP particles is highly dependent on the reaction conditions, including nature of the solvent, monomer, cross-linking agent and ligand as well as the monomer/solvent ratio, type of the imprinting metal ion salt, the stirring rate, reaction time and temperature.

Preparing the Pb(II)-IIPs typically involves interacting a proper complexing (binding) ligand with the target ion in a proper solvent to form a complex, which was next reacted with a proper monomer and an initiator to form the free radicals required for triggering the polymerization reaction, and a cross-linker After the reaction the produced IIPs precipitate, and compounds like ethylene glycol dimethyl acrylate (EGDMA) and 2,20-azobisisobutyronitrile (AIBN) are respectively used as the cross-linker and initiator. The reactions are commonly performed in oil or water baths at around 60-70°C. The reaction temperature is determined by the boiling point of the solvent and reactions may take as long as 24 h in an inert atmosphere.

The product is repeatedly washed with suitable solvents once the reaction is over, and the target species used as the template is eluted using HCl to empty the reaction sites of the IIP. The product might be further rinsed using deionized water, to the point the pH of the washing solution becomes neutral. The cleaned product is eventually dried in a vacuum desiccator.

3. IIP-BASED ELECTROCHEMICAL SENSORS FOR Pb(II)

Using IIP in electrochemical transducing platforms has given rise to the development of measuring devices for the detection and analysis of various cationic species in water solutions. The resulting sensors are believed to possess considerable absorption capacities which naturally enhance their sensitivity towards the analytes.

According to the citations accessible on the Scopus database, 11 reports have been published on the development of IIP-based Pb(II) sensors before the beginning of 2022. Table 1 lists provide a summary of IIPs used and the results obtained using the sensors.

The first report on the application of an IIP for the construction of a lead sensor involved the use of a novel nano-structured IIP, which was formed through copolymerizing the complex of methacrylic acid and Pb^{2+} ion with ethylene glycol dimethacrylate in a precipitation polymerization procedure. In this case, methacrylic acid had a dual role of a ligand and a functional monomer, so that selective sites were formed in the resulting cross-linked IIP to interact with Pb(II) ions. The resulting polymer nanoparticles were used in developing a modified carbon paste electrode for the analysis of lead ions, and the electrode was used in differential pulse stripping voltammetry analysis of the target species. The analysis involved an initial sorption of lead ions under open-circuit conditions followed by a reduction step to form metallic lead. A blank CPE composed of a non-imprinted polymer electrode was also used in the experiments and the IIP based CPE considerably outperformed the blank electrode in terms of response and selectivity. This was attributed to the presence of selective and efficient recognition sites in the IIP present in the modified CPE. The factors influencing the function of the electrode were optimized and it was found to produce a linear response over the range of 1.0×10^{-9} to 8.1×10^{-7} M. The detection limit of the electrode was at S/N=3 was reported as 6.0×10^{-10} M, and it was successfully used in the analysis of Pb(II) in various samples [48].

Another report exists on the application of a molecularly imprinted film of a self-assembled monolayer (SAM) of a complex of lead ions and a Schiff's base prepared using l-cysteine and salicylaldehyde on a gold film [49]. The reversible interactions of the target metal ion and the donor atoms of the amino and carboxyl groups (i.e. N and O atoms) make the sites of the Schiff's base capable of efficiently interacting with the ions, which can be used to modify various electrodes, including the gold used in this case (Figure 2).

Table 1. Reported Pb(II) electrochemical sensors based on IIP sensing materials

Monomer and/or complexing agent	Cross-linker	Solvent	Synthesis Method	Electrode	Detection method	LR/DL	Sample	Year
Methacrylic acid	Ethylene glycol dimethacrylate	Acetonitrile	Precipitation polymerization		Differential pulse stripping voltammetry	1.0×10^{-9}-8.1×10^{-7} M LOD: 6.0×10^{-10} M	River and waste water	2011 [48]
Schiff base (monomer and complexing agent)	-	-	Surface polymerization	Au	Differential pulse voltammetry	3.0×10^{-7}- 5.0×10^{-5} M	Yellow River	2012 [49]
4-vinylpyridine (monomer)/ 4-(2-pyridylazo)resorcinol (complexing agent)	Ethylene glycol dimethacrylate	Acetonitrile	Precipitation polymerization	Carbon Paste	Differential pulse voltammetry	0.1 nM to 10 nM LOD: 30 pM	Water and waste water	2014 [50]
Methacrylic acid (mnomer)/8-hydoxyquinoline (complexing agent)	Ethylene glycol dimethacrylate	Dimethyl sulphoxide	Precipitation polymerization	Glassy carbon	Differential pulse anodic stripping voltammetry	0.05-60 μM LOD: 0.01 μM	Food and water	2016 [51]
Itaconic acid (monomer and complexing agent)	Ethylene glycol dimethacrylate	Acetonitrile	Precipitation polymerization	Carbon Paste	Square wave anodic stripping voltammetry	1.0×10^{-11}-8.0×10^{-8} M LOD: 3.8 nM	Sea and river water	2017 [52]
Vinyl functionalization of the magnetic nanoparticles (monomer)/ 2-vinylpyridine (complexinh agent)	Ethylene glycol dimethacrylate	Acetonitrile/ Dimethyl sulphoxide	Surface Imprinting Polymerization	Carbon Paste	Stripping voltammetry	3-55 μg l^{-1} LOD: 0.5 μg l^{-1}	Environmental water	2017 [53]
Methacrylic acid (monomer and complexing agent)	Ethylene glycol dimethacrylate	Acetonitrile	Precipitation polymerization	Carbon Paste	Differential pulse voltammetry	1.0×10^{-9}-7.5×10^{-7} M LOD: 1.3×10^{-11} M	Four and rice	2017 [54]
Methacrylic acid (monomer)/ 1-(2-pyridylazo)-2-naphthol (complexing agent)	Ethylene glycol dimethacrylate	Dimethyl sulphoxide	Precipitation polymerization	Glassy carbon	Differential pulse anodic stripping voltammetry	0.16 μg L^{-1}-0.50 μg L^{-1}	Tap and mineral water, physiological serum Urine	2017 [55]
Vinyl functionalized MWCNTs	NNMBA	Water	Surface imprinting polymerization	Pt	Differential pulse voltammetry	2×10^{-2} μM	Lake water, mining effluent, food and cosmetics	2018 [56]
2,2′:6′,6″-terpyridine (monomer and complexing agent)	Ethylene glycol dimethacrylate	Dimethyl foramide	Precipitation polymerization	Graphite paste	Differential pulse anodic stripping voltammetry	10 nM to 1.0 μM LOD:0.11 nM	Water	2018 [57]
4-vinyl pyridine (monomer)/ 2-(2-aminophenyl)-1H-benzimidazole (complexing agent)	Ethylene glycol dimethacrylate	Acetonitrile	Precipitation polymerization	Glassy carbon	Differential pulse voltammetry	0.1–80 ng mL^{-1} LOD: 0.05 ng mL^{-1}	Fruit juice	2020 [58]

To form the SAM on the electrode $PbNO_3$ and the Schiff-base were dissolved in a 1:1 mixture of ethanol and water so that the Pb^{2+}/Schiff's base ratio was 2. The electrodes were polished using an alumina powder slurry and washed with distilled water each prior to use, and were conditioned through voltammetric cycling from +0.40 V to +1.20 V at 100 mV/s in 0.50 mol/L H_2SO_4 solution until a stable cyclic voltammogram (CV) was obtained. Next, the gold electrodes were dipped in the above-mentioned solution and kept in this state for 10 h, before being voltammetrically cycled from +0.40 V to +1.20 V once more (at 100 mV/s) in the solution until a stable CV was obtained. Then the electrodes were washed with ethanol to remove the loosely adsorbed molecules. Finally, the electrodes were immersed in dodecanethiol for 30 minutes to "seal" their surface, and then washed using a 0.10 M aqueous solution of EDTA to remove the lead ions. The researchers also used a control electrode, prepared in an identical fashion except for the use of the template.

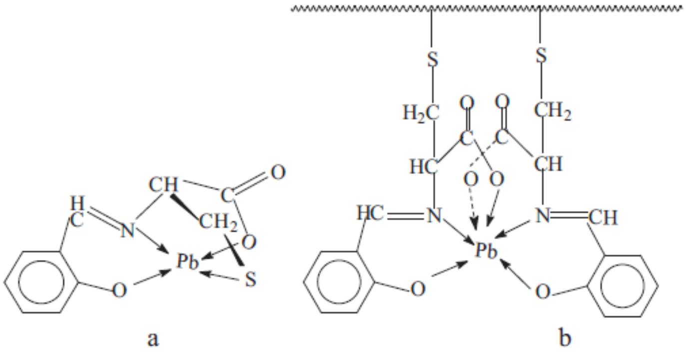

Figure 2. (a) Pb^{2+}–Schiff base and (b) Pb^{2+}–Schiff base complex on the surface of the gold electrode; Reprinted with permission from [49]

The differential pulse voltammetry (DPV) analyses were run in solutions further containing 5 mM $K_3[Fe(CN)_6]$ and 0.2 M KCl, in a voltage range of −0.7 to −0.2 V, applying a pulse amplitude and width of 50 mV and 0.05 s. The pulse repetition time was 0.2 s. Two reduction peaks were observed for Pb^{2+} at −0.28 V and −0.42 V on a bare gold electrode; while in the case of the SAM-modified gold electrode, the reduction peak appeared at −0.54 which was attributed to the overpotential of the electrode. The SAM modified electrode proved to be more sensitive than the bare electrode, reflecting the strong adsorption of Pb^{2+} ions on the modified electrode due to the coordination interactions. The control electrode did not reportedly produce any response.

The modified electrode had a dynamic linear range of 3.00×10^{-7} to 5.00×10^{-5} M under optimal conditions, and the redox process was determined to be controlled by the surface reactions, in the case of the modified electrode. The researchers reported storing the electrodes in a dilute Pb^{2+} solution. The modified electrode was used in the determination of Pb^{2+} in Yellow River water [49].

In another report a lead(II)-selective modified carbon paste electrode was prepared for the differential pulse voltammetry (DPV) analysis of lead ions using lead(II))-imprinted polymer nanoparticles (IP-NPs)prepared through the precipitation polymerization of 4-vinyl pyridine as a functional monomer, ethylene glycol dimethacrylate as the cross-linker, 2,2'-azobisisobutyronitrile as initiator, 4-(2-pyridylazo)resorcinol as a ligandin the presence of lead ions in acetonitrile. The lead ions in the product were leached using a dilute HCl solution. The modified CPE had good selectivity in the presence of common interfering species.

The electrode was prepared using a mixture of 15% wt. of the IIP, and a 55:30% wt. mixture of graphite powder and paraffin oil. The resulting paste was filled into a 2mm wide and 5 mm deep whole made at one end of a Teflon rod with a hole and the electrical connection was established by a copper wire passing through the rod.

The electrode was used in the differential pulse stripping voltammetry analyses after an initial open-circuit sorption of the analyte on the surface of the modified electrode. The electrode had a markedly improved behavior in comparison to a control electrode composed of non-IP-NPs.

The optimal electrode produced linear responses in the concentration ranges of 0.1 nM to 10 nM and 10 nM to 10 μM with various respective sensitivities of 49.179 nA/nM and 30.305 μA/μM and a detection limit of 30 pM (at S/N =3). The selectivity and applicability of the modified electrode were tested using environmental water samples spike with traces of lead ion [50].

In another report a Pb(II)-IIP was prepared using methacrylic acid (monomer), ethylene glycol dimethacrylate (crosslinker) and azobisisobutyronitrile (initiator) together with 8-hydoxyquinoline (ligand), and the product was used as to prepare an impregnated glassy carbon electrode for the selective voltammetric detection of trace amounts of Pb(II)

The IIP powder involved reacting a solution of $Pb(NO_3)_2$ and 8-hydroxyquinoline dimethyl sulfoxide, followed by admixing proper amounts of the monomer, and cross-linking agent while the reactions solutions were agitated through bubbling N_2 for 15 min. Next, the initiator (azobisisobutyronitrile) was added to the mixture under mixing with nitrogen gas in 7–10 minutes. After this stage, the reaction vessel was sealed and stored at 60°C in a thermostatic water bath for one day. The polymer produced in this way was next isolated and washed with a 2M solution of HCl to leach the templating lead ions, followed by washing absolute ethanol, before drying in a vacuum oven at 60°C and grounding to 45–55 μm particles. A nonimprinted polymer sample was also prepared in the same fashion in the absence of the template.

Next, the impregnated glassy carbon electrode was prepared using a bare GCE. The bare electrode was polished and then washed with water and was then subjected to sonic oscillations for 5 minutes in the presence of a 50%, v/v solution of nitric acid in water, absolute ethanol and water. The prepared bare GCE was covered with 4 μL of the agent. To this end, a mixture of 20 mg of powdered IIP with 1% chitosan in an acetic acid solution was prepared under sonication, and a proper amount of the solution was deposited on the glassy electrode using a microinjector, and then dried under ambient conditions for one day.

The electrode was used in differential pulse voltammetry (DPV) analyses. Prior to use, the electrode was dipped in a solution containing lead, 4 mL of a 2.0 M solution of KNO_3, 3 mL of 0.2 M solution of acetic acid/sodium acetate buffer (pH 4.5) and kept there for 15 minutes while the solution was being stirred and then kept idle for 15 s, before beginning the analyses. The analyses were performed after applying a pre-potential of -1.2 V to the electrode for 10 minutes to reduce the target ions, followed by performing the DPV analyses in a potential window of -1.2 – -0.4 V.

The optimal electrode had 3 orders of magnitude better adsorption of the analyte, in comparison to a control electrode impregnated with non-imprinted polymer (NIP). It was also reported to show good Pb(II) selectivity in the presence of other heavy metal ions like Hg(II), Cd(II), Cu(II). The electrode had a linear calibration curve in the concentration window of 0.05-60 μM and a its detection limit was as low as 0.01 μM [51].

In a later research a Pb(II)-IIP was prepared through precipitation copolymerization of a complex of itaconic acid (as both a ligand and functional monomer) and Pb^{2+} together with ethylene glycol dimethacrylate. The nanoparticles of the polymer were then used in modifying a carbon paste electrode, also containing multi walled carbon nanotubes (MWCNTs) and the resulting electrode was used in square wave anodic stripping voltammetry (SWASV) analysis of lead ions. The analysis was preceded with an open circuit sorption of the analyte onto the electrode prior to the reduction step. The modified CPE was described as having a considerably higher response as opposed to nonmodified control electrodes incorporating similar yet non-imprinted polymer. The optimal composition of the electrode was reported to be a mixture of 7% wt. of IIP, 6% wt. of MWCNT, 74.8% wt. of graphite powder and 12.2% wt. of paraffin oil.

The factors influencing the electrode were optimized and it was reported to have a linear response in the concentration range of 1.0×10^{-11}-8.0×10^{-8} M with a detection limit as low as 3.8×10^{-12} M at S/N=3. The electrode also had good sensitivity, its response was not considerably affected by the commonly occurring heavy metal ions (Co^{2+}, Ag^{+}, Ni^{2+}, Cd^{2+}), although it was reported that 50-fold excess of Fe^{2+}, Zn^{2+} and 40-fold excess of Cu^{2+} caused considerable interference on the response. The modified CPE had a minimum 5-month life time. To further confirm the practical applicability of the sensor, it was successfully applied for the trace lead determination in sea and river water samples [52].

Another modified carbon paste electrode was prepared using particles of a novel surface ion-imprinted polymer (IIP) and the resulting electrode was used in stripping voltammetric detection of Pb^{2+}.

The Pb(II) LLP was synthesized by initially vinyl functionalizing magnetic nanoparticles through reacting coupling agent KH-570 with Fe_3O_4 nanoparticles in acetonitrile at 60 °C for one day under stirring. The product was isolated using a magnet and stored. In a parallel process, proper amounts of $Pb(NO_3)_2$ and the 2-vinyl pyridine (monomer) were dissolved in a 1:2 mixture of dimethyl sulfoxide and aniline to form a complex, followed by adding and dispersing proper amounts of vinyl functionalized Fe_3O_4 under sonication. Then proper amounts of ethyleneglycol dimethacrylate and 2,2′-azobisisobutyronitril were added to the reactor under mixing while nitrogen gas was bubbled to purge oxygen. Next, the mixture was heated at 60 ºC and the product was isolated and washed with ethanol, and its Pb(II) content was removed using a solution containing 0.5 M of HCl. Finally, the particles were repeatedly rinsed with ultra-pure water and dried at 60 ºC, and used as an ingredient of the modified CPE.

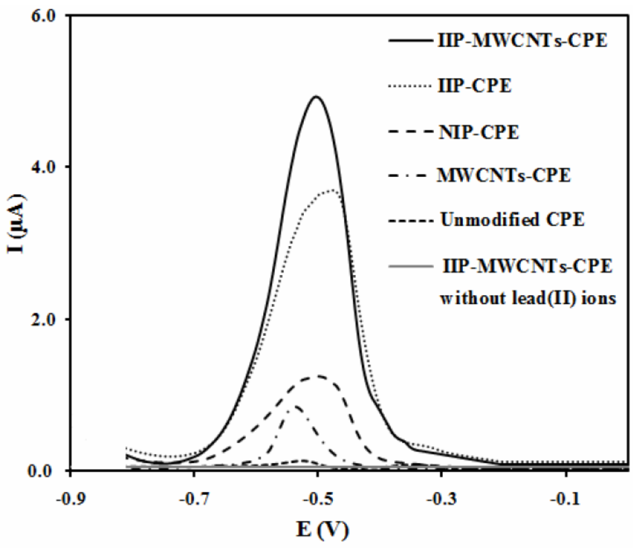

Figure 3. Results obtained using normal CPE, MWCNTs-CPE, IIP-CPE, IIP-MWCNTs-CPE, NIP-CPE in the differential pulse voltammetry (DPV) of a 25 µg l^{-1} Pb^{2+} solution (Stripping solution = 0.1 M KNO_3 and 0.1 M acetate buffer (pH=4.0), Stripping time = 10 min at -0.9 V (*vs*. Ag/AgCl), scan window -0.8 - 0.0 V, scan rate = 50 mV s^{-1}, pulse amplitude and permission 0.1 V and 4 ms); Reprinted with permission from [53]

The CPE further contained multi-walled carbon nanotubes (MWCNTs)and it produced the best response when it comprised 7% wt. of the IIP, 10% wt. of the MWCNTs, 53% wt. of graphite powder and 30% wt. of paraffin oil. The analyses were performed in a 0.1 M acetate buffer solution (pH = 4.5) and a 15 min extraction step was performed prior to the analyses. The analyses had linear response in the Pb(II) concentration range of 3-55 µg l^{-1} and the detection limit of the analyses was as low as 0.5 µg l^{-1} with an RSD of 3.1%. The response of various electrodes is can be seen in Figure 3 [53].

A later work involves the development of a Pb^{2+}-selective CPE composed of an IIP prepared based on methacrylic acid as both a ligand and function monomer, ethylene glycol dimethacrylate as a cross-linking agent, 2,2-azobisisobutyronitrile as the initiator and lead ions.

The preparation of the IIP involved initially reacting methacrylic acid and a solution of $PbCO_3$ in acetonitrile and aging the solution under stirring at room temperature for one day to form the complex. Then a mixed solution of ethylene glycol dimethacrylate (cross-linker) and 2,2-azobisisobutyronitrile (initiator) in acetonitrile was added to the supernatant of the above solution, while N_2 was bubbled to purge oxygen for 20 minutes. The polymerization reaction was performed at 65 °C in an oil bath for one day and the product was isolated and cleaned, leached using HCl and thiourea solutions, and finally washed, dried, and stored for further use (Figure 4). Non-imprinted polymer particles were also prepared for comparative studies. The optimal electrode was used in differential pulse voltammetry (DPV) analyses in a three-step procedure including the incubation of the electrode in a Pb^{2+} solution at pH=5.0 for 80 s, followed by rinsing and transferring of the electrode into the electrochemical cell containing HCl. Finally, a negative −1.0 V prepotential was applied to the working electrode for 40 s and then the DPV scan was applied from −0.8 V to 0.0 V. Under these conditions, the electrode had a linear response in the range of 1.0×10^{-9} to 7.5×10^{-7} M, with a detection limit of 1.3×10^{-11} mol L^{-1} (S/N = 3) [54].

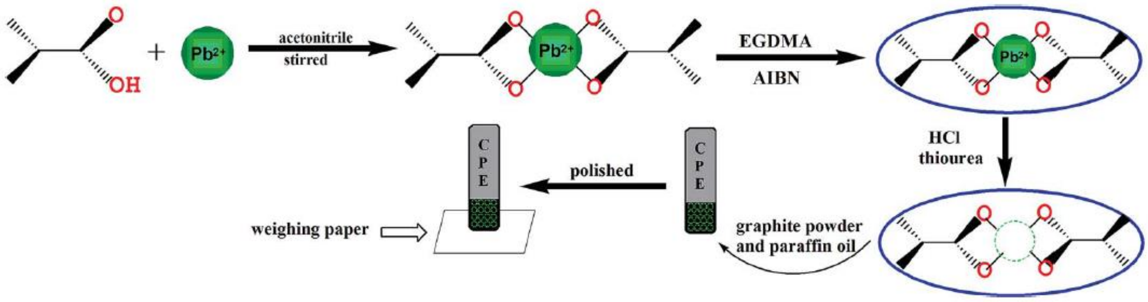

Figure 4. Preparation of the IIP and modified CPE; Reprinted with permission from [54]

In another research, a highly selective to IIP-modified GCE was prepared. The modification of the GCE was performed using a suspension of an IIP loaded with 1-(2-pyridylazo)-2-naphthol (PAN) (IIP-PAN) and MWCNT.

The IIP and a non-imprinted polymer sample were prepared through precipitation polymerization, involving the mixing solutions of 1-(2-pyridylazo)-2-naphthol (the chelating agent) in dimethyl sulfoxide and $Pb(NO_3)_2$ in water, followed by adding proper amount of methacrylic acid (monomer), 2,2′-azobisisobutyronitrile (initiator) and ethylene glycol dimethacrylate (crosslinking agent), under purging with N_2 gas bubbles. Next, the reaction vessel was sealed and the polymerization reaction started at 60 °C in an oil bath for one day. The product was next isolated, washed, ground, and leached, and stored for later use in modifying the electrode.

As in other cases, the analysis of lead started with a 20-minute open-circuit preconcentration of the analyte (in 0.05 M Tris-HCl buffer solution, pH=6.0). The DPV analyses were next performed at -1.2 V in a 0.05 M HCl solution, followed by subsequent differential pulse anodic stripping voltammetric analysis from -0.8 to -0.3 V.

Selectivity assessments were performed using binary Pb^{2+}/Cu^{2+}, Pb^{2+}/Cd^{2+}, Pb^{2+}/Ni^{2+}, and Pb^{2+}/Zn^{2+}solutions and respective relative selective coefficients (k′) of 301, 13.3, 9.5, 63.0 and

133.3 were reported. The analyses based on the electrode had detection and quantification limits of 0.16 μg L^{-1} and 0.50 μg L^{-1}, respectively, and the electrode was used in the analysis of water and synthetic urine samples with satisfactory recovery values of 95 and 103%. Further accuracy tests were conducted on standard reference material 1643e Trace Elements in Water NIST [55].

Using muti-walled carbon nanotube as the backbone, another IIP based modified platin electrode was prepared for lead ions. The template was used to modify the solid matrix of N,N'-methylenebisacrylamide (NNMBA)-crosslinked polyacrylamide on the MWCNTs backbone. Electrodes lacking IIP and MWCNT were also prepared, all of which produced inferior results.

The MWCNT-IIP was prepared through polymerizing IIP onto the surface of vinyl grafted MWCNT. Suitable amounts of MWCNT-CH=CH_2, Pb(II) ion and NNMBA were used in the synthesis, which involved the following steps. First aqueous solutions of lead and acrylamide were prepared and added to MWCNT-CH=CH_2 under stirring. Then NNMBA and initiator 2, 2' azobisisobutyronitrile were also added and the reaction temperature was elevated 70 °C. The reaction continued for 5 hours before the product was centrifuged and washed, then its Pb(II) content was removed through further washing before desiccation for 24 h.

The modified platinum electrodes were prepared by first cleaning the bare platinum electrodes using 3.0 M nitric acid for 10 min, followed by rinsing with water. After drying the polymer paste was formed through mixing the powder with Nafion in a mortar, and the paste was placed the platin electrodes and kept for 30 min for drying. The electrode was used in cyclic voltammetry (CV) and differential pulse voltammetry (DPV) analyses and the electrode was yield a detection limit as low as 2×10^{-2} μM. The electrode was satisfactorily used in the analysis of lake water, mining effluent, food samples and cosmetics [56].

In a later study, a graphite paste electrode was modified using a highly selective lead-imprinted polymer through thermal precipitation polymerization, using a terpyridine-based ligand. The resulting electrode was successfully used in the differential pulse anodic stripping voltammetry (DPASV) of Pb(II) ions.

The nano particles of the IIP were prepared through the reaction of ethylene glycol dimethacrylate (cross-linker), 2,2′-azobisisobutyronitrile (free radical initiator), and 2,2′:6′,6″-terpyridine (terpy) as the so-called recognition element.

The electrochemical analyses were conducted by immersing the modified-GPE in an acetate buffer solution (pH=5) containing a known quantity of lead ions for 6 min under stirring at -1 V *vs.* Ag/AgCl, to accumulate and reduce the Pb^{2+} ions onto the surface of the electrode. The DPV analyses were performed through potential sweeps in the range of -0.8 to -0.3 V (pulse amplitude and width were 0.1 V and 0.01 s; the scan rate was 0.1 V s^{-1}). The results were found to be linear in the two concentration windows of 0.4 to 10 nM (sensitivity= 693.95 nA nM^{-1} cm^{-2}), and 10 nM to 1.0 µM (sensitivity=580.25 µA μM^{-1} cm^{-2}). The detection limit of the method was 0.11 nM for S/N = 3, and it was used in the analysis of various water samples. No considerable interferences were also reported [57].

A novel modified glassy carbon electrode has been recently reported for the analysis of lead ions The electrode was modified using a selective magnetic ion-imprinted polymer (Fe_3O_4@SiO_2@IIP), which was prepared a ligand (2-(2-aminophenyl)-1H-benzimidazole) and a functional monomer (4-vinyl pyridine) (Figure 5).

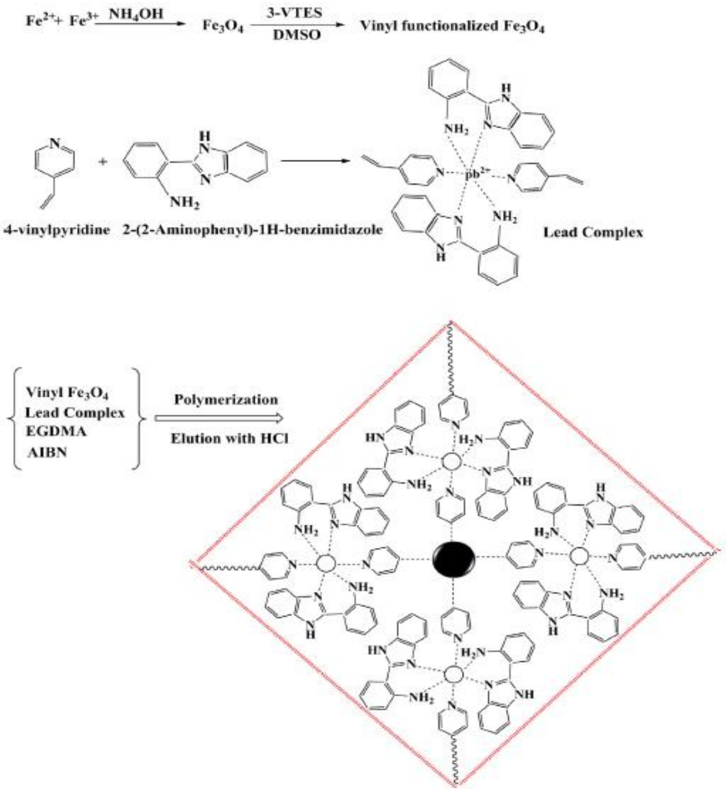

Figure 5. The synthesis process of Fe_3O_4@SiO_2@IIP nanoparticles; Reprint with permission from [58]

After preparing magnetic nanoparticles they were modified by reacting with 3-vinyltriethoxysilane in dimethyl sulfoxide under sonication for 24 hours under ambient temperature. The modified Fe_3O_4@VTES nanoparticles were isolated using a magnet and washed with ethanol and distilled water and then left to dry at ambient temperature.

Next, the Pb^{2+}-IIP was prepared through precipitation polymerization by dropwise addition of a solution of $Pb(NO_3)_2$ into an acetonitrile solution of 2-(2-aminophenyl)-1H-benzimidazole (ligand) and 4-vinyl pyridine (functional monomer) in 5 hours while stirring. Then suitable amount of Fe_3O_4@VTES and ethylene glycol dimethylacrylate (cross-linker) and AIBN (initiator) were added to the mixture of the ligand and template and the reaction was allowed to proceed at 65°C in an oil bath under stirring at 400 rpm for one day in while N_2 was bubbled to purge oxygen. The produced polymer was isolated and repeatedly washed with a 1:4 (v/v) methanol/ distillated water mixture and then its lead content was leached using a 1M HCl solution. The product was once again and desiccated. The GCE was modified after polishing with an alumina slurry, washing, sonication in an ethanol/water mixture for 5 minutes and drying. The modification involved dispersing 1.0 mg of the prepared IIP in 1 mL dimethyl fumarate through 30 min of sonication, and casting 5 µL of the mixture on the surface of clean GCE, and resting the resulting electrode to dry in air.

DPV analyses were performed in 10 mL 0.1 M acetate buffer (pH=5.6) containing various concentrations of lead ion. A pre-concentration step was performed at −1200 mV vs Ag/AgCl under stirring for 6 minutes. After this stage stirring was ceased and the solution was allowed to rest for 60 s at the target ions' reduction potential, before DPV scans -800 and -400 mV, at 30 mV s^{-1}, with a pulse amplitude and pulse period of 100 mV and 40 ms. The peak current occurred around -600 mV.

The function of the electrode was optimized using the Box–Behnken design (BBD) and under the optimal conditions the electrode showed an exceptional performance a detection limit of (0.05 ng mL^{-1}), and a linear calibration curve in the range of 0.1-80 ng mL^{-1}. The electrode was used in the analysis of Pb(II) concentration in natural water and in fruit juice and the results were very satisfactory [58].

4. CONCLUSION

Given the adverse effects of heavy metals on animals and plants, trace analyses of these species are key in controlling their emission and effects. Electrochemical sensors constitute useful options for this purpose, yet they need to be highly selective. Ion imprinted polymers are good candidates for such purposes. As important examples Pb-IIPs can be used for introducing selectivity and increasing sensitivity through pre-concentration of the target species, i.e. lead ions. Since various IIPs have been used individually and in combination with other materials in the preparation of modified metallic, glassy carbon, or carbon paste electrodes, reviewing these reports can offer more insight to researchers for further research. Based on a thorough study IIP-modified electrodes offer considerable sensitivity in electroanalysis of lead ions, as well as very good selectivity against commonly occurring interfering species allowing for efficient applicability for various samples.

REFERENCES

[1] S. Khan, Q. Cao, Y. M. Zheng, Y. Z. Huang, and Y. G. Zhu, China Environ. Pollut. 152 (2008) 686.
[2] M. Jamil, M. S. Zia, and M. Qasim, J. Chem. Soc. Pak. 32 (2010) 370.
[3] M. A. Belarra, C. Crespo, M. Resano, and J. R. Castillo, Spectrochim. Acta B 55 (2000) 865.

[4] H. F. Maltez, D. L. Borges, E. Carasek, B. Welz, and A. J. Curtius, Talanta 74 (2008) 800.

[5] L. A. Portugal, H. S. Ferreira, W. N. L. dos Santos, and S. L. C. Ferreira, Microchem. J. 87 (2007) 77.

[6] M. G. A. Korn, G. L. dos Santos, S. M. Rosa, L. S. G. Teixeira, and P. V. de Oliveira, Microchem. J. 96 (2010) 12.

[7] J. Biasino, J. R. Dominguez, and J. Alvarado, Talanta 73 (2007) 962.

[8] E. R. Yourd, J. F. Tyson, and R. D. Koons, Spectrochim. Acta B 56 (2001) 1731.

[9] D. K. Korkmaz, N. Ertaş, and O. Y. Ataman, Spectrochim. Acta B 57 (2002) 571.

[10] M. Shamsipur, F. Raoufi, and H. Sharghi, Talanta 52 (2000) 637.

[11] W. H. Chan, R. H. Yang, T. Mo, and K. M. Wang, Anal. Chim. Acta 460 (2002) 123.

[12] Z. Dehghani, M. Hosseini, J. Mohammadnejad, and M. R. Ganjali, Anal. Meth. 11 (2019) 684.

[13] M. R. Ganjali, N. Motakef-Kazami, F. Faridbod, S. Khoee, and P. Norouzi, J. Hazard. Mater. 173 (2010) 415.

[14] M. R. Fathi, F. Darviche, and M. R. Ganjali, Anal. Lett. 33 (2000) 1025.

[15] M. R. Ganjali, M. Hosseini, F. Basiripour, M. Javanbakht, O. R. Hashemi, M. F. Rastegar, M. Shamsipur, and G. W. Buchanen, Anal. Chim. Acta 464 (2002) 181.

[16] F. Faridbod, M. R. Ganjali, B. Larijani, M. Hosseini, K. Alizadeh, and P. Norouzi, Int. J. Electrochem. Sci. 4 (2009) 1528.

[17] M. R. Ganjali, and N. Davarkhah, Anal. Bioanal. Electrochem. 8 (2016) 256.

[18] E. Kirowa-Eisner, M. Brand, and D. Tzur, Anal. Chim. Acta 385 (1999) 325.

[19] Y. Wu, N. B. Li, and H. Q. Luo, Sens. Actuators B 133 (2008) 677.

[20] M. R. Ganjali, P. Norouzi, F. Faridbod, M. Rezapour, and M. R. Pourjavid, J. Iranian Chem. Soc. 4 (2007) 1.

[21] H. A. Zamani, M. R. Ganjali, P. Norouzi, and M. Adib, Sensor Lett. 5 (2007) 522.

[22] F. Faridbod, and A. L. Sanati, Curr. Anal. Chem. 15 (2019) 103.

[23] M. R. Ganjali, A. Roubollahi, A. R. Mardan, M. Hamzeloo, A. Mogimi, and M. Shamsipur, Microchem. J. 60 (1998) 122.

[24] F. Faridbod, M. R. Ganjali, B. Larijani, M. Hosseini, and P. Norouzi, Mater. Sci. Eng. C 30 (2010) 555.

[25] H. A. Zamani, M. Rohani, M. Mohammadhosseini, M. R. Ganjali, F. Faridbod, and S. Meghdadi, Sensor Lett. 9 (2011) 1745.

[26] H. A. Zamani, B. Feizyzadeh, F. Faridbod, and M. R. Ganjali, Sensor Lett. 9 (2011) 1767.

[27] M. R. Ganjali, M. Rahimi, B. Maddah, A. Moghimi, and S. Borhany, Anal. Sci. 20 (2004) 1427.

[28] M. R. Ganjali, P. Norouzi, F. Faridbod, M. Yousefi, L. Naji, and M. Salavati-Niasari, Sens. Actuators B 120 (2007) 494.

[29] H. A. Zamani, F. Malekzadegan, and M. R. Ganjali, Anal. Chim. Acta 555 (2006) 336.

[30] M. R. Ganjali, S. Rasoolipour, M. Rezapour, P. Norouzi, A. Tajarodi, and Y. Hanifehpour, Electroanalysis 17 (2005) 1534.

[31] M. R. Ganjali, Z. Memari, F. Faridbod, R. Dinarvand, and P. Norouzi, Electroanalysis 20 (2008) 2663.

[32] M. R. Ganjali, P. Norouzi, M. Adib, and A. Ahmadalinezhad, Anal. Lett. 39 (2006) 1075.

[33] S. Lee, S. Bong, J. Ha, M. Kwak, S. K. Park, and Y. Piao, Sens. Actuators B 215 (2015) 62.

[34] K. Pokpas, N. Jahed, O. Tovide, P. G. Baker, and E. I. Iwuoha, Int. J. Electrochem. Sci. 9 (2014) 5092.

[35] L. Fan, J. Chen, S. Zhu, M. Wang, and G. Xu, Electrochem. Commun. 11 (2009) 1823.

[36] F. Zavarise, D. Merli, and A. Profumo, Anal. Chim. Acta 668 (2010) 177.

[37] Z. Hu, C. J. Seliskar, and W. R. Heineman, Anal. Chim. Acta 369 (1998) 93.

[38] S. Senthilkumar, and R. Saraswathi, Sens. Actuators B 141 (2009) 65.

[39] M. Ghiaci, B. Rezaei, and R. J. Kalbasi, Talanta 73 (2007) 37.

[40] S. Yuan, W. Chen, and S. Hu, Talanta 64 (2004) 922.

[41] I. Cesarino, J. Braz. Chem. Soc. 18 (2007) 810.

[42] G. Vlatakis, L. I. Andersson, R. Müller, and K. Mosbach, Nature 361 (1993) 645.

[43] T. P. Rao, R. Kala, and S. Daniel, Anal. Chim. Acta 578 (2006) 105.

[44] M. Khadem, F. Faridbod, P. Norouzi, A. R. Foroushani, M. R. Ganjali, R. Yarahmadi, and S. J. Shahtaheri, J. Anal. Chem. 75 (2020) 669.

[45] M. Khadem, F. Faridbod, P. Norouzi, A. Rahimi Foroushani, M. R. Ganjali, S. J. Shahtaheri, and R. Yarahmadi, Electroanalysis 29 (2017) 708.

[46] M. R. Ganjali, M. Rezapour, F. Faridbod, and P. Norouzi, Molecularly Imprinted Polymers as Biomimetic Molecules: Synthesis and their Pharmaceutical Applications. In Handbook of Polymers for Pharmaceutical Technologies, Wiley 1 (2015) pp. 267-326.

[47] T. Alizadeh, A. R. Sharifi, and M. R. Ganjali, RSC Advances 10 (2020) 4110.

[48] T. Alizadeh, and S. Amjadi, J. Hazard. Mater. 190 (2011) 451.

[49] Z. Wang, Y. Qin, C. Wang, L. Sun, X. Lu, and X. Lu, Appl. Surf. Sci. 258 (2012) 2017.

[50] M. K. Bojdi, M. H. Mashhadizadeh, M. Behbahani, A. Farahani, S. S. H. Davarani, and A. Bagheri, Electrochim. Acta 136 (2014) 59.

[51] S. Hu, X. Xiong, S. Huang, and X. Lai, Anal. Sci. 32 (2016) 975.

[52] T. Alizadeh, N. Hamidi, M. R. Ganjali, and F. Rafiei, J. Environ. Chem. Eng. 5 (2017) 4327.

[53] M. Ghanei-Motlagh, and M. A. Taher, Anal. Bioanal. Chem. Res. 4 (2017) 295.

[54] X. Luo, W. Huang, Q. Shi, W. Xu, Y. Luan, Y. Yang, H. Wang, and W. Yang, RSC Adv. 7 (2017) 16033.

[55] C. R. T. Tarley, A. M. Basaglia, M. G. Segatelli, M. C. Prete, F. A. C. Suquila, and L. L. G. de Oliveira, J. Electroanal. Chem. 801 (2017) 114.

[56] M. Sebastian, and B. Mathew, J. Mater. Sci. 53 (2018) 3557.

[57] M. Shamsipur, L. Samandari, A. Besharati-Seidani, and A. Pashabadi, Chem. Pap. 72 (2018) 2707.

[58] Z. Dahaghin, P. A. Kilmartin, and H. Z. Mousavi, Food Chem. 303 (2020) 125374.