Optimization of Oil Palm-based Cellulose and Hydroxyapatite-Carbon Composite Electrode for Trace Pb(II) Ions Detection in Aqueous System

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An electroanalytical technique was devised using oil palm-based cellulose and hydroxyapatite as modifiers to carbon electrodes for Pb(II) ions detection in an aqueous system. The cyclic voltammetry scan suggested increased active binding sites and faster electron transfer with quasi-reversible redox peaks with a larger anodic current peak and smaller oxidation potential values. The optimal conditions were attained using 10% modifier at pH 2 in 0.1 M HCl, −1.2 V deposition potential, 270 s deposition time, 25 Hz frequency, 0.020 V amplitude, rotation speed of 700 rpm, and the step potential of 0.005 V. The square wave anodic stripping voltammetry established at optimum level exhibited excellent selectivity and stability from 10 ppb to 100 ppb for Pb(II) ions detection. Sharp anodic peaks were observed at -0.48 V for Pb(II) ions with the detection limit of 0.095 ± 0.32 ppb and limit of quantitation of 0.32 ± 0.32 ppb.

Keywords: Metal ion; Carbon composite electrode; Cellulose; Hydroxyapatite; Square-wave voltammetry

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INTRODUCTION

Heavy metal contamination is a type of hazardous environmental pollution that has major impacts on health, soil, and water ecosystems, with long-term economic and financial repercussions. The amount of heavy metal sludge constitutes approximately 4.9% of 1.7 million metric tons of total sewage wastes generated in Malaysia (Fen and Mahmood Mat Yunus 2013). Among these, lead (Pb) exhibits strong chemical toxicity on nervous, gastrointestinal, immune, and reproductive systems and can be detrimental even at low concentrations. As the water system contaminated with the toxic metals may finally enter the marine and human food chain, the detection must be sensitive and selective with the possibility of extending it for *in situ* and on site applications (Fen and Mahmood Mat Yunus 2013; Ajab *et al.* 2019; Khan *et al.* 2019). Conventional techniques using complicated instrumentations such as atomic absorption spectrometry (AAS) or inductively coupled plasma mass spectrometry (ICP-MS) are expensive and not suitable for on-site analysis. These also require well-controlled experimental conditions, time-consuming preparation steps, and operated by specialized personnel (El Mhammedi *et al.* 2010).

Reliable techniques for environmental sample analyses are important for knowledge-based and well-informed decision making to safeguard the health of public, accelerate developments in technology, and for the improvement of environmental quality.

Mercury-based electrodes have been utilized for the measurement of both organic and inorganic analytes due to the high reproducibility and sensitivity (Lee and Hu 2014). However, the health and safety considerations with regards to mercury's toxicity has prompted efforts to develop an alternative that is eco-friendly. The trend is towards the adoption of real-time electrochemical monitoring based on green analytical chemistry (Wang 2002). The carbon paste electrode (CPE) is not only cost-effective, but it also offers stability and ease of handling and packing. Chemically-modified electrodes (CMEs) incorporating modifiers, such as functionalized nanomaterials, ion exchangers, and various ligands, have been used to improve the performance (Khan and Abdullah 2013; Xu *et al.* 2013; Tarley *et al.* 2017; Zhao *et al.* 2017; Khan *et al.* 2019; Ajab *et al.* 2018, 2019). Plant tissue or biomaterial of plant origin is attractive as a modifier in the CMEs due to its biocompatibility and biodegradability.

In Malaysia, palm oil industries produce large amounts of oil palm empty fruit bunches (EFBs), at 19.8 million tonnes annually (Ng *et al.* 2011). Utilization, extraction, and conversion of biomass wastes and residues into value-added materials could meet the target of sustainable development goals and address the issues of recycling, treatment, and remediation of wastes. The autoclave pretreatment of EFBs has yielded 64% cellulose (Nazir *et al.* 2013), which has been explored as polypropylene composite materials (Abdullah *et al.* 2016), magnetic biosorbents (Daneshfozoun *et al.* 2017), diesel desulphurization (Nazir *et al.* 2018), and carbon composite electrode sensors for the detection and validation of trace Pb(II) ions in blood serum (Ajab *et al.* 2018) and palm oil mill effluent (POME) (Ajab *et al.* 2019).

The objectives of the study were to carry out the fabrication and optimization of cellulose-hydroxyapatite (HAp) carbon composite electrode for Pb(II) ions detection in an aqueous system, using cyclic voltammetry (CV) and square wave anodic stripping voltammetry (SWASV).

EXPERIMENTAL

Materials and Chemicals

The materials and chemicals used were as reported before (Ajab *et al.* 2018, 2019). The testing solutions were prepared in double deionized water (18.2 MΩ water conductivity) (Elga Purelab Ultra, High Wycombe, UK). The tap water for validation was obtained from Universiti Teknologi PETRONAS, Malaysia.

Synthesis of Electrode Modifiers

The preparation of cellulose was performed using a previously reported method (Nazir *et al.* 2013). The HAp was synthesized *via* a wet chemical technique. A 500 mL solution of 0.6 M $(NH_4)_2HPO_4$ was added dropwise to a 500 mL solution of 1.0 M $CaCl_2 \cdot 2H_2O$ at 70 °C, for 4 h. The pH was set at 11 by adding NH_4OH, and the reaction mixture was stirred for 8 h at 70 °C, before leaving to room temperature. The precipitate obtained were filtered, dried at room temperature, and washed using isopropyl alcohol and water (Mohan *et al.* 2012).

Fabrication of Working Electrode

For the preparation of CPE, fine graphite powder and paraffin were mixed at a ratio of 75:25 (w/w) using a pestle and mortar (Bagheri *et al.* 2013). The paste was later packed into a cavity (3 mm internal diameter and 2 mm inner cavity) of a Teflon tube, which was later polished. The tube containing the paste was later drilled for 1 mm diameter to insert the copper wire. The spill-over paste was mechanically removed. The copper wire was inserted through the length of 5 cm and cleaned thoroughly for the inner part of a graphite-filled tube to provide electrical contact. Before application, the electrode surface was polished with a smooth weighing paper. For modification, different composition of modifiers (HAp and cellulose at 1:1 ratio (w/w)) at 5, 10, 15 and 20%, was introduced to the graphite in the paste preparation at room temperature. The CPE and CME with 10% modifiers were selected for optimization using CV and SWASV analyses for Pb(II) ion detection.

Electrochemical Setup

Electrochemical measurements were carried out using a potentiostat (Autolab type-III Ecochemie, Utrecht, Netherlands), linked to a programming system (Nova 1.10, Metrohm Autolab, Herisau, Switzerland) (Fig. 1). The cell contained a working electrode (WE) made of cellulose-HAp carbon composite electrode in the space where the analyte was to be detected. It also contained an inert counter electrode (CE) that was made of graphite bar to allow the current to pass through between the CE and the WE. In addition, a reference electrode (RE), which was the Ag/AgCl electrode (Metrohom), was also used. The pH was measured with a pH meter (WalkLab, TI 9000 pH/Mv/Temp.meter. I Trans Instruments, Petro Centre, Singapore).

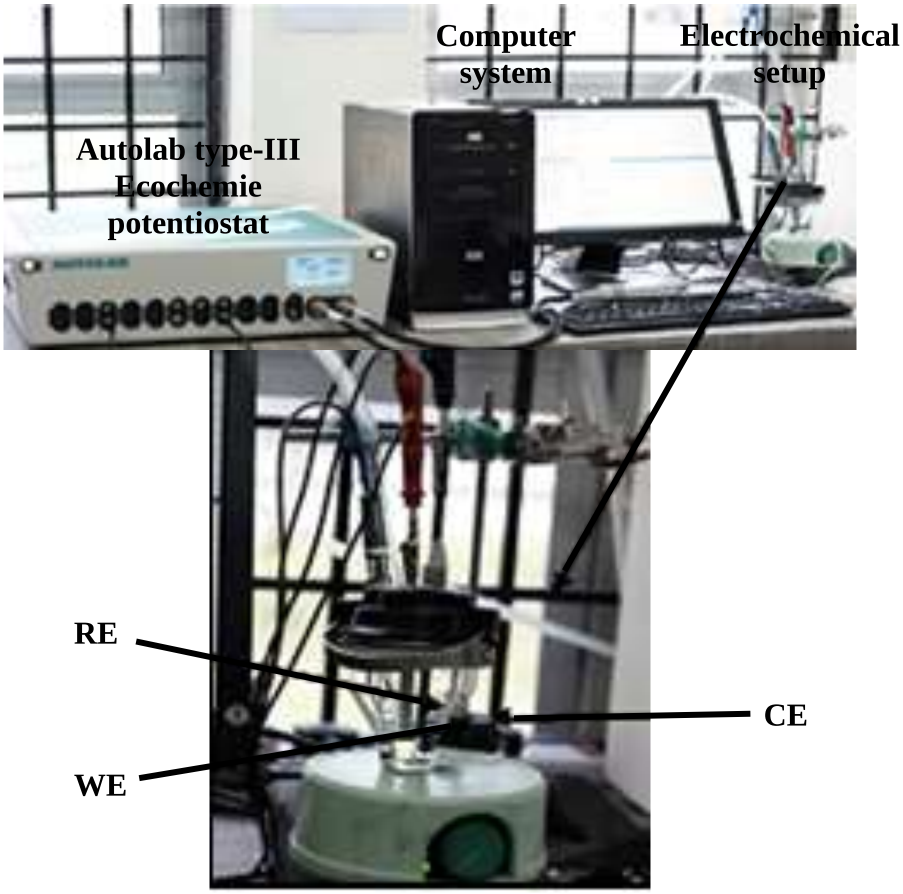

Fig. 1. Electrochemical setup

Preparation of Stock and Working Solutions

The Pb(II) ion solutions and the supporting electrolytes were prepared fresh before each experiment in deionized water. For Pb(II) ion analyses, a sample solution (8 mL), and 0.1 M HCl (2 mL) were transferred to the cell, and the pH was adjusted to pH 2.

Voltammetric Analyses

The CV was run at 5 mV/s to 1000 mV/s for the scan rate and from - 0.6 V to + 0.6 V for the potential scan. The analyte pre-concentration was measured by submerging the CME in 5 mM $K_3Fe(CN)_6$ dissolved in 0.1 M KCl (10 mL) at pH 5.5. The N_2 purging was done to remove air.

SWASV

The SWASV was performed in 10 mL of 0.1 M HCl (pH 2) with N_2 purging for 5 min as follows: (a) the pre-conditioning step to ensure the residual deposits on the CME surface were dissolved at 0.6 V *vs.* Ag/AgCl for 40 s (with 700 rpm rotation speed); (b) the pre-concentration step at -1.2 V *vs.* Ag/AgCl for 270 s (25 Hz, 5 mV step potential (ΔE), 20 mV amplitude with 15 s rest period; (c) the SWASV analyses, unless otherwise stated, from -1.0 V to -0.2 V *vs.* Ag/AgCl, for the Pb(II) ion peak current at -0.48 V *vs.* Ag/AgCl, at 25.0 ± 0.1 °C. The standard addition method with reagent blanks were used for the determination of Pb(II) ion concentrations.

Process Parameters

The SWASV was employed to evaluate the following process parameters: electrolytes (CH_3COONa, KCl, HCl, $HClO_4$, and KNO_3), pH (1 to 8), and deposition potential (-1.6 V to +0.6 V), deposition time (60 s to 360 s), rotational speed (100 rpm to 1000 rpm), amplitude (0.005 V to 0.030 V), frequency (10 Hz to 40 Hz), and step potential (0.001 V to 0.008 V).

RESULTS AND DISCUSSION

Cyclic Voltammetric Analysis

Figure 2 shows the CV of cellulose-HAp-CMEs using 5 mM $K_3Fe(CN)_6$ in 0.1 M KCl at the scan rate of 50 mV/s. A pair of well-defined redox peaks were observed and the change in the electron transfer can be distinguished between cathodic and anodic potentials. The 50 mV/s scan rate was adequate to achieve fast electron transfer.

The two main indicators - the peak current (I_p), and the peak-to-peak potential separation ($\Delta E_p = E_{pa}$-E_{pc}), reflect the properties of the charge transfer at the electrode surface (Jian *et al.* 2013). The higher the ΔE_p, the lower the electron transfer rate and *vice versa*.

The anodic peak current I_{pa} at 13.6 µA for cellulose-HAp-CME was greater than the CPE, cellulose-CME and HAp-CME (9.71 µA, 10.1 µA, and 9.78 µA, respectively), suggesting the higher active binding sites. The ΔE_p of cellulose–HAp-CME (91.9 mV) was also lower than the CPE, cellulose-CME, and HAp-CME (156.2 mV, 102.5 mV, and 114.7 mV, respectively), signifying the higher electron transfer rate.

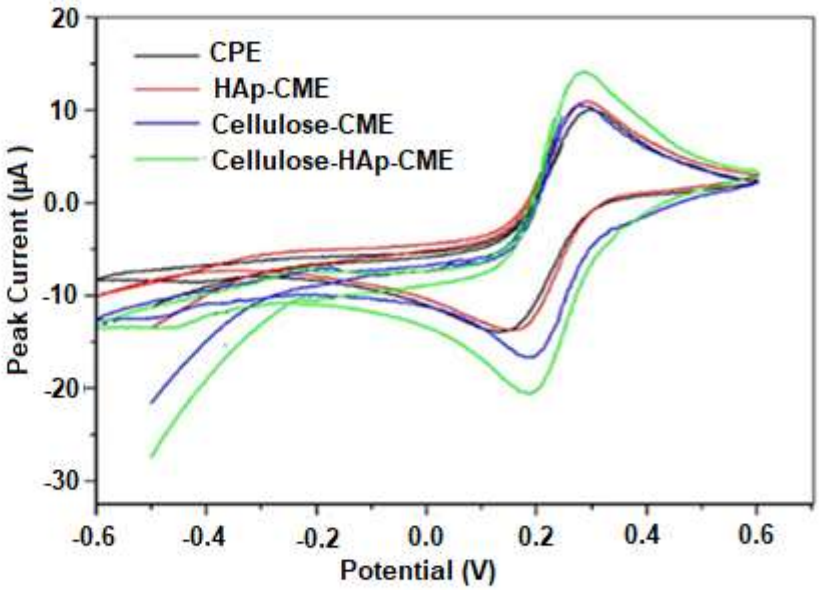

Fig. 2. Cyclic voltammograms of cellulose-HAp-CME in comparison to other electrodes for 5 mM $K_3Fe(CN)_6$ in 0.1 M KCl and scan rate of 50 mV/s

Optimization of Parameters by SWASV

For the quantitative study of the trace Pb(II) ions detection (in ppb range), SWASV is appropriate for the selectivity and pre-concentration step. The ratio of the binder (mix of graphite powder and paraffin) with the modifiers must be optimized first. The cellulose and HAp (1:1 ratio (w/w)) added to the carbon pastes exhibited increased I_p intensity with increasing modifier contents up to 10%, before decreasing at 15% to 20% level. Therefore, the 10% (w/w) level was selected as the optimum modifier composition. Different electrolytes, such as KCl, HCl, $HClO_4$, NaOAc buffer, and KNO_3, at 0.1 M concentration were examined at various pHs for Pb(II) ion detection at 40 ppb. A distinct peak was produced with 0.1 M HCl, while broad peaks were observed with KNO_3, KCl,, $HClO_4$, and NaOAc at pH 2, suggesting the different degree of metal ion complex formation in different supporting electrolytes (Xu *et al.* 2013). The difference is likely due to the metal ions forming complexes with different supporting electrolytes (Xu *et al.* 2013). The signals obtained with 0.1 M HCl were more developed in both height and shape. The Cl^- ions present in HCl may have stronger affinity towards the ionic lead, resulting in oxidation at the interface to form $PbCl_3^-$ species (Dai *et al.* 2004).

The mechanism of Pb sorption onto the HAp-modified electrode starts with a rapid Pb(II) ion complexation at the P-OH sites on the apatite surface, leading to a reduction in pH, followed by partial dissolution of Ca and apatite precipitation, resulting in the formation of $Ca_{10-x}Pb_x(PO_4)_6(OH)_2$ complex (Sandrine *et al.* 2007). Acidic medium is appropriate for the dissociation of Pb(II) (Eq. 1) where the ions leak out of HAp and are detected directly through the reduction of Pb(II) into Pb (Eq. 2) (El Mhammedi *et al.* 2009).

$$\text{HAp-Pb(II)} \rightarrow \text{HAp} + Pb^{2+} \quad (1)$$

$$Pb^{2+} + 2e^- \rightarrow Pb^{\circ} \quad (2)$$

Upon the modification of CPEs with cellulose, the presence of carbonyl and hydroxyl functional groups add to the availability of binding sites (Ajab *et al.* 2018, 2019). These functional groups facilitate the cation binding in the interaction with the aqueous system (Nazir *et al.* 2018). The conductivity showed the highest signal at 0.1 M, where the Cl^- ions bound on the electrode layer could have acted as a link with the Pb(II) ions. The 40 ppb Pb(II) ion detection in 0.1 M HCl, at 270 s and -1.2 V showed an optimal pH 2 for maximal I_p, suggesting improved sensitivity in strong acidic conditions. The deposition potential of -1.2 V and the optimum deposition time of 270 s were chosen for subsequent analysis to avoid electrode saturation and to attain an adequate limit of detection (LOD) with broader response range. The I_p was optimum at 700 rpm rotational speed for sufficient agitation to allow for optimal Pb(II) ions accumulation on the surface.

Calibration and Validation

The SWASV voltammograms of Pb(II) ions in aqueous medium are shown in the range of 10 ppb to100 ppb (Fig. 3) under optimal conditions. Distinct peaks around -0.48 V were observed with good signal to background ratio suggesting that it was relatively free from any interferences. The calibration was done by successive additions of 10 ppb of Pb (II) ions into 10 mL of the electrolyte in the cell. Linear increase of the I_p with increasing Pb(II) ions concentrations was observed (R^2 of 0.9976) with a linear regression model of $y = 10.097x – 1.2053$. The LOD was 0.095 ± 0.32 ppb, and the LOQ was 0.32 ±0.32 ppb. These are well below the Pb(II) ions limit in the drinking water of 10 ppb (World Health Organization 2011). The eco-toxicological detection is important as a part of strategies for environmental remediation, and a number of materials have been explored for Pb(II) ion analytes.

Based on the LOQ and LOD (Table 1), the cellulose-HAp-CME developed in this study was comparable or better than other electrodes. The evaluation on selectivity and interference, repeatability, reproducibility, stability and robustness, has shown that the analyte concentration range, slope and response time are stable and consistent, even after more than 3 months (Ajab *et al.* 2019). The composite structure based on cellulose isolated from the EFBs (Nazir *et al.* 2013; Abdullah *et al.* 2016) and blended with HAp and carbon, has proven to be effective, novel, cheap, and eco-friendly, for use in the Pb(II) detection of water system, blood serum (Ajab *et al.* 2018), and POME (Ajab *et al.* 2019).

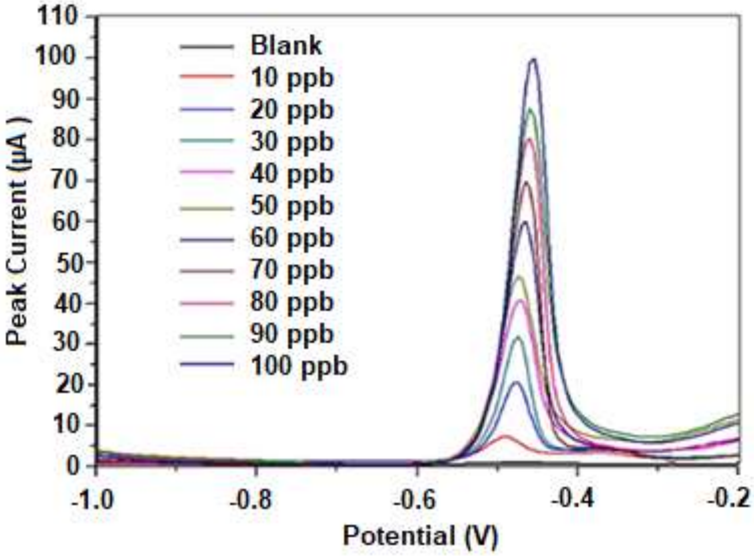

Fig. 3. Stripping voltammograms of cellulose-HAp-CME for Pb(II) ions at optimal conditions

Table 1. Comparison of LOD for Pb(II) Ions in Aqueous Medium Between Cellulose-HAp-CME and Different Electrodes

Electrode	Analytical Technique	LOD (ppb)	Refs
Cellulose/hydroxyapatite-carbon composite	SWASV	0.11 ± 0.36 (Pb(II) in serum)	Ajab *et al.* 2018
Cellulose/hydroxyapatite-carbon composite	SWASV	0.11 ± 0.37 (Pb(II) in POME)	Ajab *et al.* 2019
Bismuth-HAp / CME	SWASV	5	Khan and Abdullah 2013
Nanocellulosic fibers-CPE	SWASV	33	Rajawat *et al.* 2013
Bismuth nanoparticle-porous CPE	SWASV	0.65	Niu *et al.* 2015
CPE / Bentonite	SWASV	62.16	Ourari *et al.* 2018
CNT/rGO/Bi composite	SWASV	0.2	Xuan and Park 2018
Nafion-coated flexible bismuth	ASV	1.68	Wang *et al.* 2018
IIP and MWCNT	DPASV	0.16	Tarley *et al.* 2017
Cellulose/hydroxyapatite-carbon composite	SWASV	0.095	This work

NB: CNT = Carbon nanotube; rGO = Reduced graphene oxide; IIP = Ion imprinted polymer particles; MWCNT = Multi-walled carbon nanotube; DPASV = Differential pulse ASV

CONCLUSIONS

1. An oil palm-based cellulose and hydroxyapatite-carbon composite electrode (cellulose-HAp-CME) was successfully developed, fabricated and optimized for the detection of trace Pb(II) ions in an aqueous system.
2. The deposition of modifiers enhanced the active sites on the electrode surface and promoted the rate of electron transfer and improved the selectivity and sensitivity of detection.
3. The developed electrode achieved higher and reproducible current response with wide linear range at LOD of 0.095 ppb for Pb(II) ions detection in aqueous system.

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REFERENCES CITED

Abdullah, M., Nazir, M., Raza, M., Wahjoedi, B., and Yussof, A. (2016). "Autoclave and ultra-sonication treatments of oil palm empty fruit bunch fibers for cellulose extraction and its polypropylene composite properties," *J. Clean. Prod.* 126, 686-697. DOI: 10.1016/j.jclepro.2016.03.107

Ajab, H., Khan, A. A. A., Nazir, M. S., Yaqub, A., and Abdullah, M. A. (2019). "Cellulose-hydroxyapatite carbon electrode composite for trace plumbum ions detection in aqueous and palm oil mill effluent: Interference, optimization and validation studies," *Environ. Res*. 176, Article ID 108563. DOI: 10.1016/j.envres.2019.108563

Ajab, H., Dennis, J. O., and Abdullah, M. A. (2018). "Synthesis and characterization of cellulose and hydroxyapatite-carbon electrode composite for trace plumbum ions detection and its validation in blood serum," *Int. J. Biol. Macromol.* 113, 376-385. DOI: 10.1016/j.ijbiomac.2018.02.133

Bagheri, H., Afkhami, A., Khoshsafar, H., Rezaei, M., and Shirzadmehr, A. (2013). "Simultaneous electrochemical determination of heavy metals using a triphenylphosphine/MWCNTs composite carbon ionic liquid electrode," *Sensors. Actuat. B- Chem.* 186, 451-460. DOI: 10.1016/j.snb.2013.06.051

Dai, X., Nekrassova, O., Hyde, M. E., and Compton, R. G. (2004). "Anodic stripping voltammetry of arsenic (III) using gold nanoparticle-modified electrodes," *Analyt. Chem.* 76, 5924-5929. DOI: 10.1021/ac049232x

Daneshfozoun, S., Abdullah, M. A., and Abdullah, B. (2017). "Preparation and characterization of magnetic biosorbent based on oil palm empty fruit bunch fibers, cellulose and *Ceiba pentandra* for heavy metal ions removal," *Ind. Crop. Prod*. 105, 93-103. DOI: 10.1016/j.indcrop.2017.05.011

El Mhammedi, M., Achak, M., and Chtaini, A. (2009). "$Ca_{10}(PO_4)_6(OH)_2$-modified carbon-paste electrode for the determination of trace lead (II) by square-wave voltammetry," *J. Hazard. Mater.* 161(1), 55-61. DOI: 10.1016/j.jhazmat.2008.03.057

El Mhammedi, M. A. Achak, M., and Bakasse, M. (2010). "Square wave voltammetry for analytical determination of cadmium in natural water using $Ca_{10}(PO_4)_6(OH)_2$-modified platinum electrode," *Am. J. Anal. Chem.* 1(3), 150–158. DOI: 10.4236/ajac.2010.13019

Fen, W. Y., and Mahmood Mat Yunus, W. (2013). "Surface plasmon resonance spectroscopy as an alternative for sensing heavy metal ions: A review," *Sensor. Rev.* 33(4), 305-314. DOI: 10.1108/SR-01-2012-604

Jian, J.-M., Liu, Y.-Y., Zhang, Y.-L., Guo, X.-S., and Cai, Q. (2013). "Fast and sensitive detection of Pb^{2+} in foods using disposable screen-printed electrode modified by reduced graphene oxide," *Sensors* 13(10), 13063-13075. DOI: 10.3390/s131013063

Khan, A. A. A., Ajab, H., Yaqub, A., and Abdullah, M. A. 2019. "Bismuth/ hydroxyapatite-modified carbon screen-printed electrode for heavy-metal ion detection in aqueous media," *E3S Web of Conferences*, *EDP Sciences* 76, Article ID 02001. DOI: 10.1051/e3sconf/20197602001

Khan, A. A., and Abdullah, M. A. (2013). "Bismuth-modified hydroxyapatite carbon electrode for simultaneous *in-situ* cadmium and lead analysis," *Int. J. Electrochem. Sci.* 8(1), 195-203.

Lee, Y. H., and Hu, C. C. (2014). "Mercury drop electrodes," *Encyclopedia of Applied Electrochemistry*, Springer, New York. DOI: 10.1007/978-1-4419-6996-5

Mohan, L., Durgalakshmi, D., Geetha, M., Narayanan, T. S., and Asokamani, R. (2012). "Electrophoretic deposition of nanocomposite ($HAp+TiO_2$) on titanium alloy for biomedical applications," *Ceram. Int.* 38(4), 3435-3443. DOI: 10.1016/j.ceramint.2011.12.056

Nazir, M., Ajab, H., Raza, M., and Abdullah, M. (2018). "Surface modification of cellulose fibers from oil palm empty fruit bunches for heavy metal ion sorption and diesel desulphurization," *Desalin. Water. Treat.* 107, 241-256. DOI: 10.5004/dwt.2018.22170

Nazir, M. S., Wahjoedi, B. A., Yussof, A. W., and Abdullah, M. A. (2013). “Eco-friendly extraction and characterization of cellulose from oil palm empty fruit bunches,” *BioResources* 8(2), 2161-2172. DOI: 10.15376/biores.8.2.2161-2172

Ng, F. Y., Yew, F. K., Basiron, Y., and Sundram, K. (2011). “A renewable future driven with Malaysian palm oil-based green technology,” *J. Oil Palm. Environ. Health.* 2, 1-7. DOI: 10.5366/jope.2011.01

Niu, P., Fernández-Sánchez, C., Gich, M., Ayora, C., and Roig, A. (2015). “Electroanalytical assessment of heavy metals in waters with bismuth nanoparticle-porous carbon paste electrodes,” *Electrochim. Acta* 165, 155-161. DOI: 10.1016/j.electacta.2015.03.001

Ourari, A., Tennah, F., Ruíz-Rosas, R., Aggoun, D., and Morallón, E. (2018). “Bentonite modified carbon paste electrode as a selective electrochemical sensor for the detection of cadmium and lead in aqueous solution,” *Int. J. Electrochem. Sci.* 13(2), 1683-1699. DOI: 10.20964/2018.02.35

Rajawat, D. S., Kardam, A., Srivastava, S., and Satsangee, S. P. (2013). “Nanocellulosic fiber-modified carbon paste electrode for ultra-trace determination of Cd (II) and Pb (II) in aqueous solution,” *Environ. Sci. Pollut. Res.* 20(5), 3068-3076. DOI: 10.1007/s11356-012-1194-4

Tarley, C. R. T., Basaglia, A. M., Segatelli, M. G., Prete, M. C., Suquila, F. A. C., and De Oliveira, L. L. G. (2017). “Preparation and application of nanocomposite based on imprinted poly (methacrylic acid)-PAN/MWCNT as a new electrochemical selective sensing platform of Pb2+ in water samples,” *J. Electroanal. Chem.* 801, 114-121. DOI: 10.1016/j.jelechem.2017.07.033

Wang, J. (2002). "Real-time electrochemical monitoring: Toward green analytical chemistry," *Acc. Chem. Res.* 35, 811-816. DOI: 10.1021/ar010066e

Wang, L., Jing, G., and Cui, T. (2018). “Nafion coated flexible bismuth sensor for trace lead and cadmium determination,” *Microsyst. Technol.* 24, 3697-3704. DOI: 10.1007/s00542-018-3822-5

World Health Organization (2011). *Guidelines for Drinking Water Quality*, 4th Edition, World Health Organization, Geneva, Switzerland.

Xu, R. X., Yu, X. Y., Gao, C., Jiang, Y. J., Han, D. D., Liu, J. H., and Huang, X. J. (2013). “Non-conductive nanomaterial enhanced electrochemical response in stripping voltammetry: The use of nanostructured magnesium silicate hollow spheres for heavy metal ions detection,” *Anal. Chim. Acta* 790, 31-38. DOI: 10.1016/j.aca.2013.06.040

Xuan, X., and Park, J. Y. (2018). “A miniaturized and flexible cadmium and lead ion detection sensor based on micro-patterned reduced graphene oxide/carbon nanotube/bismuth composite electrodes,” *Sensors. Actuat. B- Chem.* 255(2), 1220-1227. DOI: 10.1016/j.snb.2017.08.046

Zhao, G., Wang, H., and Liu, G. (2017). “Direct quantification of Cd^{2+} in the presence of Cu^{2+} by a combination of anodic stripping voltammetry using a bi-film-modified glassy carbon electrode and an artificial neural network,” *Sensors* 17(7), Article number 1558. DOI: 10.3390/s17071558

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