

Recent Advanced Techniques for the detection of Heavy metal ions in Water

*Priyanka Gupta¹, Gaurav Tamrakar²

¹Department of Chemistry, Kalinga University, Naya Raipur, Chhattisgarh, India

²Department of Mechanical Engineering, Kalinga University, Naya Raipur, Chhattisgarh, India

priyanka.gupta@kalingauniversity.ac.in, gaurav.tamrakar@kalingauniversity.ac.in

Abstract

The availability of drinkable water, which is a basic requirement for healthy life, has grown more challenging over time as a result of moderate to severe human activity and, to a lesser degree, environmental factors. Polluted water contributes to the continual universal loss in the presence of abundant potable water in contrast to becoming one of the major world causes of disease, infections, and fatality. In numerous nations all around the world, research have been conducted to monitor and investigate why environmental variables impact the concentrations of metalloids and the physical and chemical properties of watercourses. Toxic elements metals including copper, zinc, nickel, lead, cadmium, and mercury have a negative impact on the ecosystem. We shall now assess the cutting-edge tools currently present for such measurement of hazardous metals in water because metal ions are perhaps the most harmful and widespread pollutants. The much more popular methodological approaches include very, liquid chromatography, inductively-coupled plasma-mass spectrometry, gas chromatography, and atomic absorption spectroscopy (ICP-MS). Additionally, a thorough discussion of sustainable materials and approaches for determination of heavy metals from natural waters is presented.

Keywords: Water resources, Heavy metals, Detection Techniques

1.Introduction

A healthy life, commonly referred to as the basic needs of humans, depends on having having availability to freshwater resources [26][4]. Water is regarded as a crucial element in the ecosystem. In addition to urbanisation and industrial expansion since the 1990s, poisoning of all water bodies has played a significant influence in the world's population growth rates. In the past year, environmental experts have increasingly focused on heavy metals (HM) contamination of water [33][26]. Since about 85% of Indians depend on groundwater for drinking, groundwater quality is a significant problem that must be solved separately. Without conducting an appropriate risk assessment, groundwater in India was thought to be largely safe and frequently used for drinking. Arsenic, mercury, and cadmium are just a few examples of the heavy metals and metalloids that are widely dispersed in the environment, including drinking water sources, and which pose a major health issue to people by seriously harming the liver, kidneys, digestive systems, and nervous systems. Such dangerous metals are categorised as toxicants because they have a propensity to accumulate in nature and endanger both human health and environment. [13][45]

2.Major Contaminant of Water

The term "toxic" refers to freshwater that has been altered by undesirable substances as a consequence of anthropogenic activity[17]. This can be caused by a variety of things, including toxins, gravel, microbes, pathogens, medications, fertilisers, and petroleum. Although it is undetectable, groundwater pollution differs to surface water pollution in that resource conservation is difficult with existing technologies. Most freshwater pollutants often have no flavour and no pigment. The impacts of polluted waters on public health are also lengthy and challenging to detect[8].

Based on a research conducted in China, the quantity of F found in well water in 2000 was 21.5 mg L⁻¹, but it is currently just 0.01 - 6.30 milligrammes per liters in a number of Tianjin regions[55][56]. Elevated levels of F have also been reported in certain locations in Nigeria, Kenya, and Japan[37][20][13]. In some rural areas of Iran, F levels (0.17 to 2.2 mg/L) were greater above the WHO limit (0.5 mg/L)[38]. Hexavalent Cr is present in about 40percent of total of California's freshwater resources. In China close to Jin Zhou city, stomach and lung cancer cases have been reported as a result of drinking water exposure to hazardous Cr(VI). In China, adjacent to Jin Zhou city, gastrointestinal and pulmonary cancer cases have been reported as a result of groundwater exposure to hazardous Cr(VI).

3.Status of Water in India

India's farming and drinkable water safety are completely reliant on aquifers. Water table is used for over 62percent of agriculture, 85percent of total of water resource,of rural areas and 50percent of urban freshwater supply. Because of the high amount of Arsenic in the water, West Bengal is one of the worst-affected states in India. Nine of the state's 19 districts have a significant illness[50][

4. Types of Water Pollutants

4.1 Organic Pollutants

Carbon-based organic pollutants, such those produced by plants and animals, are found in water and contaminate it. From trees to tiny insects, all living things are biological. Organic substances include things like the food we consume, petroleum products, and material that is alive or has historically been alive. A specific test has been developed by experts in water quality to quantify the amount of organic material in the water sample. Agricultural waste, urban wastewater, industrial wastewater, and sewage are all sources of organic compounds[14].

4.2 Inorganic Pollutants

For developing countries, the contamination of drinking water with harmful compounds including nitrogenous compounds, and toxic metals is a concern. The high quantities of nitrogen - rich pollutants and salts of phosphorus in ground water caused by the drainage of agricultural areas, release of municipal/industrial sewage, etc. are responsible for a number of health issues[41].

4.3 Thermal Pollution

The term "thermal water pollution" refers to changes in a temperature of water bodies. It contributes in contamination of water as well. It is the alteration of water's physical characteristics. A few occurrences happen spontaneously, but the majority are caused by human activity. The biggest thermal contaminants of freshwater include power stations, nuclear weapons and hydroelectric dams, greenhouses, and rising temperatures. The discharge from thermal power plants raises the temperature of the aquatic system by 10 °C. Aquatic life is so seriously impacted by the thermal effects of global warming[39].

5. Heavy Metal Causing Water Pollution

5.1 Arsenic

Due to the mobilisation of As in groundwater and aquifers, the contamination of As can spread improperly into the water bodies. Consequently, its residues may have an impact on a huge number of people[44]. Due to its high toxicity and wide distribution groundwater, arsenic (As) poses a health risk. Humans who are exposed to high quantities of As may experience a range of health issues, including genetic damage, anaemia, and other issues[9].

Investigations have also revealed problems with the nasal passages, cardiovascular and neurological diseases, consequences of diabetes, skin diseases, and aberrant babies as a consequence of consuming As-contaminated water[8][5]. In West Bengal, India, freshwater poisoning with arsenic was first discovered in 1980. In 79 blocks spread across 8 districts in West Bengal, the allowed limit for arsenic is 0.05 mg/l. Besides from Bengal, the states of Assamese, Chhattisgarh, Bihar, Jharkhand, Karnataka and UP have all been confirmed to have As poisoning in their water supply. In arsenic-contaminated aquifer, arsenic acid (H₃AsO₄), arsenous acid (H₃AsO₃), and its compounds are frequently found.

5.2 Iron

In topsoil and sediments, iron is primarily found as insoluble oxide of Iron and iron sulphide. When ferrous carbonate and water Carbon dioxide interact, Fe^{2+} solutions are released. The second most prevalent element in the layers of the earth is iron[19]. The biggest issue with water that contains Fe is the brown appearance of groundwater after it has been extracted from aquifers. The decomposition of organic matter produced a reducing environment that caused the water's colour to change to cloudy, then brown. The solubility of minerals containing Fe increases in lowering circumstances It promotes a rise in the concentration of iron.

Excessive Iron concentrations in the freshwater are the source of the unpleasant taste, discoloration, sedimentation, and equipment problems in the water system.. Red rot disease may be brought on by high Fe concentrations in water. Bacterial precipitation of ferric ion hydrate oxide is the root cause of red rot disease. When pumped, iron-containing water appears clear, but when it is exposed to the air, the iron precipitates out and causes turbidity in the water[22].

5.3 Copper

Copper is a crucial trace element that contributes in the metabolism of people, animals, and plants. It's likely that aquifer resources including feldspar, biotite, and muscovite minerals enrich water naturally with copper (Cu). Copper contamination in drinking water can occasionally be primarily caused by copper pipe corrosion. Farming pesticide sprays frequently contain organic and inorganic copper compounds. Wilson's illness may be triggered by a high Zn intake. A high Cu content increases the risk of human lung cancer while also causing pipe and equipment corrosion and discoloration.

5.4 Lead (Pb)

The major source of lead in the environment is industry, specifically lead storage batteries, metal plating, construction materials, ceramics and colourants, paints, glassware, and petroleum oil[23]. Lead is a teratogen which is not biocompatible and may be contributing to increasing Pb levels of contamination through sorption process of Pb on bottom sediments, soot transmission through the surrounding air, subsequent cementation of mineral of continental shells, rainfall, and accumulation of Pb-containing aerosolized aerosol particles. If ingested out over long period of time, low amounts that are stored and accumulated in vertebrae may be harmful to people[32].

5.5. Nickel

Since it is unclear why nickel might be present in potable water, its abundance has not been sufficiently recorded. Thus according multiple past studies[1][12][34], Potable water tests obtained from different sources have revealed Ni pollution. Although plumbing materials are the primary contributor of nickel in freshwater resources, minerals that possess nickel may cause it to leak into groundwater[51][16]. The discharge of nickel into potable water is anticipated to rise over period as metal usage increases. Ni intake can result in a several of

health complications, such as skin irritation, cardiovascular illness, liver toxicity, and lung infections[28][16][12][42].

5.6. Manganese

While a high Mn content in drinking water may not have much of an impact on adults, it has a major impact on embryos and newborns. In water with CO₂, manganese dioxide is extremely insoluble. Mn and Fe have a positive correlation, and It is an element that the both animals and vegetation require. The Manganese in freshwater is released by ferromagnesium minerals. A excessive Manganese quantity affects organisms centralnervous system. In acidic groundwater under lowering conditions, higher manganese concentrations typically occur[30].

5.7 Chromium

Chromium (Cr), a found in nature element which is extensively used in industrial operations, is among the most toxic and hazardous metals. The two primary forms in which it can be liberated from environmental Chromium sources, mainly from the earth crust are and hexavalent chromium [Cr(VI)] and trivalent chromium [Cr(III)] . The Cr(VI) version is heighly toxic, transportable, and soluble than that of the type trivalent chromium resulting in more damaging effect on both humans and animals[35]. Manufacturers generate a large amount of sewage, which contains solid sediment and Cr-containing waste. For example, tanneries are a significant global generator of Cr pollution[53]. Cr contamination of groundwater and surface aquifers may occur often due to both biological and man-made factors[49]. Water contamination might result through industrial machinery polishing, inappropriate residual mining material handling, or Cr(IV) leaks from chromite mines. Chromium has the ability to undergo number of changes in the water habitats through the mechanisms of adsorption, desorption, redox, solubility, and precipitation[46][24].

6. Analytical Technique for Detection of heavy metal ions in water

Monitoring the level of water contamination is essential to preventing health problems. While there are many different methods for doing this, a quicker method of analysing the water's quality is needed for regular pollution level control.

6.1 Atmoic Absorption Spectroscopy(AAS)

Analysing heavy metals has traditionally been done using AAS. AAS uses a variety of methods to determine the atomic composition by assessing the gaseous state's unbound atoms' ability to absorb specific electromagnetic wavelengths[3][31][55] .Based on the intensity of the absorption, the identified components' concentration levels in the sample can be calculated.[3][56].AAS is able to identify more than 70 elements in samples in a variety of physical states, including solid or solution phases.

6.2. ICP-MS

ICP-MS is an Atomic Emission Spectroscopic method that atomizes material using plasma. Positive ions and an enormous number of electrons in plasma neutralise and cancel out

molecules. The energised and ionised gases that make up plasmas are created in inert gases like argon. They contribute with atom dissociation, ionisation, and excitation to produce atomic and ionic emission.

ICP offers lower detection limits than AAS, but it also requires a highly experienced operator. The main flaw in all atomic spectroscopy techniques is that they give no information on the element's oxidation state or speciation. This approach, like AAS, also needs a highly competent operator and extensive sample preparation.

6.3. High Performance Liquid Chromatography

In this technique, a specimen is moved all over a chromatographic section by a mobile liquid solution. A specimen is a liquid or solid that has been mixed in a specific solvent. Isolation is governed by interactions between both the liquid and stationary phase.

Usually, a one movable phase formulation that really is effective for all substances is difficult to locate. It only remains single choice: use a gradient component. The basic chemical composition of the solvent system is slightly polar and allows separation of the reverse phase. Through all these separations, the migratory phase's makeup is even less polar as the separation advances. Identical to Gas Chromatography, a variety of sensors, including spectroscopic sensors electrochemical finders, and continuing mass spectrometry improvements, have been created for observing HPLC separation. Due to this, interest in is expanding LC-MS. These hplc techniques are frequently used to examine different compounds. Liquid chromatography techniques are extremely sensitive and successful, especially when combined with Mass Spectroscopy, but they also require costly, sophisticated instruments and expert operators[18].

6.4. Gas Chromatography

Gas chromatography is a widely adopted technique in chemical analysis for the separation and investigation of compounds that may vaporize without disintegrating (GC). The homogeneity of a material or the separation of the distinct components in a mixture are routinely determined by GC[18]. To extract pure compounds within a mixture, preparative chromatography can be used[28].

Gas chromatography is a technique used to isolate substances in mixtures by introducing either liquid or gaseous specimens into a moveable phase, sometimes referred to as the gaseous state, and then passing the gas through a solid matrix. Most frequently, a non-reactive gas such as He, Ar, N₂, or H₂ makes up the mobile phase.

7. Metal Nanoparticle

For the spectrometric determination of metals, new nanostructured materials (NPs) of gold, platinum and silver are widely used[52]. One can modify the optical characteristics of metallic. By altering particle dimension, shape, molecular make-up, and distribution, nanostructures can be formed. These are useful because they make it easier to create spectrophotometric sensor devices that operate in the relevant spectral region. This has been proven that ag nano - particles treated with 11-mercaptoundecanoic acid (MUA) are capable of detecting Pb(II) ions spectrophotometrically. The detection limits for this method was 2.07

ppm, which was a lot higher than the values that the WHO allowed. It employed a camera to capture the photographs, but there was no visual programme to analyse them. For quick and accurate strip-based immunosensing of Pb(II) ions in potable water, such constraints were conquered by utilising anti-Pb(II)-ITCBE monoclonal antibody on twin non-uniformly scaled Gold Nanoparticle probes[11].

8.Organic Ligands

To monitor toxic metals in groundwater, natural linkers/ligands attach to particular toxic elements using heteroatoms (Carbon, Nitrogen, Hydrogen, Oxygen, and Sulphur) in their framework to form a stable complex[21]. One can determine Nickel(II), Copper(II), and Chromium (VI) using metal-selective chromogenic linkers such as bathocuproine, 1, 5-diphenylcarbazide (DPC)[52].

9.Carbonaceous Quantum Dots

Due to their easy preparation, low experimental expenses, user- as well as eco-friendly character, and coupling of carbon quantum dots (Carbon dots) as a detecting component for spectrophotometric identification of toxic elements, this sector primarily focuses on this topic. Metal recognition has been investigated using CQD-based spectrophotometric sensing depending on ratiometric methods. Elevated nano crystalline carbon quantum dots and (NCQDs) are synthesised using watersoluble chitosan, a biocompatible precursor, as dual-mode Hg(II) ion sensing probes. A ratiometric paper strip consisting of red p-phenylenediamine-functionalized CQDs (r-CQDs) and was also used for the colorimetric detection of Copper(II) ions[10].

10.Conclusion

Since heavy metal water pollution has dramatically increased over the previous few decades, it is especially concerning. Therefore, it is essential to create strategies, regulations, technologies, and materials to address this issue without having any negative consequences on the environment or human health. Fast, inexpensive, and reliable procedures that are appropriate for spot and in situ measurement of heavy metal ions must be researched and developed. This would enable us to comprehend and assess the seriousness of the contamination from heavy metals pollution issues in various ecosystems. This study examined the treatment methods that can effectively remove heavy metals from water. In-depth explanations were given regarding the treatment method's capacity to absorb both single- and multi-component heavy metals. It also highlighted the benefits, drawbacks, and restrictions of various therapeutic modalities to determine the reliable way for heavy metal removal. The results of this research should enable the advancement of current water treatment techniques and the development of cost-effective, safe, cutting-edge, environmentally friendly, and efficient technologies that make use of residues, advanced materials, and natural resources.

Reference

1. N.Abeera, S. A.Khana, S.Muhammad, A.Rasool, and I.Ahmadd, "Health risk assessment and provenance of arsenic and heavy metal in drinking water in Islamabad, Pakistan." *Environ Technol Innov* (2020), 20:101171. <https://doi.org/10.1016/j.eti.2020.101171>
2. M.T.Alarcón-Herrera, D.A.Martin-Alarcon, M.Gutiérrez, L.Reynoso-Cuevas, A.Martín-Domínguez, M.A.Olmos-Márqueze, and J.Bundschuh, "Co-occurrence, possible origin, and health-risk assessment of arsenic and fluoride in drinking water sources in Mexico: geographical data visualization." *Sci Total Environ*, (2020)698:134–168
3. A.Baysal, N. Ozbek, and S. Akman, "Determination of trace metals in waste water and their removal processes. " *Waste water-treatment technologies and recent analytical developments*, (2013) pp 145–171
4. E. Bazrafshan, F. K. Mostafapour, M. Esmaelnejad, G. Reza Ebrahimzadeh and A. H. Mahvi, "Concentration of heavy metals in surface water and sediments of Chah Nimeh water reservoir in Sistan and Baluchestan province, Iran." *Desalination and Water Treatment*, (2015), Volume 57, <https://doi.org/10.1080/19443994.2015.1027958>
5. S. Bhowmick, S. Pramanik, P. Singh, P. Mondal, D. Chatterjee and J. Nriagu, "Arsenic in groundwater of West Bengal, India: a review of human health risks and assessment of possible intervention options." *Sci Total Environ* (2018), 612:148–169
6. K.K. Borah, B. Bhuyan, and H.P. Sarma (2010) "Lead, arsenic, fluoride, and iron contamination of drinking water in the tea garden belt of Darrang district, Assam, India." *Environ Monit Assess*, (2010), 169(1-4), 347–352
7. D. Chakraborti, M. M. Rahman, B. Das, A. Chatterjee, D. Das, B. Nayak, A. Pal, U. K. Chowdhury, S. Ahmed, B. K. Biswas, M. K. Sengupta, Md. A. Hossain, G. Samanta, M. M. Roy, R. N. Dutta, K. C. Saha, S.C. Mukherjee, S. Pati, P. B. Kar, A. Mukherjee and M. Kumar, "Hydrogeology Journal, (2017), volume 25, pages 1165–1181
8. D.Chakraborti, M.M.Rahman, A.Mukherjee, A.Manzurul, M.Hassan, R.N.Dutta, S.Pati, S.C.Mukherjee, S.Roy, Q.Quamruzzman, M.Rahman, S.Morshed, T.Islam, S.Sorif, Md.Selim, Md. R.Islam, Md. M. Hossain, "Groundwater arsenic contamination in Bangladesh—21 years of research." *J Trace Elem Med Biol* (2015) 31:237–248
9. D. Chatterjee, S. Adak, N. Banerjee, A.K. K.Bandyopadhyay and A. K.Giri, "Evaluation of health effects, genetic damage and telomere length in children exposed to arsenic in West Bengal, India." *Mutation Res Genet Toxicol Environ Mutagen* (2018)836:82–88
10. C. Liu, D. Ning, C. Zhang, Z. Liu, R. Zhang, J. Zhao, T. Zhao, B. Liu, Z. Zhang, *ACS applied materials & interfaces* 9 (2017) 18897
11. C. Fan, S. He, G. Liu, L. Wang, S. Song, "A Portable and Power-Free Microfluidic Device for Rapid and Sensitive Lead (Pb²⁺) Detection, *Sensors*, 12 (2012) 9467
12. W. Dong, Y Zhang, X Quan, "Health risk assessment of heavy metals and pesticides: a case study in the main drinking water source in Dalian, China." *Chemosphere*, (2020), 242:125113. <https://doi.org/10.1016/j.chemosphere.2019.125113>
13. S.Dwivedi, S. Mishra and R.D. Tripathi, "Ganga water pollution: A potential health threat to inhabitants of Ganga basin." *Environment International*, 117(May), (2017), 327–338. <https://doi.org/10.1016/j.envint.2018.05.015>

14. A.K.Ekevwe, A. Isaaci, G. Baertholomew, and O. Aroh, "Review of organic pollutants in wastewater along the Course of River Gwagwarwa and River Rafin Malam in Kano State-Nigeria. *Journal of Biotechnology and Bioengineering*, (2018), 2, 36–39
15. C.P.G. Emenike, I.T. Tenebe and P. Jarvis, "Fluoride contamination in groundwater sources in Southwestern Nigeria: assessment using multivariate statistical approach and human health risk." *Ecotoxicol Environ Saf*, (2018), 156:391–402
16. G. Genchi, A. Carocci, G. Lauria, M.S. Sinicropi and A. Catalano, "Nickel: human health and environmental toxicology. *Int J Environ Res Public Health*, (2020) 17. <https://doi.org/10.3390/ijerph17030679>
17. Government of Canada (2017) Groundwater contamination. <https://www.canada.ca/en/environment-climate-change/services/water-overview/pollution-causes-effects/groundwater-contamination.html>. Accessed 17 Oct 2020
18. D. Harvey, *Modern analytical chemistry*. New York: (2000) McGraw-Hill Higher Education
19. D. Hossain, M.S. Islam, N. Sultana and T. Tusher, "Assessment of iron contamination in groundwater at Tangail municipality, Bangladesh. " *J Environ Sci Nat Resour*, (2013), 6(1):117–121
20. S. Hossain, T. Hosono, H. Yang and J. Shimada, "Geochemical processes controlling fluoride enrichment in groundwater at the western part of Kumamoto area, Japan., (2016), *Water Air Soil Pollut* 227(10):385
21. H. Wang, Y.-j. Li, J.-f. Wei, J.-r. Xu, Y.-h. Wang, G.-x. Zheng, *Analytical and bioanalytical chemistry* 406 (2014) 2799
22. C.K. Jain, A. Bandyopadhyay, and A. Bhadra, "Assessment of ground water quality for drinking purpose, District Nainital, Uttarakhand, India." *Environmental Monitoring and Assessment*, (2010), 166(1–4), 663–676
23. M. Jaishankar, T. Tseten, N. Anbalagan, B.B. Mathew, and K.N. Beeregowda, "Toxicity, mechanism and health effects of some heavy metals. *Interdisciplinary Toxicology*," (2014) 7(2), 60–72
24. B. Jiang, Q. Niu, C. Li, N. Oturan and M.A. Oturan, "Outstanding performance of electro-Fenton process for efficient decontamination of Cr (III) complexes via alkaline precipitation with no accumulation of Cr (VI): important roles of iron species. *Appl. Catal., B Env.*, (2020), 272, 119002
25. L. Kaur, M.S. Rishi and A.U. Siddiqui (2020) Deterministic and probabilistic health risk assessment techniques to evaluate non-carcinogenic human health risk (NHHR) due to fluoride and nitrate in groundwater of Panipat, Haryana, India. *Environ Pollut*, (2020), 259:11371
26. K. Khan, Y. Lu, H. Khan, S. Zakir, S. Khan, A.A. Khan, L. Wei and T. Wang, "Health risks associated with heavy metals in the drinking water of Swat, northern Pakistan." *Journal of Environmental Sciences*, (2013) 25(10): p. 2003-2013.
27. S. Khan, M. Shahnaz, N. Jehan and S. Rehman, "Drinking water quality and human health risk in Charsadda district, Pakistan." *Journal of Cleaner Production*, (2013). 60: p. 93-101
28. C. Lidén, "Nickel allergy following EU regulation - more action is needed". *Br J Dermatol*, (2013), 169:733. <https://doi.org/10.1111/bjd.1253>
29. L. Wang, B. Li, F. Xu, X. Shi, D. Feng, D. Wei, Y. Li, Y. Feng, Y. Wang, D. Jia, *Biosensors and Bioelectronics* 79 (2016)

30. P.B.McMahon, K.Belitz, J.E. Reddy and T.D.Johnson, "Elevated manganese concentrations in United States groundwater, role of land surface–soil–aquifer connections." *Environ Sci Technol* (2018),53(1):29–38
31. B.Michalke and V. Nischwitz, "Liquid Chromatography: Speciation and Element-Specific Detection " Elsevier Inc., New York (2013)
32. N. C. Mondal, V. S. Singh, S. C. Puranik & V. P. Singh, " Trace element concentration in groundwater of Pesarlanka Island, Krishna Delta, India." *Environmental Monitoring and Assessment*,(2010), 163(1–4), 215–227
33. S. Muhammad, M.T. Shah, and S. Khan, " Health risk assessment of heavy metals and their source apportionment in drinking water of Kohistan region, northern Pakistan." *Microchemical Journal*, 2011. 98(2): p. 334-343
34. L.Nakaona, K.K. Maseka, E.M.Hamilton and M.J. Watts, "Using human hair and nails as biomarkers to assess exposure of potentially harmful elements to populations living near mine waste dumps." *Environ Geochem Health*,(2020) 42:1197–1209. <https://doi.org/10.1007/s10653-019-00376>
35. E.Nakkeeran, C. Patra, T. Shahnaz, S. Rangabhashiyam, and N.Selvaraju, "Continuous biosorption assessment for the removal of hexavalent chromium from aqueous solutions using *Strychnos nux vomica* fruit shell. *Bioresour. Technol. Rep.*(2018), 3, 256–260
36. M.F.Naujokas, B. Anderson, H. Ahsan, H.V. Aposhian, J.H.Graziano, C. Thompson and W.A. Suk, " The broad scope of health effects from chronic arsenic exposure: update on a worldwide. public health problem." *Environ Health Perspect.*,(2013) 121(3):295–302. <https://doi.org/10.1289/ehp.1205875>
37. L.A.Olaka, F.D. Wilke, D.O. Olago, E.O. Odada, A. Mulch, and A. Musolf, " Groundwater fluoride enrichment in an active rift setting: central Kenya Rift case study." *Sci Total Environ.*,(2016), 545:641–653
38. M.Qasemi, M. Afsharnia, A. Zarei, M. Farhang M. and Allahdadi, "2019) Non-carcinogenic risk assessment to human health due to intake of fluoride in the groundwater in rural areas of Gonabad and Bajestan, Iran: a case study." *Hum Ecol Risk Assess. Int. J.*(2019), 25(5):1222–1233
39. D.S.Rao, " Thermal pollution—Impact on living organisms. *International Journal of Engineering Research and Sports Science*, 2,(2015)
40. A.Rashid, A.Farooqi, X. Gao, S. Zahir, S. Noor and J.A.Khattak, "Geochemical modeling, source apportionment, health risk exposure and control of higher fluoride in groundwater of sub-district Dargai, Pakistan." *Chemosphere*, (2020),243:125409
41. V.C. Rekha Kathal, L Kumar, A Puri, R BaishyaR, & P.L.Uniyal, " Pollution Status of Yamuna River, India—A national concern." *International Research Journal of Environment Sciences*,(2016), 5, 1–6
42. K.Renu, R.Chakraborty, H. Myakala, R. Koti, A.C. Famurewa, H. Madhyastha, B. Vellingiri, A. George, A. Valsala Gopalakrishnan, " Molecular mechanism of heavy metals (lead, chromium, arsenic, mercury, nickel and cadmium) - induced hepatotoxicity – a review." *Chemosphere*, (2021), 271:129735. <https://doi.org/10.1016/j.chemosphere.2021.12973>
43. H.A.Rowland, E.O. Omoregie, R. Millot, C. Jimenez, J. Mertens, C. Baciu, S.T.Hug and M.Berg, " Geochemistry and arsenic behaviour in groundwater resources of the Pannonian Basin (Hungary and Romania)." *Appl Geochem*,(2011), 26(1):1–17

44. S. Murcott, “ Arsenic Contamination in the World.” *An International Sourcebook*, IWA Publishing, London, UK, 2012
45. N.Saha, M.S. Rahman, M.B. Ahmed, J.L. Zhou, H.H. Ngo, & W. Guo, “ Industrial metal pollution in water and probabilistic assessment of human health risk.” *Journal of Environmental Management*, (2015), 185, 70–78. <https://doi.org/10.1016/j.jenvman.2016.10.023>
46. C. Sneddon, “Chromium and its Adverse Effects on the Environment. Case Study.” *Department of Earth Sciences*, (2012), Montana State University
47. S.Y. Stambulska, M.M. Bayliak and V.I. Lushchak, “Chromium (VI) toxicity in legume plants: modulation effects of rhizobial symbiosis.” (2018), *BioMed Res. Int.* <https://doi.org/10.1155/2018/8031213>, 2018
48. F. Tatti, M.P. Papini, V. Torretta, G. Mancini, M.R. Bon and P. Viotti, “Experimental and numerical evaluation of groundwater circulation wells as a remediation technology for persistent, low permeability contaminant source zones.” *J Contam Hydro*, (2019), 222:89–10
49. M. Tumolo, V. Ancona, D.D. Paola, D. Losacco, C. Campanale, C. Massarelli, V.F. Uricchio, “Chromium pollution in European water, sources, health risk, and remediation strategies: an overview.” *Int. J. Environ. Res. Publ. Health*, (2020), 17, 5438
50. M.K. Upadhyay, A. Majumdar, A. Barla, S. Bose, S. Srivastava, “An assessment of arsenic hazard in groundwater-soil-rice system in two villages of Nadia district, West Bengal, India.” *Environ Geochem Health*, (2019), 41(6):2381–2395
51. W.H.O., “ Nickel in drinking water. Draft Background document for development of WHO guidelines for drinking-water quality.” (2019), Geneva
52. X. Sun, B. Li, A. Qi, C. Tian, J. Han, Y. Shi, B. Lin, L. Chen, *Talanta* 178 (2018) 426X. Yuan, H. Wang, Y. Wu, G. Zeng, X. Chen, L. Leng, Z. Wu, H. Li, *Applied Organometallic Chemistry* 30 (2016) 289
53. M. Yoshinaga, H. Ninomiya, M.A. Al Hossain, M. Sudo, A.A. Akhand, N. Ahsan, M.A. Alim, M. Khalequzzaman, M. Iida, I. Yajima, N. and N. Ohgami, “A comprehensive study including monitoring, assessment of health effects, and development of a remediation method for chromium pollution.” *Chemosphere*, (2018), 201, 667–675s
54. M. Yousef, S. Ghalehaskar, F.B. Asghari, A. Ghaderpoury, M.H. Dehghani, M. Ghaderpoori, A.A. Mohammadi, “ Distribution of fluoride contamination in drinking water resources and health risk assessment using geographic information system, northwest Iran.” *Regul Toxicol Pharmacol*, (2019), 107:104408
55. L. Zhang, L. Zhao, Q. Zeng, G. Fu, B. Feng, X. Lin, Z. Liu, Y. Wang, and C. Hou, “ Spatial distribution of fluoride in drinking water and health risk assessment of children in typical fluorosis areas in north China.” *Chemosphere*, (2020) 239:124811
56. Y. Zhang, R. Qiao, C. Sheng and H. Zhao, “ Technologies for detection of HRP in wastewater, High-risk pollutants in wastewater.” *Elsevier, New York*, (2020) pp 79–100