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REVIEW

Detection and removal of heavy metal ions: a review

Lateef Ahmad Malik[1] · Arshid Bashir[1] · Aaliya Qureashi[1] · Altaf Hussain Pandith[1]

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Abstract

In aqueous systems, heavy metal ions, when present in excess than permissible limits, are dangerous for human beings and aquatic life. Heavy metals cannot be degraded. Rather, they accumulate in living organisms either directly or through the food chain. Inside the body, metal ions can be converted to more toxic forms or can directly interfere with metabolic processes. As a result of metal toxicity, various disorders and damage due to oxidative stress triggered by metal ions have been witnessed. Toxic effects of metallic pollution coupled with the need of pure water for the survival and sanitation have thus prompted researchers to take every possible step to uphold the quality of water. In this regard, various strategies have been developed for the detection and the removal of metal ions from aqueous systems. Here we review metal-free water and methodologies used for rapid detection at low levels. Also, the application of benign materials and methods for metal removal from aqueous systems is detailed. Electrochemical methods, especially stripping and cyclic voltammetry, are commonly used methods for detection, while adsorption and ion exchange methods are quite effective for removal.

Keywords Heavy metal ions · Cyclic voltammetry · Anodic stripping · Removal of metal ions · Adsorption · Ion exchange

Introduction

Increased anthropogenic activity has led to the release of many hazardous substances into water resources that has put aquatic ecosystem and environment at risk (Nagajyoti et al. 2018). Heavy metal ions are the most serious contributors of water pollution as they are highly toxic, non-degradable and have a tendency to bioaccumulate and biomagnify as a result of food chain (Ayangbenro and Babalola 2017; Ali and Khan 2018; Kahlon et al. 2018). Their presence in aquatic ecosystems is sufficient to affect living systems directly or indirectly. Even in the soil environment, heavy metal ions are quite dangerous to both plants and animals as they are adsorbed by plants and finally reach to animals and humans (Dubey et al. 2018; Mallampati et al. 2013). In the soil environment, sorption of these heavy metals by soil constituents is considered to be a vital process in reducing the mobility of these pollutants to water, crops, vegetables and the threat to human beings and animals (Zhu et al. 2019; Lair et al. 2007). The impacts of this water pollution have forced researchers to develop suitable techniques for the detection and quantification of heavy metal contaminants. Many techniques have been used for the detection of heavy metal ions which can be divided into three main categories; spectroscopic detection techniques, electrochemical detection techniques and optical detection techniques. Spectroscopic methods for heavy metal ion detection include atomic absorption spectroscopy, atomic emission spectroscopy, inductively coupled plasma mass spectrometry (Lebedev et al. 2003), cold vapour atomic fluorescence spectrometry, which are quite sensitive but are expensive and require laborious pre-treatment processes (Harrington et al. 2011). Electrochemical methods on a contrary are more cost-effective, time economic, user-friendly, reliable and suitable for in-field applications and include techniques such as amperometry, voltammetry, potentiometry, impedance measurement and coulometry for heavy metal ion detection (Zhu et al. 2015). These electrochemical techniques allow simple procedures and are also fast in terms of short analytical time as compared to other spectroscopic techniques. Among various electrochemical techniques, anodic stripping voltammetry has been widely used for the analysis of heavy metal ions at trace levels because it possesses good selectivity, portability, low cost, fast analysis speed and excellent sensitivity (Zhu et al. 2012; Zhang et al. 2015; Yao et al. 2014; Liu et al. 2014a, b; Xu

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✉ Altaf Hussain Pandith
altafpandit23@gmail.com

[1] Department of Chemistry, University of Kashmir, Hazratbal, Srinagar, Kashmir 190006, India

et al. 2013). In optical methods of detection, metal ions can be detected by conventional methods of absorption, reflection or luminescence spectrometry. Selective chromogenic reagents and indicator dyes are often used in optical detection methods, where they react with a specific metal ion. In addition, optical fibres, integrated optics, capillary-type devices, etc., are also helpful in the detection of metal ions.

In addition to the detection of heavy metal ion, their removal from aqueous systems is essentially a highly important concern. Water contaminated with highly toxic heavy metal ions such as Hg^{2+}, Pb^{2+} and Cd^{2+} is detrimental and hazardous for human health and requires highly efficient and specific methods of removal from aqueous systems. There are many such methods which can be employed for removal process such as precipitation, flocculation, membrane separation, ion exchange, evaporation. Every method has its own advantages and limitations in terms of efficiency, sensitivity, selectivity and specificity (Pujol et al. 2014; Crini and Lichtfouse 2019). Among many of these methods, adsorption is more often a method of choice, because of its low cost, simple design and strong operability, especially its high removal efficiency from dilute solutions (Wang et al. 2013). At several occasions, the surface of materials is modified so as to enhance the removal efficiency towards metal ion uptake (Elfeky et al. 2017; Ojemaye et al. 2017).

Here we present an overview of metal ion pollution scenario in aqueous systems and potential consequences of these increasing levels of pollution on living system and the overall quality of life. Various methodologies that can be used in the detection purpose and the advantages of each method have been highlighted. Finally, some important methods which are quite useful for the removal of heavy metal ions from water have been discussed threadbare in this review paper.

Though metals are important to carry out cellular functions, their concentration window has a great impact on human health. Concentrations below the toxicity range is not going to have many adverse effects, but when it goes beyond the permissible limits, it becomes dangerous and leads to various cytological and physiological effects (Sumner et al. 2005). The effects of heavy metal ions on living beings along with their toxicity range according to World Health Organization (WHO) and Bureau of Indian Standards (BIS) are given in Table 1.

Table 1 lists various sources and effects of some most toxic heavy metal ions like lead (Pb), cadmium (Cd), mercury (Hg), arsenic (As) and chromium (Cr) which are the cause for many of the heavy metal-related diseases (Flora et al. 2008; Flora 2009; Bashir et al. 2016). “Presence” of heavy metal ions is not an issue; rather, it is “excess” that is creating the problem. It has been reported in the literature that in most cases, trace levels of metals are important in the biological functioning of cells such as transportation and cell signalling (Valko et al. 2005). However, when present in excess, these metal ions move out of the main metabolic pathway and can bind with protein sites other than natural binding sites, breaking the cell cascade, thereby, leading to toxicity in living things (Sevcikova et al. 2011; Gemma et al. 2006; Singh et al. 2010).

So considering the toxic effects of heavy metal ions when present in excess than the permissible limits, it is prior requirement to detect, quantify and then remove these heavy metal ions by applying suitable methodological procedures.

Detection

A metal ion detector is a device or instrument designed to detect the presence of metal ions in its surroundings and sometimes may also be useful to quantify these metal ions. As already mentioned the importance of metal ion free water systems, it is very essential to develop a strategy for making water bodies safe to use for living beings. Prior to removal of these toxic metal ions from water samples, we need to have a technique available that could detect their presence and also help in making a quantitative estimate of the level of pollution possible so that a suitable method is chosen for the removal. For this purpose, detection process should be developed which are time- and cost-effective besides being environmentally green. Also a detection technique must be sensitive enough to detect even traces of metal ions with a good accuracy. A number of techniques are available for detection of heavy metal ions, but a particular technique applicable for all the ions is rather missing.

Methods of detection

Heavy metal ion detection techniques can be broadly divided into three main categories:

Spectroscopic detection

Spectroscopic detection of heavy metal ions includes highly sensitive techniques like atomic absorption spectroscopy (Gong et al. 2016; Array and Merkoci 2012), inductively coupled plasma mass spectroscopy (Wang et al. 2015), X-ray fluorescence spectrometry (Sitko et al. 2015), neutron activation analysis and inductively coupled plasma-optical emission spectrometry (Losev et al. 2015; Poikyo and Permki 2003). They are versatile in terms of simultaneous determination of heavy metal ions concentration for a large range of elements with very low detection limits. However, these techniques are quite expensive and require trained personnel to work on the complex equipments. Flame atomic absorption spectroscopic technique has been used to determine Cu, Pb and Cd ions in water where limit of detection has been

Table 1 Limits, sources and effects of various heavy metal ion contaminations. Reproduced with permission from Gumpu et al. (2015). Copyright 2015 Elsevier

Metal	WHO limits[a] (mg L^{-1})	BIS limits[b] (mg L^{-1})	Common sources	Effects
Lead (Pb)	0.05	0.05	PVC[c] pipes in sanitation, agriculture, recycled PVC lead paints, jewellery, lead batteries, lunch boxes, etc	Penetrates through protective blood brain barrier (BBB) and is proving to be a risk factor for Alzheimer's disease and senile dementia, also leads to neuro-degenerative diseases, decreases intelligence quotient, kidney damage, decreases bone growth, behavioural issues, ataxia, hyperirritability and stupor
Cadmium (Cd)	0.005	0.01	Paints, pigments, electroplated parts, batteries, plastics, synthetic rubber, photographic and engraving process, photoconductors and photovoltaic cells	Renal toxicity, hypertension, weight loss, fatigue, microcytic hypochromic anaemia, lymphocytosis, pulmonary fibrosis, atherosclerosis, peripheral neuropathy, lung cancer, osteomalacia, osteoporosis and hyperuricemia
Mercury (Hg)	0.001	0.001	Combustion of coal, municipal solid waste incineration and volcanic emissions	Impaired neurologic development, effects on digestive system, immune system, lungs, kidneys, skin and eyes, Minamata, acrodynia, increases salivation, hypotonia, hypertension
Arsenic (Ar)	0.05	0.05	Wooden electricity poles that are treated with arsenic-based preservatives, pesticides, fertilizers, release of untreated effluents, oxidation of pyrite (FeS) and arseno pyrite (FeAsS)	Causes effects on central nervous system (CNS), peripheral nervous system (PNS), cardiovascular, pulmonary diseases, gastrointestinal tract (GI), genitourinary (GU), haemopoietic, dermatologic, foetal and teratogenic diseases, anorexia, brown pigmentation, hyper-pigmentation, localized oedema and skin cancer
Chromium (Cr)	0.05	0.05	Leather industry, tanning and chrome plating industries	Reproductive toxicity, embryotoxicity, teratogenicity, mutagenicity, carcinogenicity, lung cancer, dermatitis, skin ulcers, perforation of septum and irritant contact dermatitis
Silver (Ag)	0.1	0.1	Refining of copper, gold, nickel, zinc, jewellery and electroplating industries	Argyria, gastroenteritis, neuronal disorders, mental fatigue, rheumatism, knotting of cartilage, cytopathological effects in fibroblast, keratinocytes and mast cells
Zinc (Zn)	5	5	Soldering, cosmetics and pigments	Respiratory disorders, metal fume fever, bronchiolar leucocytes, neuronal disorder, prostate cancer risks, macular degeneration and impotence
Copper (Cu)	1.3	1.3	Fertilizers, tanning and photovoltaic cells	Adreno-corticol hyperactivity, allergies, anaemia, alopecia, arthritis, autism, cystic fibrosis, diabetes, haemorrhaging and kidney disorders

[a] World Health Organization recommended permissible limits for heavy metal ions in water

[b] Permissible limits for heavy metal ions as per Bureau of Indian Standards

[c] Polyvinyl chloride, a strong lightweight polymer

reported to be 2, 3 and 0.2 μg dm^{-3} for Cu^{2+}, Pb^{2+} and Cd^{2+} ions, respectively (Shirkhanloo et al. 2011). High-resolution surface plasmon resonance spectroscopy combined with anodic stripping voltammetry has been used to detect lead, copper and mercury ions from parts per million down to subparts per billion levels (Wang et al. 2007). Some of the important spectroscopic methods used for the detection of heavy metal ions are explained below.

Atomic absorption spectrometry

In atomic absorption spectroscopy, a specific wavelength is used to excite isolated atoms from ground state to excited state and the amount of energy absorbed during this excitation is measured which is proportional to the concentration of atoms present in the sample. A block diagram of a typical atomic absorption spectrometer is shown in Fig. 1. It consists of a primary light source, atomizer to produce gas-phase atoms or ions for analysis, a monochromator, a detector and an electronic "readout" system.

Atomic absorption spectroscopic determination of elements can only be performed on gaseous medium in which the individual atoms or ions are well separated from each other. Plasmas, flames and electrothermal atomizers are used to generate gas-phase analyte atoms/ions. This process in which sample is volatilized and decomposed in such a way so as to produce gas-phase atoms and ions is called as atomization. A specific light source is used to excite atoms or ions of a particular element and these light sources usually use a hollow cathode lamp or an electrodeless discharge lamp of the same element, which is to be analysed. Many lamps are also available that can be used to determine more than one element without changing the lamp. Solid-state detectors or photomultiplier tubes have been used as detectors in atomic absorption spectroscopy. For the determination of mercury, a modified atomic absorption spectroscopic technique, called as flow injection mercury systems, is used. Spectroscopic detection of some metal ions by the help of atomic absorption spectroscopy is summarized in Table 2.

Graphite furnace atomic absorption spectrometry

Graphitic furnace consists of a cylindrical graphitic tube that is open at both the ends and has a central hole for introduction of samples. The sample is introduced directly into a graphite tube where it is heated to remove the solvent and matrix components, and then atomization of the sample takes place. The atomized sample is then analysed in the same way as reported in flame atomic absorption spectroscopy. In graphitic furnace atomic absorption spectroscopy, atomization occurs in an environment where temperature is not changing rapidly as sample is no longer directly on furnace wall, as a result of which more reproducible signals are obtained. The disadvantages of graphitic furnace atomic absorption spectroscopy as a detection tool for heavy metal ions are in terms of analysis times which are longer than those for flame sampling and the numbers of elements that can be determined by this method are fewer. Graphitic furnace atomic absorption spectroscopy was used for the determination of lead, cadmium, copper, arsenic and mercury with detection limits of 0.28, 0.014, 0.49, 0.19 and 0.061 mg L^{-1}, respectively (Nie et al. 2008). A graphite furnace technique was also used for the analysis of lead in "Yin Qiao Jie Du" tablets where LOD for Pb was found to be of the order of 0.1 ppb (Yuan et al. 2009). Graphitic furnace atomic absorption spectroscopy as an effective method for the detection of some heavy metal ions is reported in Table 2.

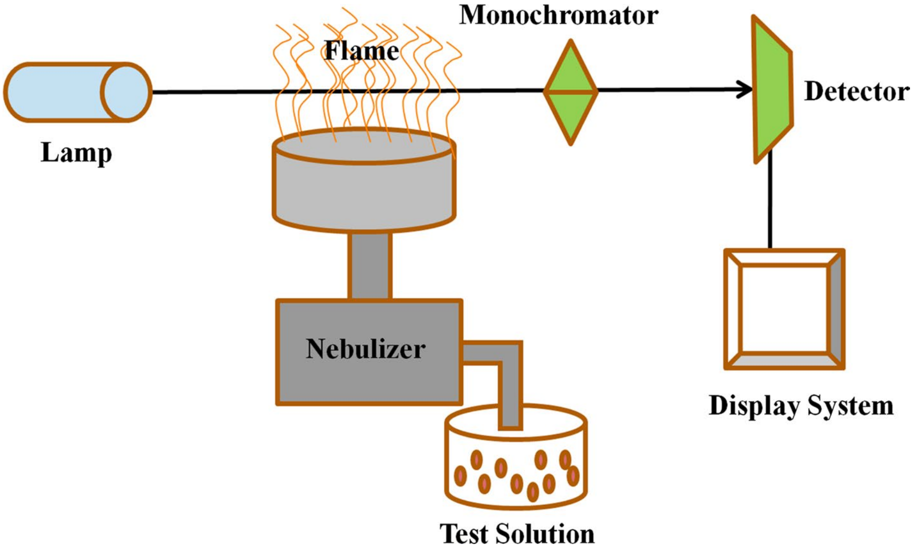

Fig. 1 Single-beam atomic absorption spectrophotometer used to detect metal ions. It consists of a primary light source, atomizer to produce gas-phase atoms or ions for analysis, a monochromator, a detector and an electronic "readout" system

Table 2 Detection of toxic heavy metal ions from various sources by atomic absorption spectroscopy (AAS) and graphitic furnace atomic absorption spectroscopy (GF-AAS)

Metal ion/ions	Source	Technique	References
Mn, Pb, Cr, Cd	Kulufo River, Arbaminch, Gamo Gofa, Ethiopia	AAS[a]	Tsade (2016)
Pb, Sb, Al, As	Tube wells of District Pishin, Balochistan, Pakistan	AAS	Tareen et al. (2014)
Pb, Cd, Zn, Ni, Cr, Mn, Fe	Water and therapeutic mud	AAS	Radulescu et al. (2014)
Cd, Cu, Fe, Ni, Pb, Zn, Tl	Seawater	AAS	Kojuncu et al. (2004)
Pb, Cd, Cr, Cu, Ni	Chinese tea	GF-AAS[b]	Zhong et al. (2016)
Ca, Mg, Fe, Cu, Zn	Chinese tablets	AAS	Dong and Zhu (2002)
Ca, Mg, Fe, Mn, Cu, Zn, Cd	Chinese taponin tablet recipe	AAS	Dong and Zhu (2003)
Co, Ni	Water samples	GF-AAS	Minami et al. (2003)
Pb	Water sample	GF-AAS	Chen et al. (2005)
Pt	Rocks	GF-AAS	Odonchimeg et al. (2016)
V	Wine	GF-AAS	Wierzbicki and Pyrzynska (2002)
Cd	Wine	GF-AAS	Cvetkovi et al. (2006)
Cr	French wine and grapes	GF-AAS	Cabrera-Vique et al. (1997)
Hg	Muscle samples of fish	GF-AAS	Moraes et al. (2013)
Fe	Natural and mineral waters	AAS	Tautkus et al. (2004)

[a] Atomic absorption spectroscopy

[b] Graphitic furnace atomic absorption spectroscopy

Atomic fluorescence spectrometry

Atomic fluorescence spectrometry is different from atomic absorption spectrometry in principle and working. Like atomic absorption spectroscopy, in atomic fluorescence spectrometry a sample solution is first atomized and then the atoms are illuminated with a light source leading to the excitation of atoms. These excited atoms undergo radiative deactivation and emit characteristic radiations that fall on the detection device, and the atomic fluorescence is measured by the detector. For mercury determination, cold vapour atomic fluorescence spectrometry can be used in which carrier gas like argon is used to take free mercury atoms to the cell where these atoms are excited by a collimated ultraviolet light source. The excited atoms re-emit the absorbed energy as fluorescence which is measured by the help of photomultiplier tube detector or a UV photodiode detector. The major advances in the field of metal detection using atomic fluorescence spectrometry are highlighted in Table 3.

X-ray fluorescence spectrometry

When a material is irradiated with X-rays or gamma rays, it leads to the ionization of the material. Such a bombardment of material with high energy radiations can even eject electrons from inner orbitals of K or L shell as shown in Fig. 2. These vacancies are fulfilled by electrons from higher energy shells which is accompanied by the emission of photon or fluorescence called as X-ray fluorescence spectrometry, which is measured.

Since each element has a unique set of energy levels, each element produces its own fluorescence spectrum with a unique set of energies associated with multiple peaks of different intensities. Thus, XRF is quite useful technique to determine the elemental composition of a sample quite easily. The block diagram of X-ray fluorescence spectrometer which is composed of an X-ray source, sample chamber, fluorescence detector, data processing and display system is shown in Fig. 3.

XRF technique has been used to screen and identify toxic elements in various FDA-regulated products (Palmer et al. 2009) and many other such sources which are summarized in Table 3.

Electrochemical methods of detection

Electrochemical techniques are economic, user-friendly and reliable and involve simple procedures for monitoring of contaminated samples. The other advantage offered by electrochemical methods is the very short analytical time as compared to other spectroscopic techniques (Pujol et al. 2014). However, these electrochemical techniques have some drawbacks like they possess lower sensitivity and higher limits of detection (LOD) as compared to spectroscopic and optical techniques. Also, these techniques often in certain cases require developments and modifications in the design to improve their performance in detection of heavy metal ions (Bansod et al. 2017). For example, various electrochemical techniques have to be coupled with different biosensing electrodes in order to improve

Table 3 Detection of some toxic heavy metal ions by atomic fluorescence spectrometry (AFS) and X-ray fluorescence spectrometry (XRFS)

Metal ion/ions	Sample	Analytical technique	References
Cd	Brown rice	AFS[a]	Hafuka et al. (2017)
Pb	Water samples	AFS	Beltran et al. (2015)
As	Chicken meat	AFS	Sanchez-Rodas et al. (2006)
Cu, Pb	Aqueous solution	XRFS[b]	Hutton et al. (2014)
As	Mining polluted soils	AFS	Ruiz-Chancho et al. (2005)
Fe, Ni, Mn, Cu, Zn, Pb	Coastal seawaters	XRFS	Yuan-Zhen et al. (2012)
As, As	Acid mine drainage, Beltran	AFS	Oliveira et al. (2006)
As, As	Seafood	AFS	Schaeffer et al. (2005)
As, Cr, Cu, Ni, Pb, V, Zn	Soil	XRFS	Ene et al. (2010)
Se	Cow milk	AFS	Muniz-Naveiro et al. (2007)
As, Pb, U	Aerial parts of *Origanum sipyleum* L	XRFS	Durmuşkahya et al. (2016)
Sc	Sesame seeds	AFS	Kapolna et al. (2007)
Sb, Sb	Marine algae, molluscs	AFS	de Gregoi et al. (2007)
As, Cd, Cr, Cu, Ni, Zn, Pb	Soils	XRFS	Taha (2017)
Cr, Ni, Cu, Zn, Zr, Rb, Y, Ba, Pb, Sr, Ga, V, Nb.	surface soil samples	XRFS	El-Bahi et al. (2013)
Hg	Water	AFS	Logar et al. (2002)
Pb, As, Cu, Zn	Soil samples	XRFS	Radu and Diamond (2009)
Cr, Ni, Cu, Zn, Hg, Pb	Fish tissues	XRFS	Zarazúa et al. (2014)
Hg	Wastewater samples	XRFS	Marguí et al. (2010)

[a] Atomic fluorescence spectroscopy

[b] X-ray fluorescence spectrometry

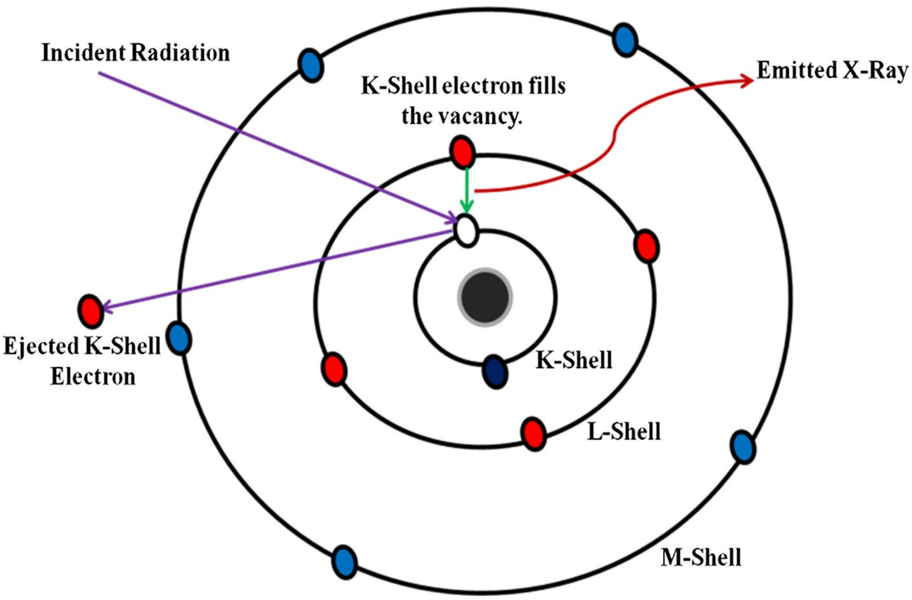

Fig. 2 A block diagram of K-capture involved in X-ray fluorescence spectrometry (XRF) where the high-energy X-rays or gamma rays eject electrons from K-shell of an atom, creating a vacancy which is being filled by the electron of next higher energy level

their sensitivity and limits of detection by modifying the electrode material. The presence of heavy metal ion in water usually brings the change in electrical parameters like current, voltage, electrochemical impedance, charge and electroluminescence (Cui et al. 2015) in the electrochemical setup. Based on that electrical signal has been affected by the presence of heavy metal ions, these techniques can be categorized into potentiometric, amperometric, voltammetric, coulometric, impedance measurement and electrochemiluminescent techniques. Some important electrochemical techniques are presented below.

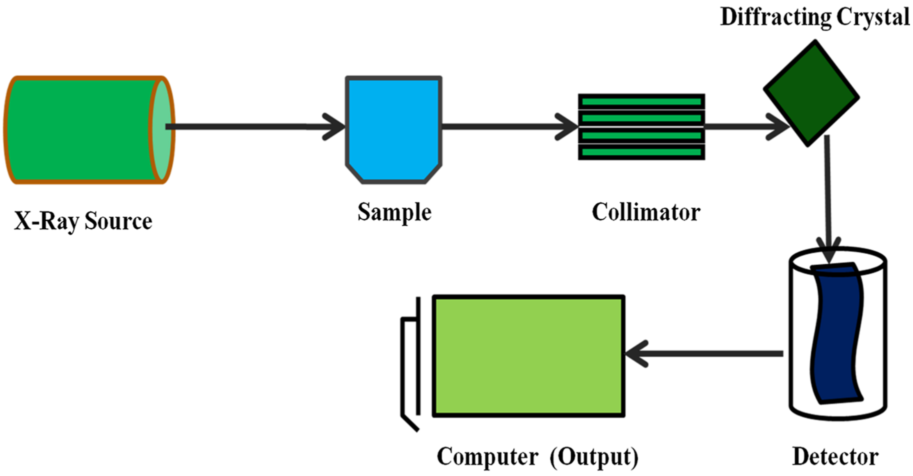

Fig. 3 A block diagram of X-ray fluorescence spectrometer, composed of X-ray source, sample chamber, fluorescence detector, data processing and display system used to determine the elemental composition

Potentiometry

This technique is based on the measurement of electromotive force (EMF) without applying any electric current for such measurements. Potentiometric techniques are generally used for quantitative analysis of ions in solutions. However, it is also quite effective in the detection of heavy metal ions because of its advantages like low cost, short response time, high selectivity and broad range of response (Array and Merkoci 2012). High detection limits and reduced sensitivity are some drawbacks associated with this technique, and efforts have been carried out in order to overcome such problems. Use of modified electrodes especially with carbon nanotubes and metal nanoparticles has been found promising in this regard (Düzgün et al. 2011; Bakker and Pretsch 2008). Such modified electrodes have been reported with enhanced sensitivity and also lower down the limits of detection for heavy metal ions as shown in Table 4.

Amperometry

Amperometry is a potentiostatic technique in which a fixed potential difference is applied between working and reference electrode in the solution containing electroactive species, and the flow of very small currents due to reduction of these heavy metal ions is measured. The current is recorded as a function of time, and such experiments are called amperometry techniques. By this technique, one particular metal ion is detected among various electroactive species due to fixed potential of the working electrode. The analyte to be detected undergoes a faradic reaction at some desired polarity and magnitude of the potential applied. However, due to less surface area of the working electrode, this faradic reaction is incomplete and only a fraction of analyte reacts. To overcome this problem, electrode surface has been modified by several means. In one such case, a highly sensitive screen-printed electrode modified with a nanostructured carbon black film has been used for the detection of Hg^{2+} with the detection limit of 5 nM (Arduini et al. 2011). In another

Table 4 Detection of heavy metal ions by potentiometry

Metal ion	Electrode modification	Limit of detection (mol L^{-1})	References
Hg	Thiourea-functionalized nanoporous silica-modified carbon paste electrode	7×10^{-8}	Javanbakht et al. (2009)
Hg	Screen-printed electrode modified with zirconium antimonate ionophore	5×10^{-8}	Aglan et al. (2018)
Hg	Tribromomercurate–rhodamine B PVC membrane electrode	2.4×10^{-6}	Othman (2006)
Hg	Modified palm shell activated carbon paste electrode based on Kryptofix®5*	1.0×10^{-7}	Ismaiel et al. (2012)
Cd	Multiwalled carbon nanotubes functionalized by dithizone-modified electrode	1.0×10^{-7} mol	Karimi et al. (2012)
Cd	PVC-based polyaniline Sn(IV) silicate composite cation exchanger ion-selective membrane electrode	1×10^{-7}	Naushad et al. (2014)
Pb	PVC-based carboxymethyl cellulose Sn(IV) phosphate composite membrane electrode	1×10^{-6}	Inamuddin et al. (2015)
Pb	Zirconium(IV) iodosulphosalicylate-based electrode	4.07×10^{-6}	Lutfullah and Rahman (2012)
Pb	Polypyrrole-modified electrode	7.0×10^{-7}	Mazloum-ardakani et al. (2012)

case, amperometric biosensors which utilize biologically modified electrodes have also been used in the detection of heavy metal ions (Mohammadi et al. 2005). Electrodes have been modified so as to enhance their sensitivity towards metal ion detection by amperometric technique, as reported in Table 5.

Voltammetry

Among electrochemical techniques, voltammetry is commonly used technique for the detection of heavy metal ions. In voltammetric techniques, current is measured at different applied potentials to obtain a current–voltage curve. Voltammetry is widely used technique for heavy metal ion detection because of its high accuracy, lower limit of detections and high sensitivity. There are various forms of voltammetry, though the basic procedure, i.e. measuring the current by varying the potential, is same for the all. Some of the modes in which voltammetry is conducted for the analysis of heavy metal ions are described below.

Cyclic voltammetry In cyclic voltammetry, applied potential is swept first in one direction and then in the reverse direction. The current in the forward and reverse scan is recorded and is plotted against applied potential to obtain cyclic voltagram. From this cyclic voltagram, some important parameters like cathodic and anodic peak potentials and corresponding currents are obtained. Gold nanoparticles-thiol functionalized reduced graphene oxide-modified glassy carbon electrode (GCE/rGO-SH/Au nanoparticles) was used for selective detection of Hg^{2+} by employing cyclic voltammetry (Devi et al. 2018). The sensor showed linear response for Hg^{2+} detection in concentration range of 1–10 µM in phosphate buffer saline (PBS) solution, and the low detection limit of 0.2 µM was obtained. Cyclic voltammetric response of GCE/rGO-SH/Au nanoparticles was compared to the one with no thiol functionalization GCE/rGO/Au nanoparticles, and a drastic change in the anodic peak potential was obtained as shown in Fig. 4. The higher anodic currents obtained in case of GCE/rGO-SH/Au nanoparticles electrode system may be due to higher loading of Au nanoparticles as the –SH group on the rGO sheets has a strong affinity towards the Au nanoparticles.

Pulse voltammetry The use of pulse of voltage signal having different shapes and amplitudes in voltammetric measurement gives rise to another type of voltammetry known as pulse voltammetry. Pulse voltammetry is further subcategorized into normal pulse voltammetry, reverse pulse voltammetry, differential pulse voltammetry, etc. Out of various pulse voltammetric methods, differential pulse is most commonly used due to its high sensitivity towards detection of heavy metal ions. Simultaneous determination of copper, lead and cadmium was carried out at a carbon paste electrode modified with hexagonal mesoporous silica (HMS)-immobilized quercetin (HMS-Qu/CPE) by employing differential pulse voltammetry (Xia et al. 2010). Voltammetric response at querectin-modified carbon paste electrodes (Qu/CPE) and querection/ionic liquid-modified carbon paste electrode (QuIL/CPE) is shown in Fig. 5, and a comparison was drawn between the voltammetric response shown by these modified electrodes towards Cu^{2+}, Pb^{2+} and Cd^{2+} ions. The peak currents of copper, lead and Cd at HMS-Qu/CPE showed a good enhancement which apparently may be due to the cooperative effect of HMS and Qu.

Stripping voltammetry Stripping voltammetry eventually consists of two main steps: electrodeposition where analyte solution from well-stirred solution is deposited on the electrode and voltammetric step where analyte is stripped off and can be analysed by any of the VM methods. The stripping voltammetry is further characterized into anodic

Table 5 Amperometric detection of heavy metal ions using various modified electrodes

Metal ion	Electrode modification	Limit of detection (mol L^{-1})	References
Hg	Pt/CeO_2/urease-modified electrode	1.8×10^{-8}	Gumpu et al. (2017)
Pb		1.9×10^{-8}	
Hg	Poly(vinylferrocenium) (PVF(+))-modified platinum electrode	5×10^{-10}	Celebi et al. (2009)
Hg	L-tyrosine-modified platinum electrode	1.4×10^{-8}	Majid et al. (2002)
Cd	Microwater/polyvinylchloride-2-nitrophenylethyl ether (PVC–NPOE) gel interfaces-based tape ion sensor.	1.78×10^{-7}	Lee et al. (2009)
Cd, Co, Ni, As, Cr, Pb	Glucose oxidase-functionalized cobalt oxide-modified glassy carbon electrode	50[a]	Mugheri et al. (2016)
Pb,	Single carbon fibre electrode	1.3×10^{-6}	Li et al. (2007)
Cd,		3.3×10^{-6}	
Cu		7.4×10^{-6}	

[a] Parts per billion (ppb)

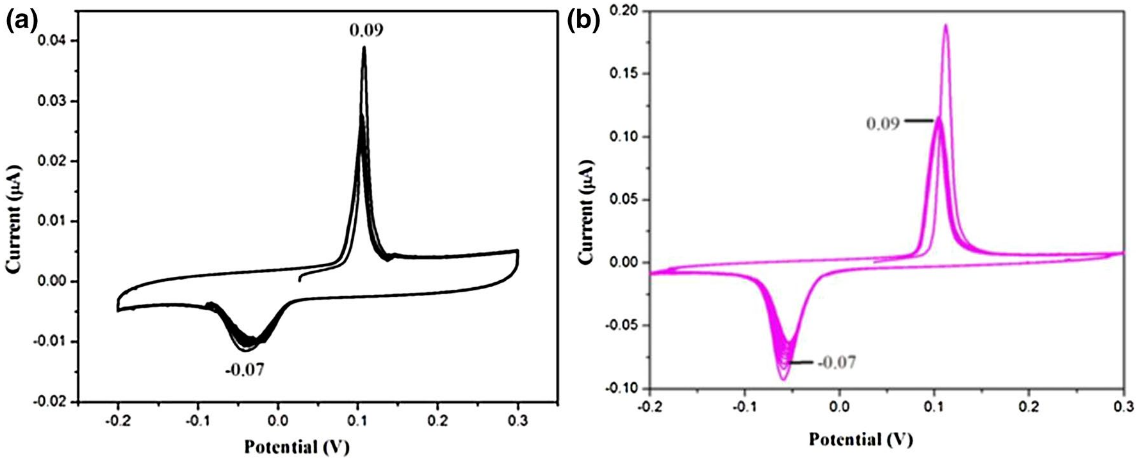

Fig. 4 Detection of Hg^{2+} ions by the help of cyclic voltammetry using modified glassy carbon electrode. Cyclic voltagrams of **a** GCE/rGO/Au nanoparticles and **b** GCE/rGO/-SH/Au nanoparticles recorded in 0.1 M KCl solution in the potential range from −0.2 to 0.3 V at a scan rate of 50 mV s^{-1}. Reproduced with permission from Devi et al. (2018). Copyright 2018 Electrochemical Society

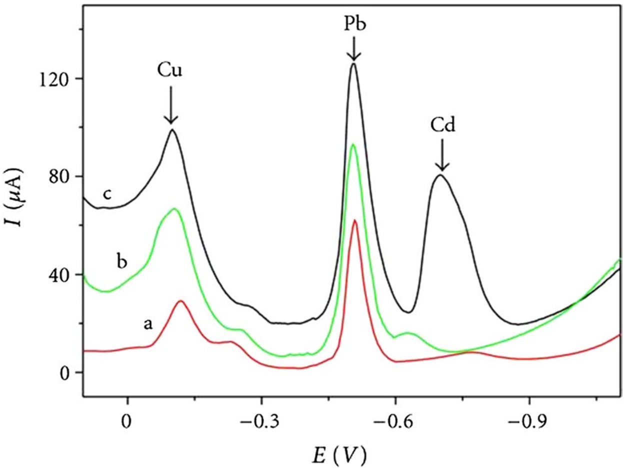

Fig. 5 Detection of Cu^{2+}, Pb^{2+} and Cd^{2+} ions by differential pulse voltammetric technique. The differential pulse voltammograms of 1.0 μM (each) multicomponent $Cu^{2+}/Pb^{2+}/Cd^{2+}$ solution at (a) Qu/CPE, (b) QuIL/CPE and (c) HMS-Qu/CPE. Adapted from Xia et al. (2010)

stripping voltammetry (ASV) or cathodic stripping voltammetry (CSV) by applying anodic potential scan or a cathodic potential scan, respectively. In addition to a very low limit of detection, stripping voltammetry requires relatively simple and inexpensive instrumentation, with exceptional suitability for miniaturization (Jothimuthu et al. 2011). Anodic stripping voltammetry for the detection of zinc ions was carried out in acetate buffer by using disposable copper-based electrochemical sensor (Pei et al. 2014). Besides good sensitivity and lower limit of detection, the sensor was able to detect and measure the concentration of Zn^{2+} in blood serum as well. Anodic stripping voltammograms at various concentrations of Zn^{2+} ion are shown in Fig. 6.

Stripping methods in combination with voltammetric techniques Stripping methods can be used in combination with various pulse voltammetric techniques that give rise to new detection techniques like linear sweep anodic stripping voltammetry, differential pulse anodic stripping voltammetry,

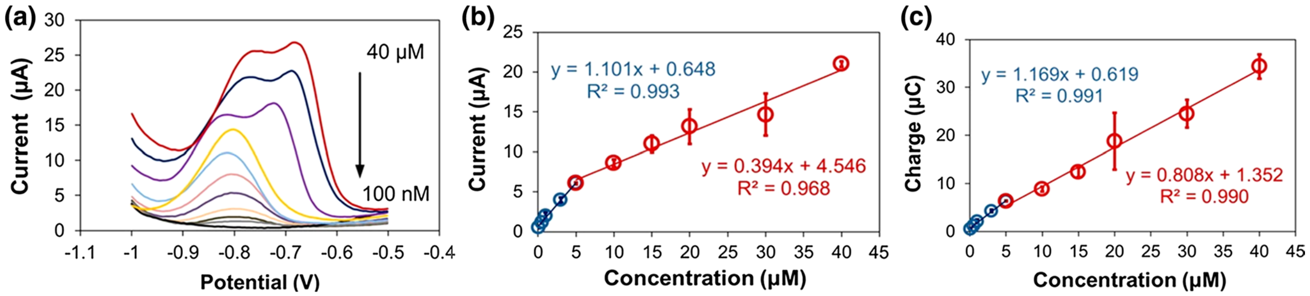

Fig. 6 Anodic stripping voltammetric detection of zinc ions by using disposable copper-based electrochemical sensor: **a** anodic stripping voltagram of Zn^{2+} samples in a range from 100 nM to 40 μM range, **b** calibration curves for Zn^{2+} using peak height and **c** peak area of stripping voltammograms. Reproduced from Pei et al. (2014). Copyright 2014 American Chemical Society

square-wave anodic stripping voltammetry, etc., which are quite effective for trace level detection of heavy metal ions with very low limits of detection. Square-wave anodic stripping voltammetry has been performed for the detection of heavy metal ions such as Zn^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+}, on cubic and octahedral Fe_3O_4 nanocrystal-modified electrodes (Yao et al. 2014). According to Yao et al., in comparison to cubic Fe_3O_4 nanocrystal-modified electrode, octahedral Fe_3O_4 nanocrystals show better electrochemical sensing performances towards these investigated heavy metal ions as shown in Fig. 7. Also the electrochemical performance of octahedral Fe_3O_4 nanocrystals showed dominating performance towards detection of Pb^{2+} ions with higher sensitivity and lower limit of detection compared to other metal ions.

Other electrochemical methods include linear sweep voltammetry (LSV) which involves conventional electrodes linear sweep of potential (10 mV s^{-1} to about 1000 mV s^{-1}) to obtain I–V curve and polarography, where one of the electrodes used is polarizable dropping mercury electrode (DME) whose potential changes from its reverse value and the other electrode used is non-polarizable electrode such as calomel electrode. Some of the important electrochemical techniques along with the electrode system used for detection of some toxic heavy metal ions are highlighted in Table 6.

Galvanostatic techniques

In galvanostatic techniques, it is electric potential that is measured while applying electric current. A current source (galvanostat) is used to control the current between the working electrode and counter electrode, and resulting potential is measured across the working and reference electrodes. Galvanostatic technique employees simple instrumentation as compared to the potentiostatic techniques; however, these techniques have the disadvantage of large double-layer charging effects that occur throughout the experiment. Galvanostatic stripping chronopotentiometry (SCP) is one of the most applied galvanostatic techniques for heavy metal ion detection. It has been reported that SCP is less sensitive to the presence of organic matter (Estela et al. 1995), as a result of which SCP has been extensively used for detection of

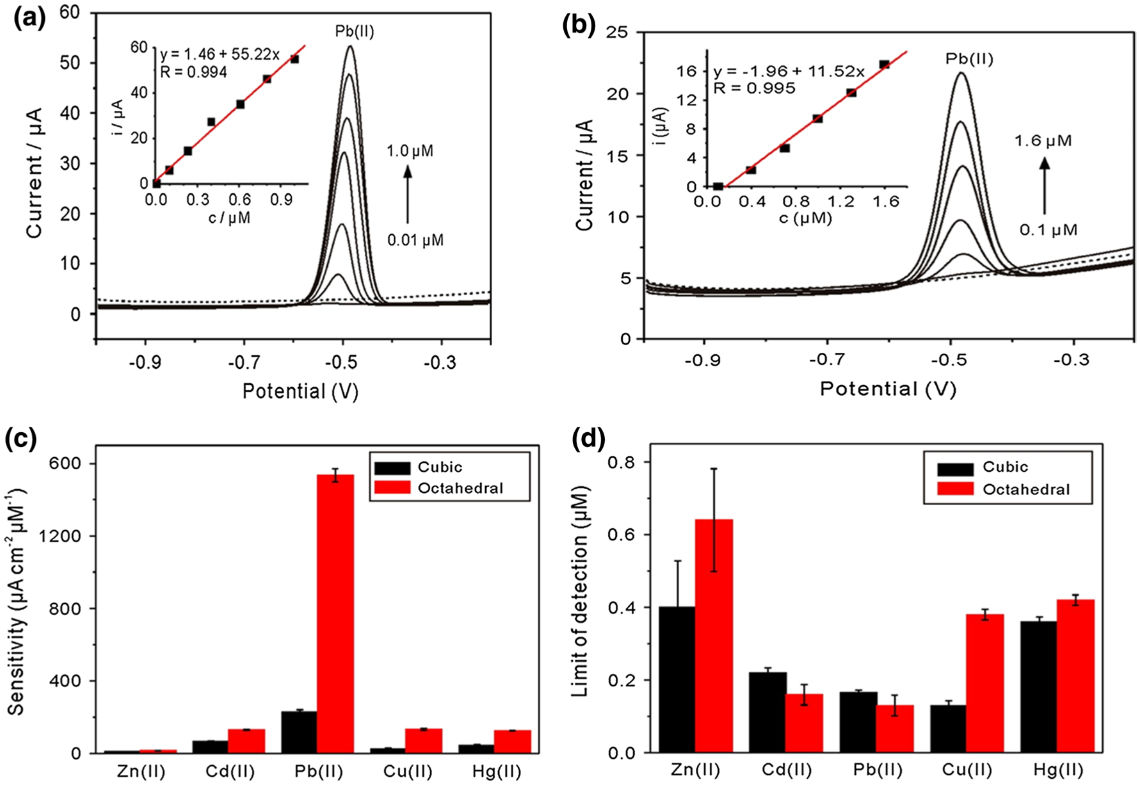

Fig. 7 Detection of various heavy metal ions by the help of square-wave anodic stripping voltammetry. Square-wave anodic stripping voltammetric response of **a** octahedral and **b** cubic Fe_3O_4 nanocrystals-modified GCE for determination of Pb(II), comparison of **c** sensitivity and **d** limit of detection (3σ method) for SWASV detection of Zn^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+} at Fe_3O_4 cubic and octahedral nanocrystals, respectively (Insets in **a** and **b** are the corresponding linear calibration plots of peak current against concentrations). Adapted with permission from Yao et al. (2014). Copyright 2014 American Chemical Society

Table 6 Detection of heavy metal ions by various voltammetric techniques

Metal ion	Electrode system	Technique	Detection limit (mol L^{-1})	References
Hg	Hydroxyapatite (HA) nanoparticles-modified glassy carbon electrode (GCE)	SWV[a]	1.41×10^{-7}	Kanchana et al. (2015)
Hg	Indium tin oxide (ITO) electrodes modified by gold nanoparticles (Au nanoparticles)	LSV[b]	1×10^{-6}	Ratner and Mandler (2015)
Hg	Graphene-modified glassy carbon electrode	CV[c]	1×10^{-9}	Talat et al. (2018)
Cd	Bi/glassy carbon electrode (Bi/GCE)	SWASV[d]	NA	Zhao et al. (2017)
Pb	Montmorillonite-bismuth-carbon electrode	SWASV	1.8×10^{-9}	Luo et al. (2010)
Cd			3.1×10^{-9}	
Cd	A boron-doped diamond electrode modified by 0.5 mM 4-aminomethyl benzoic acid	ASV[e]	1.8×10^{-9}	Innuphata and Chootoa (2017)
Pb	Graphitic carbon modified with 4-amino salicylic acid	CV & DPASV[f]	9×10^{-8}	Kempegowda and Malingappa (2012)
Cd			10.7×10^{-9}	
Pb	Clay nanoparticle anthraquinone—GC thin film	DPASV	1×10^{-9}	Yuan et al. (2004)
Cd			3×10^{-9}	
Pb	A solid paraffin-based carbon paste electrode modified with 2-aminothiazole-functionalized silica gel	ASV	7.3×10^{-9}	Silva et al. (2011)
Cu			90×10^{-9}	
Pb	Glassy carbon electrode modified with novel calix [4] arene	ASV	6.1×10^{-9}	Jian-Qua et al. (2003)

[a] Square-wave voltammetry

[b] Linear sweep voltammetry

[c] Cyclic voltammetry

[d] Square-wave anodic stripping voltammetry

[e] Anodic stripping voltammetry

[f] Differential pulse anodic stripping voltammetry

heavy metal ions like cadmium, lead and copper in foods and biological samples (Szlyk and Czerniak-Szydlowska 2004).

Optical methods of detection

The optical effects of the materials may be detected by conventional methods of absorption, reflection or luminescence spectrometry. Optical fibres, integrated optics, capillary-type devices, specific indicator dyes, ionophores, etc., are more often used for optical detection of heavy metal ions. Optical ion sensing, though suitable for detection of some heavy metal ions, has its own limitations (Wolfbeis 2002). There are many non-selective optical indicators that react with more than one metal ion, and also many metal ion indicators combine with hydrogen ions so pH has to be controlled in a proper way so that an appropriate correction factor can be applied. To overcome the poor selectivity of indicator dyes, masking agents may be put into use. For example, fluoride may be co-immobilized in sensor membranes so that undesired interferences by other metal ions are suppressed or to make use of test strips containing reducing agents that convert analyte into a different species or oxidation state for which a selective indicator is available (Oehme and Wolfbeis 1997).

Indicator dye-based sensors

Such type of sensor is based on the binding reaction of heavy metal ion with the indicator dye that leads to change in the absorption or fluorescence of such binding reagents. In such type of heavy metal ion sensors, indicator plays the role of a transducer for the heavy metal ion for which direct optical determination is not possible. In another group of indicators, heavy metal ions act as “quenchers” where both static and dynamic quenching of luminescence of indicator dye takes place when the two combine together (Lakowicz 1983). In case of static quenching, a quencher interacts with fluorophore in its ground state, while in dynamic quenching, the interaction between the two occurs in the excited state only. The process of dynamic quenching is reversible in the sense that the dye is not consumed. Fluorescent indicators provide advantage of improved sensitivity and selectivity; however, their disadvantages cannot be ruled out. Many indicators are not selective and can bind with more than one metal ion. Some indicators cannot be used in optical sensing of heavy metal ions because of unfavourable analytical wavelengths, poor stability, the need for additional reagents and their non-availability in pure form required for sensing applications. Many indicators bind irreversibly or only at high or low pH values. The main problem associated with indicator dye-based sensors is that for each particular heavy metal ion, a specific dye, and hence a different analytical wavelength, has to be used every time, which complicates the overall procedure of detection (Oehme and Wolfbeis 1997).

Ionophore-based sensors

Because of many limitations of indicator reagents, ion-complexing organic molecules, ionophores have been employed for heavy metal ion detection by optical means. Ion carrier, complexing properties of these ionophores and their ability to bind with selective ions have made them capable for heavy metal ion specification. There are several sensing schemes where ionophores can be made as effective metal ion sensors like the introduction of chromogenic or fluorogenic moieties into ionophores or combining the ionophores with suitable dyes. Another way which is most suitable for detection of heavy metal ions is the extraction of ions into membranes using ion carriers (Lerchi et al. 1992, 1994: Hisamoto et al. 1995). In such optical sensors, selective binding of heavy metal with ionophores is responsible for recognition of heavy metal ion, while the optical signal is provided by a proton-selective chromo-ionophore. During the binding of heavy metal ions, protons equivalent to the charge of metal ion are released from the chromo-ionophore resulting in a change in the colour or fluorescence of the chromo-ionophore. The heavy metal ions bind to ionophore through coordination bonds with various heteroatoms (nitrogen, oxygen, sulphur) which are present in ionophores.

Review on optical sensors

An optic chemical sensor containing a sensitive layer of 5,10,15,20-tetra(*p*-sulphonatophenyl) porphyrin covalently immobilized onto a polymeric matrix has been used for the detection of Cd^{2+}, Pb^{2+} and Hg^{2+}. The complexation of these heavy metal ions with the sensor results in different absorbance spectra and thus changes the reflection behaviour of the sensor (Czolk et al. 1992). A novel Hg^{2+} ion-selective chemosensor bearing a rhodamine and two tosyl groups was synthesized and was successfully used for the detection of Hg^{2+} ions (Fig. 8). Interaction of Hg^{2+} with the sensor induces a visual colour change as well as significant enhancement in fluorescence of the sensor. The selectivity of the sensor lies in its ability of producing no or much smaller spectral changes on interacting with metal ions other than Hg^{2+} (Lee et al. 2007).

The detection of zinc ions by highly selective optical sensor based on the tris-triazole trimethylamine derivative with three pyrene fluorophores is based on the sharp change in the intensity ratio of the monomer (376 nm) and excimer (465 nm) emissions upon binding of metal cations in acetonitrile (Ingale and Seela 2012). Azobenzene derivative containing two amino groups is able to coordinate to Hg^{2+} ion. This coordination gives rise to a metal-induced intramolecular charge transfer in which free amino group serves as the electron donor. Coordination of Hg^{2+} induces a 100 nm bathochromic shift of the absorption maximum and red colouring of the solution. The colour change is specific to Hg^{2+} ions (Fu et al. 2007). Hemicyanine dye, containing aniline (electron-donating group) and a benzothiazolium (electron-withdrawing group), has been used to perform selective optical detection of Hg^{2+} in aqueous solutions at neutral pH (Tatay et al. 2006). A naked eye detection of Hg^{2+} ion was successfully achieved by using a bis(ferrocenyl) azine, as chromogenic molecule, supported on solid cellulose fibre (Fig. 9). The sensor is metal specific and produces a spectacular colour change upon binding with Hg^{2+} ion. The colour change is also helpful to determine the concentration of the ion either by naked eye or spectroscopically (Díez-Gil et al. 2007).

The addition of Hg^{2+} to such ligand leads to a hypsochromic shift of the absorption band and also a colour

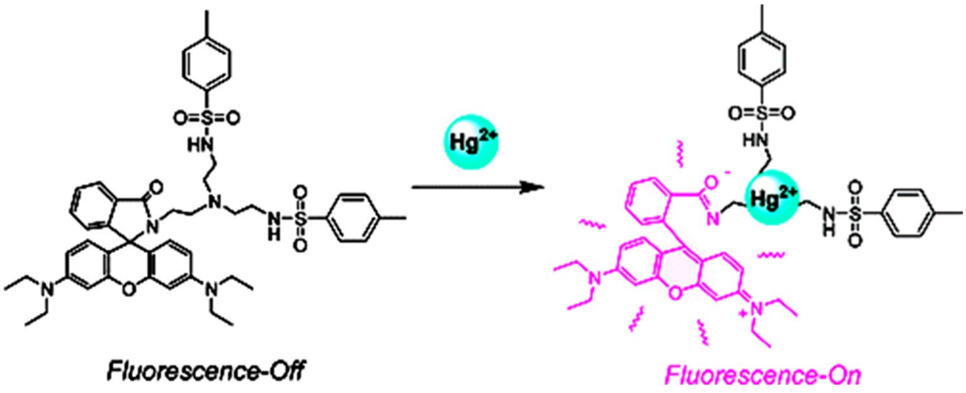

Fig. 8 Detection of Hg^{2+} ion by the optical method where a “tren-based tripodal chemosensor” depict spectral changes on interaction with Hg^{2+} ion. Adapted with permission from Lee et al. (2007). Copyright 2007 American Chemical Society

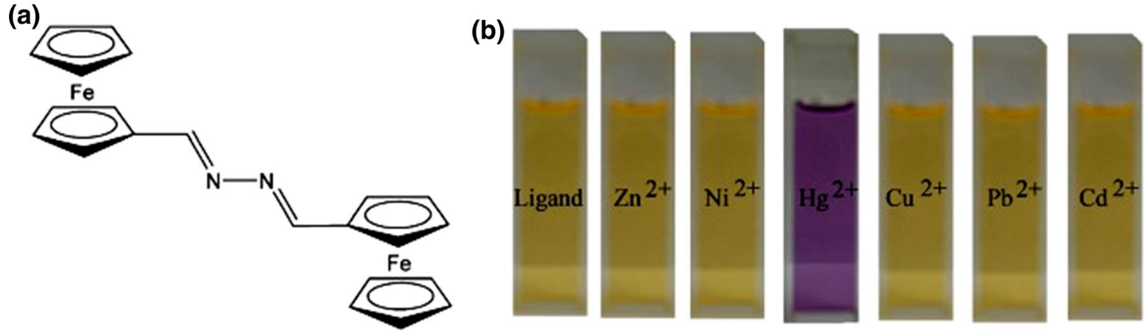

Fig. 9 A highly selective optical detection of Hg^{2+} ion achieved by using a bis(ferrocenyl) azine, as chromogenic molecule **a** 1,4-disubstituted azine bearing two ferrocene groups, highly selective and chromogenic mercury sensor, **b** colour change due to binding of sensor with Hg^{2+} in comparison with other divalent metal cations. Reproduced with permission from Díez-Gil et al. (2007)

change of solution from pink to green. Dithiacrown ether based on 1, 8-dihydroxyanthraquinone has been used for selective detection of Cd^{2+} and Hg^{2+} ions. The detection is based on the increase in the fluorescence intensity (Kadarkaraisamy and Sykes 2007). Crown ether fused to 1, 8-dihydroxyanthraquinone has been used as a fluorescent sensor for Pb^{2+} ions (Kadarkaraisamy and Sykes 2006). The coordination of Pb^{2+} to such crown ether changes the energy of excited states and increases the fluorescence intensity by many folds. In addition, a bathochromic shift of the emission band maximum as a result of coordination has also been reported.

Removal of metal ions

Once the presence of a particular metal ion and its quantity in water is tested by any of the above-mentioned detection techniques, it is very essential to remove it so that water can be made safe for use. Removal process is as important as detection because a slight excess of metal ion from its permissible limit can prove dangerous to human health. A proper technique of removal has to be followed for a particular metal ion to ensure its complete removal from the aqueous system; besides, care has to be taken to select the technique which is safe to use, environmental friendly and economical.

Methods of removal

Many methods have been used to remove heavy metal ions from water. Among these, the most remarkable ones are chemical precipitation, adsorption, ion exchange, etc., which are most often used for the removal of metal ions from aqueous systems.

Chemical precipitation

It is one of the effective techniques for removal of heavy metals from wastewater. In this process, chemical reagents are used which react with the heavy metal ions present in wastewaters and form an insoluble precipitates. These precipitates are removed by sedimentation or filtration technique to get toxic metal ion free water. The heavy metal ions may be precipitated either by hydroxide precipitation or sulphide precipitation methods. A variety of hydroxides has been used to precipitate metals from wastewater, based on the low cost and ease of handling. For example, $Ca(OH)_2$ and NaOH were used in removing Cu(II) and Cr(VI) ions from wastewater (Mirbagheri and Hosseini 2005). Sometimes, the addition of coagulants such as alum, iron salts and organic polymers can enhance the removal of heavy metals as hydroxide precipitates from wastewater (Charerntanyarak 1999). Hydroxide precipitation is a pH-dependent process, and for mixed metals, it may create a problem as an ideal pH for one metal may put another metal back into solution. Sulphide precipitation is also an effective process for the treatment of toxic heavy metals ions. The solubility of the metal sulphide precipitate is dramatically lower than hydroxide precipitate, and also by this method metal ion can be removed selectively with faster reaction rate. Sulphide precipitation method has been used to remove Cu^{2+}, Cd^{2+} and Pb^{2+} ions using pyrite and synthetic iron sulphide as precipitating agents (Özverdi and Erdem 2006). As an alternative, chelating precipitants like trimercaptotriazine, potassium/sodiumthiocarbonate and sodiumdimethyldithiocarbamate can be used to precipitate heavy metals from aqueous systems (Matlock et al. 2002a). Some new chelating precipitants have also been synthesized as commercial heavy metal precipitants may not possess necessary binding sites. For example, a new thiol-based compound, 1,3-benzenediamidoethanethiol (BDET2) has been synthesized and was used effectively to precipitate mercury ions in wastewater (Matlock et al. 2002b).

Ion exchange method

Ion exchange is another technique of interest for the removal of toxic heavy metal ions from wastewater because of high removal efficiency and fast kinetics of ion exchanger materials (Kang et al. 2004). Ion exchange resins, synthetic or natural, have been used for this purpose; however, synthetic resins are preferred as they are more effective in removing the heavy metals from the solution (Alyüz and Veli 2009). These cation exchangers are either strongly acidic resins with sulphonic acid groups (–SO_3H) or weakly acid resins with carboxylic acid groups (–COOH) where H^+ ions in the sulphonic group or carboxylic group of the exchanger get exchanged with the heavy metal ions. Factors like pH, temperature, initial metal concentration, contact time and charge of the metal ion have a good role to play in the uptake of heavy metal ions by ion exchange resins (Gode and Pehlivan 2006; Abo-Farha et al. 2009; Pathania et al. 2014). Ion exchange capabilities of thermally stable acrylamide zirconium(IV) sulphosalicylate (AaZrSs) composite material for the removal of various metal ions have been carried out by our research group (Ahad et al. 2016). Out of various metal ions tested, the exchanger was found to have maximum retention potential for Cd^{2+} ion with the recovery efficiency of around 98%. The effect of doze, contact time, initial metal ion concentration and pH on the adsorption behaviour of the exchanger has also been investigated (Fig. 10).

Ion exchange capabilities of zirconium resorcinol phosphate synthesized by reverse micelle method have been carried out by our research group (Bashir et al. 2016). The nanocomposite was found to be Cd^{2+} ion selective with high distribution coefficient (Kd) value in aqueous system as well as in other solvents. As a result, the ion exchanger was not

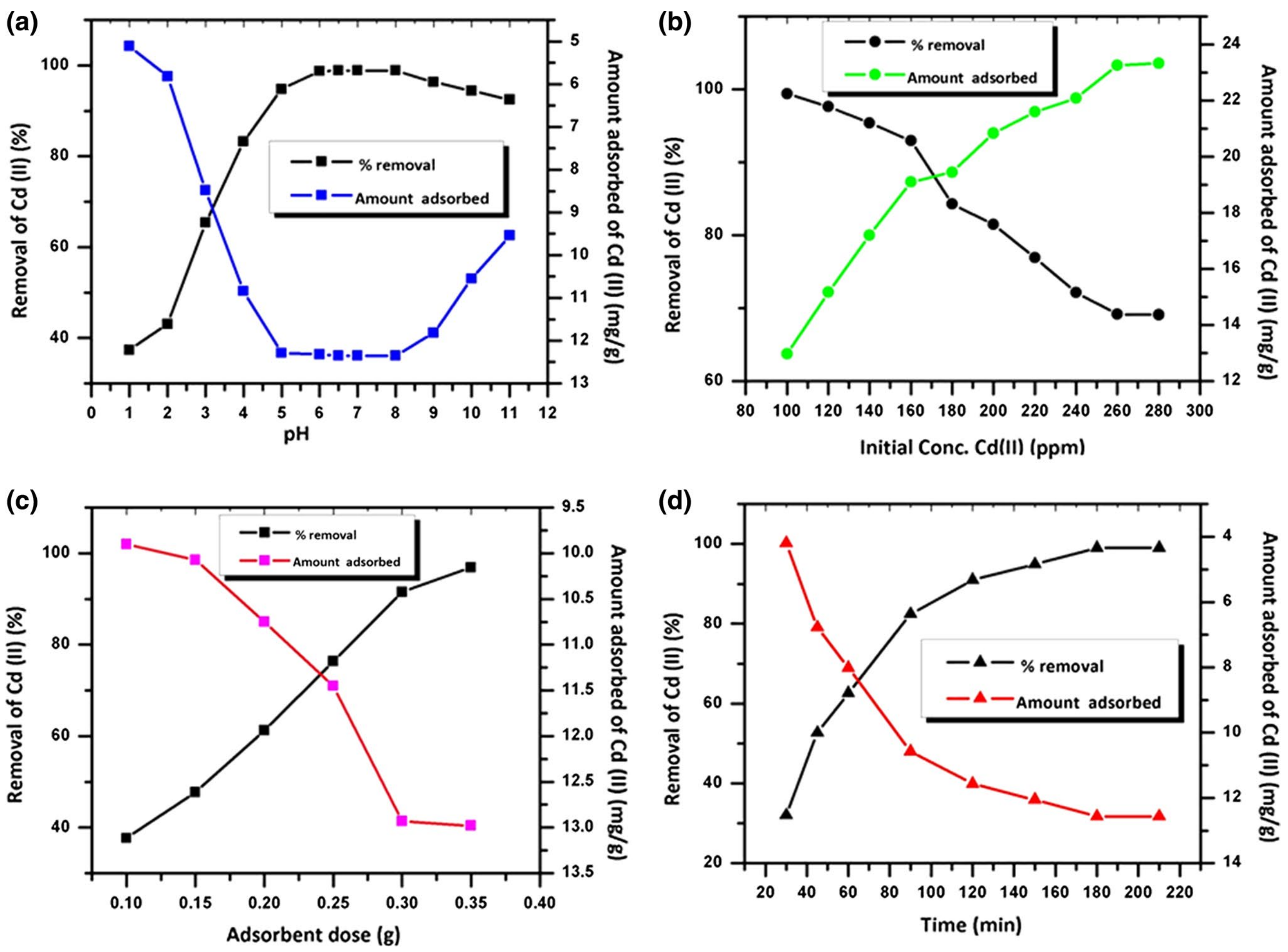

Fig. 10 Removal of various metal ions by ion exchange method while using thermally stable acrylamide zirconium(IV) sulphosalicylate (AaZrSs) as ion exchanger. Effect of **a** pH, **b** initial metal ion concentration, **c** adsorbent dose and **d** contact time on the percentage removal of Cd^{2+} by the hybrid material: acrylamide zirconium(IV) sulphosalicylate (AaZrSs). Adapted with permission from Ahad et al. (2016). Copyright 2016 Royal Society of Chemistry

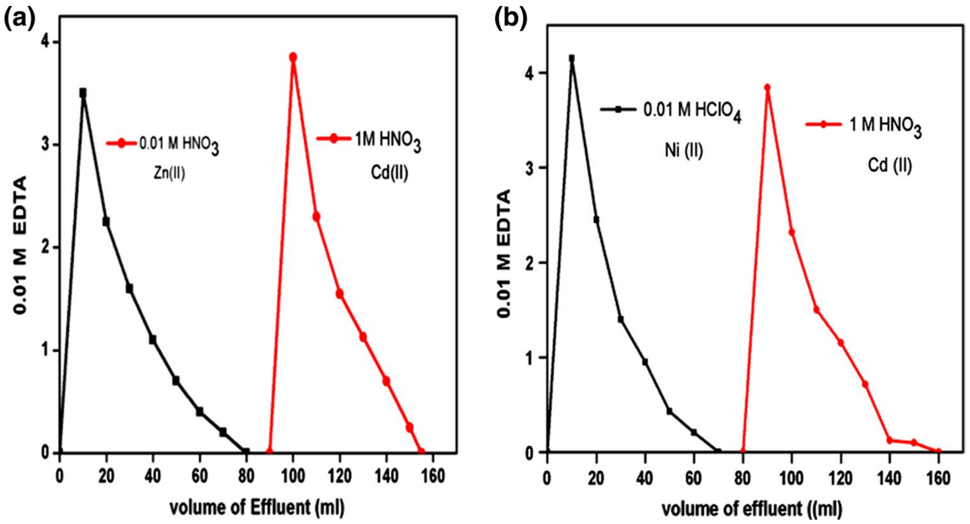

Fig. 11 Binary mixture separation capabilities of zirconium resorcinol phosphate nanocomposite. Separation of **a** Cd^{2+}/Zn^{2+} ion mixture and **b** Cd^{2+}/Ni^{2+} ion mixture. Adapted with permission from Bashir et al. (2016). Copyright 2016 American Chemical Society

only capable of removing Cd^{2+} ions from wastewater but also can be effectively used to separate binary mixtures like Cd^{2+}/Zn^{2+} and Cd^{2+}/Ni^{2+} as shown in Fig. 11.

Al-Othman et al. (2011a, b) have successfully synthesized an organic–inorganic-type composite cation exchanger, poly-*o*-toluidine Zr(IV) tungstate, and used this hybrid material for the removal of Hg(II) ions. In addition to its high thermal stability and rapid elution of exchangeable H^+ ions, the cation exchanger was possessing high selectivity for Hg(II) ion and was quite efficient for metal ion separation in case of binary mixtures. Naushad et al. (2015a, b, c) used Nernst–Planck approximation to study kinetics of Cd^{2+}, Co^{2+}, Cu^{2+} and Pb^{2+} ions on the surface of acetonitrile stannic(IV) selenite composite cation exchanger. From these kinetic studies, various physical parameters like fractional attainment of equilibrium, self-diffusion coefficients, energy of activation and entropy of activation were estimated to evaluate the mechanism of ion exchange on the surface of composite ion exchange material. In similar studies, Nernst–Planck equation was applied to study the heavy metal ion exchange kinetics over the surface of nylon 6,6 Zr(IV) phosphate and poly-*o*-methoxyaniline Zr(IV) molybdate composite cation exchanger (Al-Othman et al. 2011a, b, 2013). Various useful ion exchange kinetic parameters were evaluated in order to validate the practical use of this ion exchanger in the field of wastewater treatment and to predict the ion exchange process occurring on the surface of the cation exchanger. A polymeric–inorganic cation exchanger, acrylonitrile stannic(IV) tungstate with good ion exchange capacity, higher stability, reproducibility and selectivity for heavy metals, is another important ion exchanger that has been used for the removal of metal ions from water (Nabi et al. 2009). Its practical application was demonstrated in the quantitative separation of Fe^{3+} and Zn^{2+} contents of a commercially available pharmaceutical, Fefol-Z sample. Zeolites have also been found good cation exchangers for heavy metal ions under different experimental conditions (Motsi et al. 2009). A schematic representation of zeolite involving ion exchange process for the removal of Co(II) ions from wastewaters is shown in Fig. 12.

Clinoptilolite which is a natural zeolite has received extensive attention in this field due to its selectivity towards heavy metal ions. Some other ion exchanger materials used for the removal of heavy metal ion are summarized in Table 7.

Adsorption method

In many cases conventional methods, including chemical precipitation, flocculation, membrane separation, ion exchange, etc., are not desirable because of low capacities and low removal rates for metals other than Hg(II). Adsorption method is considered to be quite attractive in terms of the low cost, simple design and strong operability, especially its high removal efficiency from dilute solutions (Wang et al. 2013). Adsorbents which have been mostly used for heavy metal removal are activated carbon, biomaterials, layered double hydroxide (LDH), carbon nanotubes (CNT)-based materials, etc.

1. Activated carbon.

   Activated carbon has proved an efficient adsorbent for the removal of metal contaminants present in the aquatic environment. Because of its high surface areas, it is widely used in the treatment of wastewaters. The effectiveness of activated carbon in cleaning up polluted water is due to its well developed porosity structure as well as the presence of a wide spectrum of surface functional groups. Al-Malack et al. (2017) carried out adsorption studies on activated carbon and obtained

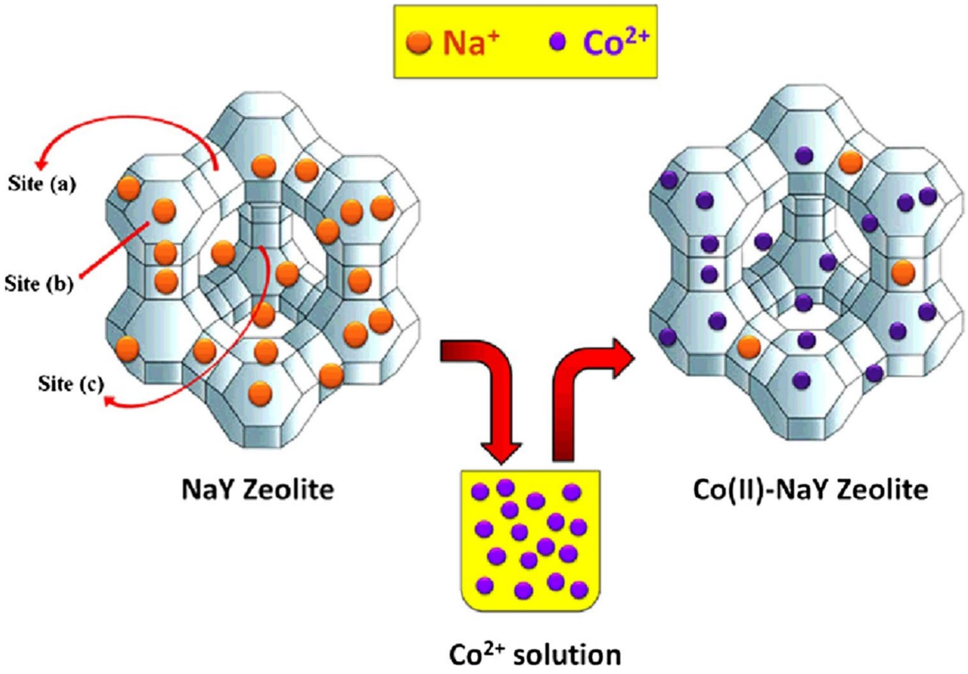

Fig. 12 Metal ion removal capabilities of zeolites involving ion exchange process. Schematic representation of Co^{2+} ions distribution on the extra-framework sites in the Co(II)–NaY zeolites. Reproduced with permission from Sanaeepur et al. (2015). Copyright 2015 Elsevier

Table 7 Heavy metal ion removal performance of some ion exchange materials

Ion exchanger	Metal ion	Removal percentage	References
Clinoptilolite	Pb^{2+}	55	Inglezakis et al. (2007)
Purolite C100	Pb^{2+}	99	Badawy et al. (2009)
Amberjet 1200 Na	Ni^{2+}	98	Zewail and Yousef (2015)
	Pb^{2+}	99	
Acidic cation exchange resin	Ni^{2+}	97	Shaidan et al. (2012)
Clinoptilolite	Zn^{2+}	100	Athanasiadis and Helmreich (2005)
Duolite GT-73 Resin	Hg^{2+}	30–40	Chiarle et al. (2000)
Acrylamide zirconium(IV) sulphosalicylate (AaZrSs) composite	Cd^{2+}	98	Ahad et al. (2016)
Sodium dodecyl sulphate acrylamide Zr(IV) selenite (SDS-AZS)	Pb^{2+}	90	Naushad (2014)

adsorption efficiency of 78% and 94% for Cd^{2+} and Pb^{2+} ions, respectively. Activated carbon prepared from peanut shell was used to remove Cr(VI) from water where Cr(VI) adsorption was found to be pH dependent (AL-Othman et al. 2012). Effective adsorption of Cr(VI) was found to occur in the pH range of 2–4. Some other examples of activated carbon as adsorbent for metal ions are summarized in Table 8.

2. Biosorption

Biosorption of heavy metals from aqueous solutions can be considered as an alternative technology in industrial wastewater treatment; dry biomass is used to extract toxic heavy metals from industrial effluents. In biosorption of heavy metal ions, physisorption and chemical adsorption play an important role in the adsorption mechanisms of metal ions (Sahmoune 2018). The term biosorption is used to describe the passive non-metabolically mediated process of metal binding to living or dead biomass (Rangsayatorn et al. 2002). A variety of low-cost biomass has been developed and commercialized for controlling pollution. Low-cost ash and magnetite-modified ash developed from agricultural products have been used for the removal of Pb^{2+} ions from water where their highest removal capacities of 25 and 30 mg g^{-1}, respectively, were reported for this toxic metal ion (Ghasemi et al. 2014a, b). Some other important biomaterials used for controlling heavy metal ion pollution include anaerobically digested sludge (Tokcaer and Yetis 2006), fungi (Garcia et al. 2005), algae (Elifantz and Tel-Or 2002), hemp-based biosorbents (Morin-Crini

Table 8 Removal percentages of different metal ions using activated carbon as adsorbant at neutral pH

Source of activated carbon	Metal ion	Removal efficiency (%)	References
Sigma-Aldrich	Cd^{2+}	86	Karnib et al. (2014)
	Pb^{2+}	83	
	Cr^{3+}	50	
	Ni^{2+}	90	
Coconut shell	Pb^{2+}	100	Bernard et al. (2013)
	Fe^{2+}	76	
	Cu^{2+}	71	
	Zn^{2+}	26	
Oil palm and coconut shells	Pb^{2+}	86	Rahman et al. (2014)
	Ni^{2+}	82	
	Cr^{3+}	70	
African palm fruit	Cd^{2+}	93	Abdulrazak et al. (2017)
	Cu^{2+}	97	
	Ni^{2+}	92	
	Pb^{2+}	95	
Fig sawdust	Pb^{2+}	80.6	Ghasemi et al. (2014a, b)

et al. 2019) and bacterial biomass (Oves et al. 2013). In addition, agricultural materials including rice bran, soybean, cottonseed crop milling waste, jute, leaves–derived biosorbents (Anastopoulos et al. 2018), sawdust, spent mushrooms substrates (Kulshreshtha 2018), coconut shell, cellulose-based adsorbents (Varghese et al. 2018), maize cob and groundnut husk (Saeed et al. 2005; Okieimen et al. 1985; Okieimen and Okundaye 1989; Shukla and Pai 2005; Marshall and Johns 1996; Ogunsuyi et al. 2001) have also been found extremely useful in this field. Phytoremediation, a plant-based technology is an efficient, eco-friendly and economic biosorption method to tackle the heavy metal pollution (Muthusaravanan 2018). Biosorption is receiving much more attention in the field of metal ion removal because it offers advantages like cost-effectiveness, selectivity, easy availability, efficient removal of metals even at low concentrations, less production of unwanted secondary sludge, etc. (Bashir et al. 2018; Escudero et al. 2019).

3. Layered double hydroxides

Layered double hydroxides (LDH) are a type of anionic clay mineral with lamellar structures having general formula $[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2]^{X+}\,(A^{n-})_{x/n}\cdot mH_2O$, where M^{2+} and M^{3+} represent divalent and trivalent metal cations, respectively, A^{n-} represents an interlayer anion, x represents the molar ratio of $M^{3+}/(M^{2+}/M^{3+})$, and m represents the number of water molecules between the layers (He et al. 2018). Metal cations in the laminates of the LDHs as well as anions in the interlayers can be substituted by other metal cations and anions, respectively (Fig. 12a). As a result, different LDHs with different interlayer spacings can be obtained. The adsorption of heavy metal ion mainly depends on the exchangeability of the interlayer anions of LDHs; besides, type of cations in the laminates, the type of interlayer anions and the nature of surface groups also play an important role in the removal performance of LDHs towards heavy metal ions. Usually small anions, such as ethylenediaminetetraacetate (EDTA), citrate, glutamate, malate, are preferred for interlayer anions as they are effective for the leaching of heavy metals due to the formation of chelate complexes (Mosekiemang and Dikinya 2012). In situ oxidative polymerization was carried out for the synthesis of polyaniline/Mg/Al layered double hydroxide (PANI/LDH) and was used for the efficient removal of Cr(VI) as depicted in Fig. 12b (Zhu et al. 2016). The composite was found to have maximum adsorption capacity of 393.7 mg g^{-1} for Cr(VI) (Fig. 13).

Table 9 highlights some of the important LDHs having different interlayer anions that have been used to remove various heavy metal ions.

4. Carbon nanotubes (CNTs)

CNTs can be considered as a graphite sheet that has been rolled into a tube. There are two types of CNTs: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) (Fig. 14).

CNTs possess highly porous and hollow structure, large specific surface area and light mass density. Also, there are four possible interaction sites present in CNTs: internal sites, interstitial channels, grooves and outside surface (Gadhave and Waghmare 2014). As a result of these additional sites, a strong interaction between CNTs

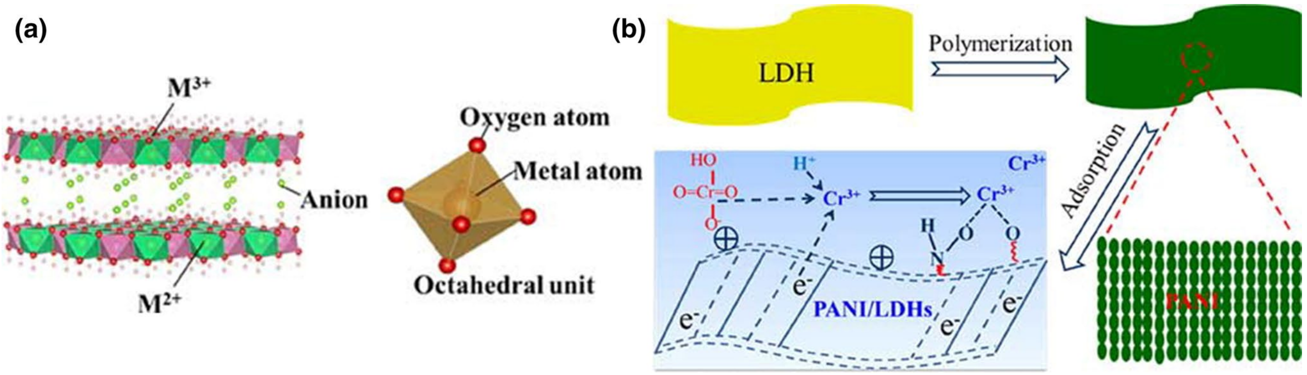

Fig. 13 Use of layered double hydroxides (LDHs) for the removal of heavy metal ions from aqueous systems. **a** Schematic diagram of LDH, **b** preparation of PANI/LDHs hybrid material by an in situ oxidative polymerization procedure and its efficient use for Cr(VI). Reproduced with permission from He et al. (2018). Copyright 2018 Taylor & Francis

Table 9 List of some layered double hydroxides (LDHs) and their use in heavy metal ion removal

LDH	Inter layer anion	Heavy metal Ion removed	Removal efficiency (mg g^{-1})	References
Mg–Al LDH	Glutamate	Pb^{2+}	68.49	Yanming et al. (2017)
Mg–Zn–Al LDH	CO_3^{2-}	Cr(IV)	33.82	Eshaq et al. (2016)
Mg/Al LDH	MoS_4^{2-}	As^{3+}	99	Ma et al. (2017)
		As(V)	56	
		Cr(VI)	130	
Al–Mg LDH	Cl^-	Cr(VI)	112.0	Li et al. (2009)
Ca–Al LDH	Dodecyl sulphate	Ni^{2+}	143.8	Chen et al. (2016)
Zn–Fe LDH	Citrate	Pb^{2+}	94.3	Rahmanian et al. (2018)
Mg–Al LDH	MoS_4^{2-}	Hg^{2+}	500	Ma et al. (2016)

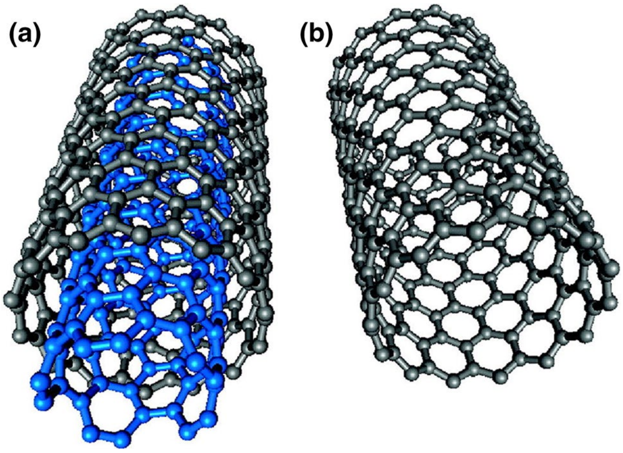

Fig. 14 Highly porous and hollow structure with large specific surface area of carbon nanotubes. Structure representations of **a** MWCNT and **b** SWCNT. Reproduced with permission from Ihsanullah et al. (2016). Copyright 2015 Elsevier

and pollutant molecules can take place very easily (Li et al. 2005). Owing to these properties, CNTs find a role in removal of hazardous pollutants from aqueous systems. Oxygen-containing functionalized carbon nanotubes (F-CNTs) were modified with chitosan so as to obtain chitosan-coated carbon nanotube (CHIT/F-CNTs). The chitosan-modified CNTs were not only found to be a good adsorbant for Cu(II) and Cr(VI) ions but metal-loaded chitosan-coated oxygen-containing functional carbon nanotubes were successfully used to develop a supercapacitor electrodes through a facile heavy metal ion adsorption and carbonization procedure (Hao et al. 2018). The scanning electron micrographs and schematic representation of chitosan-modified CNTs for heavy metal ion adsorption are shown in Fig. 15.

Some important other CNT-based materials useful for adsorption of heavy metal ions are given in Table 10.

5. Other adsorbant materials

In addition to these adsorbant materials for heavy metal ions, there are so many other adsorbants, which have shown excellent performance in the field of wastewater treatment. Some of these adsorbants are not only

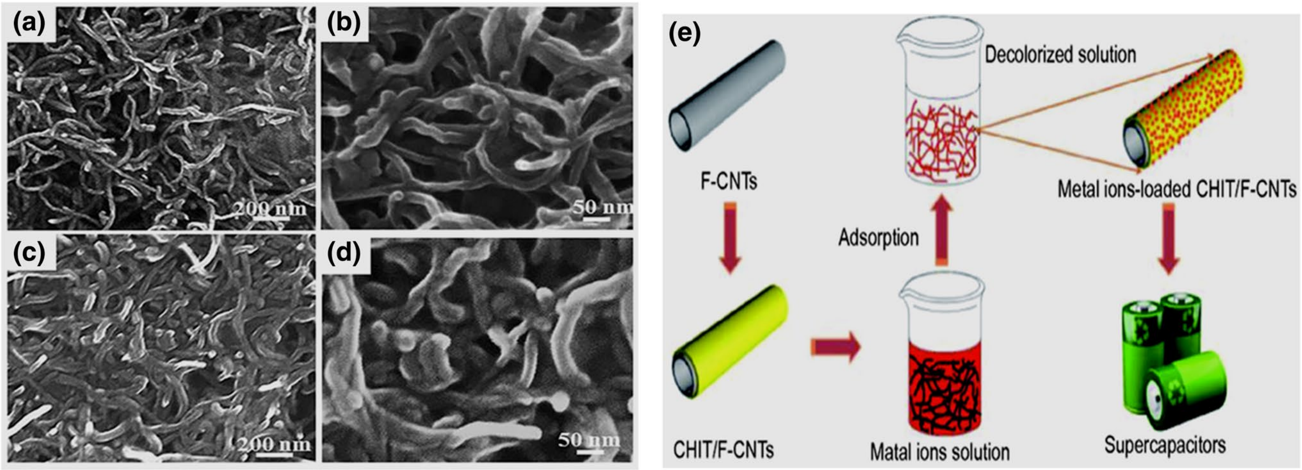

Fig. 15 Use of modified carbon nanotubes for the removal of Cu(II) and Cr(VI) ions. SEM images of **a**, **b** oxygen-containing functionalized carbon nanotubes (F-CNTs), **c**, **d** chitosan-coated carbon nanotube (CHIT/F-CNTs) and **e** schematic representation of chitosan-modified CNTs as a heavy metal ion adsorbant. Reproduced with permission from Hao et al. (2018). Copyright 2018 Springer

Table 10 Removal of some toxic heavy metal ions by CNT-based materials

CNT material	Metal ion	Adsorption capacity	References
Amino-modified MWCNTs	Pb^{2+}	58.26	Vukovic et al. (2011)
Activated alumina CNT nanoclusters	Cd^{2+}	229.90	Sankararamakrishnan et al. (2014)
MWCNTs	Ni^{2+}	3.72	Yang et al. (2009)
CNT supported by activated carbon (AC)	Cr(VI)	9.00	Bahr et al. (2001)
Oxidized CNTs	Pb^{2+}	63.29	Liu et al. (1998)
	Cu^{2+}	23.89	
	Cd^{2+}	11.01	
MWCNTs/ThO_2	Pb^{2+}	–	Mittal et al. (2016)

having high adsorption capacities for the highly toxic metal ions like Hg^{2+} but can also be regenerated without much loss in their adsorption capacities (Naushad et al. 2016). Since in adsorption process, adsorbents can be recreated by the desorption process because it is reversible technique, adsorption is considered as an environmentally acceptable method for recovery and separation of heavy metal ions (Carolin et al. 2017). Metal ions like Hg^{2+} possess strong affinity towards O, N and S atoms containing ligands, so the materials coated with polymers or resins can prove effective in increasing their efficiency and selectivity towards various metal ions (Naushad et al. 2015a, b, c). Crystal violet-modified amberlite IR-120 resin have been effectively used for the removal of Co(II) ions from aqueous systems (Naushad et al. 2015a, b, c), while polyaniline Sn(IV) silicate composite has been found very much effective for the removal of Cd(II) ion (Naushad et al. 2013). Some other adsorbants that have been used for the metal ion removal are summarized in Table 11.

Membrane filtration

Membrane filtration is useful for removal of suspending solids and organic molecules, but its role in metal ion removal can't be ignored. There are various types of membrane filtration such as ultrafiltration, nanofiltration and reverse osmosis that can be employed for heavy metal removal from wastewater. In ultrafiltration, permeable membrane is used to separate heavy metals or macromolecules on the basis of the pore size and molecular weight (Barakat 2011). Lower driving force and a smaller space requirement due to its high packing density are some of the advantages offered by ultrafiltration. Ultrafiltration can be modified so as to improve its removal efficiency. One such modification involves polymer-supported ultrafiltration where water soluble polymeric

Table 11 List of the various adsorbants for heavy metal ion removal

Adsorbant	Metal ion/s	Max. adsorption Capacity (mg g^{-1})	References
Fe_3O_4@TAS[a]	Cd(II)	286	Alqadami et al. (2017a, b)
	Cr(III)	370	
	Co(II)	270	
Alizarin red-S-loaded amberlite IRA-400 resin	Hg(II)	303.03	Naushad et al. (2015a, b, c)
($NiFe_2O_4$-NC)[b]	Hg(II)	476.2	Naushad et al. (2017)
DSDH[c] anchored on mesoporous silica	Pb(II)	169.34	Shahat et al. (2015)
(Fe_3O_4@AMCA-MIL53(Al)[d]	U(VI)	227.3	Alqadami et al. (2017a, b)
	Th(IV)	285.7	

[a] 3-[2-(2-Aminoethylamino)ethylamino] propyl-trimethoxysilane

[b] Nickel ferrite bearing nitrogen-doped mesoporous carbon

[c] *N*,*N*′di(3-Carboxysalicylidene)-3,4diamino-5-hydroxypyrazole

[d] Magnetic metal–organic framework nanocomposite

ligands bind metal ions and form macromolecular complexes (Rether and Schuster 2003). Many polymeric complexing agents such as pectin, alginate, chitosan, polyacetic acid, polystyrene, polyethyleneimine, polyvinyl alcohol have been found very effective to increase the efficiency of metal removal by ultrafiltration (Garba et al. 2019). This modification provides advantages like low-energy requirements and fast reaction kinetics and also improves selectivity. In reverse osmosis pure solvent is forced through semi-permeable membrane by applying pressure, while solute particles are retained. The membranes used for reverse osmosis have a dense barrier layer in the polymer matrix where most of the separation process takes place. Reverse osmosis has been employed to remove Cu^{2+} and Cd^{2+} ions from wastewater where more than 90% removal has been reported (Maximous et al. 2004). In another case ceramic ultrafiltration membrane was used in the recovery of mixtures of Fe^{2+} and Fe^{3+}, Cu^{2+} and Cr^{3+} by using ultrafiltration technique (Crini et al. 2017). Polymer-supported ultrafiltration is a technique of choice where metal ions form stable chelates with enhanced selectivity. The schematic representation of polymer-supported ultrafiltration is shown in Fig. 13a. Resins containing amino and imino groups are well known to form stable chelates with copper, nickel and other transition metal ions.

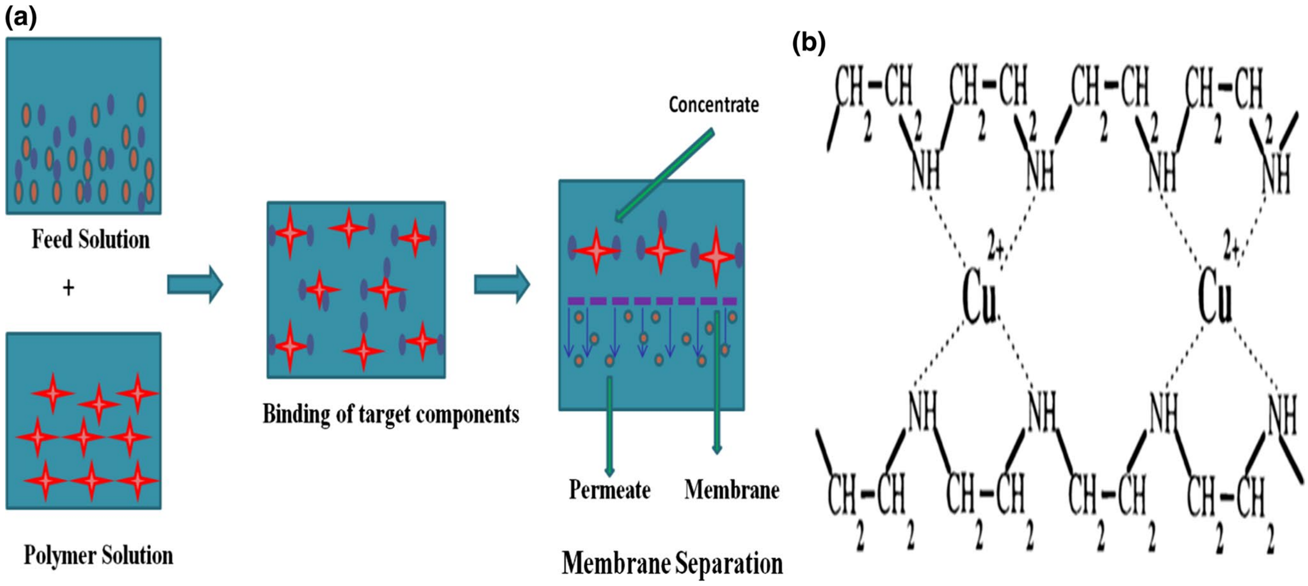

Fig. 16 Polymer-supported ultrafiltration as a tool for the removal of heavy metal ions from water. **a** Schematic representation of the polymer-supported ultrafiltration separation technique and **b** idealized structure of the polymeric complex poly(ethylenimine) with copper (II) ions. Adapted with permission from Geckeler and Volchek (1996). Copyright 1996 American Chemical Society

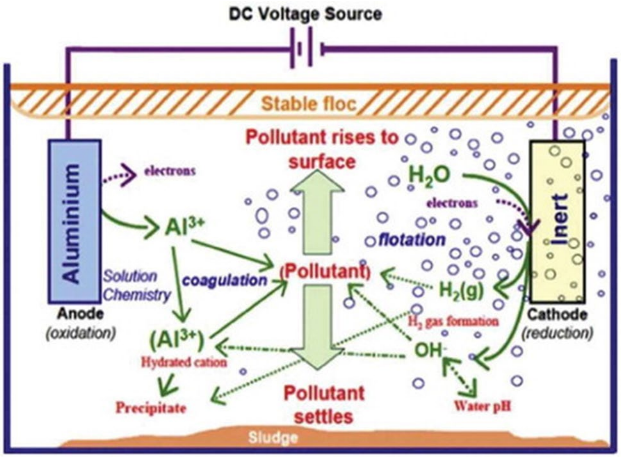

Fig. 17 Schematic diagram of an electrocoagulation cell showing the main reactions involved in the electrocoagulation process, possessing a carbonaceous material cathode. Reproduced with permission from Al-Qodah and Al-Shannag (2017). Copyright 2017 Taylor & Francis

Poly(ethylenimine) (Fig. 13b) is one such example which has been used in connection with polysulphone or polyamide membranes for heavy metal ion removal (Geckeler and Volchek 1996). Molecules of poly(ethylenimine) form chelates with transition metal ions with no interference from the presence of alkali and alkaline earth metals (Fig. 16).

Electrochemical method

Electrolytic recovery is one of the methods used to remove metals from wastewaters. This process uses electricity to pass through an aqueous metal-bearing solution. Electrochemical treatments of wastewater involve electrodeposition, electrocoagulation, electrofloatation and electro-oxidation (Shim et al. 2014). In this process, consumable electrode is used to supply ions into the wastewater, where they neutralize the charges of the particles (Tran et al. 2017). These ions remove the undesirable contaminants by means of chemical reaction, coagulation or precipitation as depicted in Fig. 17. In electroprecipitation method heavy metals present in wastewater are precipitated as hydroxides with the supply of electricity.

Copper, chromium and nickel ions have been removed from wastewater by using electrocoagulation process with 100% removal efficiency in a time span of 20 min (Akbal and Camci 2011). Nearly 100% removal efficiency has also been reported for Cd^{2+}, Cu^{2+} and Ni^{2+} ions by electrocoagulation method using batch cylindrical iron reactor (Un and Ocal 2015). The electrochemical method has some advantages over the traditional flotation and coagulation such as better removal rate and larger probability of coagulation as the electricity applied to the system sets the whole process in motion, reduced sludge production, no requirement for chemical use and ease of operation. On the other hand, chemical precipitation requires a large amount of chemicals to reduce metals to an acceptable level for discharge.

Conclusion

Pollution by heavy metal ions is one of the serious environmental problems. Heavy metal ion toxicity has been reported to cause many health issues to living beings which has motivated researchers to develop various strategies for detection and removal of these heavy metal ions from aqueous systems to make water safe for use. Many materials and methods have been adopted earlier for these purposes which have shown promising performance, but are having many drawbacks as well. Such materials and methods have been modified from time to time in order to improve their performance and to overcome the associated limitations. Search for new materials and methods, which are more efficient, environment friendly, easy to operate and cheap, is a continuous ongoing process to lower down the concentrations of these heavy metal ions below the level where they cannot prove dangerous to living beings.

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