ScienSage

Journal of Advanced Scientific Research

Available online through http://www.sciensage.info

ISSN
0976-9595
Review Article

NANOMATERIAL SENSORS FOR ENVIRONMENTAL POLLUTANTS

Sajith Kumar Chandran
Department of Chemistry, Jai Hind College, A-Road, Churchgate, Mumbai, Maharashtra, India
**Corresponding author: sajithkchandran@gmail.com*

ABSTRACT
Nowadays, global environment of water, soil, and atmospheric systems has continuously been deteriorating due to the incessant release of toxic chemicals from various constructed sources. The existence of heavy metal ions in the environment poses serious threats to human health and the ecosystem. Therefore, this review focuses on the advent of nanotechnology that has given immense opportunities for developing advanced nanomaterials with unique functionalities. This review reports on the development of sensing techniques based on nanomaterials including metal and metal oxide nanomaterials, quantum dots, carbon nanomaterials and polymer nanocomposites. Nanomaterials well possess excellent electrical, optical, thermal, catalytic properties and strong mechanical strength, which offer great opportunities to construct nanomaterials-based sensors or devices for environmental pollutants. The nanosorbents themselves should be nontoxic, the sorbents present relatively high sorption capacities and selectivity to the low concentration of pollutants. The adsorbed pollutants can be removed from the surface of the nanoadsorbent easily and sorbents infinitely recycled.

Keywords: Nanomaterials, Sensing, Environmental pollutants, Heavy metals.

1. INTRODUCTION
The extensive release of heavy metals into water bodies has been prevalent for past many decades. Heavy metal toxicity is becoming a severe threat to humans and the environment. Due to their long-lasting half-life, potential growth in different parts of the body, and non-biodegradability, metal ions are being obvious entities that can cause numerous hazardous health risks. Various methods have been developed for detecting heavy/ hazardous metals based on sensors. Among the variety of new technologies, a chemical and optical nanosensor is promising technology to detect poisonous heavy metals. Several nanosensors have been developed using nano-materials, synthesized from green or chemical methods. The nanosensors are suitable to arrange and give superior limit of detection, limit of quantification, and onsite detection [1]. The enormous increase of heavy metals in the environment for past few years is due to the enhancement in industrial and mining activities. Moreover, metals can be discharged through other natural sources that can intensively increase the release of toxic metals into waters systems. Heavy metals can cause pollution in soil, air and water leading to severe toxic effects and health issues [2-3]. Over the past decade, various conventional analytical methods have been established for detecting heavy metals at low and ultra-low level employing different techniques such as liquid chromatography, UV/Vis spectroscopy, X-ray fluorescence spectroscopy (XFS), capillary electro-phoresis (CE), microprobes (MP), anodic stripping voltammetry (ASV), atomic absorption spectroscopy (AAS), inductively coupled plasma mass spectroscopy (ICP-MS), and inductively coupled plasma optical emission spectroscopy (ICP-OES). However, these analytical tools suffer from several limitations including sample preparation, clean-up, pre-concentration processes, expensive instruments, and professional personnel [4-5]. Alternatively, facile, inexpensive, and time -consuming procedures are also being employed for metal detection, such as electrochemical colorimetric and fluorescence detection [6]. Recently, nano material-based sensors have shown great potential in detection of heavy metals due to their high surface reactivity, large surface area, strong adsorption capacity, and high catalytic efficiency. Various nanomaterials such as metal and metal oxide nanoparticles, polymeric nanomaterials, silicon, and carbon based nanomaterials have been used to design special nanosensors for detecting toxic metal ions. [7]. This review reports the development of sensing techniques based on nanomaterials including metal and metal oxide nanomaterials, quantum dots, carbon nanomaterials and polymer nanocomposites. Nano-

materials possess excellent electrical optical, thermal, catalytic properties and strong mechanical strength, which offer great opportunities to construct nano-materials-based sensors or devices for environmental pollutants.

2. SOURCES OF HEAVY METALS POLLUTANT

Heavy metals are found naturally on Earth's crust since Earth's formation. In the astounding increase in the use of heavy metals, it has resulted in an imminent surge of metallic substances in both the terrestrial environment and aquatic environment. Heavy metal pollution has emerged due to anthropogenic activity, which is the prime cause of pollution, primarily due to mining the metal, smelting foundries, and other industries that are metal-based, leaching of metals from different sources such as landfills, waste dumps, excretion, livestock and chicken manure, runoffs, automobiles and road works. Heavy metals use in the agricultural field has been the secondary source of heavy metal pollution, such as the use of pesticides, insecticides, fertilizers, and more. Natural causes can also increase heavy metal pollution, such as volcanic activity, metal corrosion, metal evaporation from soil and water and sediment re-suspension, soil erosion, geological weathering [8-13].

3. TRANSPORT OF POLLUTANTS INTO THE ECOSYSTEM

Pollutants enter the ecosystem in various ways and will enter the hydrosphere, lithosphere and atmosphere. Apart from also entering natural ways as previously said, through volcanic activity and weathering of rocks, anthropogenic activity is a major cause of pollutants entering the environment. They can be an unintended release such as in shipwrecks, oil spills, mining and fires; in the intended application of biocides such as vector controls; and waste disposals such as industrial effluents and sewage disposal. Movement of heavy metals or any other pollutants in water sources depends on temperature, movements and direction of surface waters, circulation of air masses and the speed of the wind. Apart from these, there are other physicochemical factor which influences the distribution and movement of pollutants, such as partition coefficient, polarity, vapor pressure and molecular stability [15].

3.1. Soil pollution

Soil pollution can be deliberate or unintentional. Deliberate pollution includes wastewater irrigation, pesticides, animal manures, fertilizers, leaching paint, mine ore waste (mine tailing), sewage sludge, spillage of petroleum distillates, coal combustion residues, waste dumping. Using sewage and wastewater that are not treated have caused many heavy metals in our agricultural lands and thus have been absorbed by the crops that tend to be eaten by humans themselves. Non-deliberate pollution is brought about through flooding of seas and rivers that brings sewage and contaminated water to the land and accidents involving vehicles transporting toxic chemicals. Since heavy metals are non-degradable, since they cannot undergo and microbial or chemical degradation, they stay in the soil for a long time. The ecosystem is being ruined to the fact that the heavy metals are entering the food chain. Heavy metals also affect the biodegradability of organic pollutants, making them less degradable and thus having double the effect of polluting the environment. These metals present in the soil cause risks to all the biosphere and are taken up through direct ingestion, absorbed by plants that can be hazardous to the plant and to the food chain that eats the plant, altering the properties of the soil such as the pH, colour, porosity and natural chemistry thus impacting the quality of the soil, and contaminating the water [15-19].

3.2. Water pollution

Two major origins are the culprits of water contamination: urbanization and industrialization. The metals are transported by the runoffs from villages, towns, cities and industries that accumulate in the sediments of water bodies. Even if traces are transported to water bodies, they still are toxic to human beings and other ecosystems. The toxicity of heavy metals depends on many factors such as nature of the metal present, the biological role of the metal, the organism exposed and duration of exposure. Exposure of one organism will affect all the organisms in the food chain. Since humans are the last of the food chain, the accumulation of heavy metal is at large proportions, as the concentration increases along the food chain. Both industrial and domestic wastes are usually expelled into the sewage system. Heavy metals are found in high concentrations in raw sewage, and these are not degraded in the sewage treatment. They are removed either in the final effluent or else in the sludge produced. The properties and contaminants of sewage that enters the water depend on the treatment of the sewage. Several controls have been set up due to the problems caused by sewage elimination into the rivers and sea without being treated. Stringent regulations have been placed, and better technology has been developed to decrease the number of pollutants that are thrown in the waters. [15, 20-21].

3.3. Air pollution

Like water contamination, air pollution has been caused due to urbanization and industrialization. Pollutants enter the atmosphere in different forms. They can enter as particles, droplets, or the gaseous form, or association with particles or droplets. Particles and droplets do not travel long distances and fall on the ground after a short distance, though if small can travel a longer distance. Particles in the gaseous state can be transported over long distances due to air masses. Natural and anthropogenic activity has released particulate matters (PMs), especially fine particles, and dust. Particulate matter present through natural activity are released through sand storms, volcanic activity, soil erosion and weathering of rocks. While particulate matters due to human activity are released through industrial activity, burning of fossil fuels, vehicle exhaust, smelting and more. The particulate matters can precipitate severe health problems and cause infrastructure deterioration, the formation of acid rain, corrosion, eutrophication due to particulate matters falling in the water when it rains, and it can cause haze. Chimneys are one of the main sources of atmospheric pollution where a number of gases are released. The height of the chimney and weather, make a difference in how far the pollutant travels. The Smokestack, further the pollutant travels. The warmer climate is and the windier it is, the farther away the pollutants travel since convection currents occur and the side currents help it move further away. In cold and foggy weather the pollutants travelling short distances. Other sources of atmospheric pollution are internal combustion and jet engines. Catalytic converters and unleaded petrol have helped reduced pollution from vehicles, apart from an improvement of engines though diesel engines, old cars and too many cars still cause a problem. Pesticide application is another source of pollutants with refrigerators, aerosols and radioactive pollution [14-15]. The atmosphere is divided into five main layers, though the troposphere and stratosphere are essential for pollutant transportation. The troposphere is the first layer closest to the Earth and stratosphere is above it where at the top the ozone layer lies. In the troposphere, vigorous vertical mixing occurs, with a consistent air pattern of circulation, and pollutants can be transported in a small amount of time. There is little vertical mixing in the stratosphere. Pollutants released close to the Earth tend not to travel far due to turbulence and confined airflow. Though pollutants eliminated at a higher distance can travel further due to the circulating air. Air pollutants can thus travel far when entering air circulation and cause global issues. Soluble particles can then react with the rain and fall back into waters and land [15].

4. CHEMICAL, ELECTRONIC, AND OPTICAL PROPERTIES OF NANOMATERIAL

Chemical properties of two-dimensional nanomaterials are closely related to the structural defects, especially surface defects. These determine a series of reactions involved in the recognition events of sensors to a large extent. Generally, the structural defects of two-dimensional nanomaterials are located at low coordinated steps, edges, terraces, kinks and corner atoms [22-23]. For perfect two-dimensional nanomaterials, there are no dangling bonds within basal surfaces; therefore, the active sites are mainly located at the plane edges [23]. The structural defects play a critical role in affecting the sensor performance. For any sensor system, surface defects are involved in the surface or interface reactions including the modifications and recognition events between heavy metals ions and sensing probes or elements. Adsorption processes on the surface or interface can to a large extent affect the performance of sensors. Due to the decreased thickness or energy fluctuation, the increased active sites can facilitate the adsorption processes. In return, the surface functionalization by physical and chemical adsorption can be immediately and sensitively reflected in the electronic and optical properties because the adsorption can result in the p-dopants or n-dopant effects [24-25]. These unique properties lead to two-dimensional nanomaterials based sensors with high sensitivity. Optical and electronic properties have an intertwined and bidirectional relationship [26]. They are associated with all sensing applications mentioned in this review. Optical and electronic properties well reflected by the electronic band structure. Generally, the crystal structure determines the movement behaviour of electrons and photons in the bulk. For example, the atomic thickness leads to excellent optical transparency, but at the same time decreases charge mobility due to enhanced electron scattering [27]. Optical and electronic properties are flexibly regulated due to the sensitive surface states of 2D nanomaterials. Their thickness, chemical component, and the atomic arrangement can be controlled by a hybrid with other nanomaterials, surface functionalization, or other treatment processes (electrochemical etching and plasma treatment). Further, these strategies can improve the electronic and optical properties for sensor applications [22, 28-30].

5. NANOMATERIALS FOR HEAVY METAL IONS SENSING

Many advances have been achieved in the development of nanomaterial-based techniques to monitor heavy metal ions in various samples (standards and real world samples) with various sensing strategies. These strategies have been established with diverse classes of nano-materials, such as metal nanoparticles, quantum dots, nanometal organic frameworks (NMOFs), magnetic nanoparticles, carbon nanotubes, and nano- composites. Metal nanoparticles have unique physical and chemical properties which have been widely applied for many applications. Various metals such as Au, Pt, Pd, Ag, Cu, Co, including rare earth metals have been employed for sensing [31]. Metal nanoparticles-based sensors provide a strong potential with increasing both sensitivity and selectivity via tuned signal amplifications. The design of metal nanoparticles, bio-functionalized nanoparticles and nanocomposites has attracted research focused on nanosensors. Numerous advanced analytical methods were developed for environmental monitoring and food safety applications [32]. Noble metals with outstandingly resistant to corrosion and oxidation, even at elevated temperatures include the metals of groups VIIb, VIII and 1b of the second and third transition series of the periodic table i.e. rhodium (Rh), ruthenium (Ru), palladium (Pd), silver (Ag), osmium (Os), iridium (Ir), platinum (Pt), and gold (Au) [33]. Au nanoparticle modification of glassy carbon electrodes can help eliminate the memory effect and interferences from intermetallic compounds. It has been seen that the Au nanoparticle-modified electrodes have a sensitivity of higher magnitude than macro-electrodes for detecting As (III) [34]. Bi nanoparticles modified electrode for heavy metal detection showed improved sensitivity of the electrode with a drop-in particle size of Bi nanopowder. It gives a higher electro active surface area [35]. In the reported work using Bi nanoparticles, simultaneous detection of Zn, Cd and Pb is done and the sensitivity and LOD of sensor electrodes are improved with smaller particle size distribution. Several heavy metal ions are highly dangerous for the environment and human beings. One of the most lethal is mercury and many recent works have been published in this field. One example is an ultra-sensitive colorimetric detection of Hg(II) based on silver nanoparticles functionalized with mercaptobenzo heterocyclic compounds (mercaptobenzooxazole (MBO), mercaptobenzoimidazole (MBI) and mercaptobenzo-thiazole (MBT)) that has been recently reported [36]. A similar mechanism is presented in [37] for Hg (II), has also been used for Ni (II) detection. Here, triangular silver nanoprisms were synthesized by a modified seed-mediated growth method, and upon addition of Ni (II) ions these triangular nanostructures showed a significant colorimetric change from blue to yellow as a function of the Ni (II) ion concentration. Ni (II) ions serve as a catalyst for the generating of H_2O_2 in a citrate-capped triangular silver nanoprisms colloidal solution. The oxidative etching with H_2O_2 formed in the colloidal solution sculptured the sharp corners/edges of the prisms to produce circular Ag nanodisk. The sensor showed a high linearity for Ni (II) concentration in the range of 0 to 30 μM with a limit of detection of 21.6 nM in aqueous solution [38]. Copper is another dangerous ion that can contaminate water and functionalized silver NPs can effectively help in the detection of this contaminant. For example, recently the detection of Cu (II) ions based on coordination reactions of copper ions with casein peptide-functionalized silver nanoparticles has been reported. This system leads to a distinct color change of the solution from yellow to red. Such a system has a good detection limit of about 0.16 μM with a high linearity in the 0.08-1.44 μM concentration range [39]. Silver NPs can also be used for colorimetric determination of Fe (III) ions as recently reported by some authors. The first example is based on chitosan-capped silver nanoparticles [40]. Such functionalized NPs exhibit a strong surface plasmon resonance band, which disappears in the presence of increasing concentrations of Fe (III) ions. The system showed a visually detectable color change from brownish-yellow to colorless for the selective deter-mination of Fe (III). The distinct color change can be observed. It shows good selectivity for Fe (III) with the lowest detection concentration of 0.53 μm and the system was successfully applied for the determination of Fe (III) in real samples. Ag NPs are found to be highly sensitive for Hg (II) and Mn (II) ions with the detection limit for these ions are 16 nM. Another system is based on alginate-stabilized silver nanoparticles, which act as a label-free colorimetric sensor for the quantification of Mn (II) metal ions with excellent selectivity and sensitivity and detection in aqueous solution in the range of 1-10 μM. Here, the binding forces between functionalized AgNPs and Mn (II) ions bring the silver nanoparticles closer, decreasing the interparticle distance and causing slight agglomeration, with a color change from pale yellow to brownish yellow [41].

Carbon based nanomaterials have excellent properties such as good conductivity, high stability, low cost, wide potential windows and easy surface functionalization

[42]. Carbon nanotubes (CNTs), graphene and nano/ mesoporous carbon were used for various electro-analytical applications. Their nanostructures provide efficient exposure of surface groups for the binding between analyte molecules and transduction material, leading to high detection performance for environmental pollutants [43-44].

Carbon nanotubes (CNTs) are one of the most important materials because of their unique electronic, chemical, and mechanical properties, since discovered by Sumio Iijima in 1991. CNTs are a 2D nanomaterial possessed sp2 carbon units with several nanometers in diameter and many microns in length. Many techniques for the production of single, double and multi-walled CNTs such as electrical arc discharge, laser ablation, and chemical vapour deposition method are available. These CNTs can have conductivity properties of metals or semi-conductors, depending on the diameter and degree of chirality. They have high electronic conductivity for electron transfer reactions and better electrochemical and chemical stabilities in both aqueous and non-aqueous solutions [45]. Carbon nanotubes (CNTs) [46], carbon nanofibers [47] and graphene [48] are also used as materials for the electrode to detect heavy metals. Bui *et al.* [46] demonstrated the electrochemical determination of Cd^{2+} and Pb^{2+} metal detection on pristine single-walled CNTs electrodes with a LOD of 2.2 ppb and 0.6 ppb for Cd^{2+} and Pb^{2+} respectively. These can be used as disposable electrodes for simultaneous detection of multiple heavy metals. Chen *et al.* [49] reported a thermally reduced graphene oxide field-effect transistor (FET) for detecting mercury (Hg) and its compounds. There are various advantages for CNTs and graphene such as large surface area, small size, excellent electron transfer ability and easy surface modification. Being excellent sorbents for heavy metal ions, CNTs are promising candidates for the construction of electrochemical sensors by employing electrodes modified with CNTs or graphene for heavy metal detection [50].

The composite material of MWCTs has also utilized for the adsorption of heavy metal ions from water. The MWCNTs-Fe_2O_3, MWCNTs-ZrO_2, MWCNTs-Fe_3O_4, MWCNTs-Al_2O_3 and MWCNTs-MnO_2-Fe_2O_3 nano-composite has been successfully applied for the removal of heavy metal ions of Cr^{6+}, As^{3+}, Ni^{2+} , Pb^{2+} and Cu^{2+} ions from water [51-54].

Oxidized MWCNTs have also shown exceptionally high sorption capacity and efficiency for Pb^{2+}, Cd^{2+}, and Cr^{6+} from water. The sorption efficacy of MWCNTs with acid treatment increases the potential to remove lead, chromium and cadmium ions with the oxygen functional group making the complexes of ions or precipitates of salts on surfaces [55]. Another modification reported for MWCNTs is functionallization with hydroquinoline and their application for the removal of copper, lead, cadmium and other toxic ions [56]. The carbon nanotubes alone as well as in their oxidized and composite forms have tremendous ability to absorb heavy metal ions, and many researches are in progress for their application in purification of water. Elsehly et al. Applied commercial MWCNTs for the removal of Manganese and Iron, which reach 71.5% and 52% respectively, with a concentration in aqueous solution of 50 ppm of these metal ions [57]. In another study, CNT-Based nanocomposites have been applied for the removal of iron and manganese from water [58].

Graphene is a unique two-dimensional nanostructure that allows fast electron transport. It has potential applications in the field of electrochemical sensors and biosensors [59]. It has a theoretical surface area of 2630 $m^2 g^{-1}$, which is approximately 260 times greater than graphite and twice that of carbon nanotubes. Besides, it is a semiconductor with a zero band-gap, exhibiting an ambipolar electric field effect with high charge carrier mobility (15,000-20,000 cm^2/Vs). Graphene also possesses superior mechanical and thermal characteristics. Thus, graphene increases the electrochemical catalytic activity of materials by greatly enlarging the surface area [60]. Many economical processes and high-yield production of grapheme are available such as the Hummers method rGO, electrochemical reduction, and chemical vapor deposition (CVD) [61].

Tabish et al. designed porous graphene and applied it as an adsorbent for the removal of heavy metal ions and other pollutants from water. This material applied for As^{3+} removal from water and found 80% efficiency. The material was found to retain its water treatment properties after regeneration and recycling [62]. Guo et al. designed a nanocomposite of partially reduces graphene oxide by fabrication with Fe_3O_4 via in situ co-precipitation method and applied it to the removal of Pb^{2+} ions from water. The designed nanocomposite was found to be excellent in removing the Pb^{2+} ions from aqueous solution with an adsorption capacity of 373.14 mg/g [63]. Zhang et al. functionalized the reduced graphene oxide with 4-sulpfophenylazo (rGOs) and applied it to the removal of various heavy metal ions from aqueous solution.The designed material showed maximum adsorption capacity of 689,59,66, 267 and 191 mg/g for the Pb^{2+}, Cu^{2+}, Cd^{2+} and Cr^{3+} respectively [64]. Mousavi et al. reported nanocomposites of graphene oxide with iron oxide magnetite nanoparticles Fe_3O_4 and applied them for the removal of Pb^{2+} ions from water and the material showed 98% removal efficiency with a capacity of 126.6 mg/g [65]. Considering functionalized graphene as an adsorbent to remove Pb^{2+} ions from an aqueous medium, the highest record of Pb^{2+} ion removal over graphene is 406.6 mg/g at a pH of 5.0 in 40 min [66].

Porous carbon was characterized by a high surface area, accessible surface chemistry, and short pathway for mass and electron transfer. It has attracted considerable attention in the field of electrochemical sensors. According to the International Union of Pure and Applied Chemistry (IUPA) classification, porous materials can be divided into three classifications based upon their pore sizes microporous <2 nm, 2 nm < mesoporous <50 nm, and macroporous more than 50 nm [67]. Niu et al. [68] have synthesized bismuth porous carbon nanocomposite based screen-printed electrodes (SPEs) for heavy metal detection. The nanocomposite was synthesized via a combined onestep sol-gel and pyrolysis process, followed by milling down to a specific particle size distribution for the screen printing ink. The resulting electrodes showed high sensitivity toward the detection of Pb^{2+} and Cd^{2+} ions at concentration levels below 4 ppb in tap-drinking water and wastewater systems. Veerakumar et al. [69] fabricated Pd nanoparticles (Pd NPs) dispersed on porous activated carbons (PACs) for the monitoring of toxic metal ions. The PACs are effectively employed as solid support for the dispersion of Pd nanoparticles. They have high porosities, high surface area and large pore volumes. They are suitable for applications as nanosensors for detecting multiple Cd^{2+}, Pb^{2+}, Cu^{2+}, and Hg^{2+} metal ions with nanomolar detection limits.

The nanostructures electrochemical sensors and biosensors based on polymeric and biomaterials showed high performance with rapid response and selectivity is attributed to their radiant, electrical, catalytic, mechanical, thermal and physical properties [70] based on structural and functional complexity of polymeric and biomaterials, it is difficult to determine the desired sensing properties. Using polymeric and bio-nanomaterials, the fabrication of electrochemical sensors can be achieved through the combination of novel analytical and scientific methods, including that of combinatorial and high-throughput materials screening with micro- and nanofabrication and microfluidics [71].

Porous materials, such as metal-organic frameworks (MOFs), have also been investigated for heavy metal ions detection. MOFs are crystalline porous (or potentially porous) materials consisting of metal ion or metal clusters (as nodes) and multidentate organic ligands. The porous nature of MOFs and their ability to be designed and modified with appropriate ligands or metal ions has led to intense research on subjects such as storage, separation, and gas catalysis. A wide range of available metal ions and bridging ligands allows for the introduction of properties such as luminescence and magnetism to MOFs. Additionally, bridging ligands can easily be synthetically modified to decorate the pores with various functional groups, making them highly selective to specific guests. Thus, luminescent MOFs have emerged as a new class of materials showing great promise for sensing applications [72-73] in the recent survey of MOFs as luminescent sensor for heavy metal ions. The scaffold of the aluminum-based MOF-253 was used to sense Hg^{2+} ions [74]. A honeycomb-type luminescent MOF was synthesized from terbium with a synthetically modified amino-terephthalate ligand with a side group suitable for binding metal ions. This MOF selectively responds to Fe^{3+} and Al^{3+} ions through different detection mechanisms [75].

6. CONCLUSION AND FUTURE PROSPECTIVE

Nanomaterials have been extensively exploited to sensing heavy metals in environmental pollutants owing to their exceptional properties. In this work, various nano-materials, including carbon-based nanomaterials, zero-valent metal nanomaterials, metal oxide materials, and nanocomposites were discussed. The development in nanomaterial science and custom engineering of recognition components will further extend the area of practical and consistent sensing techniques for hazardous heavy metal ions. In the future, it may be crucial to develop enhanced nanomaterials and to perform detailed investigations about their sensing properties. Therefore, it is anticipated that intense research efforts will be directed toward nanomaterials and their composites with emphasis on their practical applications in this field.

Conflict of Interest

There are no conflicts of interest

7. REFERENCES

1. Buledi JA, Amin S, Haider SI et al. *Environ Sci Pollut Res*, 2020; 1-9.
2. Lin W-C, Li Z et al. *Anal Chem,* 2017; **89(17):**8748-8756.

3. Poornima V, Alexandar V, et al. *RSC Adv,* 2016; **6(52)**:46711-46722.
4. Hoang CV, Oyama M, Saito O, Aono M, Nagao T. *Sci Rep,* 2013; b: 1175.
5. Kaur B, Srivastava R, Biswarup S. *New J Chem*, 2015; **39(7)**:5137-5149.
6. De Acha N, Elosúa C, Corres JM, Arregui FJ. *Sensors,* 2019; **19(3)**:599.
7. Borah SB, Bora T, Sunandan B, Joydeep D. *Ground-water Sustain Dev,* 2015; **1(1-2)**:1-11.
8. Masindi V, Muedi KL, *InTech,* 2018.
9. Jessica B, Emmanuel S, Renald B. *Heliyon,* 2020; **6(9)**:e04691.
10. Tchounwou PB, Yedjou CG, Patlolla AK, Sutton DJ. *Clinical and Environmental Toxicity. In EXS* 2012; **101**:133-164.
11. Shallari S, Schwarts C, Hasko A, Morel JL. *Sci Total Environ,* 1998; **209**:133-142.
12. Herawati N, Suzuki S, Hayashi K, Rivai IF, Koyama H. Bull. *Environ Contam Toxicol*, 2000; **64**:33-39.
13. He ZL, Yang XE, Stoffella PJ. *J Trace Elem. Med Biol,* 2005; **19**:125-140.
14. Gautam PK, Gautam RK. Chattopadhyaya MC, Banerjee S, Pandey JD. *Heavy metals*, 2016; 1-27.
15. Walker CH, Sibly RM, Hopkin SP, DBP. Group,T. and F., Ed.; 4th Edition, CRC Press;2012.
16. Aronsson P, Perttu K. *For Chron*, 2001; **77**:293-299.
17. Jackson AP, Alloway BJ. *Air. Soil Pollut*, 1991; **57**:873-881.
18. Muchuweti M, Birkett JW, Chinyanga E, Zvauya R, Scrimshaw MD, Lester JN. *Agric Ecosyst Environ*, 2006; **112**:41-48.
19. Gupta N, Khan DK, Santra SC. *Environ Monit Assess*, 2012; **184**:6673-6682.
20. Carrondo MJT, Lester JN, Perry R, Stoveland S. *Anal Chem Act A,* 1979; **106**:309-317.
21. Marcello Di B. *Environmental Geochemistry*, 2008; 251-286.
22. Gan X R, Lee LYS, Wong KY, Lo TW, Ho KH, Lei DY, Zhao HM. ACS *Appl Energy Mater*, 2018; **1(9)**:4754-4765.
23. Sun YF, Gao S, Lei FC, Xie Y. *Chem Soc Rev*, 2015; **44(3)**:623-636.
24. Hu ZH, Wu ZT, Han C, He J, Ni ZH, Chen W. *Chem Soc Rev,* 2018; **47(9)**:3100-3128.
25. Kiriya D, Tosun M, Zhao PD, Kang JS, Javey A. *J Am Chem Soc,* 2014; **136(22)**:7853-7856.
26. Wang QH, Kalantar-Zadeh K, Kis A, Coleman JN, Strano MS. *Nat Nanotechnol*, 2012; **7(11)**:699-712.
27. Gan XR, Zhao HM, Quan X. *Biosens Bioelectron,* 2017; **89**:56-71.
28. Zhou ZX, Shang QW, Shen YF, Zhang LQ, Zhang YY, Lv YQ, et al. *Anal Chem*, 2016; **88(11)**:6004-6010.
29. Gan XR, Zhao HM, Wong KY, Lei DY, Zhang YB, Quan X. *Talanta,* 2018; **182**:38-48.
30. Lin Z, Carvalho BR, Kahn E, Lv RT, Rao R, Terrones H, et al. *2D Materials,* 2016; **3**:022002
31. Franke ME, Koplin TJ, Simon U. *Small,* 2006; **2**:36.
32. Wang Y, Tong MM, Zhang D, Gao Z. *Sensors*, 2011; **11(1)**:19 -31.
33. Azharuddin M, Zhu GH, Das D, Ozgur E, Uzun L, Turner APF, et al. *Chem Com*, 2019; **55**:6964-6996.
34. Dai X, Compton RG. *Electroanalysis*, 2005; **17**:1325-1330.
35. Lee GJ, Kim CK, Lee MK, Rhee CK. *Electroanalysis,* 2010; **22**:530-535.
36. Bhattacharjee Y, Chatterjee D, Chakraborty A. *Sens. Actuators B Chem,* 2018; **255**:210-216.
37. Chen L, Fu X, Lu W, Chen L. *ACS Appl Mater Interfaces*, 2013; **5(2)**:284-290.
38. Yoon SJ, Nam YS, Lee HJ, Lee Y, Lee KB. *Sens. Actuators B Chem,* 2019; **300**: 127045.
39. Ghodake GS, Shinde SK, Saratale RG, Kadam AA. *Beilstein J. Nanotechnol,* 2018; **9**:1414-1422.
40. Tashkhourian J, Sheydaei O. *Anal Bioanal Chem Res*, 2017; **4**:249-260.
41. Narayan KB, Han SS, *Res Chem Intermed,* 2017; **43**:5665-5674.
42. Pan Z, Sun F. *Adv Eng Res*, 2018; **164**:34.
43. Zhang W, Luque R, Han S, Hu L, Xu G*, Chem. Soc. Rev*, 2016; **45**:715-752.
44. Ramnani P, Mulchandani A. *Chemosphere*, 2016; **143**: 85-98.
45. Brett CMA. *Pure Appl Chem*, 2001; **73(12)**:1969-1977.
46. Bui MPN, Li CA, Han KN, Pham XH, Seong GH. *Anal. Sci*, 2012; **28**:699-704.
47. Wanekaya AK. *Analyst,* 2011; **136**:4383-4391.
48. Shao Y, Wang J, Wu H, Liu J, Aksay IA, Lin Y. *Electroanalysis,* 2010; **22**:1027-1036.
49. Chen K, Lu G, Chang J, Mao S, Yu K, Cui S, Chen J. *Anal. Chem,* 2012; **84(9)**: 4057-4062.
50. Song W, Zhang L, Shi L, Li DW, Li Y, Long YT. *Microchim Acta*, 2010; **169**:321-326.
51. Shitong Y, Jiaxing Li, Dadong S, Jun Hu, Xiangke W. *J Hazard Mater*, 2009; **166(1)**:109-116.

52. Ntim SA, Mitra S. *J Colloid Interface Sci*, 2012; **375 (1)**:154-159.
53. Tang WW, Zeng GM, Gong JL, Liu Y, Wang XY, Liu YY, et al. *Chem Eng J,* 2012; **211-212**:470-478.
54. Luo C, Tian Z, Yang B, Zhang L, Yan S. *Chem Eng J.* 2013; **234**:256-265.
55. Moosa AA, Ridha AM, Abdullha IN**.** *Int J Innovative Res Sci Eng Technol,* 2015; 275-282.
56. Bullo S, Alina C, Arundhati M, Bullo N, Sharida F, Sanjib B, and Mohd Z H. *Molecules,* 2017; **22(10)**:1560-1571.
57. Elsehly EMI, Chechenin NG, Bukunov KA, Makunin AV, Priselkova AB, Vorobyeva EA, et al. *Water Supply*, 2016; **16(2)**:347-353.
58. Rahman MM, Sime SA, Hossain MA et al. *Arab J Sci Eng*, 2017; **42**:261-269.
59. Rao CNR, Sood AK, Subrahmanyam KS, Govindaraj A. *Angew Chem,* 2009; **48**:7752.
60. Chen XM, Wu GH, Jiang YQ, Wang YRC. *Analyst,* 2011; **136**:4631.
61. Low CTJ, Walsh FC, Chakrabarti MH, Hashim MA, Hussain MA, *Carbon*, 2013; **54**:1-21.
62. Tabish TA, Memon FA, Gomez DE et al. *Sci Rep,* 2018; **8**:1817.
63. Guo T et al. *Adsorption Sci Technol*, 2018; 1031-1048.
64. Zhang CZh, Chen B, Yuan B, Jing X. *Sep Sci Technol*, 2018; **53(18)**:2896-2905.
65. Seyyed MM, Seyyed AH, Ali MA, Hossein E, Younes G, Aziz B, Fatemeh M, Omid A. *Phys Chem Res*, 2018; **6(4)**:759-771.
66. Thakur S, Penny PG, Messai AM, Sigitas T, Yogendra Kumar M, Thakur V. *Vacuum,* 2017; **146**:342-355.
67. Lee J, Kim J, Hyeon T. *Adv Mater*, 2006; **18**:2073.
68. Niu P, Gich M, César FS, Navarro-Hernandez C, Fanjul-Bolado P, Roig A. *Microchim Acta*, 2016; **183**:617-623.
69. Veerakumar P, Veeramani V, Chen SM, Madhu R, Liu SB, *ACS Appl Mater Interfaces*, 2016; **8(2)**:1319-1326.
70. Yang J, Dou B, Yuan R, Xiang Y. *Anal Chem*, 2016; **88**:8218-8223.
71. Wang Z, Zhu W, Qiu Y, Yi X, Von dem Bussche A, Kane A, et al. *Chem Soc Rev*, 2016; **45**:1750-1780.
72. Hu Z, Deibert BJ, Li J. *Chem Soc Rev*, 2014; **43**:5815-5840.
73. Kumar P, Deep A, Kim KH. *Anal. Chem*, 2015; **73**:39-53.
74. Xu XY, Yan B. *J. Mater. Chem. C,* 2016; **4**:1543-1549.
75. Cao LH, Shi F, Zhang WM, Zang SQ, Mak TC. *Chem A: Eur J*, 2015**; 21(44)**:15705-15712.