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A Review

Green electrochemical sensors based on ionic liquid nanocomposites for detection of environmental pollutants

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Industrialization and globalization have caused a huge burden on the limited natural resources, which releases various environmental pollutants such as toxic metal ions and pesticides. World Health Organisation (WHO) has set a maximum permissible limit for these toxic pollutants in water, above which, it is unsuitable for drinking purpose. There are various techniques available for the determination of such pollutants like ICP-MS, HPLC, FAAS *etc*. that are costly, cumbersome, and time consuming. Whereas, electrochemical sensors are portable, fast and can perform multi-analyte sensing. Electrochemical sensor can be made selective by fabricating with nanocomposites having different functional groups. Nowadays, trend of utilizing greener materials in research field is being highly appreciated in accordance with the principles of green chemistry for the application and development of electrochemical sensors. Ionic liquids having non-volatility, low toxicity, wide potential window, high electrochemical stability and conductivity have shown sustainable electrochemical sensing applications. Nanocomposite of these ionic liquids as a sensing platform have been extensively used in electrochemical detection of various pollutants. This work provides a literature survey of different ionic liquid nanocomposite based sensing platform for electrochemical detection of toxic pesticides and heavy metals. They have demonstrated good sensitivity with detection limit below WHO guidelines.

Keywords: Green electrochemical sensors, Ionic liquid, Nanocomposites, Pollutants

Introduction

Ionic liquids (ILs) are low-melting salts typically consisting of huge asymmetric organic cations with organic or inorganic anions. The inclusion of positive and negative ions, combined together in a liquid state is the main characteristic of ILs. An arbitrary definition frequently used for ILs describe them as molten salt shaving melting point below 100°C. ILs with melting point below room temperature are often called room temperature ionic liquids (RTILs). It is important to note that ionic liquids are not simple liquids, their ions are generally asymmetric with delocalized electrostatic charges. ILs include various types of organic cations such as imidazolium, pyridinium and phosphonium *etc*. with a relatively small anion which can either be a single atom like Cl^- or larger molecules like ethyl sulphate, tetrafluoroborate, hexafluorophosphate *etc*. First IL was prepared by Walden in 1914 having a melting point of 12°C. These ILs have additional benefits over conventional organic solvents as they have very low vapour pressure and higher temperature range. The ionic components induce polarity which help in dissolving wider range of organic and inorganic compounds. The ionic interactions such as electrostatic attraction and repulsion decides their solubility with polar compounds whereas the alkyl chain on cationic part control their miscibility for non-polar substances. As the characteristics of these solvents can be tuned based on our requirement they are also famously known as “designer solvents”. Because of their charged nature they are being efficiently used in both synthesis as well as electrochemical field. Their high solvation ability, along with good thermal and ionic conductivity have attracted the interest of research community related to chemical synthesis and electrochemical fields[1]. The various applications of ILs in different fields of chemistry can be seen in (Fig. 1).

These ILs can be combined with different materials such as silica, carbon based nanomaterials, zeolites, Metal-Organic Frameworks (MOFs) *etc*. to form composites with desired characteristics. ILs interact with the surface of these porous material and as a consequence, the important characteristics of ILs such as physicochemical, rheological, thermophysical and conductivity can be tuned. In such hybrid systems, the

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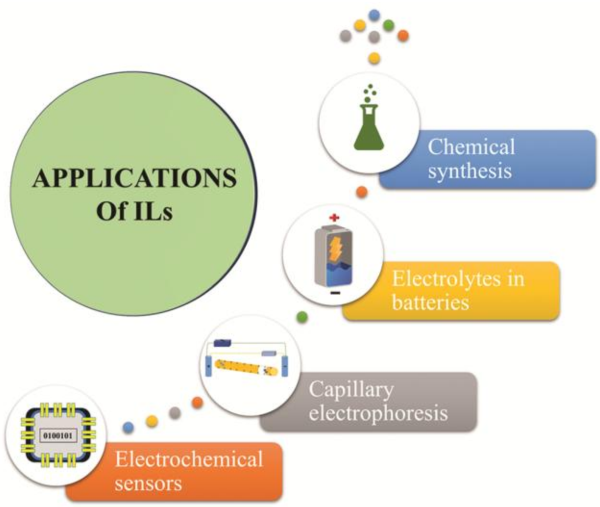

Fig. 1 — Applications of Ionic Liquids

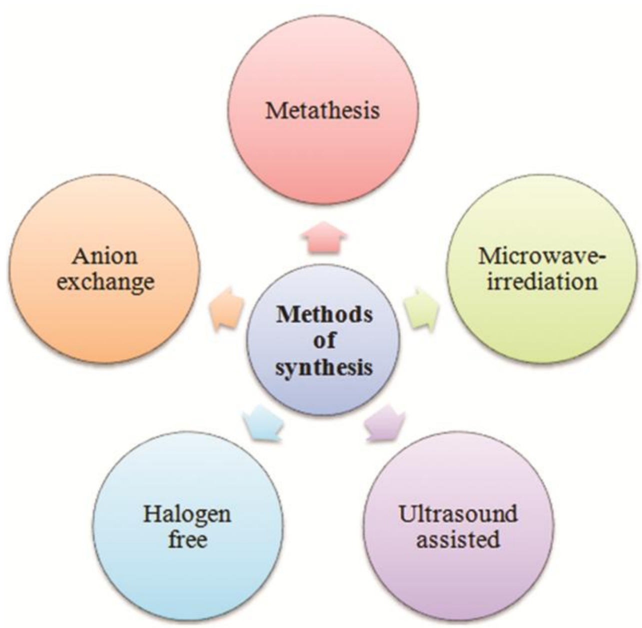

Fig. 2 — Methods of synthesis of ILs

porous material not only ensures thermal and mechanical stability but also improves absorption capacity and selectivity towards specific analytes. So, the ILs composites can be effectively used in fabricating electrochemical sensor for the selective determination of various environmental pollutants.

Synthesis of ionic liquids

The low volatility and melting point of ILs causes difficulty in their preparation. However, there are various routes through which ionic liquids can be prepared depending on the requirement such as anion exchange, microwave irradiation and ultrasound assisted synthesis which will be discussed in more detail in subsequent sections (Fig. 2).

Anion exchange

In this method Lewis acid base ILs are formed *via* the anion exchange reaction between halide ions and Lewis acids. The most studied and widely used Lewis acid based ILs are of $AlCl_3$ based salts. Lewis acid and halide ions are simply mixed and results in formation of more than one anionic species depending upon the different ratio of Lewis acid and quaternary halide salt. Three types of ILs, anionic, cationic and neutral are formed based on ratio of halide ions and $AlCl_3$. Anionic ILs are formed when the halide are present in molar excess over $AlCl_3$. Cationic ILs are formed when the $AlCl_3$ molar excess over Lewis acid and when they are present in equimolar, neutral ILs are formed[2].

Microwave irradiation

The microwave irradiation synthesis of ILs is a greener approach as it is fast, selective and highly energy saving as compared to conventional heating methods. It is safe heating source which works in solvent free condition and produces high yield in minimum time. Thus, it's an environmental friendly method of synthesis. Various ILs have been synthesized using this method. In 2002, Khadilkar and co-workers synthesized imidazolium and pyridinium cation based ILs using microwave irradiations method under solvent free condition[3]. Similarly, imidazolium based ILs like calamitic-calamitic (alkoxycyanobiphe), calamitic-discotic and discotic-discotic (triphenylene) moieties were synthesized using microwave irradiations method[4].

Ultrasound-assisted synthesis

The Ultrasound assisted synthesis of ILs is gaining more attention in various chemical and pharmaceutical industries due to its advantages over other methods. The Ultrasound assisted synthesis of ILs takes place under solvent free condition and the obtained yield is also high. In this method of synthesis, the ultrasound works at the interfacial layer of two immiscible liquids which enhances the material transformation and this ultimately improves the rate of reaction. Hence, the other advantage is the time required for synthesis of ILs is very less and its environment friendly[5]. In 2014, N-methyl-2-pyrrolidinium hydrogensulphate-based IL was synthesized using an ultrasound-assisted method without solvent with good yield[6].

Environmental pollutants and their determination

The population of the world has increased tremendously which have reduced the arable land and natural resources at a faster rate. To meet the demands of such a huge population excessive industrial and mining activities are going on, which releases several environmental pollutants, including heavy metal ions. Also, to ensure food safety various pesticides are being used at a large scale. These environmental pollutants are generally non-biodegradable and persists in the environment for a long time. These pollutants can be easily absorbed by plants and can enter our food chain which causes health problems. World Health Organisation (WHO) and United States Environmental Protection Agency (US EPA) have set maximum permissible limit for these environmental pollutants in drinking water above which it is unsafe.

Important environmental pollutants

The term 'pollutant' is referred to any substance that when introduced in the environment shows adverse effects. The common environmental pollutants include toxic metals, pesticides, volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), *etc*. Among these environmental pollutants toxic heavy metals and pesticides are of serious concern because of their tendency to cause harmful effects even at very low concentration. Heavy metal ions are used in industries for manufacturing of utensils, machines, vehicles, paints, *etc*. Pesticides are mainly used in agriculture for the safety of crops from pests, insects and weeds *etc*. These are deadly poisons which transmit in living organisms through soil, water and air. A brief discussion on the toxicity and maximum permissible limit of these pollutants is provided in subsequent sections[7].

Heavy metals

The toxic heavy metals like arsenic, cadmium, lead, mercury *etc*. are being used in various industrial processes and are released in the environment without pre-treatment. These metals affect our body either by making the active enzymes inactive or by replacing the essential metal ions, which leads to various health issues and chronic diseases also can lead to death. '*Minamata'* and '*Itai-Itai'* are some of the deadly known disease that are caused by the exposure of mercury and cadmium respectively. Certain metals in adequate amount are essential for various physiological functions and comes in the category of essential elements such as zinc, copper, iron *etc*. However, the imbalance of these essential metals in our body can lead to serious health problems *e.g*. copper in excess can lead to '*Wilson disease'*[8]. A maximum permissible limit for these toxic heavy metal ions in drinking water is set by WHO and US EPA as shown in (Table 1)[9,10].

Table 1 — Maximum permissible limit of toxic metal ions as per WHO and US EPA for drinking water

Metals	EPA standard limit (mg L^{-1})	WHO standard limit (mg L^{-1})
Arsenic	0.010	0.010
Cadmium	0.005	0.003
Chromium	0.1	0.05
Copper	1.3	2.0
Lead	0.015	0.010
Mercury	0.002	0.001
Thallium	0.002	-

Pesticides

A pesticide is a substance used to kill, repel, or control certain forms of plant or animal life that are considered to be pests. Many pesticides can be grouped into chemical families. Based on the chemical constituents, pesticides are classified as organochlorine, organophosphate, carbamate, synthetic pyrethroids, and inorganic pesticides *etc*. Pesticides can also be classified on the basis of the target against which it is applied like insecticides, nematicides, fungicides, weedicides in addition to miscellaneous other substances. There is another class of pesticides which is produced from natural materials such as bacteria, plants *etc*. having pesticidal applications and are known as biopesticides, for example baking soda and canola oil.

Prominent insecticide families include organochlorines, organophosphates, and carbamates. Pesticides are extensively used in agriculture worldwide to control pests in agricultural crops as insecticide, acaricide and herbicides and increase the agricultural production yield. Due to their large persistence and high toxicity, pesticides are considered as the most dangerous of environmental pollutants. Naturally, their residues can persist in the environment for a longer period due to their lower solubility and higher stability. For example, parathion (organophosphates) and DDT (organochlorides) can be easily recovered even after twenty years of their usage. Among the large variety of synthetic pesticides, organophosphorus pesticides (OPs) are the commonly used toxic one. It inhibits acetylcholinesterase which plays a crucial role in central nervous system of insects and humans that result in accumulation of acetylcholine at nerve endings. Excess acetylcholine at synaptic junctions in neurons can lead to cholinergic dysfunction and disrupts normal neural transmission. At synapses the excess accumulation of acetylcholine can result in jammed and over stimulated nerves. Long exposure of organophosphate pesticide have found to result in increased cancer cases, suppression of immune system, kidney diseases, endocrine disorders, sterility among females and males, neurological disorders among children. Carbamate pesticides also have similar toxicity mechanism as organophosphates but they are less harmful. Due to their lower toxicity, the minimum concentration for poisoning is on the higher side for carbamate pesticides as compared to organophosphorus compounds. Due to the lack of timely degradation and less water solubility, they persist in the ecosystem which is harmful for the environment. As these pesticides causes serious health problems to both humans and animals, so developing monitoring techniques for these compounds is highly crucial[11]. Guideline value as set by WHO for some of the pesticidesin drinking water are mentioned in (Table 2)[12]. Hence, more focus on developing cost effective, faster, portable and sensitive method for the monitoring of pesticides is under progress.

Electrochemical determination of pollutants

Numerous techniques have been developed for the determination of pesticides and toxic metal ions. Such techniques include gas chromatography (GC), high performance liquid chromatography (HPLC), inductively coupled plasma (ICP), flame atomic absorption spectroscopy (FAAS), mass spectrometry and electrochemical sensing to detect these environmental pollutants at low level. Though HPLC, FAAS, GC and ICP shows good detection limit but have certain drawbacks like they have complex analytical procedure, bulky and costly. Electrochemical sensors in addition to solving above problems can perform speciation and multi-sensing of analyte. Electrochemical sensors have gained lot of attention in the field of analytical chemistry as they can be used to monitor in real environmental samples because of their portability[13]. Electrochemical sensors represent themselves as a low-cost alternative for the detection of pesticides and toxic metal ions in contrast to another techniques. So, the focus of the review is centred around the recent development of electrochemical sensor fabricated using IL composites for the sensing of toxic metals and pesticides.

Table 2 — WHO guideline value of pesticides for drinking water

Pesticides	WHO standard limit (μg L^{-1})
Atrazine	2
Carbofuran	7
Diquat	10
Isoproturon	9
Methoxychlor	20
Metoclachlor	10

Application of electrochemical sensors

- They provide instant information of the analyte in the real environment.
- The handling and sampling methods of the instrument is easy.
- Simultaneous sensing of different analyte is possible.
- Due to miniaturization, they can be easily used for monitoring of bio-systems.
- Gas sensing is also possible using electrochemical sensors.

Electrochemical sensing of pollutants

Electrochemical sensing requires a sensing platform for the detection of environmental pollutants that measures the interaction qualitatively as well as quantitatively to provide an electrical signal which can be used for further studies. The sensitivity of such sensing platforms can be enhanced by fabricating it with numerous modifiers containing various functionalities such as biomolecules, nanomaterials, ligands, ionophores andionic liquids *etc.* Such modifiers can be concurrently used to prepare a composite material which have individual characteristics for more benefits. Also, there are different types of electrochemical sensing techniques like voltammetric, potentiometric and conductometry which have their own advantages. Based on the transduction method of electro-analytical technique, conductometry is a bulk method while voltammetry and potentiometry are interfacial method[14]. The electrochemical set up used in these techniques are usually compact and portable which makes monitoring of these environmental pollutants outside the laboratory feasible[15].

Advantages of ionic liquid in fabricating electrochemical sensor

ILs are being efficiently used in electrochemical sensing technologies as they are widely used in manufacturing electrochemical equipment such as super capacitors, batteries, dye sensitized solar cells (DSSCs) and fuel cells[16]. They are extensively utilised to make electrode materials and electrolytes in these types of devices. The constituents of ILs show stable responses towards wide range of reduction and oxidation potential and can be applied in a larger potential window. Moreover, these ILs can replace non-conductive binding agents such as mineral oil, polymer compounds and paraffin as they possess high viscosity and good conductivity. They provide excellent electrochemical response due to high conductivity and are efficient in trace level detection of analytes. As they have high solvation characteristics that can help in dispersing various nanomaterials like carbon, metal oxide nanomaterials, *etc*. which is further helpful in fabricating electrode uniformly. Taking all these advantages into consideration, ILs and their composites can be a promising candidate for the preparation of electrochemical sensor[17].

Ionic liquid nanocomposite as sensing platform for environmental pollutants

RTILs are cationic and anionic salts in molten state, that have opened new realms in the field of electrochemistry because of their various sustainable advantages. They have high thermal stability, nonvolatility, low toxicity and high conductivity. Additionally, they possess high dielectric and ionic characteristics that help in stabilizing different nanoparticles that is beneficial for fabricating electrode with various hybrid IL-nanocomposites to induce selectivity. Due to their high viscosity, they are being widely used as a binding agent for electrode preparation nowadays. Also, immobilization of various modifiers such as nanomaterials and biomolecules on electrode surface becomes a lot easier with the help of viscous ionic liquid.

Ionic liquid-carbon based nanocomposite

Traditional carbon based sensors include glassy carbon electrodes, carbon fibers and pyrolytic graphite. Recently carbon based nanomaterials have been one of the excellent electrode modification materials owing to large specific surface area and strong electron transmission performance. Carbon having catenation property can bind with other carbon atoms in different manner to give different allotropes. By combining different allotropic forms of carbon at the nanoscale it is possible to have tailor made surfaces with unique properties. These novel materials have shown high potential especially in the electrochemical sensing. They can be deposited on electrode surface through dip coating, drop casting or can be directly grown on surface. There is a huge focus on carbon nanotubes (CNTs), graphene, carbon dots and carbon fibers. Carbon-based nanomaterials have excellent conductive properties with high surface to volume ratio and are highly preferred in fabricating electrochemical sensors. They are already being used as conducting material in environmental, medicinal and engineering field efficiently[18]. The IL-CBNMs hybrids allows to harness desired benefits of each material in order to prepare sensing platform for detection of heavy metals and pesticides.

Heavy metals

There is a large number of already published work where researchers have used IL-Carbon nanomaterial hybrid nanocomposites for the detection of heavy metals in electrochemical sensors. Khani *et al*. developed an ion selective electrode by incorporating ionophore (1-(2-ethoxyphenyl)-3-(3-nitrophenyl) triazene), conductive binder (BMIM·BF_4) and a conductivity enhancing material (MWCNTs) for the determination of Hg(II). The fabricated potentiometric sensor showed a detection limit of 2.5×10^{-9} M and linearity range of 1.0×10^{-4} - 5.0×10^{-9} M. Apart from decent analytical performances the sensor has good shelf life of at least 55 days and was applied to determine Hg(II) in real water samples and dental amalgam[25]. Similarly, Bagheri *et al*. have constructed an electrode for simultaneous detection of Cd(II), Pb(II) and Hg(II) using a composite electrode having triphenylphosphine functionalised MWCNTs with RTILs as a binding agent. The fabricated sensor was able to show linearity for these pollutants from 0.1 to 150 nM. The limit of detection for Pb(II), Hg(II) and Cd(II) was found to be 6.0×10^{-5}, 9.2×10^{-5} and 7.4×10^{-5} μM under optimised conditions using SWASV, respectively[29]. Zhao and Liu fabricated an electrochemical sensor for simultaneous detection of lead and cadmium by modifying GCE with a homogenous mixture of L-cysteine functionalised MWCNTs, nafion and ionic liquid. The prepared sensor showed detection limit of 0.05 and 0.08 μg L^{-1} for Cd(II) and Pb(II), respectively, within a concentration range from 0 to 50 μg L^{-1} under optimised conditions. The authors confirmed that sensor possess high selectivity with good stability and finally applicability of the sensor was checked in real water samples for detection of both ions that showed good recovery[35]. Pandey *et al*. used GCE modified with IL (BMIM-PF_6), graphene oxide and nafion as binding agent to prepare an electrochemical sensor for detection of Cd(II).The sensor showed a sensitivity, detection limit and linear range of 0.0711 mA/ppb, 0.33 ppb and 2.4 -70 ppb for Cd(II) respectively.

Similarly, a sensitivity, detection limit and linear range of 0.0371 mA/ppb, 0.42 ppb and 5-15 ppb for Pb(II), respectively. Also, the sensor exhibited good reproducibility, stability and selectivity under optimised conditions[36].

Pesticides

Electrochemical sensor based on IL-Carbon nanomaterial hybrid nanocomposites have been used extensively for the detection of pesticides and other similar toxic compounds. Zheng *et al*. prepared an electrochemical biosensor by immobilizing acetylcholinesterase with the help of glutaraldehyde on ionic liquid-graphene composite that is further used to modify GCE to detect carbaryl and monocrotophos. The fabricated sensor showed good sensitivity towards both the pesticides with a limit of detection of 5.3×10^{-15} M and 4.6×10^{-14} M for carbaryl and monocrotophos, respectively, at optimised condition using amperometry technique. The authors found that it showed good stability with a low-cost alternative for analysing the pesticides[39]. Rasdi *et al*. developed a carbon paste electrode with cyclodextrin functionalised ionic liquid to detect 2,4-dichlorophenol, a precursor in preparing biocides. The sensor is highly effective and specific that showed a detection limit of 1.2 μMol L^{-1} under optimised conditions. Finally, the sensor's applicability was tested in lake and mineral water samples that gave good results[40]. Zhao *et al*. fabricated an electrochemical sensor for determination of imidacloprid by modifying GCE with ionic liquid monomer immobilised MWCNTs and graphene-IL nanocomposite. They reported that the sensor exhibited a good detection limit of 0.08 μM, sensitivity of 0.71 μA μM^{-1} mm^{-2} and a linearity range of 0.2-24 μM at optimised condition. The authors stated that it showed good reproducibility and selectivity with efficient performance in determination of imidacloprid in real samples[44]. Nasr-Esfahani *et al*. on the other hand developed an electrochemical sensor by modifying GCE with graphene quantum dots, MWCNTs and ionic liquid for the determination of imidacloprid. Further polyaniline film is electropolymerized with help of cyclic voltammetry. The sensor showed a detection limit of 9 nmol L^{-1} and a linearity range of 0.03 - 12.0 μmol L^{-1} under optimised conditions using DPV technique[50]. The other reported ionic liquid-carbon nanocomposite based electrochemical sensor for the determination of toxic metals and pesticides is enlisted in (Table 3) with their analytical performance.

Ionic liquid-Metal/Metal Oxide nanocomposite

Owing to the fast response time, superior sensitivity, easy integration on wearable/flexible substrate and low cost of fabrication, these

Table 3 — Ionic liquid-Carbon nanocomposite based electrochemical sensors for the determination of metals and pesticides

Metals

Electrode	Analyte	Technique	LOD (μM)	LR (μM)	Ref
IIP/Carbon IL electrode	Hg	DPASV	0.1×10^{-3}	$0.5\times10^{-3} - 10\times10^{-3}$	[19]
HQ-IL-CPE	Cd	DPASV	5.0×0^{-3}	0.03 – 2.0	[20]
$L/MWCNTs/CPE_{IL}$	Cd	DPASV	0.08 *	0.2 – 23 *	[21]
OMC-IL2-chitosan/CILE	Pb	DPASV	25×10^{-3}	0.05 – 1.4	[22]
Hollow fiber-graphite supported nanomagnetite/ionic liquid electrode	Pb & Cd	DPV	0.19 & 0.61*	0.6 – 6500 & 2 –13000*	[23]
P123-SH/ILs/GCE	Cd	LSV	1×10^{-3}	$29 - 0.87\times10^{-3}$	[24]
ENTZ/IL/MWCNTs/CPE	Hg	Potentiometric	2.5×10^{-3}	$100 - 5.0\times10^{-3}$	[25]
IIP/IL/MWCNTs/Nanosilica/ Graphite/CPE	Cd	Potentiometric	2.00×10^{-1}	$10^{-1} - 1000$	[26]
ionic-liquid/Schiff base/MWCNTs/ nanosilica/CPE	Pb	Potentiometric	2.51×0^{-3}	$5\times10^{-3} - 100000$	[27]
SBA-15/ Ionic Liquid/MWCNTs/Graphite	Cr	Potentiometric	1.0	10 – 100000	[28]
PPh_3/MWCNTs/IL/CPE	Pb, Hg & Cd	SWASV	6.0×10^{-5}, 9.2×10^{-5} & 7.4×10^{-5}	$10^{-4} - 0.15$, $10^{-4} - 0.15$ & $10^{-4} - 0.15$	[29]
IL/Gr/L/CPE	Tl, Pb & Hg	SWASV	3.57×10^{-4}, 4.50×10^{-4} & 3.86×10^{-4}	$1.25\times10^{-3} - 2.0\times10^{-1}$	[30]

(*Contd.*)

Table 3 — Ionic liquid-Carbon nanocomposite based electrochemical sensors for the determination of metals and pesticides (*Contd.*)

Electrode	Analyte	Technique	LOD (μM)	LR (μM)	Ref
Metals					
GR/IL-SPE	Pb & Cd	SWASV	0.1 & 0.08 *	1.0 – 80.0 *	[31]
GR/IL-SPE	Cd	SWASV	3 *	5.0 – 70.0 *	[32]
BiF/IL/CPE	Cd & Pb	SWASV	0.1 & 0.12 *	1.0 μg L^{-1} – 100.0 *	[33]
BI/MWNT-IL/SPCE	Cd & Pb	SWASV	0.5 & 0.12 *	1.0 – 60 *	[34]
SWCNs/l-cysteine/Nafion-IL/GCE	Cd & Pb	SWASV	0.05 & 0.08 *	0 – 50 *	[35]
IL/GO/GCE	Cd & Pb	SWASV	0.33 & 0.42 *	2.4 – 70 & 5 – 15 *	[36]
BiPs-CNFs/[EMIM][NTf2]/CPE	Pb & Cd	SWASV	0.12 & 0.25 *	2 – 120 *	[37]
HAP-CILE	Pb & Cd	SWASV	2×10^{-4}& 5×10^{-4}	1×10^{-3} – 1×10^{-1}	[38]
Pesticides					
AChE/IL-GR–Gel/GCE	Carbaryl & Monocrotophos	Amperometry	5.3×10^{-9}& 4.6×10^{-8}	1.0×10^{-8} – 1.0×10^{-2}& 1.0×10^{-7} – 5.0×10^{-2}	[39]
Cyclodextrin/IL-CPE	2,4-dichlorophenol	Amperometry	1.2	4 – 100	[40]
AChE/MWCNTs/IL/SPE	Chlorpyrifos	CV	0.05 *	0.05 – 1.0×10^{-5}*	[41]
Carbon paste electrode modified with 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	Carbendazim	DPASV	1.7 *	10 – 247 *	[42]
MWCNTs–IL-GCE	Pyrimethanil	DPV	1.6×10^{-2}	1.0×10^{-1} – 100	[43]
MWNTs@RAFT-MIP-GR-IL/GCE	Imidacloprid	DPV	0.08	0.2 – 24	[44]
IL/CCE	Imidacloprid	DPV	31×10^{-3}	5×10^{-2} – 7	[45]
AChE/PEDOT/RGO/IL/FTO	Chlorpyrifos, Malathion & Methyl parathion	DPV	0.04, 0.117 & 0.108 *	-	[46]
Cl/iron porphyrin -modified MWCNTs/AChE/GCE	Monocrotophos	DPV	3.2×10^{-5}	1.0×10^{-4} – 1.0×10^{-1}	[47]
GCE/GQDs/IL/MWCNTs/PANI	Imidacloprid	DPV	9×10^{-3}	0.03 – 12.0	[48]
IL–GNs/GCE	Methyl parathion	DPV	1.1 *	5.3 – 2600 *	[49]
MIP–IL–EGN/GCE	Methyl parathion	DPV	6×10^{-3}	0.010 – 7.0	[50]
DNA-Carbon Ionic Liquid	Paraquat	DPV	3.6×10^{-3}	5×10^{-2} – 70	[51]
poly-pPDs-IL/CPE	Carbaryl	DPV	0.09	0.5 – 200	[52]
GO-IL/GCE	Carbaryl	SWV	0.02	0.10 – 12.0	[53]
PIL/ZIF-8/CPE	Parathion	SWV	2.0 *	5.0 – 700 *	[54]
MWCNTs/IL/GCE	2-Chlorophenol	SWV	0.1	0.5 – 12.0	[55]

*ppb

nanomaterials possess numerous applications in electrochemical sensing, degrading waste, water splitting, photovoltaic solar cells and various enhanced imaging technologies like MRI, optical imaging *etc*. for diagnostic purposes. It has been reported that wide range of metal and metal oxide nanomaterials have been used to develop potentiometric, conductimetric, voltammetric sensors *etc*. They can be further modified by various modifiers like ligands, binding agents, antibodies *etc*. to give them selectivity and delivering properties. They are generally composed of noble metals like Pt, Pd, Ag, Au *etc*. and on the other hand metal oxides like TiO_2, MnO_2, WO_3, CeO_2, *etc*. They are chemically stable and possess high surface area which is ideal for electrochemical sensing of various pollutants. Metal and metal oxide nanomaterials can be easily electrodeposited on electrode which makes the sensing process fast and cost effective.

Heavy metals

Numerous IL-Metal/Metal Oxide hybrid nanocomposites have been successfully applied as electrochemical sensors for the detection of heavy metals. Zhou *et al*. prepared a Hg(II) electrochemical sensor by modifying GCE with gold nanoparticles

(AuNPs), graphene oxide and ionic liquid. They stated that there is a synergic effect between the modifiers which resulted in to provide a lower detection limit of 0.03 nM over a linear range of 0.1-100 nM using anodic stripping voltammetry[57]. Xiong *et al*. prepared a composite electrode containing an irradiated attapulgite [$(OH_2)_4$ (Mg, Al, $Fe)_5$ (OH)·$2Si_8O_{20}$]·4H2O and ionic liquid ([C4dmim] [NTf2]) for simultaneous detection of Cu(II), Pb(II), Cd(II) and Hg(II) using SWV technique. The proposed sensor showed a limit of detection of 0.06, 0.8, 0.5 and 0.2 nM respectively which is much lower than limit set by WHO[61]. Whereas, Gao *et al*. have reported a cheap alternative for conventionally used noble metal in a strong acid for detection of As(III). They confirmed that SPCE modified with a composite of RTILs ([C4dmim] [NTf2], [C4mim] [FAP], [C4mim] [NTf2], and [N2113] [NTf2]) and Fe_3O_4 showed better results than the previously reported methods. The sensor showed a detection limit of 8×10^{-4} ppb and a sensitivity of 4.91 μA ppb^{-1} with a linearity range from 1 to 10 ppb using SWASV[62]. Similarly, Yang et al. designed a sensing interface by preparing amine functionalised porous SnO_2 nanowires and RTIL nanocomposite for detection of Cd(II). The fabricated sensor showed a detection limit of 0.0054 μM with a sensitivity of 124.03 μA μM^{-1} and a linearity range between 0.01 –0.2 μM with the help of SWASV technique. The author suggested that the sensor is able to detect Cd(II) ions much below the desirable concentration limit set by WHO (0.0267 μM)[63].

Pesticides

Electrochemical sensor based on IL-Metal/Metal Oxide hybrid nanocomposites have been largely reported for detection of pesticides, herbicides *etc*. Huang et al. modified GCE with molybdenum disulfide (MoS_2), ionic liquid and gold/silver nanorods to prepare electrochemical sensor for detection of 2,4-dichlorophenol (2,4-DCP). The found that modified electrode showed better performance compared to bare one. Detection limit of 2.6 nM was obtained with a linearity range of 0.01-50 μM. Finally, the sensor was applied in tap and river water samples to detect 2,4-DCP that gave satisfactory result[67]. Zheng *et al*. fabricated an electrochemical biosensor by immobilizing acetylcholinesterase on GCE with ionic liquid functionalised graphene, chitosan and Co_3O_4 nanoparticles for detection of organophosphate pesticides. The sensor showed a detection limit of 1.0×10^{-13} M with a linearity range 5.0×10^{-12} to 1.0×10^{-7} M using DPV technique. They also stated that the proposed sensor exhibited good stability and sensitivity for the determination of organophosphate pesticides[68]. Bolat and Abaci prepared a sensitive platform based on gold nanoparticles (AuNPs), IL and chitosan composite on pencil graphite electrode for determination of Malathion. The fabricated sensor showed a detection limit of 0.68 nM along with two linear range 0.89-5.94 nM and 5.94-44.6 nM representing two binding positions of analyte. Finally, the sensor was applied on apple and tomato samples to demonstrate its applicability in real analysis[70]. Kardas *et al*. developed a voltammetric sensor with a carbon paste electrode fabricated using CuO NPs and IL for determination of atrazine. The sensor exhibited a very low detection limit of 2.0×10^{-12} M and linearity range between 1.0×10^{-11}-2.0×10^{-9} M using SWV technique. Also, the feasibility of the sensor was checked in wastewater that showed good recovery[71]. The other reported ionic

Table 4 — Ionic liquid-Metal/Metal Oxide nanocomposite based electrochemical sensors for the determination of metals and pesticides

Metals

Electrode	Analyte	Technique	LOD	LR(μM)	Ref
NILHgFE	Pb & Cd	AdSV	0.12 & 0.13 *	0 – 16 *	[56]
AuNPs/GO-IL/GCE	Hg	ASV	0.03×10^{-3}	0.1 – 100×10^{-3}	[57]
SPSbFE/IL	Hg	ASV	0.36 *	20 – 140 *	[58]
Bi/Fe_3O_4/ILSPE	Cd	DPV	0.05 *	0.5 – 40 *	[59]
TBA/CeO_2–MWNTs–$EMIMBF_4$/GCE	Pb	DPV	5×10^{-3}	1.0×10^{-2} – 10	[60]
IAP30/RTIL electrode	Pb, Cd, Cu & Hg	SWASV	0.8×10^{-3}, 0.5×10^{-3}, 0.2×10^{-3} & 0.06×10^{-3}	0.1 – 2.5	[61]
Fe_3O_4-RTIL/SPCE	As	SWASV	8×10^{-4}*	1 – 10 *	[62]
NH_2/SnO_2-RTIL/GCE	Cd	SWASV	0.0054	0.01 – 0.2	[63]
IL-Mg/Al-GCE	Cd, Cu, Hg & Pb	SWASV	0.25, 0.025, 0.25 & 0.016 *	0.5 – 20, 0.05 – 20, 0.5 – 20 & 0.05 – 20 *	[64]

(*Contd*.)

Table 4 — Ionic liquid-Metal/Metal Oxide nanocomposite based electrochemical sensors for the determination of metals and pesticides

Pesticides

Electrode	Analyte	Technique	LOD	LR(μM)	Ref
TiO_2–P3HT–IL modified GCE	Herbicide & Acetochlor	Amperometry	0.2×10^{-3}	0.5 – 20	[65]
$NiCo_2O_4$/rGO/IL/GCE	Pyrimethanil	DPV	11×10^{-3}	0.1-10.0	[66]
MoS_2-IL-Au/Ag NR electrode	2,4-dichlorophenol	DPV	2.6×10^{-3}	0.01 – 50	[67]
AChE/Co_3O_4/CHI/GCE	Organophosphate pesticides	DPV	10^{-7}	5.0×10^{-6} – 1.0×10^{-1}	[68]
MIP/GR-IL-Au/CS-AuPtNPs/GCE	Carbaryl	DPV	8×10^{-3}	0.030 – 6.0	[69]
AuNPs-CS-IL/PGE	Malathion	SWV	0.68×10^{-3}	0.89 – 5.94×10^{-3}	[70]
CuO NPs/ILs	Atrazine	SWV	2.0×10^{-6}	10^{-5} – 2.0×10^{-3}	[71]
$NdFeO_3$ nano-perovskite/ionic liquid crystal modified carbon paste electrode	Hydroquinone & Catechol	SWV	0.118 & 0.252	10 – 180	[72]

liquid-metal/metal oxide nanocomposite based electrochemical sensor for the determination of toxic metals and pesticides is enlisted in (Table 4) with their analytical performance.

Conclusion

Both toxic metal ions and pesticides possess harmful effects on environment and humans after a certain permissible limit. In excess they can alter or inhibit various biological processes essential for the living organisms. Toxicity of these environmental pollutants depends on several factors such as exposure time, route and dose level. These pollutants enter our food chain through various natural and anthropogenic means. They can interact with various functional sites of amino acids and enzymes which makes them inactive. Electrochemical sensors allow simultaneous determination and speciation of these environmental pollutants. In addition to this they are highly portable and can be used in real environmental conditions. Electrochemical sensor's sensitivity can be enhanced by modifying the electrodes with different efficient conductive materials. Trend of using green materials is gaining a lot of attention these days and RTILs having good conductive properties are excellent choice for making environment friendly electrochemical sensors. Also, metal, metal oxide and carbon based nanomaterials possess high surface area, excellent conductivity and are ideal option for fabricating the electrodes. Hybrid nanocomposite of RTILs with these nanomaterials provide desired characteristics of both materials in the electrochemical sensor. In conclusion from above discussion it can be said that hybrid ionic liquid nanocomposite have showed excellent performance and can be a good alternative in fabrication of electrochemical sensor to deal with environmental issues related to toxic metal ions and pesticides.

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Conflict of interest

All authors declare no conflict of interest.

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