Research Article

Removal of Chlorinated Phenolic Compounds from the Environment and Desulfurization of Oil with Carbon Nanoporous

Ghasem Zolfaghari

Department of Environment Science and Engineering, Faculty of Environmental Sciences, Hakim Sabzevari University, Sabzevar, Iran.

Abstract:

In this research, SBA-16 nanoprocesses were first synthesized and then the surface of this nanostructure was modified using aminopropyltrimethoxysilane and melamine (Me-ASBA-16). The synthesis of SBA-16 has been carried out by two surfactants F127 and P123. In addition, Amino-ASBA-16 was used to remove 2,4-dichlorophenol from polluted water, and the effect of the initial concentration of the pollutant and contact time on the amount of pollutant absorption was investigated. Furthermore, Au-doped mesoporous carbon, Au-OCMK-3, was prepared for desulfurization and denitrogenation of refinery fuels. The synthesis of ordered mesoporous carbon, OMC, was performed using SBA-15 silica as the hard template and sucrose as the carbon source. The structural order and textural properties of the prepared materials were studied by X-ray fiffraction (XRD), Scanning Electron Microscopy (SEM), and N_2 adsorption-desorption. Au-doped oxidized mesoporous carbon has been studied as a nanoabsorbent for removal of dibenzothiphene from n-heptane solutions as fuel model at room temperature. Batch adsorption studies were carried out to study the effect of contact time and initial concentration. The uptake capacity of dibenzothiphene and carbazole followed the order: Au-OCMK-3> CMK-3. The results showed that the synthesized compounds are suitable for removing phenolic and sulfur compounds.

Keywords: amino-asba-16 ; desulfurization; 2,4-dichlorophenol; au-ocmk-3

1. Introduction:

Various studies have been conducted in the field of environmental pollution [1]. In recent years, the contamination of aromatic pollutants such as phenolic compounds in aquatic ecosystems has attracted increasing attention. Phenolic compounds are toxic and carcinogenic and cause unpleasant taste and smell in drinking water. The US Environmental Protection Agency has listed eleven types of phenols as highly toxic substances, among which chlorophenols are the most toxic and carcinogenic [2]. The reported sources of phenol pollution include rain water, surface water, underground water, soil, gases from burning wood, exhaust gas from cars, wastewater from many industries such as pharmaceutical, petrochemical, wood, metal forming, paint, electrical coating of surfaces, resins, plastics, rubber and glue industries [3-4]. Wastewaters containing phenolic compounds are considered a serious problem due to their high toxicity, low degradability and ecological aspects [1]. Contamination of soils and waters by fossil fuels or their derivatives a widespread problem in many industrialized countries. Commercial gasoline and diesel contain a large amount of organic sulfur compounds with a concentration of 300 and 500 ppmw (parts per million by weight) [5]. One of the goals of the U.S.

EPA is to decrease the content of sulfure in diesel oil to 30 ppm. These sulfur compounds present in the fuel oils can cause serious environment pollution because they will be turned into SOx species during combustion. Sulfur compounds also result in the severe corrosion of reactors and equipment in the oil processing step. It promotes investigation of new techniques of separations because low concentrations cannot be achieved using hydrodesulfurization (HDS). HDS is not able to remove aromatic hetrocyclic sulfur compounds to the required levels [6]. Thus, desulfurization, i.e. removal of organic sulfur compounds from fuel oils, is a required practice across the world and has become an important unit operation in petroleum refining [5]. Among those compounds, dibenzothiophene is considered as refactory species. Recently investigated methods have been oxidation with hydrogen peroxide in the presense of litanium oxides [7] or reaction-enhanced adsorption on undisclosed reactive adsorbent [8]. In the latter method, a proprietary adsorbent attracts sulfur and withdraws it from dibenzothiophene and an aromatic hydrocarbon is released to the system [9].

Some of the methods that have been used so far to remove the phenolic compounds from water sources include absorption, chemical oxidation, photolysis, sedimentation, filtering, osmosis, and ion exchange [10-11]. Recently, many types of nanostructured carbons have been produced through templating approaches [12, 13, 14]. Ryoo et al. reported the first preparation of new type of mesoscopically ordered carbon molecular sieves CMK-1 and CMK-3 (cubic and hexagonal, respectively) by carbonizing sucrose inside the pores of the cubic MCM-48 and hexagonal SBA-15 mesostructured silica materials [15, 16]. The ordered mesoporous carbon replicas of cage-like mesoporous silicas SBA-1 [17], SBA-7 [18], SBA-16 [19], and FDU-12 [20] were reported as well. Furthermore, chemical vapour deposition (CVD) was applied using liquid petroleum gas (LPG) as the carbon source and HMS as the template to prepare ordered mesoporous carbon (OMC) as well as carbon nanotubes (CNT) [21]. Also Anbeia and Moradi (2009) modified ordered mesoporous carbon with HNO_3 and used for removing naphthalene-derived compounds [22]. Here, we report the preparation of CMK-3 from SBA-15 as hard template and sucrose as the carbon source. CMK-3 was modified with HNO_3 and functionalized with gold solution by post-synthesis treatment. Au-doped oxidized mesoporous carbon, Au-OCMK-3, for removing dibenzothiphene from oil model was investigated. Furthermore inn this research, SBA-16 nanostructure was first synthesized and then the surface of this nanostructure was modified using 3-aminopropyl trimethoxy silane (ASBA-16). Next, the resulting material was treated with melamine resins (Me-ASBA-16). The synthesized material was used to remove 2,4-dichlorophenol from polluted water.

2. Exprimental:
2.1. Materials:

The reactants used in this study were gold solution ($HAuCl_4$), tetraethyl orthosilicate (TEOS) as a silica source, Pluronic® P123 ($EO_{20}PO_{70}EO_{20}$) and F127 ($EO_{106}PO_{70}EO_{106}$) as surfactant, H_3PO_4 (85%), deionized water for synthesis of mesoporous silica (SBA-15), sucrose as a carbon source, and sulfuric acid as a catalyst for synthesis of ordered mesoporous carbon.

2.2. Synthesis of SBA-15, SBA-16, and modification:

The method of Kim et al. [15] was used for the synthesis of SBA-16. The synthesis procedure of SBA-15 involves the use of Pluronic P123 ($EO_{20}PO_{70}EO_{20}$; BASF) as the template agent, which is dissolved in distilled water and H_3PO_4 (85%) (Aldrich) obtaining initial solutions with the following molar compositions: 1:0.017:1.5:208 $SiO_2/P123/H_3PO_4/H_2O$ [24]. To modify SBA-16 with propylamine, 2 g of SBA-16 is spread in 70 mL of dry toluene, and then 1 g of aminopropyltrimethoxysilane is added to the mixture under nitrogen vacuum (Amino-SBA-16) [25]. Diisopropylethylamine was used for the for the synthesis of melamine resins on silicate nanoprous modified with propylamine (Me-SBA-16).

2.3. Synthesis of CMK-3 and functionalization:

The synthesis method for CMK-3 was to dissolve 1.25 g sucrose and 0.14 g H_2SO_4 in 5.0 g H_2O, and to add this solution with 1 g SBA-15 [15]. The texture and surface chemistry of synthesized CMK-3 was modified by means of oxidation treatment in liquid phase. Au-doped OCMK-3 was prepared by mixing 5000 ppm of $HAuCl_4$ and OCMK-3 for 10 h. The solid was separated by filtration, washed and vacuum dried. These samples were reduced to form nanoparticles of Au using 0.1 M $NaBH_4$ solution.

2.4. Adsorption tests:

To investigate the adsorption process, the amount of 0.9 g/L of the synthesized adsorbent was mixed with solutions of 2,4-dichlorophenol in concentrations of 10, 20, 30, 50, 100, 150 and 200 mg/L and in time 15, 30, 60, 120, 180, 240 and 300 minutes were mixed by a mechanical stirrer. Then the adsorbent was separated from the solution with the help of filter paper and the amount of absorption was measured (adsorbent dose = 0.9 g/L, temperature: 40 ℃, and pH = 7). Also, to investigate the effect of adsorbent dose, the amounts of 0.2, 0.4, 0.6 and 0.8 g/L were tested at a concentration of 10 mg/L of the pollutant at a temperature of 40 ℃ and a pH of 7. Pollutant adsorption percentage (R) was calculated using following equation:

$$R = \frac{C_0 - C_e}{C_0} \times 100$$

where C_0 and C_e are the initial and equilibrium concentrations of the compound in mg/L, V is the solution volume in L, and m is the adsorbent mass in g. Measurement of absorbance was analyzed by UV-Vis spectrophotometer. In the case of Au-OCMK-3, the absorption process was carried out under the same conditions.

3. Results and discussion:

Figure 1 shows the XRD pattern obtained for SBA-16, Amino-SBA-16 and Me-SBA-16 compounds. These three materials show regular silicate structure. In this figure, three XRD peaks corresponding to the reflections of 110, 200 and 211 of the three-dimensional space group are observed. The matching of the XRD pattern found in the reported studies for the compound SBA-16 proves the correctness of the synthesis of this compound. The low-angle XRD patterns of CMK-3 and Au-OCMK-3 are shown in Fig.

1. The nitrogen adsorption–desorption isotherms performed at 77K for the CMK-3 before and after modification are showed in Fig. 2. Both mesoporous materials yield a type IV isotherm. The type IV isotherm (IUPAC classification) is typical for mesoporous systems [26].
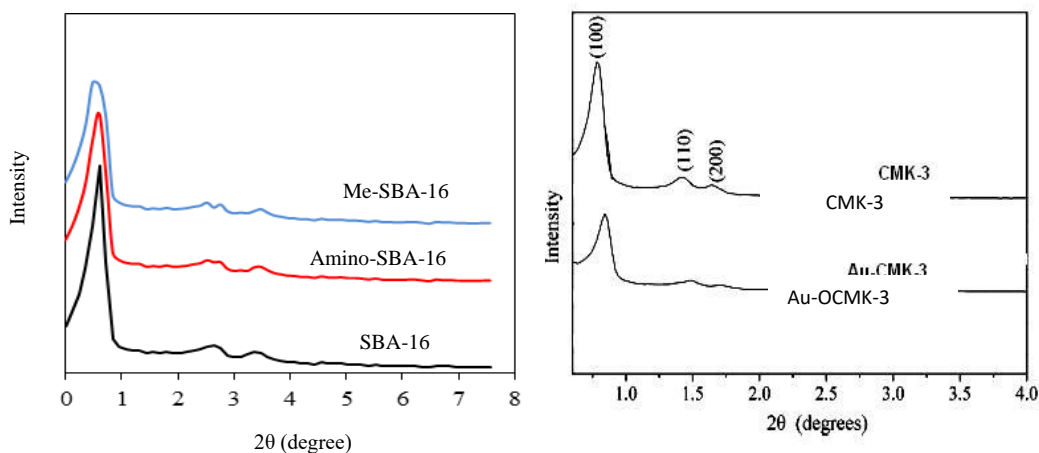
Figure 1: XRD patterns of synthesized materials.
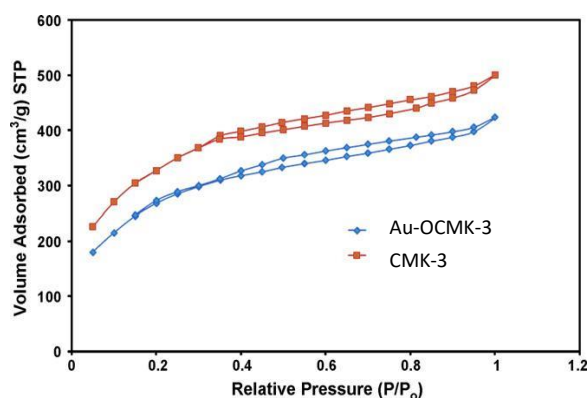
Figure 2: Nitrogen adsorption–desorption isotherms of CMK-3 and Au-OCMK-3.

In order to determine the equilibrium time in the absorption of 2,4-dichlorophenol, the amount of absorption has been studied as a function of time and in different initial concentrations (Fig. 3A). After 2 hours, increasing the contact time has no effect on increasing the amount of absorption, and this indicates that the reaction has reached equilibrium. It can be seen that the absorption process is fast at first and becomes slower as the equilibrium time is reached [27]. This is related to the fact that in the initial stages of adsorption, more active sites are available, so the adsorption happens quickly, after this time, due to the repulsion between the adsorbed species and the species in the mass, the adsorption becomes difficult. Adsorption in different concentrations has also been shown. The amount of adsorption decreased with increasing concentration. To investigate the effect of adsorbent amount on absorption capacity, different amounts of Me-SBA-16 adsorbent (0.2, 0.4, 0.6 and 0.8 g/L) were added to 25 mL of 200 mg/L solution of the pollutant. Figure 3B shows that the amount of absorbed phenolic compound increases significantly with increasing amount of absorbent.

The desulfurization performance of as received and modified mesoporous carbon was valuated using model oils in a batch type adsorption setup. For a typical run, the adsorption conditions are as followes: room temperature; adsorption time 30, 60, 120, 180 and 240 min. The sorption of dibenzothiphene on Au-OCMK-3 was more than CMK-3 (Fig. 4). Au species contribute to an increase in the number of active centers, which improve the adsorption of dibenzothiphene on mesoporous carbon. The results of the study conducted by Zolfaghari et al. [28] show that OCMK-3 functionalized with zinc oxide is an effective adsorbent for removal of lead and mercury.
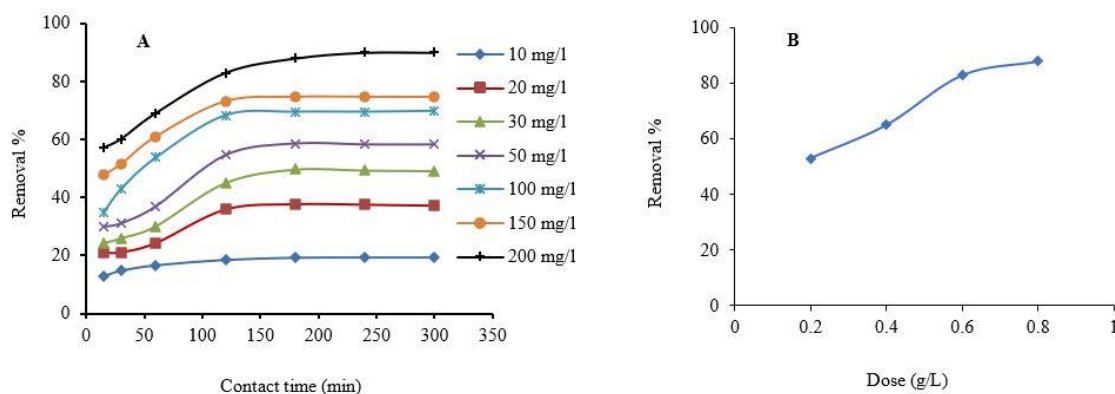
Figure 3: The effect of initial concentration and time on the absorption of 2,4-dichlorophenol by Me-SBA-16 (adsorbent dosage = 0.9 g/L, temperature: 40 ℃, pH = 7) (A) and the effect of adsorbent dose on the absorption of 2,4-dichlorophenol by Me-SBA-16 (initial concentration= 10 mg/L, contact time: 120 minutes, temperature: 40 ℃, pH = 7) (B).
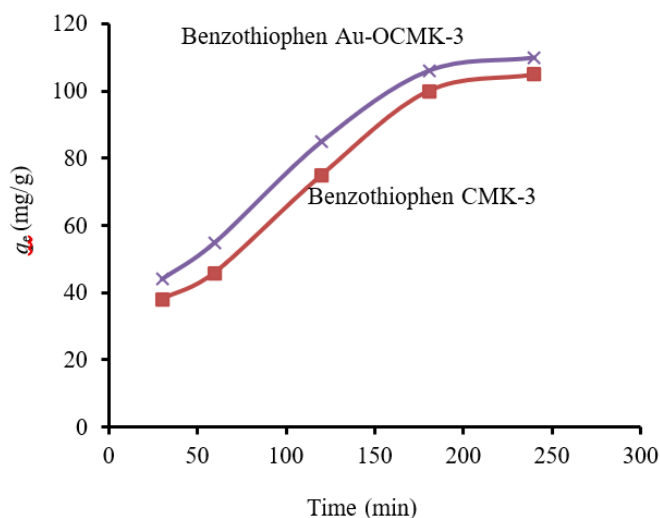
Figure 4: The sorption of dibenzothiphene on nanoadsorbent studied (Effect of contact time on removal of DBT (dose of 0.7 g/L and temperature of 25 ℃).

4. Conclusion:

In this research, the synthesis of nanoporous silicate SBA-16 has been done correctly. The XRD diagram confirms this issue. Me-SBA-16 showed that it has a high ability to absorb 2,4-dichlorophenol. Melamine groups are the reason for this ability. Further researches on this matter of identification and investigation of different dimensions of adsorption are ongoing. We demonstrate that functionalization of CMK-3 with gold is possible. The present study shows that the Au-OCMK-3 some deal is an effective adsorbent for the removal of dibenzothiphene.

References:

1. Zolfaghari G, Esmaili-Sari A, Ghasempouri SM, Hassanzade Kiabi B (2009). Multispecies monitoring study about bioaccumulation of mercury in Iranian birds (Khuzestan to Persian Gulf): effect of taxonomic affiliation, trophic level and feeding habitat. Environ Res 109:830-838.
2. WHO, Guidelines for Drinking-Water Quality, 1984.
3. Sabio, E., et al, Influence of regeneration temperature on the phenols adsorption on activated carbon, Colloid Interface Science. Vol. 242, 2001, pp. 31-35.
4. Podkoscielny, P., et al, Heterogeneity of activated carbons in adsorption of phenol aqueous solutions, Applied Surface Science, Vol. 205, 2003, pp. 297-301.
5. R.J. Farrauto, C.H. Bartholomew. Fundamentals of Industrial Catalytic Processes, Chapman and Hall, New York, 1997.
6. M. Seredych, T.J. Bandosz. *Energy and Fuels* 2009, 23, 3737–3744.

7. Y. Shirashiri, H. Hara, T. Hirai, I, Komasawa. *Ind. Eng. Chem. Res*. 1999, 38, 1589–1595.
8. J. Gislason. *Oil Gas J.* 2001, 99, 72–76.
9. C. Song. *Catal. Today* 2003, 86, 211–263.
10. Banat, F.A., et al, Adsorption of phenol by bentonite, Environmental Pollution, Vol. 107, 2000, pp. 391-398.
11. Wu, J., et al, Oxidation of aqueous phenol by ozone and peroxidase, Advanced in Environmental Research, Vol. 4, 2000, pp. 339-346.
12. J. Lee, S.H. Yoon, S.M. Oh, C.H. Shin, T. Hyeon. *Adv Mater*, 2000, 12: 359
13. W.W. Lukens, G.D. Stucky. *Chem Mater*, 2002, 14: 1665.
14. M. Sevilla, S. Alvarez, A.B. Fuertes. *Microporou Mesoporou Mater*, 2004, 74: 49.
15. R. Ryoo, S.H Joo, S. Jun. *J Phys Chem* B, 1999, 103: 7743
16. S. Jun, S.H. Joo, R. Ryoo, M. Kruk, M. Jaroniec. *J Am Chem Soc*, 2000, 122: 10712
17. R. Ryoo, S.H. Joo, M. Kruk, M. Jaroniec. *Adv Mater*, 2001, 122: 677
18. H.C Li, Y. Sakamoto, Y.S Li, O. Terasaki, M. Thommes, S.N. Che. *Microporou Mesoporou Mater*, 2006, 95: 193
19. T.W. Kim, R. Ryoo, K.P Gierszal, M. Jaroniec, L.A. Solovyov. *J Mater Chem*, 2005, 95: 1560
20. J. Fan, C.Z. Yu, F. Gao, J. Lei, B.Z. Tian, L.M. Wang, Q. Luo, B. Tu, W.Z. Zhou, D.Y Zhao. *Angew Chem, Int Ed*, 2003, 42: 3146
21. P. Ndungu, Z.G. Godongwana, L.F. Petrik, A. Nechaev, S. Liao, V. Linkov. *Microporou Mesoporou Mater*, 2008, 116: 593.
22. M. Anbia, S.E. Moradi. *Chem. Eng. J.*, 2009, 148 (2-3), 452-458.
23. Kim, T.W., et al, Characterization of mesoporous carbons synthesized with SBA-16 silica template, Journal of Materials Chemistry, Vol. 15, Feb. 2005, pp. 1560-1571.
24. M. Colilla, F. Balas, M. Manzano, M. Vallet-Reg. *Chem. Mater.* 2007, 19, 3099-3101.
25. Anbia, M. and Lashgari, M., Synthesis of amino-modified ordered mesoporous silica as a new nano sorbent for the removal of chlorophenols from aqueous media, Chemical Engineering Journal, Vol. 150 (2-3), Feb. 2009, pp. 555-560.
26. IUPAC "Manual on Catalyst Characterization", J. Haber, *Pure and Appl. Chem.*, 1991, 63, 1227-1246.
27. Zolfaghari G, (2016). β-Cyclodextrin incorporated nanoporous carbon: Host–guest inclusion for removal of p-Nitrophenol and pesticides from aqueous solutions. Chemical Engineering Journal 283, 1434-1424 (2016).
28. Zolfaghari G, Esmaili-Sari A, Anbia M, Younesi H, Amirmahmoodi S, Ghafari-Nazari A (2011a). Taguchi optimization approach for Pb(II) and Hg(II) removal from aqueous solutions using modified mesoporous carbon. J Hazard Mater 192:1046–1055.

Mining and mineral processing industries contribute heavily to water pollution, particularly through discharge of wastes containing HMs into the surrounding aquatic environments including surface and ground water sources with inefficient or without prior treatment. Mining wastes such as tailings, slags, waste rocks, spent leach piles are the potential source of HMs in natural waters and sediments (Hudson et al., 1999). In addition, the formation of acid mine drainages (AMD) at mining sites contain HMs posing environmental threats to aquatic and terrestrial life (Esmaeili et al., 2019).

Furthermore, the increasing use of metal-based products in agriculture, homes, construction, medicine, and electronics has led to the generation of a large volume of waste containing HMs that eventually end up in water resources (Sekomo et al., 2011) . For instance, HMs-based pesticides including mercuric chloride and phenyl mercury acetate, mercuric oxide, lead arsenate, copper-arsenic complex (Paris green), sodium arsenic, and calcium arsenate are extremely and highly hazardous pesticides which are introduced in agriculture to control pests and diseases (WHO, 2020). As a result, pesticides residues have been identified in aquatic environments and in food (Codex, 2006). Equally important, the introduction of chemical fertilizers containing trace amount of HMs to the soils have led into the accumulation of these metals, which can further be transported to aquatic environments through sediment transport and soil erosion. In addition, metal scraps from construction facilities, electronic and metal workshops contribute to the source of HMs in the surrounding soil environments, which later on find their way to nearby water bodies by runoff (Achi et al., 2011).

It has been well established that natural processes such as weathering coupled with soil erosion contribute to the displacement and transport of the HMs into aquatic systems. In a stable environment, the distribution of HMs in the earth's crust varies depending on the nature of the parent rock (Cox et al., 2017). Natural weathering involves physical, biological and chemical processes that act on the rock bearing HMs and this leads to the disintegration of the parent rock into smaller particles such as sediments or ions. A common phenomenon occurs, when metal sulphide bearing rocks (ores) such as galena, zinc pyrite, copper and iron pyrites get oxidized in presence of microbes, usually *Thiobacillus ferrooxidans,* in sufficient oxygen leading to the formation of AMD. The resulting acidified medium dissolves and releases more HMs into aquatic environments (Hudson et al., 1999; Virtanem et al., 2015; Esmaeili et al., 2019).

The term "Heavy Metals" technically refers, essentially, to a group of metal and metalloid elements in the Periodic Table that have an atomic density of 6 g/cm³ (Makuleke and Ngole-Jeme, 2020) . These metals have been associated with environmental pollution and ecotoxicity. HMs are not biodegradable and thus, accumulate in the nature including aquatic systems, and can be transferred to living organisms through the food chains (Codex, 2006; Sekomo et al., 2011; Ali et al., 2015). Mercury (Hg), lead (Pb), chromium (Cr), cadmium (Cd), and arsenic (As) have been the most common HMs that induced human poisonings (Balali-Mood et al., 2021). However, other HMs such as nickel (Ni), copper (Cu), zinc (Zn), iron (Fe) and manganese (Mn) have been reported in different literature (Cox et al., 2017; Makuleke and Ngole-Jeme, 2020).

Above the background concentration, HMs can pose health risks to organisms, especially human beings. The World Health Organization (WHO) has set guidelines for the maximum concentration of these metals for safety purposes. For instance, cadmium should not exceed a concentration of 0.003 mg/L in drinking water, because it is considered unsafe to humans as this may result into cancer of the kidneys (WHO, 2008). The safe levels (WHO standards) for the selected HMs in drinking water are provided in Table 1. For precautionary reason, it is imperative to keep track on the levels of these contaminants to avoid long-term exposure due to lack of awareness of their sources.

This would help in mitigating and preventing long-term health effects caused by chronic exposure, which has been the case of arsenic in groundwater in Bangladesh and West Bengal (WHO, 2008). Therefore, measures should be taken by responsible authorities to protect the environment and human beings from the accumulation of these toxic metals in aquatic systems.

Understanding the key processes that are involved in the distribution of HMs play a fundamental role in the control and remediation of these metals in different media including aquatic environment. Few, if any, literature encompasses this indispensable need. Thus, this paper describes fully the processes involved in heavy metal distribution, chemistry as well as sources and the associated health effects of HMs; a measure of heavy metal environmental contamination; heavy metal speciation; chemical mobility and bioavailability of HMs in the environment; current remediation technologies of HMs and finally, reliable quantitative methods of analyzing HMs in the environment.

2. Heavy Metals in Aquatic Systems:
2.1. Aquatic Bottom Sediments:

Many investigators have pioneered in the study of aquatic bottom sediments in an attempt to assess their physico-chemical quality (Muhammed, 1991; Olutona et al., 2012; Sibomana et al., 2019).

Bottom sediments in water bodies are complex mixtures of various phases, namely, residues of weathering and erosion of underground materials (Sibomana et al., 2019). According to Muhammed (1991), aquatic bottom sediments have three main components, namely, clays, organic matter, and oxides of iron and manganese (Fe-MnO), which play a role in the transport of HMs. In about five decades ago, Jenne (1968) proposed that oxides of iron and manganese play a major role in controlling HMs in soils and water sediments. The author added that other controls proposed previously are the layer of silicates, organic matter, and carbonates. Recently, Abbott et al. (2019) found that clay minerals are likely to have primary influence on the rare earth elements cycling near the seafloor. The accumulation of rare earth metals in aquatic bottom sediments implies trace metal pollution, especially HMs. Therefore, bottom sediments act as a filter of overlying marine waters, and they can immobilize hazardous chemicals including HMs.

2.2. Processes Associated with Heavy Metal Distribution:

It has been agreed that man's activities and natural processes, mainly erosion have made a significant perturbation of the natural distribution of metals in the environment, such as on land and in rivers, lakes and seas. Indeed, the terrestrial and aquatic systems are surely interconnected and this makes an easy transport of metal pollutants from one system to another through several physico-chemical processes (Eggleton and Thomas, 2004). HMs get into aquatic systems through various processes, such as precipitation and or coprecipitation, dissolution, sorption, complexation and so on. Different processes involved in the distribution of HMs in aquatic systems are summarized in Figure 1.

Adsorptive behavior of metals onto different adsorbents' surfaces has been largely investigated, and proven to contribute to the metal transport in different environmental matrices such as sediments (Jenne, 1968; Muhammed, 1991; Sekomo et al., 2015) . Once in aquatic system, metals are partitioned between water-sediment phases. In doing so, some metals become hydrolyzed, complexed with organic or inorganic ligands in water, and interact with sedimentary materials by ion-exchange, coprecipitation and other adsorption reactions (Pentreath, 1985) .

Equally important, the adsorptive behavior of metals (cations) and differential solubilities of their compounds have led to the successful designs and development of various remediation technologies meant to control HMs in all media including aquatic environments. These technologies focus on improving metal stabilization, mainly by enhancing either metal sorption on natural sorbents such as sediments or metal-ion absorption through the roots of specialized plant species. The overall results were found to lower the potential mobility or bioavailability of the HMs to environment (Jenne, 1968; Pentreath, 1985,Eggleton and Thomas, 2004). Despite their drawbacks, the use of active sorbent materials, sand capping, and phytoremediation (the use of plants) methods are some of the currently recognized onsite remediation technologies for HMs (Peng et al., 2009). The remediation technologies will further be discussed in section 7.

It has been suggested that several physico-chemical factors dictate the distribution of HMs between the water-sediment phases, and the changes in these factors may alter the concentration of the metal of interest, which affects its mobility and availability (Muhammed, 1991). Such factors include, mainly pH, organic matter (OM), redox potential (ORP), temperature, salinity, concentration of other metal species and retention time (Peng et al., 2009; Nijeje et al., 2023). Literature (Jenne, 1968; Peng et al., 2009) claimed that pH, ORP, and OM are, perhaps, the most controlling factors of metal distribution. Furthermore, the changes in these factors will determine the speciation of the metals and thus, contribute to their mobility and availability (Zang et al., 2017; Aigberua et al., 2018; Nijeje et al., 2023).

3. Chemistry and Health Effects of Selected HMs:

The toxicity of a metal depends on its nature, ingested/absorbed concentration (dose), and physiology of the victim. Metal toxicity is related to the formation of complexes with proteins, in which carboxylic acid (–COOH), amine (–NH$_2$), and thiol (–SH) groups are involved (Uwamariya, 2013). HMs can cause serious health problems even at their lower concentrations. For the most kinds of

toxicity, it is believed that there is a dose below which no adverse effect will occur.

For HMs that give rise to such toxic effects, a tolerable daily intake (TDI) is an estimate of the amount of a substance (HMs) in food and drinking-water, expressed on a body weight basis (mg/kg or mg/kg of body weight), that can be ingested over a lifetime without appreciable health risk (WHO, 2020). Most reported health complications include cancer and auto-immunity caused by lead, kidney damage, and hypertension due to exposure to higher amounts of cadmium. Generally, exposure to over the recommended amounts is unhealthy. The World Health Organization (WHO, 2008)   set the guidelines for the allowable amounts/values   of metals in drinking water. Excluding other factors, these values can assist in estimating and comparing the toxicity of the HMs in terms of dosage. For instance, the order of toxicity of the HMs would be cadmium (0.003 mg/kg) > mercury (0.006 mg/kg) > arsenic (0.01 mg/kg) = lead (0.01 mg/kg) > chromium (0.05 mg/kg) > nickel (0.07 mg/kg) > copper (2.00 mg/kg) > zinc (5.00 mg/kg). In the following sections, we will see briefly the chemistry, source and toxicity of the common reported HMs in aquatic systems, namely arsenic, cadmium, copper, chromium, mercury, nickel, lead, zinc and iron respectively.

3.1. Arsenic (As):

Arsenic is one of the harmful HMs which pose a serious threat to human health. The exposure routes to arsenic can be via injection, ingestion of As contaminated food and water, skin absorption of As, inhalation of atmospheric aerosols containing As. Arsenic exists in the forms of elemental metalloid (As^0), inorganic (As^{3+} and As^{5+}), organic, and arsine (AsH$_3$). The order of increasing toxicity of As compounds is defined as organic arsenicals < As^0 < inorganic species (As^{5+} < As^{3+}) < arsine (Balali-Mood et al., 2021). Arsenic has no known nutritive benefits to human beings and animals. However, arsenic is found in the diet, particularly in fish and shellfish, in which it is found mainly in the less toxic organic form (WHO, 2008)Therefore, the presence of As in the food chain has become a serious concern for global food safety, environment and human health (Irshad et al. 2020).

Due to its high toxicity, it is primarily used as pesticides such as lead hydrogen arsenate [PbHAsO$_4$] and Paris green/copper-arsenic complex   [Cu$_4$As$_6$(C$_4$H$_6$O$_{16}$)] as   larvacides,   sodium   arsenite [NaAsO$_2$] as rodenticide, and calcium arsenate [Ca$_3$(AsO$_4$)$_2$] as insecticide (WHO, 2020). It is also notoriously known as the king of poisons and poison of kings (Balali-Mood et al., 2021). According to WHO (2008), the long-term exposure to arsenic in drinking water is causally related to increased risks of cancer in the skin, lungs, bladder and kidney, as well as other skin changes, such as hyperkeratosis and pigmentation changes.
Naturally, As occurs often as sulfides or metal arsenides or arsenates. In water, it is mostly present as arsenate (+5), but in anaerobic conditions, it is likely to be present as arsenite (+3). It is usually present in natural waters at concentrations of less than 1–2 mg/litre and in groundwaters the concentrations can be significantly elevated, because of sedimentary deposits deriving from volcanic rocks, where there are sulfide mineral deposits (WHO, 2008).

3.2. Cadmium (Cd):

Cadmium is found in group IIB with zinc in the Periodic Table. The chemistry of cadmium is broad, but the most important part is its aqueous phase. In aqueous, cadmium is present as Cd^{2+}, $CdOH^+$, $CdCO_3$ (s), (otavite) and Cd $(OH)_2$ (Uwamariya, 2013). It is reported that the species Cd^{2+}, $CdOH^+$, and Cd $(OH)_2$ contribute to the solubility of Cd in the pH range of 4 to 9. Cadmium is naturally found in all environments, namely, air, water, soils, and sediments as carbonate and sulphide ores in association with zinc as in sphalerite (Zn[Cd]S) (Bradl, 2005; Slavko et al., 2019).

The natural geological levels of Cd started to rise noticeably after it was introduced into the environment, especially by wastewater and diffuse sources from mines, metal smelters, and cadmium based industries for alloys, fertilizers, Ni/Cd batteries, pigments and in plastics (WHO, 2008; Bradl, 2005). Cadmium has no biological function to human beings, and it exhibits human toxicity at extremely low concentrations (Muhammed, 1991; Nijeje et al., 2023). Long-terms exposure to Cd can result into accumulation in human beings and causes cancer in the kidneys, whereas acute exposure to fumes containing Cd and cadmium salts can result into death. The major route of exposure to cadmium for human beings is ingestion of contaminated food and water. However, cigarette smoke is also a recognized direct exposure through the inhalation route (Narjala, 2020). Cadmium accumulates in plant tissues (leaves, roots, fruits, and seeds) and enters the food chain, where human beings and other invertebrates can easily get exposed (Ochieng, 2013). World Health Organization set the guideline for Cd in drinking water to be 0.003 mg/L (WHO, 2008).

3.3. Copper (Cu):

The chemistry of copper shows that it exists in three oxidation states, namely, unstable copper (I), the most common copper (II), and rare copper (III). In aquatic systems, copper has been known as particulate, colloidal, and soluble form of copper. Copper is a good electron acceptor, and therefore, it strongly interacts with different ligands present in the aqueous phase such as carbonate, nitrate, sulfate, chloride, ammonia, hydroxide, and humic substances.

In aqueous phase, insoluble particulate malachite $Cu_2(OH)_2CO_3$) is normally formed and could be a major factor in controlling the amount of Cu^{2+} ions. However, carbonates and hydroxides of copper are pH dependent (Nijeje et al., 2023). For example, $CuCO_3$ is stable at a pH range of 6.0− 9.0, and above this range, a complex ion of $[Cu(CO_3)_2]^{2-}$ which cannot be formed in natural waters of normal pH range is formed. In fact, Cu^{2+} free ions would increase as the pH decreases below 6.5. Naturally, copper exists as chalcopyrite $CuFeS_2$ or in clay minerals with many other minerals (Bradl, 2005; Slavko et al., 2019).

Copper is an essential nutrient to human beings and a drinking water contaminant when it exceeds its permissible concentration of 2 mg/L as established by WHO (2008). The common sources of copper include electricity and heat appliances, water pipes, roofing, kitchenware, chemicals and pharmaceutical equipment, alloys,

pesticides, paints and pigments, textile industry, and explosive (Bradly, 2005; Slavako et al., 2019). The negative effects of exposure to higher copper levels than the body can regulate causes, itching, dermatitis, keratinization of the hands and soles of the feet, vomiting, diarrhea, nausea. Some acute symptoms presumably due to local irritation by ingested copper (II) ions have been described in several cases (Uwamariya, 2013).

3.4. Chromium (Cr):

Chromium is widely distributed in the Earth's crust. According to Balali-Mood (2021), Cr can exist in valences of - 2 to +6, but its most stable forms are +3 and +6. Generally, food and water appears to be the major source of intake (WHO, 2008). The toxicity of Cr varies and depends on its chemical species. Hexavalent chromium is known to be the responsible for occupational human carcinogen via inhalation exposure. The bioaccumulation of Cr is associated with various diseases ranging from dermal, renal, neurological, and gastrointestinal (GI) diseases to the development of several cancers including lungs, larynx, bladder, kidneys, testicles, bone, and thyroid (Balali-Mood et al., 2021). The source of Cr in water bodies could originate from different industrial application of chromium, majorly in dyes as coloring agent in textile products and cosmetics. Chromium can also get into the water sources due improper waste management of laboratory and industrial waste containing Cr. The maximum permissible limit set by WHO (2008) is 0.05 mg/kg in drinking water.

3.5. Nickel (Ni):

Nickel occurs naturally in the environment at low levels. It exists in two important ores of laterite (oxide or silicate ores such as garnierite $(NiMg)_6Si_4O_{10}(OH)_8$ and sulphides (NiS) minerals). In aqueous environment, nickel can exist in +1 to +4 oxidation states. However, the most common occurrence of nickel in aquatic systems is Ni^{2+} compounds. Carbonates ($NiCO_3$) and hydroxides ($Ni(OH)_2$) of nickel are normally stable in oxidizing conditions, whereas the sulphides of nickel (NiS) are stable in reducing conditions (Slavako et al., 2019) . Therefore, redox and pH can control the Ni^{2+} levels in aqueous phase. In addition, Ni^{2+} was found to bind strongly to poorly biodegradable elthylenediaminetetraacetic acid (EDTA), carbonyls ($[Ni(CO)_4]$) and nitrilotriacetate (NTA). In aqueous, Ni^{2+} hexahydrates exist as $[Ni(H_2O)_6]^{2+}$ ion. Nickel is used for nickel alloys, electroplating, batteries, coins, industrial plumbing, spark plugs, machinery parts, stainless-steel, nickel-chrome resistance wires, and catalysts. Nickel carbonyl has severely limited use in nickel refining (Bradl, 2005, WHO, 2008). No evidence has been shown to prove nickel as an essential element to human health, although it is essential in some animal species.

Health threats resulting from long-term skin exposure to nickel were largely recognized to be associated with itching of the fingers, hands, and forearms in humans. However, inhalation of nickel compounds is carcinogenic to humans as group 1 and that metallic nickel is possibly carcinogenic as group 2B (WHO, 2008). Moreover, carbonyls are extremely hazardous because of their toxicity. When volatile carbonyls are readily taken into the body through respiratory tract or through the skin, this causes a

production of toxic carbon monoxide and toxic metal by-products (Bradl, 2005). Considering the toxicity of nickel, the maximum permissible level in drinking water is 0.07 mg/L (WHO, 2005).

3.6.   Lead (Pb):

The use of lead in water distribution systems, such as pipes, in our homes has been the most source of lead in drinking water (Slavko et al., 2019). Lead has also been used in the joining of copper tubes, and this usually solubilized lead due to faster galvanic corrosion than the usual oxidative corrosion of lead. The solubility of lead, also known as plumbosolvency in pipes, is however due to the formation of deposits of lead carbonate (Pb $(CO_3)_2$) inside the pipes. Since carbonates are governed by pH, the solubility of lead increases below the pH of 8 and with a decrease of hardness (Pueyo, 2001). Lead hydroxide is known to occur as an individual compound or as a combination with its carbonate in the environment ($PbCO_3.Pb(OH)_2$), and it is stable in oxidizing conditions (Manahan, 2000).

In aqueous environment, the solubilization of lead is thought to be caused by the introduction of strong chelating agents, such as NTA in basic conditions, forming Pb^{2+} complex ions. However, in anoxic environments, such as sediments, lead is immobile as sulphide (PbS). Apart from plumbing systems, other sources of lead are principally lead-acid batteries, organolead compounds tetraethyl/ tetramethyl lead as antiknocks, lubricating agents, and alloys (Bradl, 2005; Slavko et al., 2019). Lead is very toxic and is not essential to human health. According to WHO (2008), the permissible level of Pb is as low as 0.01 mg/L, and this explains the severity it would cause if it exceeds regulatory amounts. Severe effects from exposure to lead have been reported to occur to children and pregnant women (Baha;li-Mood et al., 2021). Some of the reported health effects were associated with toxicity to both the central and peripheral nervous systems, inducing subencephalopathic neurological and behavioural effects, inhibition of biosynthesis of iron/haem (leukemia) and vitamin D (WHO, 2008).

3.7.   Mercury (Hg):

Mercury is a heavy, silvery white, liquid metal at room temperature and pressure. Its freezing point is −**38.83 °C and boils at 356.62 °C.** This temperature range was one of the major property, in addition to its constant coefficient of thermal expansion and its high thermal conductivity, that makes Hg suitable to be used in thermometers. The chemistry of Hg depends on its oxidation states. Hg exists in three forms: elemental or metallic mercury (Hg^0), inorganic mercury (Hg^+, Hg^{2+}), and organic mercury (commonly methyl or ethyl mercury) (Balali-Mood et al., 2021).

Mercury is an extremely chemical hazard, and is known for its deadly health risks up on exposure. Vapor mercury being more toxic than liquid mercury due to exposure route via inhalation. The physical properties of Hg have attracted many manufacturers for economic applications. For example, Hg is used in lamp factories body based on EQS set for either sediments, water, and/ or biota. For example, in Norway, the chemical status for water bodies is primarily based on the national EQS set for sediments and biota,

due to its fluorescent light emission. It is also used in mining industries in the extraction of gold. Therefore, wastewater containing mercury, broken thermometers, electrical lamps containing mercury and Hg-based pesticides are the primary sources of Hg in soils and aquatic environment. Mercury is regulated (WHO, 2008) and hence, its concentration in drinking water should not exceed 0.006 mg/kg.

3.8.   Zinc (Zn):

Zinc is a very essential trace metal that we consume in food and drinking water. It is also added to our health to boost our immune system as zinc sulphate ($ZnSO_4$). Until now, no health guideline has been set for drinking water. However, consumption of Zn above 3 mg/L is considered unacceptable for human beings (WHO, 2008). In aquatic environments, the solubility of zinc depends on the pH and the level of total inorganic carbon; zinc carbonate solubilizes when pH and the concentrations of carbonate species decreases (Nijeje, 2023). Therefore, liming is enough to control zinc in water treatment plants as it removes Zn^{2+} as insoluble zinc carbonate ($ZnCO_3$). Zinc can also exist as solid oxides, sulphides, and silicates. Although zinc (II) is not very toxic to animals, it is phytotoxic (toxic to plants) from different sources of zinc-rich sewage sludge, sediments, and soils exposed to smelting industries resulting in stunting of shoots, curling and rolling of young leaves, death of leaf tips, and chlorosis (Manahan, 2000).

3.9.   Iron (Fe):

Naturally, the total content of iron is by far the highest beyond the trace level in the environment (Tessier et al., 1979). In the last centuries, it has been believed that the enormous deposits of iron oxides in the crust were responsible for liberating oxygen in the primitive atmosphere (Manahan, 2000). Fortunately, bioavailable iron is not toxic to human beings with a daily requirement of Fe ranging from $10-50$mg/L depending on age, sex, and physiological status (WHO, 2008). The deficiency of iron in plants causes chlorosis (inhibition to synthesize chlorophyll). This is because iron is an essential element to both human beings and plants. Two important naturally occurring iron compounds are iron oxides (ferric oxide, Fe_2O_3; ferric hydroxide, Fe $(OH)_3$; and ferric oxyhydroxide, FeOOH) and ferrous sulphides (mackinawite, FeS; pyrite, FeS_2 and greigite, Fe_3S_4) which occur in oxidizing and reducing conditions respectively. In anoxic environment, ferrous iron is used by iron bacteria to obtain their energy leading to deposits of slimy iron familiar in our pipes (Manahan, 2000).

4. Sediments Contamination and Environmental Quality Standards:
4.1.   Environmental Quality Standards:

Based on Environmental Quality Standards (EQS), most aquatic systems can be classified as contaminated or not. Nationally, chemical status is commonly used to define the quality of a water

whereas in Finland the chemical status of water bodies is based on the EQS set for surface water and biota, but not for sediments (Olsen et al., 2019). This is not the same in Denmark and Sweden,

where the definition of good chemical status of a water body is based on EQS set for both water, sediment and biota, although in Sweden EQS has been defined only for a few substances in biota and sediments. Table 1 shows the national environmental quality standard values for HMs in marine and freshwater sediments in the Nordic countries as well as heavy metal distribution in bottom sediments of water bodies in different countries.

In any aquatic system, the elevation of metal levels is shown mainly by an increase in their concentrations in the bottom sediments of the reservoir (Olutona et al., 2012). Studies (Nhapi, 2011; Abdel-Satar, 2005; Malik and Maurya, 2004) showed that aquatic bottom sediments are heavily polluted by HMs with some of them present in their available form. In some conditions, more than 99% of HMs entering into a river can be stored in marine and surface water sediments in various other forms (Peng et al., 2009). Therefore, the investigation of metal pollutants performed on water samples would not reveal the in-depth metal pollution aquatic system to explore more about the behavior of the HMs in question if bottom sediments are not considered.

4.2 Measure of Environmental Contamination:

The natural occurrence of metals in many environments does not give an easy assessment of contamination. This is because contamination occurs when the measured quantity of the suspect is above the level of its natural or background occurrence. Table 1 provides different concentrations of the selected HMs in bottom sediments of different aquatic systems and their natural background mean concentrations in the shale. Above the natural background concentrations, the exceeding amounts are thought to be anthropogenic induced. Apart from comparing EQS set by national regulatory agencies with the measured quantities of the metal in the investigation, a variety of normalizing techniques (grain size, total carbon, iron, aluminium, lithium, rare earth elements, and radioactive trace elements) maybe used to differentiate natural from anthropogenic sources of HMs (Schiff and Weisberg, 1999). However, iron is widely used as a geochemical normalizing element for trace metals (Amin et al., 2009; Saleem et al., 2015; Nijeje et al., 2023).

Some investigators used grain size (shale) and iron as a reference tracer (Amin et al., 2009; Saleem et al., 2015; Nijeje et al., 2023). Selecting a conservative tracer element requires several assumptions. According to Schiff and Weisberg (1999), mainly three assumptions should be considered in sediment environments:

i. The reference element co-varies in proportion to the naturally occurring concentrations of the metal of interest.

ii. The reference element is insensitive to inputs from anthropogenic sources and this can be assessed using geochemical accumulation index of that element as shown in equation 1.

iii. The reference element is stable and is not subject to environmental influences such as reduction/oxidation, adsorption/desorption, and other diagenic processes that may alter sediments properties.

Rivers/streams/lakes	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Fe (%)	Reference
Mpenge stream (Rwanda)	n.s	5.0	169.1	44.2	ns	33.3	33.	136.7	n.s	Sibomana et al. (2019)
Nyabugogo river (Rwanda)	n.s	2.9	41.0	39.7	n.s	n.s	54.0	107.0	n.s	Sekomo et al. (2011)
Saint-Pierreville river (France)	n.s	<0.1	n.s	48.6	n.s	60.2	42.5	127.0	5.0	Tessier et al. (1979)
Saint Marcel river (France)	n.s	<0.1	n.s	25.0	n.s	28.8	18.2	88.0	3.6	Tessier et al. (1979)
Nakivubo stream (Uganda)	n.s	1.1	n.s	35.8	n.s	n.s	154.6	331.7	4.1	Sekabira et al. (2010)
Mangla river (Pakistan)	n.s	4.4	25.1	22.6	n.s	70.8	30.7	127.3	0.5	Saleem et al. (2015)
Water bodies in Southern Poland	18.3	113.1	2.1	151.1	n.s	66.0	2040.8	12724.7	7.6	Machowski et al. (2019)
River Rwizi (Uganda)	n.s	1.6	n.s	108.6	n.s	39.0	33.7	112.0	3.1	Nijeje et al. (2023)
Italian coasts (Italy)	n.s	0.2	n.s	n.s	0.23	n.s	41.1	n.s	1.7	Giordano et al. (1992)
Standards[1]	18.0	2.5	660.0	84.0	0.5	42.0	150	139	n.s	Olsen et al. (2019)
Background Shale Values	13.0	0.3	90.0	46.0	0.4	65.0	20	95	4.7	Turekian & Wadephl (1961)
WHO Standards[2]	0.01	0.003	0.05	2.0	0.006	0.07	0.1	5.0	n.s	WHO (2008)

Table 1: Reported mean concentrations (mg/kg, except iron) of selected HMs in bottom sediments.
n.s: not specified, [1]National environmental quality standard values for marine and freshwater sediments in the Nordic countries

[2]WHO standards guidelines for drinking water as of WHO (2008)

Therefore, the reference elements are presumably uniformly distributed in crustal rock sources and if the above mentioned assumptions are met, the effect of anthropogenic input of trace metals can easily be assessed and determined as extent of enrichment or Enrichment Factor (EF) using the reference element. In addition to the extent of enrichment, the geochemical accumulation of HMs in soils and sediments can be assessed using an index-based technique developed by Müller (1979).

Geochemical accumulation Index (I_{geo}) is linked to the background values of HMs in the earth's crust and their measured concentrations as shown in Equation 1 and the values obtained are interpreted in Table 2. The technique has been widely used to assess the effect of anthropogenic activities on the concentration of HMs in soils and aquatic systems. The combined of all metal pollutants can therefore be calculated using pollution load index (PLI) in the equation 2. However, the determination of EF as shown in equation 3 is more important than I_{geo} , because it shows the extent of accumulation or sedimentation with reference to a stable element (Nijeje et al., 2023; Amin et al., 2009) . Background values are important in the computation of EF and or I_{geo} and draw conclusions on whether there is contamination or not. Upon determination of pollution load index, decisive actions can be taken following the guide provided in Table 3.

$$I_{geo} = log_2 \frac{C_n}{1.5B_n} \qquad (1)$$

where C_n is the measured concentration of the examined metal n[th] metal in the sediments, and B_n is the geochemical baseline concentration of the metal n[th] metal of average shale.

Calculated I_{geo}		I_{geo} Class	Interpretation
>5		6	Very strongly polluted
4-5		5	Strongly to very strongly polluted
3-4		4	Strongly polluted
2-3		3	Moderately to strongly polluted
1-2		2	Moderately polluted
0-1		1	Unpolluted to moderately polluted
<0		0	Unpolluted

Table 2: Geo-accumulation index in relation to pollution level*
*Adapted from the literature (Amin et al., 2009; Osakwe, 2011)

EF	Severity	PLI	Action
>50	Extremely severe	≥100	Immediate action to

			ameliorate pollution
25−50	Very severe	≥ 50	More details needed to monitor the site
10−25	Severe	< 50	No need for drastic rectification measures
5−10	Moderately severe	-	-
3−5	Moderate	-	-
1−3	Minor	-	-
<1	No enrichment	-	-

Table 3: Interpretation of enrichment factor and pollution load index values**

**Adapted from the literature (Amin et al., 2009; Saleem et al., 2015)

$$PLI = \sqrt[n]{CF_1 \; x \; CF_2 \; x \; ... \; CF_n} \qquad (2)$$
Then, $CF = \frac{C_{metal}}{C_{base-line}}$

where CF = contamination factor; n = number of metals; C_{metal} = metal concentration in sediment sample; $C_{base-line}$ = base-line value of that metal.

$$EF = \frac{\left(C_x/C_{Fe}\right)sample}{\left(C_x/C_{Fe}\right)shale} \qquad (3)$$

where (C_x/C_{Fe}) and (C_x/C_{Fe}) are the sample and background average shale values, respectively, with metal concentration in (µg/g) dry weight and Fe levels in (%) dry weight in the sediment sample.

5. Speciation of Heavy Metals:

Speciation of an element can simply be defined as its ability to form different chemical compounds (Jenne, 1968; Tessier et al., 1979). Speciation of metals became a satisfying approach to understand their behavior in aquatic systems. This is because the use of total concentration as a criterion to assess the potential effects of sediment contamination implies that all forms of a given metal have an equal impact on the environment; such an assumption is clearly untenable (Sibomana et al., 2019; Nijeje et al., 2023).

In around 1970's, a successful chemical speciation technique was proposed by Tessier et al. (1979) to understand the fate of HMs by fractionating and extracting selectively five distinct chemical fractions, namely exchangeable metals, carbonate bound metals, Fe-MnO bound metals, organic bound metals, and residual fraction. Speciation procedure proposed by Tessier et al. (1979) has attracted attention and it was widely used by many researchers (Aigeberua et al., 2018; Matley and Gulson, 2003; Kraus and Weigand, 2006).

Since then, some researchers modified the extraction procedures proposed by Tessier and others (1979) to exploit more about the behavior of metals as shown in Table 4.

Speciation of an element constitutes to all its chemical compounds it forms. Common chemical forms of selected HMs in aquatic bottom sediments are provided in Table 5 as obtained from the literature. Analytically, the concept of speciation technique can be thought as the partitioning of a sample material containing an element of interest into specific fractions through which the chemical forms of that element can be extracted selectively by using appropriate reagents Nijeje et al. (2023). This helps an investigator to quantify the measurable quantities of the element of interest present in the extract. The sequential extraction procedure proposed by Tessier et al. (1979)   has been widely used to understand the mobility and bioavailability of trace metals. According to the author's extraction scheme, in each extraction step, measurable amounts of metals in question as a fraction are obtained.

In the first step, the exchangeable metal fraction is obtained followed by the carbonate metal bound fraction obtained in the second step. These two fractions can be more easily mobilized than the rest and become available to plants and animals, when the equilibrium concentration of the metal between water-sediment phases in these two fractions is disturbed by any change in ionic strength and pH change, respectively (Duan et al., 2019). In the third step, a fraction of metal bound to oxides of iron and manganese (Fe-MnO) followed by extraction of metal bound to organic substrates is examined in the last step. The metals in the residues obtained from the last step are extracted by acid digestion and named residual metal fractions, and this makes a total of five distinct fractions.

After understanding the precedent extraction scheme, different modifications were made to explore various chemical forms depending on one's interests. In this material, we briefly present the possible extraction schemes currently available in the literature, and all are summarized in Table 4. Generally, the total distinct metal fractions so far extracted ranges from four up to nine fractions. Collectively, despite their limitations, these techniques have been used to explain the mobility and biological availability of metals.

Fn	Type of metal species extracted in each single fraction	Sources
4	Acid soluble; reducible; oxidizable; residual.	Pueyo et al. (2001)
5	Exchangeable; carbonate bound; Fe-Mn oxides bound; organic matter bound; residual.	Tessier et al. (1979)
6	Exchangeable; carbonate bound; easily reducible; moderately reducible; oxidizable (organic + sulphides); residual.	Kersten and Föstner (1987)
7	Mobile; exchangeable; Mn-oxide bound; organic bound; amorphous Fe oxides bound; crystalline Fe oxides bound; residual.	Matley and Gulson (2003)
8	Mobile; exchangeable bound; Mn-oxides bound; OM bound; Fe-oxides (anthropogenic) bound; Fe-oxides (geogenic) bound; sulphide bound; residual.	Kraus and Wiegand (2006)
9	Water soluble; exchangeable; carbonate bound; plant available; Mn-oxide bound; amorphous Fe-oxide bound; crystalline Fe-oxide bound; organic matter bound; residual.	(Aigberua et al. (2018)

Table 4: Different sequential extraction procedures
Fn: number of fractions

5.1.   Different Chemical Fractions of HMs in Sediments:
5.1.1.   Acid Soluble Fraction:

The method to determine the metals present in this fraction was developed by the European Commission through Certified Bureau of Reference (BCR) after Tessier et al. (1979). It extracts all metals from 1 g dry sediments that are soluble in 1.11 mol. l^{-1} of acetic acid by continuous shaking for 16 hours at 22±5 °C overnight (Pueyo et al., 2001). It combines carbonates bound metals, exchangeable, and water-soluble metal fractions Saleem et al., 2015). The advantage of this combination extraction is that it is economically reasonable, because fewer reagents are used. However, it is time consuming and does not detail the fractionation information.

5.1.2.   Water Soluble:

Water soluble metals reflect normally all free metal ions and easily bound metals to soluble organic compounds. This fraction is the most mobile fraction, and hence metals in this fraction are available to biota and environment (Aigbrua et al., 2018; Nijeje et al., 2023). They can be extracted with distilled water at pH 7.0 with continuous shaking at room temperature for 2 hours. It is essential to determine the metals in this fraction to understand the direct effect on the environment, since it is mobile. The extraction was modified from Tessier et al. (1979).

5.1.3.   Exchangeable Fraction:

According to Tessier et al. (1979), exchangeable fraction is usually extracted with either magnesium chloride, $MgCl_2$ (1 M at pH 7.0) or sodium acetate solution, NaOAc, (1 M) at a pH 8.2 for 1 hour. Exchangeable fractions can also be extracted using ammonium acetate, CH_3COONH_4, at pH 7 for 2 hours (Duan et al., 2019; Sibomana et al., 2019; Nijeje et al., 2023). However, it was found to attack carbonate fractions Tessier et al., 1979). Generally, the exchangeable fraction refers to the metals directly adsorbed on sediments or on their major constituents (clays, hydrated oxides of iron and manganese, humic acids). They are held by weak electrostatic or weak Vander Waal's interactions (Aigberua et al., 2018), and changes in water ionic composition are likely to affect sorption-desorption processes and therefore these metals can be

exchangeable and are in equilibrium with the ionic content in water (Duan et al., 2019). Generally, this fraction is usually used to represent the environmentally available components (Peng et al., 2009).

5.1.4. Carbonate Bound Fraction:

Metal carbonates are generally chemical species which are stable in slightly acidic to basic conditions. The solubility of metal carbonates is strongly affected by pH changes. The equilibria between solid metal carbonates and their ionic species are complicated for metals whose oxidation is higher.

Metal carbonates can exist with hydroxides, and the solubility of metal carbonates becomes more complex, unless the equilibria are characterized. In addition, the speciation of these carbonates depends on carbonic acid dissociation equilibria. The fraction of metal bound to carbonates was found to be released in solution when continuously extracted with NaOAc acidified with HOAc solution (1 M) to pH 5.0 for 5 hours (Aigberua et al., 2028; Nijeje et al., 2023). Therefore, pH of the pore water will greatly affect the stability of this fraction.

5.1.5. Plant Available Metals:

The metals in this fraction are associated with metal-organic complexes in plant debris/slurry. This fraction is similar to the organically bound metal. Compared to refractory organic compounds and sulfides, this fraction is easily oxidizable (Aigberua et al., 2018). To extract this metal fraction, digestion using a mixture of acids, preferably hydrochloric ($0.025M$ HCl) and sulphuric acid ($0.05M$ H_2SO_4) for 30 minutes at 28^oC can be effective (Olutona et al., 2012; Aigberua et al., 2018).

5.1.6. Bound to Iron−Manganese Oxides (Fe-MnO):

The existence of oxides, hydroxides, and oxyhydroxides of Fe and Mn in nature as scavengers (nodules or cementing agents) tend to retain some trace metals (Duan et al., 2019). This fraction is also called reducible metal fraction. However, Mn is easily reducible, while Fe is moderately reducible. For this reason, Kersten and Förstner (1987) divided this fraction according to their ease to be reduced. Martley and Gulson (2003) expanded this fraction into three fractions as metals bound to manganese oxide, bound to amorphous iron, and bound to crystalline iron in order to understand the contribution of these species in controlling trace metals as stipulated in the study by Jenne (1968). Later on in 2006, Kraus and Wiegand (2006) discovered that the idea of Martley and Gulson (2003) was useful to differentiate HMs bound to anthropogenic (metal bound to amorphous iron oxide) from geologic (metals bound to crystalline iron xide) origin. This is true because under low acidic and reducing conditions, amorphous Fe–Mn oxyhydroxides would be dissociated and release the retained metals in the solution (Aigberua et al., 2018; Zang et al., 2017; Nijeje et al., 2023).

The easily reducible metal fraction (bound to Mn-oxides) is extracted using hydroxylamine hydrochloride in acidic medium (0.1 M of $NH_2OH.HCl$, pH 2 HNO_3), 12 hours, and for moderately reducible metal fraction (bound to iron) 0.1 M oxalate buffer pH 3, 24 hours is used. According to Nijeje et al. (2023), metals bound to

Fe-MnO are extracted with strong reducing agents of either 0.3 M of $Na_2S_2O_4$ (sodium dithionite) + 0.175 M of Na-citrate + 0.025 M of H-citrate, or 0.04 M of NH_2OH-HCl in 25% (v/v) HOAc at $96^{\circ}C$ for 6 hours.

5.1.7. Bound to Organic Matter and Sulphides:

HMs in this fraction are associated with various forms of organic material such as living organisms, detritus, or coatings on mineral particles through complexation or bioaccumulation process (Peng et al., 2009). It is also known as oxidizable fraction. It is extracted with double addition of 30% hydrogen peroxide acidified with HNO_3 (adjusted to pH 2) and 0.02 M maintained at 85 $^{\circ}C$ for an interval time of 2 hours (Nijeje et al., 2023). These metals can exist in sediments as long as the organic matter and sulfides they are bound to are still stable from oxidation. For persistent organic matter, these HMs can stay for a long time in sediments and will only be released on OM oxidation.

5.1.8. Residual Fraction:

Residual fraction can be defined as metals that failed to be extracted by the precedent extraction steps. These metals are normally present as stable, strongly held metals, which do not show significant transformation in various conditions in nature. They can be quantified as a difference of total metal digested without fractionation and the sum of metals in the other fractions (Sibomana et al., 2019). However, this does not give an exact value of the present metals in the residue, because the extraction procedure does not offer 100% extraction efficiency. It is important to consider the loss of sediments during the extraction steps. Therefore, digestion of the residue using a mixture of acids is needed to quantify the metals in this fraction as done by some investigators (Olutona et al., 2012; Aigberua et al., 2018). If digestion is not a good option, an X-ray fluorescence (XRF) can be used (Sibomana et al., 2019).

HMs	Chemical Reference Forms	
As	F6 > F2 > F3 > F5 > F4 > F1	Aigberua et al. (2018)
Cd	F6 > F3 > F5 > F2 > F4 > F1	Sibomana et al. (2019)
Cu	F6 > F5 > F4 > F3 > F2 > F1	Tessier et al. (1979)and Sibomana et al. (2019)
Cr	F6 > F1 > F5 > F4 > F3 > F2	Nijeje et al. (2023)
Pb	F6> F4 > F5 > F3 > F2 > F1	Baran et al. (2019)
Hg	F6 > F5 > n.i	Giordano et al. (1992)
Ni	F6 > F5 > F3 > F2 > F4 > F1	Sibomana et al. (2019)and Nijeje et al. (2023)
Zn	F3 > F4 > F2 > F5 > F6 > F1	Olutona et al. (2012)
Fe	F6 > F4 > F5 > F3 > F2 > F1	Nijeje et al. (2023)

Table 5: Prevalent chemical forms for selected HMs in aquatic bottom sediments**.**
Note: F1: Waster-soluble; F2: Exchangeable; F3: Carbonate bound; F4: Bound to Fe-Mn Oxides F5: Organically and sulfide Bound; F6: Residual (other forms, e.g.: elemental); n.i: not identified

The use of sequential extraction procedure developed by Tessier et al. (1979) won the most popularity among different users, although more time consuming, furnishes the main information about the origin, mode of occurrence, biological and physico-chemical availability, mobilization, and transport of HMs. However, the author's method cannot explain water-soluble metal fraction (the most available), which can be used to justify the mobility and bioavailability of metals in sediment pore water. Therefore, water-soluble metal fraction together with other fractions proposed by Tessier et al. (1979) could be essential to understand the mobility and bioavailability of the metals in question.

5.2. Factors Influencing Speciation of HMs:

Sediments act as temporally immobilizing substrates of HMs in aquatic systems. In fact, a subsequent change in time of the physico–chemical as well as biological characteristics of both sediment and overlying water conditions will eventually cause some HMs re-enter the overlying water and may become environmentally available. Therefore, the speciation of HMs could be influenced by any of the factors categorized as pH, organic matter content (OM), reduction-oxidation potential (ORP) and other factors.

5.2.1. Influence of pH:

Potential in Hydrogen (pH) which is minus logarithm of the concentration of H^+ ions present in a matrix, is a measure of acidity that can be interpreted using a pH scale of 0 to 14. It is measured by a selective ion (H^+) glass electrode, and it is linked to redox potential by Equation 4.

Lower values of pH below 7 indicate higher acidity (lower basicity), a pH of 7 indicates neutral, and higher values of pH above 7 indicate lower acidity (higher basicity). Lowering of pH towards smaller values in sediments could cause the solubility of immobilized metals (Duan et al., 2029). In the bottom sediments, the pH maybe lower than the overlying water due to natural degradation of OM and the oxidation of acid volatile sulphides (AVS) as shown in Table 6. The pH of sediments may initially drop from neutral to acid, sometimes even decreasing to pH 1.2, which often results in some metals being released into water again even under stable water conditions (Peng et al., 2009).

$$E_m = E^0 - 2.3 \frac{RT}{F} pH \qquad (4)$$

Where E_m is the measured redox potential (potential difference between Ag/AgCl /solution and the Ag/AgCl/KCl reference electrode), E^0 is the standard (when the activity is 1) redox potential, R is the molar gas constant 8.314 $Jmol^{-1}K^{-1}$, T is the temperature in Kelvin and F is the Faraday's constant 96,485 C, and 2.303 is the conversion factor from natural to common logarithm (as $pH = -log\ a_{H^+}$) and a_{H^+} is the activity of hydrogen or hydronium ions which is equal to its concentration in diluted solutions of concentrations << 1M.

In fact, a pH decrease (increase in [H^+]) in sediments would cause the competition between H^+ and metal cations for an active site at the adsorbent interface or for available ligands (e.g. OH^-, CO_3^{2-}, SO_4^{2-}, Cl^-, S^{2-} and phosphates) with significant effect.

This competition would lead to a decrease in the adsorption capacity of sediment adsorbents towards the heavy metal cations. In effect, the mobility and bioavailability of the metals would then increase (Chuan et al., 1996). A study conducted by Sekomo (2011) on the effect of pH on the adsorption of four HMs showed that at pH 4, only Pb (II) was adsorbed and at pH 6, all four metals (Cd(II), Cu(II), Pb(II) and Zn(II)) were adsorbed on the adsorbent. He explained that near-neutral pH is favorable to the adsorption process because it is mainly due to displacement of the water equilibrium towards the predominance of [HO^-] ions. The behavior shown by Pb could be explained by the fact of competition between H^+ and Pb(II).

Due to the nature of every metal cation, there exists a specific pH controlling heavy metal mobility in bottom sediments. This means that the metal would be released only as its specific pH value is achieved. Therefore, under similar pH values the potential mobility of HMs in bottom sediments is significantly different. For instance, the potential mobility of these metals decreases as follows: Zn > Cd > Ni > Cu > Pb, at pH 4 (Peng et al., 2009, Sekomo et al., 2012).

5.2.2. Organic Matter (OM):

The eutrophication of water bodies often involves increased input of nutrients that results in an increase in primary production (i.e., fixation of CO_2) within the system, and if the increase in primary production are not balanced by organic matter degradation and outflow, an accumulation of organic-rich sediments can occur Gale et al., 1992). According to Gale et al. (1992), the rate and extent of organic matter decomposition in sediments is governed by the quantity and quality of organic matter present. In oxidizing conditions, organic substances are easily degraded. Thus, organic matter serves as a primary source of electrons in sediments.

Under anaerobic conditions, OM degradation can be thought of as a stepwise process where cellulose is converted to simple sugars, simple sugars to organic acids, and organic acids to CO_2 and CH_4, and any one of these steps can be rate limiting in anaerobic environments. Mainly, the role played by OM in sediments is to fix HMs by adsorption, chelation, or complexation mechanisms (Khan et al., 2012).

It is obvious that the increase in OM would also increase the fixation of HMs. However, the solubility and degradation of OM in sediments depends on pH and redox potential (DeLaume et al., 1981). And this would directly determine the overall mobility and availability of the bound HMs. Higher positive redox potential and lower pH values deplete OM (Eggleton and Thomas, 2004).

The binding of metals to soluble organic matter (dissolved organic carbons) enhances their mobility, whereas the binding to insoluble OM would lower the metal mobility. Likewise, the degradation of OM would lower their concentrations, which would therefore release some metals in sediments pore water or overlying waters (Malik et al., 2015). In natural waters, OM may appear as humic substances (humic acid, fulvic acid, humin) where they participate

in complexation reactions with HMs (Jackson et al., 1978). Therefore, HMs and OM complexation interactions are usually recognized as the most important reaction pathway determining, to a large extent, the speciation and bioavailability of HMs in natural water environment (Peng et al., 2009).

5.2.3. Redox Potential (ORP):

Redox or reduction-oxidation potential, sometimes shortened as 'ORP' is a measure (in Volts) of the tendency or the ability of a chemical species to gain electrons from or to lose electrons to an electrode and thereby be reduced or oxidized respectively. This measure shows how participating species in a redox reaction, such as that illustrated in Equation 5, compete for electrons. In general, to measure the redox potential of sediments and soils, an inert electrode (e.g.: platinum electrode) is inserted in filtrates made by mixing 1:1 sediment/soil: water, and connected to a half-cell reference electrode such as standard hydrogen electrode (SHE), saturated calomel electrode (SCE) or Silver-Silver Chloride saturated in KCl by a salt bridge and the circuit is completed by a high impedance voltmeter to record potential difference (E_m) between the two electrodes.

$$Ox + mH^+ + n\bar{e} \rightarrow Rd \tag{5}$$

Where Ox is the oxidized component or electron acceptor, Rd is the reduced component or electron donor; m is the number of hydrogen ions involved in the reaction and n is the number of electrons gained or lost in the redox reaction.

When other reference electrodes other than SHE are used, adjustment of the measured potential (E_m, mV) to SHE should be done by adding the reference redox potential (E_{ref}) of 199 mV (for Ag/AgCl/KCl) or 244 mV (for SCE) to E_m as shown in Equation 6. Experimentally, a $f_T(298 - T_m)$ product is added for the temperature compensation effect, where f_T is 0.7 and T_m is the measured temperature in Kelvin (Virtanen et al., 2015). Similarly, since redox potential is a function of pH of the medium, it essential to be taken into account. According to Abraham et al. (Abraham et al., 2015), E_h in the equation 6 can further be simplified and standardized to a fixed pH (such as pH 7) for easy reporting of the results as shown in Equation 7. Hence, E_h measurements should be accompanied by further information on the pH value and temperature at which they were taken.

$$E_h(mV) = E_m + E_{ref} + f_T(298 - T_m) \tag{6}$$
$$E_{h7} = E_h - [(7 - pH) \times \alpha] \tag{7}$$

Where E_{h7} is the redox potential at the pH 7, E_h is the redox potential at any measured pH of the medium, and α is the regression factor, which must be determined experimentally for each medium. According to the Equation 7 a pH variation of one unit modifies E_h by approximately α mV.

It should be well understood that sediment reduction-oxidation potential is a net redox potential contributed by every redox couple in the sediment system, and it is a measure of electron availability or deficit. The presence of strong oxidizing species in the sediments determine the overall redox potential in that sediments. Oxygen is the primary terminal electron acceptor (TEA) for the

microbial respiration chain (Virtanen et al., 2015). Unlike in standing waters, fast-flowing water bodies such as rivers are constantly moving and mixing. Depending on the depth of the river, the distribution of dissolved oxygen gradually decreases as you go deeper, making sediments more less in oxygen, hence some metals are mostly in their reduced form.

In the absence of oxygen, secondary TEA such as nitrates and manganese (IV) oxides, oxides of iron, sulphates, and CO_2 can, respectively, accept electrons. In anaerobic sediments (low redox potential), acid volatile sulphide (AVS) is a key component controlling the activities of some divalent cationic metals, usually present naturally (Nijeje et al., 2023; Peng et al., 2009) . The most reactive and abundant geological iron bound to these sulphides is iron monosulphide, FeS (Virtanen et al., 2015). Other sulphides such as the iron disulphide (pyrite, FeS_2) and elemental sulphur (S_8) also play a role in redox reaction in sediments as shown in Table 6. Theoretically, Peng et al. (2009) explained that in presence of divalent metals such as Cu, Ni, Pb, Cd, Zn, iron in iron sulphides is displaced by these divalent metals forming more stable metal sulphides and releasing Fe^{2+} cations to the aqueous phase. The displacement reaction does not involve electron transfer.

However, the stability of the resulting metal sulphide (MS) could be explained by its stability constant, K_s(MS). For instance, Cu^{2+} and Zn^{2+} have higher stability constants for sulphide (CuS (log K_s =−35.96) and ZnS (log K_s =−21.97) than FeS; thus, Cu^{2+} and Zn^{2+} will displace the Fe from FeS to form CuS and ZnS respectively as shown in Equation 1 in Table 6, and the resulting MS will be oxidized to form acidic sediments (Peng et al., 2009; Duan et al., 2019).

Reaction	Equation number
$M^{2+}+FeS \rightarrow Fe^{2+}+MS$	(1)[c]
$MS+ 2NO_3^- +4H_2O \rightarrow M(OH)_2+ SO_4^{2-} + N_2 +6H^+$	(2)
$CH_2O + 4Fe(OH)_3+ 8H^+ \rightarrow 4Fe^{2+}+ CO_2+11H_2O$	(3)[a,b]
$2CH_2O+ SO_4^{2-} \rightarrow H_2S + 2HCO_3^-$	(4)[b]
$Fe^{2+}+ H_2S \rightarrow FeS + 2H^+$	(5)[b,c]
$FeS + H_2S \rightarrow FeS_2 + H_2$	(6)[b]
$5FeS+ 9NO_3^- + 8H_2O \rightarrow 5 Fe(OH)_3 + 5SO_4^{2-} + 4.5 N_2 + H^+$	(7)[b]
$FeS_2 + 3NO_3^- + 2H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 1.5 N_2 + H^+$	(8)[b]
$FeS + 1.5MnO_2 +3H^+ \rightarrow Fe(OH)_3 + S^0 + 1.5Mn^{2+}$	(9)[b]
$FeS_2 + 7.5 MnO_2 + 11H^+ \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 7.5Mn^{2+} +4 H_2O$	(10)[b]
$FeS_2 + 14 Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$	(11)[b]

Table 6: Selected redox reactions that occur in anaerobic soil and sediments.

[a]DeLaune and Reddy (2005), [b]Virtanen et al. (2015), [c]Displacement reaction

The oxidation of metal sulphide can be predicted by equations in anoxic sediments in the equations (7-11) in the Table 6 above. In general, this oxidation leads to an acidic medium in the sediment pore water that eventually causes the release of secondary adsorbed HMs (Peng et al., 2009). A decrease in the redox potential of bottom sediments increases some heavy metal mobility, such as Cd, Zn, Ni, Pb, Zn, and Fe, while an increase decreases their mobility (Aigberua et al., 2018 Duyan et al., 2019; Nijeje et al., 2023) . Therefore, the redox potential can be used to understand the speciation of HMs.

5.2.4.   Other Factors:

Apart from the main factors already mentioned, the literature (Peng et al., 2009; Sekomo et al., 2012; Duan et al., 2019) suggest other factors that can affect the speciation or distribution of HMs. These factors include temperature, sediment particle size, retention time, dissolved oxygen (DO), salinity, metal species, and biological content. Temperature can be linked to adsorption mechanism and organic matter decomposition in sediments. The increase in temperature was found to decrease the adsorption capacity of sediment content (Sekomo et al., 2012) . Moreover, the influence of temperature on the distribution of HMs can indirectly be linked to the mineralization of organic matter as it has been shown to influence OM decomposition rates, with rate constants doubling for every 10 °C rise in temperature (Gale et al., 1992). Higher decomposition rates would cause depletion of organic matter leading to fixation of lower metals (Barfan et al., 2019). Hence, temperature is a thermodynamically controlling factor of many reactions involving metals.

Furthermore, adsorption is also a time-dependent phenomenon. Contact time between metals and adsorbent increases the adsorption rate. Sekomo et al. (2012) studied the adsorption kinetics of four selected HMs (Cu, Cd, Zn, Pb) for a contact time ranging from 1 to 120 hours by monitoring the percentage removal of HMs by the adsorbent. He found that metals were adsorbed at higher contact time until the equilibrium sorption was reached. Moreover, the data from the studies of Muhammed (1991) indicates that lead adsorbs more strongly than copper, cadmium, zinc, and nickel and the relative affinity of soils for various HMs increases in the following order: $Pb > Cu > Cd > Zn > Ni$ in just 15-20 minutes.

DO contributes to the distribution of metals in all media. This is because oxygen acts as the primary terminal electron acceptor for the microbial respiration chain (Virtanen et al., 2015; Nijeje et al., 2023). In the presence of oxygen in surface waters, the oxides, hydroxides, and oxyhydroxides of some metals precipitate and therefore, would settle as particulate and become part of bottom sediments. In aerobic conditions, it has been proposed that oxides of iron and manganese play a major role in the scavenging of trace amounts of HMs and make them less available to the environment (Nijeje et al., 2023).
Iron oxides collectively include hematite (Fe_2O_3), iron hydroxide ($Fe(OH)_3$), and iron oxyhydroxides (FeOOH). Since the redox potential is directly proportional to DO, the scavenged HMs would be released at very redox potential and pH conditions which would

be attained in reducing conditions or absence of oxygen (DeLaume and Reddy, 2005).

Cation exchange capacity (CEC) of sediments also affects the distribution of HMs. Due to the differences in affinity between cations and cation exchangers (sediments), their mobility would differ accordingly. Peng et al. (2009), said that Zn would be more mobile than Cd due to its lower affinity than Cd.   Equally important, when salinity (e.g.: $Mg^{2+}[Cl^-]_2$) increases in pore water, the adsorbed HMs would decrease due to competition between Mg^{2+} and heavy metal cations (M^{n+}) at the adsorption sites causing the reverse reaction of the Equation 8 would occur. Similarly, the chloro-complexation associated with M^{n+} could lead to their mobility.

On the other hand, the effect of sediment particle size on the adsorption of HMs would be explained by the surface area. The smaller the particles, the larger the surface area, and therefore the higher the adsorption capacity of the particles. Among the sediment particles, clays have smaller fine particle size containing higher amounts of iron and manganese than coarse sand (Zaki et al., 2017). Recently, in 2019, Abbott et al. proposed that the balance between dissolution and authigenesis controls the concentration, ratio of heavy and light rare earth metals abundances, and the isotopic composition of the pore waters. The authors concluded that clay mineral dissolution and authigenesis are likely the primary influences on the rare earth metals cycling near the seafloor. Therefore, sediments with higher proportion of clay content would have a more significant effect on speciation and distribution of HMs than sand-rich sediments.   According to Pentreath (1985) , HMs can also be associated with the clay substrates in the sediment matrix by ion-exchange reactions as shown by the following simplified reaction in Equation 8.

$$M^{n+} \quad + \quad [X(Clay)_n] \quad \rightleftharpoons \quad [M(Clay)_n] \quad + \quad X^{n+} \tag{8}$$
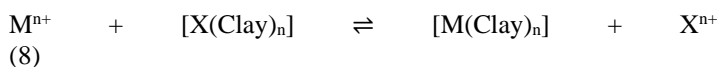
where "clay" represents an alumino-silicate particle surface with negatively charged exchange sites. M^{n+} is the heavy metal cation and X is any exchangeable metal cation such as magnesium.
Furthermore, biological content in sediments can also be indirectly linked to heavy metal distribution. For example, higher microbial activity in sediments increases biotransformation of organic matter, which in turn affects the metal distribution (Gale et al., 1992). HMs in sediments can be removed by organisms through uptake pathways such as direct absorption through their tissues and ingestion (Nabulo et al., 2008;, Tangahu et al., 2011). When these organisms die, they release the metals back into sediments and/or water (Nijeje et al., 2023) . Therefore, organisms play a part in heavy metal recycling in bottom sediments (Duan et al., 2019).

6. Mobility and Bioavailability of HMs in Aquatic Ecosystems:

HMs in aquatic environments essentially come from both natural and anthropogenic sources. Weathering coupled with soil erosion are the most natural phenomena that feed aquatic systems with heavy metal contaminants (Nijeje et al., 2023). On the other hand, industrial wastes and products containing HMs eventually end in

natural waters by different transport means such as air, water runoffs, and animals. The fate of HMs in aquatic ecosystems can be explained by their chemical speciation, which results into their transport across the water−sediments interface, and become either available or immobile.

Water bodies play an important role in different ecosystems (Sibomana et al., 2019). This is because all ecosystems are interconnected by either energy or nutrients flow (Eggleton and Thomas, 2004). Aquatic ecosystem is therefore not self–contained, and it can be connected to terrestrial ecosystems. This interconnection eases the transport of contaminants such as HMs in the form of dissolved nutrients for plants or contaminated food as energy for animals. If we draw a line on a freshwater aquatic ecosystem (lotic, lentic, and wetland), the fate of HMs can be thought as that complex interaction between them and the components of the aquatic environment that involves the contaminant transport and transformation through different pathways as shown in Figure 1.

Speciation will determine which pathway is favorable to the metal contaminant. For example, metals bound to dissolved organic carbon (Me-DOC) and in their dissolved chemical form which constitutes wholly to dissolved metal (DM) form can be transported between pore water in the surficial sediments and overlying waters as shown in Figure 1. Equally important, the insoluble forms of metals that involves carbonate bound, bound to Fe-MnO, bound to insoluble organic carbon, and other particulate forms (Me-particulate) will settle at the surficial sediments, may resuspend back to overlying water, or be buried in anoxic subsurface sediments. When sediment environment conditions change, the HMs can again be mobilized back to overlying water (Duan et al., 2019; Nijeje et al., 2023). Speciation techniques separate metal fractions according to their mobility or solubilities. Unlike water-soluble metal fraction which is already mobile, the exchangeable metal fraction and carbonate fraction are easily mobilizable. This is because the perturbation in sediment pH can directly mobilize the bound metals in aqueous phase and eventually become available to and bioaccumulate in aquatic organisms.

According to literature (Aigberua et al., 2018; Sibomaman et al., 2019; Nijeje et al., 2023), the order of mobility of the metals considering their abundance in the fractions is: water-soluble (F1) > exchangeable (F2) > bound to carbonate (F3) > bound to oxides (F4) > bound to organics (F5) > residual (F6). To determine the relationship between the mobility of a metal and its bioavailability, the mobility factor (MF) is determined and is defined as a percentage ratio of the summation of mobile fractions to the summation of all fractions (Nijeje et al., 2023). The MF is a measure of the potential mobility of a metal to become bioavailable in the environment and thus, a significant increase in MF (in percentage) of the metal would literally indicate a potential threat to the environment (Achi et al., 2011; Saleem et al., 2015; Aigberua et al., 2018). As shown by the Table 5, the order of chemical mobility of the selected HMs is Zn > Cr > As > Cd > Pb > Cu > Fe > Ni > Hg. Apart from lotic freshwater ecosystems (fast-flowing water bodies such as rivers), metal contaminants can be transported to other aquatic ecosystems such as wetlands. Toxic HMs have been identified in natural wetlands that are located in the nearby

river water catchments, where they bioaccumulate in the living tissues of fish and plants and this leads to negative impacts as they enter in the food chain.

The toxicity of a given heavy metal in the aquatic systems depends on the concentration of its available form (WHO, 2008; Dana et al., 2015; Huseen and Muhammed, 2019). Sekomo et al. (2011) , reported some HMs (Cd, Cu, Pb, and Zn) accumulation being the highest in sediments followed by accumulation in the roots of *C. papyrus*.
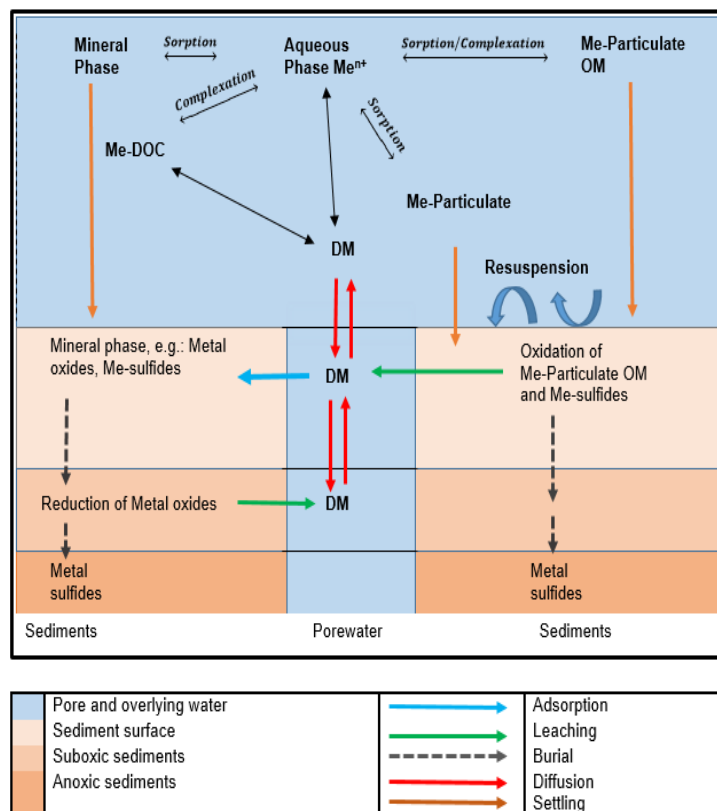
Figure 1: Transport and transformation of HMs in sediments modified from literature (Eggleton and Thomas, 2004; ,Duan et al., 2019)

According to Sekomo et al. (2011) , apart from Cu and Zn, other HMs (Cd, and Pb) concentrations were found high in fish (*Clarias sp., Oreochromis sp.*), and *Oligochaetes*. Sekabira et al. (2010) also reported higher levels of HMs (Pb, Cd, Cu, Zn, Mn) and iron (Fe) sequestrated in plant parts (leaves, stem and roots): *Commelina benghalensis (L.)* and *Cynodon dactylon (L.)* that grow in different polluted sites along the urban stream sediments of the Nakivubo drainage ecosystem in Kampala with bioaccumulation factor for Cd, Pb, and Zn in both plants. If any part of these plants or fish are eaten by domestic herbivores or human beings, they eventually enter into their bodies through ingestion, where they bioaccumulate (Dan et al., 2015). Thus, the accumulation of toxic HMs in organisms is perhaps the most concern of every individual.

7.   Remediation Technologies of Heavy Metals:

The failure to control heavy metal contamination in aquatic

reservoirs beyond permissible limits may lead to health problems to both aquatic wildlife as well as humans. The issue of heavy metal contamination in sediments has led to several studies on how to get rid of them; eventually different remediation technologies have been developed. Peng et al. (2009) categorized these remediation technologies as *in-situ* and *ex-situ* as applied for slightly and heavily polluted sediments, respectively. Traditionally, the most commonly used approach has been the removal of contaminated sediments by dredging and excavation and disposal/treatment off-site (Olsen et al., 2019).

Through technological advancement, after the removal of sediments from the water body, the sediments undergo some of these *ex-situ* treatments such as washing, electrochemical separation, thermal treatment, ultrasonic assisted extraction, or immobilization of dredged sediments. However, despite the fact that most *ex-situ* remediation technologies for soil or mineral ores can be used for dredged sediments, different authors (Peng et al., 2009; Khalid et al., 2017; Olsen et al., 2019) have claimed many disadvantages of *ex-situ* technologies including higher treatment costs, complexity, and aquatic ecological disruption. This is because of a higher volume of sediments to be treated and the lack of enough machinery resources to apply these technologies, especially in both undeveloped and developing countries.

Marine sediments are naturally important habitats for aquatic organisms. For these reasons, polluted sediments should be treated *in-situ* to maintain the proper functioning of the aquatic ecosystems. According to Akcil et al. (2015), the main advantages of *in-situ* remediation are: relatively inexpensive, usually results in less resuspension of contaminated sediments than removal technologies, poor environmental conditions for treatment treats, does not contain, contaminants and reduces handling and exposure of sediments. On the other hand, the disadvantages include lack of process control, poor environmental conditions for treatment, lower treatment efficiency than *ex-situ* treatment, and limited experience with *in-situ* treatments. Moreover, while it is inappropriate to apply neither ex-situ nor *in-situ* technologies, the natural treatment and land use control measures are needed to protect the aquatic environment (Olsen et al., 2019).

The monitored natural recovery (MNR) has been developed along with erosion controls to counteract further sediment contamination in some countries. The following discussion sections will provide some information on *in-situ* and monitored natural recovery as the best choice to get rid of HMs in sediments and soils and their comparisons are given in Table 7.

7.1. *In-situ* Amendment:

Unlike *ex-situ* remediation technologies which mostly focus on the separation of HMs from sediments, *in-situ* remediation technologies aim at improving metal stabilization/ immobilization, in which mainly by enhancing metal sorption, precipitation and complexation capacity in sediments, the potential mobility or bioavailability of toxic metals to the environment are lessened (Peng et al., 2009). These remediation technologies (*in-situ*) are: sediment capping, use of active materials (adsorbent), stabilization, beneficial importance such as gaining new land (; Akcil et al.,

and bioremediation and are, respectively, discussed.

7.1.1. Capping of Contaminated Sediments:

Capping is one of the *in-situ* amendment technologies. Capping involves the placement of one or several layers of clean (inert or active) material over the contaminated sediments with the purpose of reducing the dispersal of contaminants to a level that is environmentally acceptable, and to reduce the exposure of benthic fauna to an acceptable level (Olsen et al., 2019). These clean materials may range from clay, sand, gravel to fine stone. The efficiency of the technique increases with the increasing thickness of the capping layer. When properly designed, it can reduce the transfer rate of metals from sediments to overlying water. For example, Peng et al. (2009) argued that a good cap thickness was approximately 50 cm; and through capping the sediments by sand materials, the heavy metal concentration in water could be reduced to 80%.

7.1.2. Active Materials (sorbents):

Another *in-situ* amendment technology is the use of active materials (sorbents) in contaminated sediments. Sediment capping offers some disadvantages including resuspension of contaminated sediments in the water column, contaminated sediment residuals, contaminant transport through the cap and destruction of existing benthic ecosystems, new techniques offering greater flexibility in contaminated sediment management have been developed (Olsen et al., 2019).

This technique allows the use of minerals with higher sorption capacity, lower solubility, higher stability under reducing and oxidizing conditions, and lower cost (Duan et al., 2019; Olsen et al., 2019; Irshad et al., 2020). In sand capping, the immobilization of metals in sediments maybe low, and the sorbents used in this technique need to be added in active caps that are designed to use active materials.

Most commonly used clean materials include activated carbon, apatite, zeolite, and organoclay to strengthen their adsorption and degradation capacity (Virtanen et al., 2015). Natural geological materials such as volcanic rocks have been proven effective for the removal of HMs from textile wastewater (Sekomo et al., 2012). Through these fixing processes, apatite minerals can effectively immobilize and reduce both the mobile metal fractions of Pb, Cu, Cd, Zn, Ni and their bioavailability to benthic organisms in polluted sediments (Peng et al., 2009; Olsen et al., 2019).

7.1.3. Stabilization:

Unlike other *in-situ* amendments which immobilize HMs, this technique stabilizes the sediment and its matrix to increase the physical strength of the sediments, reduce the permeability, and reduce the leakage of some contaminants (Olsen et al., 2019). Under this technique, we have cement stabilization and redox stabilization to prevent the formation of methylated mercury. Although it is a very costly method, cement stabilization offers

2015; Khalid et al., 2017). However, in some cases, the chemical

composition of the cement can disrupt the aquatic life.

On the other hand, redox stabilization involves the introduction of a redox buffer into the polluted sediments to prevent any significance changes that may cause immobile HMs to become mobile under increased redox potential, for instance for contaminated sediments with mercury. This buffer is composed of $FeOOH$, MnO_2, or NO_3^- (Olsen et al., 2019).

7.1.4. Bioremediation:

The increasing need to fully maximize the efficiency and effective means of heavy metal remediation in the aquatic environments has led to the exploitation of biological processes whereby selected microbes or plants (phytoremediation) are applied in this technique.

For microorganisms, they usually combine this technique with amendments such as capping where the microbes mobilize inactive HMs by destroying the adsorbents to which these metals are bound, thereby making them available to the capping systems. Capping systems contain different sorbents and microorganisms (Olsen et al., 2019). On the other hand, the selected plants are used to absorb HMs from polluted soils and waters. In this process, the selected plant: extracts, sequesters, and/or detoxifies metal pollutants from contaminated sediments.

Tangahu et al. (2011) depicted the uptake mechanisms of both organics and inorganics contaminants using phytoremediation technology. Both organic and inorganic contaminants uptake occur similarly by phytostabilization, rhizofiltration, phytodegradation, and phytovolatilization; the difference being rhizodegradation and phytoaccumulation for organic and inorganic contaminants respectively. Some plants accumulate extremely high levels of specific trace metals, and those accumulating more than 1.00 mg/g of dry weight are called hyperaccumulators (Manahan, 2000).
Nickel and copper both undergo hyperaccumulation in some plant species. As an example of a metal hyperaccumulator, *Aeolanthus biformifolius DeWild* growing in copper-rich regions of Shaba Province, Zaire, contains up to 1.3% copper (dry weight) and is known as a "copper flower". In most literature, the authors (Peng et al., 2009; Dana et al., 2015; Olsen et al., 2019) agree that phytoremediation is an environmental friendly, effective and affordable technological solution used to extract or remove inactive metals and metal pollutants from contaminated soil and water.

In the review of Tangahu et al. (2011) some of the investigated plants on field trials for polluted water phytoremediation include aquatic plant species, *Lepironia articulata*, *Pandanus helicopus*,

Scirpus grossus, *Cabomba furcata*, and *Nelumbo nucifera* (on Cd, Cu, and Pb); for polluted soils are terrestrial Willow (Salix spp.) on Ni, Cu, Cd, Zn and *Paulowni fortunei* (seem) on Cu, Pb, Cd, and Zn. Although most of the plants used in phytoremediation are applied on polluted soils, more researches are still being done on the effectiveness of other plants to remediate HMs from polluted water and sediments.

7.2.   Monitored Natural Recovery (MNR):

Though cost effective and environmentally friendly, all technologies do not offer 100% efficiency. In addition, continuous pollution of sediments in rivers would eventually reduce the effectiveness of *in-situ* amendment technologies. In some countries, the natural treatment methods coupled with land use measures are applied. Using natural processes, the monitored natural recovery is a solution to polluted sediments (Khalid et al., 2017).

During natural attenuation, pollutants are transformed to less harmful forms or immobilized by a wide range of processes that include biodegradation, dispersion, dilution, sorption, volatilization, radioactive decay, and chemical or biological stabilization, transformation, or destruction of contaminants (Khalid et al., 2017; Olsen et al., 2019).

Some users of this method may apply some amendments or active materials along with MNR to enhance its efficiency in removing HMs over time. Perhaps the enhanced MNR (EMNR) improves its selective capacity for a particular contaminant depending on the material applied along with. However, the use of MNR/EMNR requires adequate control practices on the sources of contaminants such as soil erosion control and integrated waste management (IWM). Moreover, the aquatic systems, including river, streams, lakes, and oceans under MNR should be free from any disturbing activities and therefore, good practices of catchment management and buffering of the water bodies are considered effective for the restoration of natural resources (Khalid et al., 2017) .

Therefore, this review revealed the cost involved, long-term effectiveness, general acceptability, applicability to high metal, and multimetal contaminated sites, which are the key factors that affect the applicability and selection of remediation technologies as shown in Table 7. The cost for removal of HMs in contaminated sediments by each technique can be minimized by gaining a better understanding of the mechanisms/processes involved in remediation through research works and the various options available at different steps during remediation

Technique	Advantages	Limitations	Applicability	Acceptance	Multi-metal sites
Capping	Prevent off-site transport of HMs, Effective for highly contaminated soils and sediments.	Costly, soil clean up still needs further engineering measures, effectiveness varies with the type of capping barriers.	Small scale, and short to long term.	Very low: limited to highly contaminated soils and sediments	Effective
Use of active sorbent materials	Fast and easy applicability, relatively low costs, covers a broad spectrum of inorganic pollutants.	Temporary solution and permanent monitoring are necessary.	Small to medium scale and short-term	High public acceptability	Can be effective. Depends on the type of soils and sediments, metal and sorbents materials.
Stabilization	Fast and easy applicability, relatively low costs, covers a broad spectrum of inorganic pollutants.	Temporary solution and permanent monitoring are necessary.	Small to medium scale and short-term	High public acceptability	Can be effective. Depends on the type of soils and sediments, metal and immobilizing amendment.
Bioremediation	Economical and less disruptive.	Temporary solution, effectiveness varies with soils and sediments, plant and metal type.	Small to medium scale and short-term	Medium public acceptability	Very low, but use of microbes is more effective than phytoremediation.
Monitored Natural Recovery	Economical and less disruptive.	Temporary solution and permanent monitoring of sources is necessary.	Within reasonable Timeframe	High public acceptability	Depends on natural processes to decrease chemical contaminants in sediment to acceptable levels within a reasonable timeframe.

Table 7: Comparison of different soil and sediments heavy metal clean-up methods*
*Adapted from the literature (Peng et al., 2009; Khalid et al., 2017; Olsen et al., 2019)

8. Analysis of Heavy Metals:

The quantitative analysis of a heavy metal associated with each fraction can be analyzed using a preferable analytical method. The growing realization of the importance of even extremely small amounts of HMs in the environment has led to ever-increasing demand for the determination of these metals at trace level concentrations, and the levels to be detected range from parts per million to parts per billion (Muhammed, 1991). To achieve this, robust methods of high sensitivity and selectivity were developed. The selection of a suitable method also depends on its accuracy and reliability and preferably they should also be convenient and economical. These methods include but not limited to atomic absorption spectroscopy techniques (AAS), X-ray fluorescence spectroscopy, neutron activation analysis, and electroanalytical techniques (Siboimana et al., 2019). The capabilities and limitations of each method make it suitable for a given analyst. However, atomic absorption spectrometry (AAS) is the most frequently used method, because it combines high sensitivity, selectivity, simplicity with low cost, routine application, and speed of analysis.

8.1. Atomic Absorption Spectroscopy (AAS):

Atomic spectroscopy is a technique for determining the elemental composition of an analyte by its electromagnetic or mass spectrum (PerkinElmer, 2018). There are four atomic absorption spectroscopic techniques, namely, flame atomic absorption spectroscopy (FAAS), graphite furnace atomic absorption spectroscopy (GFAAS), inductively coupled plasma optical emission spectroscopy (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS). When studying trace metals, a technique of the highest selectivity and lowest detection limit would be preferred. According to PerkinElmer (2018), the lower detection limits of all techniques are in the order of ICP-MS>GFAAS>ICP-OES>FAAS. Although FAAS has a lower detection limit compared to the rest others, its environmental detection limit is accepted by many agencies.

FAAS is a popular method due to the fact that it is very easy to use, widely accepted, extensive application, information available, and relatively inexpensive, but has low sensitivity, single-element analytical capability, and cannot be left unattended to. Levinson (2002), provides comprehensive techniques of analyzing elements using Flame Atomic absorption spectroscopy.

The working principle of this analytical instrument is that the flame aspiration technique is applied for the atomization (a system to produce free atoms) of the sample, and hence the name 'Flame' comes into existence. It measures the concentrations of a chemical element (analyte) in a sample by using specific wavelengths of light emitted by atoms of the similar element from a lamp to be absorbed by the analyte in the sample. This wavelength corresponds to the energies needed to promote electrons from one energy level to the next higher energy level (Agilent, 2017). Atoms of different elements will always absorb in specific wavelengths of light.

When analyzing a sample for a particular element, a light beam from that element is normally used (Levinson, 2002; PerkinElmer, 2018). For example, with copper, a lamp containing copper (as cathode) is used to emit light beam from excited copper (cathode filament) atoms that produce the right mix of wavelengths to be absorbed by any copper atoms present in the sample. The sample is atomized (using acetylene or nitrous oxide as fuel); i.e., converted into ground state, free atoms in the vapor state, and a beam of electromagnetic radiation emitted from excited copper atoms is passed through the vaporized sample. Some of the radiation is absorbed by the copper atoms in the sample. The greater the number of atoms in the vapor, the more radiation is absorbed. That is, the amount of light absorbed is proportional to the number of copper atoms. A calibration curve is constructed by running several samples of known copper concentration (standard samples) under the same conditions as the unknown. The calibration curve therefore, enables the calculation of the copper concentration in the unknown sample.

8.2. Digestion of Sediments Samples:

Prior to analyzing samples by AAS, sample digestion is always required. Digestion simply means "breakdown". It has been extensively applied in chemistry to refer to a breaking down of sample matrices (soil, sediments, solid waste, wastewater) to release/dissolve chemical species in aqueous phase using appropriate reagents. Acid digestion is the breakdown of the sample matrix using an oxidizing agent (normally strong acid is used) individually or mixed with other digestion reagents such as other acid and/ or hydrogen peroxide. Various standard acid digestion methods were established by United States Environmental Protection Agency (EPA,1996a,1996b) and International Standard Organization (ISO, 2001; EPA, 2007). Each method can be used according to its efficiency in dissolving the analyte to be determined by a specific instrument. Although the total content of metals in sediments or soil (or other matrix) samples was named as pseudo-total (Virtanen et al., 2015; Saleem et al., 2015), a digestion method that gives a better metal recovery should be selected. Three most common acid digestion methods

developed by US-EPA are HNO_3-H_2O_2-HCl, method 3050 (EPA, 1996a) ; Aqua-regia 3:1 HNO_3-HCl assisted microwave, method 3051 (ISO, 2020); 3:1 HNO_3-HF assisted microwave, method 3052 (EPA, 1996b). On the other hand, two ISO digestion methods are aqua-regia 3:1 HNO_3-HCl, ISO11466.3 (ISO, 2020) and use of hydrofluoric, HF, and perchloric acids, $HClO_4$, ISO 14869-1 (ISO, 2001).

The question that most investigators meet while selecting the best digestion is how efficient is the selected method. Some comparative studies (Peña-icart et al., 2012; Uddin, 2016) were done to evaluate their efficiencies in recovering HMs. Peña-icart et al. (2012) compared US-EPA method 3050 to ISO 11466.3 (aqua regia) with the total content of Cu, Ni and Pb in marine sediments, and found that similar amounts of Cu were extracted by both methods; while leaching of Ni and Pb were different. The author noticed that the US-EPA method extracted more Ni than the ISO method. In contrast, Pb was extracted in a larger amount by the ISO method. Peña-icart et al. (2012) recommended the use of both methods for analytical performances with combination of FAAS. In (2016), Uddin et al. compared the efficiency of three acid digestion methods using different solvents. Method A (a combination of nitric perchloric acid HNO_3–$HClO_4$ in a ratio 2:1), method B (only nitric acid HNO_3), and US-EPA method 3050, C (a mixture of nitric hydrochloric acids HNO_3–HCl in a ratio 1:3), to recommend the most efficient digestion method that gains the highest analyte recovery. The analysis was carried out on arsenic (As), cadmium (Cd), lead (Pb), nickel (Ni), zinc (Zn), and iron (Fe) atomic absorption spectrometry (AAS). In his findings, he found out that HNO_3–HCl in a ratio 1:3 had good recovery for all metals ranging from 94.5 to 108%. Besides, US-EPA digestion method (EPA, 1996a), indicated the suitability of the method and the appropriate analytical technique of AAS to be used for each element.

In many cases, the non-extracted metal fraction is associated with the silicate mineral phase of the sediments, which is poorly attacked by the acids by US-EPA method 3050 and method 3051. The author emphasizes that US-EPA method 3052 microwave-assisted acid digestion of siliceous and organically based matrices is normally a better choice for absolute total metal determination.

9. Conclusion:

Heavy metal contamination in aquatic ecosystems is primarily due to increasing anthropogenic activities. Water pollution is of a general concern as it causes adverse effects on the environment and human beings. The knowledge about speciation of HMs is an essential tool to understand their behavior, fate, and transport, control and remediation and thus, the bio-geochemical behavior, nutritional bioavailability, and toxicity of HMs are widely dependent on their chemical speciation. The bottom sediments of aquatic systems act as sinks of HMs; the concentration of HMs in overlying water only indicates the available forms of HMs present on a time scale. In this review, it was found that the potential mobility of the selected HMs would be estimated to be in the order of Zn > Cr > As > Cd > Pb > Cu > Fe > Ni > Hg in aquatic environments.

This signifies that at a certain time, the measured concentration of HMs in surface waters would vary depending on the environmental factors that dictate their release and/or retainment in the bottom sediments. The dominant mobile chemical forms of the studied HMs appear in exchangeable and carbonate forms and their water-soluble forms being in lower concentrations, except for Cr, which tend to appear in its water-soluble forms in high concentration. Heavy metals in the water-soluble forms are easily available to plants, fishes, and other benthic invertebrates, which results into their accumulation in the food chain.

Remediation technologies are widely applied to control HMs in aquatic environment. In order to control heavy metal pollution in aquatic systems without disturbance of its natural ecological system, *in-situ* amendment, including stabilization, active sorbents, sand capping, and bioremediation as well as MNR are more preferred than *ex-situ* technologies. However, the MNR coupled with soil erosion control measures as well as effective waste management strategies are the most applied and sustainable remediation technologies due to their economical and ecofriendly benefits.

10. Future Prospects:

Still, water pollution is ubiquitously inevitable and thus, the assessment of heavy metal pollution in sediments, water, and aquatic biota should be conducted in order to take necessary measures to protect human beings and the environment from adverse effects for future resilience. In fact, remediation technologies have evolved in the last decades. However, the need for effective, affordable, and environmental friendly remediation techniques for HMs such as adsorbents as well as the discovery of new species for phytoremediation has not been fully met. It is expected that successful application of these techniques could significantly reduce the spread of HMs in the aquatic environment. Extensive research on new different remediation technologies are therefore, strongly encouraged to scale down the spread of HMs in the future.

Availability of Data and Materials:
The source of all the data used in this study is provided in the manuscript, and no other supplementary material is available.

Author Contributions:
Eustache Nijeje; **Sylivester Jonathan Sahan** and **Amos Senyonjo** have made equal substantial contributions to conception and design, acquisition of data, as well as analysis and interpretation of data. All authors drafted the manuscript, revised it critically for important intellectual content; and made approval of the final version to be submitted for publication.

Conflict of Interest:
All authors declare no conflict of interest.

References:

1. Abbott, A.N., Löhr, S., & Trethewy, M. (2019). Are Clay Minerals the Primary Control on the Oceanic Rare Earth Element Budget? *Frontiers in Marine Science*, 6, 1–43.
2. Abdel-Satar, M. A. (2005). Quality of River Nile Sediments From Idfo To Cairo. *Egyptian Journal of Aquatic Research*, *31*(2), 182–199.
3. Abraham, S., Cachon, R., Jeanson, S., Ebel, B., & Michelon, D. et al. (2013). A Procedure for Reproducible Measurement of Redox Potential (Eh) in Dairy Processes. *Dairy Science & Technology*, 93 (6), 675-690.
4. Achi, M.M., Uzairu, A., Gimba. E.C., & Okunola, J. O. (2011). Chemical Fractionation of Heavy Metals in Soils Around the Vicinity of Automobile Mechanic Workshops in Kaduna Metropolis, Nigeria. *Journal of Environmental Chemistry and Ecotoxicology*, *3*(7), 184–194.
5. Agilent, T. (2017). Flame Atomic Absorption Spectrometry. *Analytical Methods*, 16–121. Retrieved January 20,
6. Aigberua, A.O., Tarawou, J.T., & Abasi, C. Y. (2018). Effect of Oxidation-Reduction Fluctuations on Metal Mobility of Speciated Metals and Arsenic in Bottom Sediments of Middleton River, Bayelsa State, Nigeria. *Journal of Applied Sciences and Environmental Management*, *22*(9), 1511–1517.
7. Akcil, A., Erust, C., Ozdemiroglu, S., Fonti, V., & Beolchini, F. (2015). A Review of Approaches and Techniques Used in Aquatic Contaminated Sediments: Metal Removal and Stabilization by Chemical and Biotechnological Processes. *Journal of Cleaner Production*, *86*, 24–36.
8. Ali, Z., Malik, R.N., Shinwari, Z.K., & Qadir, A. (2015). Enrichment, Risk Assessment, and Statistical Apportionment of Heavy Metals in Tannery-affected Areas. *International Journal of Environmental Science and Technology*, *12*(2), 537–550.
9. Amin, B., Ismail, A., Arshad, A., Yap, K.C., & Kamarudin, S. M. (2009). Anthropogenic Impacts on Heavy Metal Concentrations in the Coastal Sediments of Dumai, Indonesia. *Environmental Monitoring and Assessment*, *148*(1–4), 291–305.
10. Balali-Mood, M., Naseri, K., Tahergorabi, Z., Khazdair, M.R., & Sadeghi, M. (2021). Toxic Mechanisms of Five Heavy Metals: Mercury, Lead, Chromium, Cadmium, and Arsenic. *Front. Pharmacol*, 12, 643972.
11. Baran, A., Mierzwa-Hersztek, M., Gondek, K., Tarnawski, M., Szara, M., Gorczyca, O., & Koniarz, T. (2019). The Influence of the Quantity and Quality of Sediment Organic Matter on the Potential Mobility and Toxicity of Trace Elements in Bottom Sediment. *Environmental Geochemistry and Health*, *41*(6), 2893–2910.
12. Bradl, H.B. (2005). Sources and Origins of Heavy Metals. *Interface Science and Technology* 6, (3), 1–27.
13. Chuan, M.C., Shu, G.Y., & Liu, J. C. (1996). Solubility of Heavy Metals in a Contaminated Soil: Effects of Redox Potential and pH. *Water, Air, and Soil Pollution*, *90*, 543–556.
14. Codex. (2006). Joint FAO/WHO Food Standards Programme. Report of the Seventh Session of the Codex Committee on Milk and Milk Products 29.
15. Cox, S., McKinley, J., & Rollinson, G. (2017). Mineralogical Characterization to improve Understanding of oral Bioaccessibility of Cr and Ni in Basaltic Soils in Northern

Ireland. J*ournal of Geochemical Exploration* 183, 166–177.

16. Dana, J.M., Banadda, N., Kiggundu, N., & Asuman, R. (2015). Lead Uptake of Water Plants in Water Stream at Kiteezi Landfill Site, Kampala (Uganda). *African Journal of Environmental Science and Technology*, *9*, 502–507.

17. DeLaune, R.D. & Reddy, K. R. (2005). Redox Potential in Soil and Sediment Environment. In: Hillel, D. (Ed.), *Encyclopedia of Soils in the Environment* (pp. 366–371). Amsterdam: Elsevier Ltd.

18. Duan, L., Song, J., Liang, X., Yin, M., Yuan, H., Li, X., Ren, C., & Zhou, B., Kang, X., & Yin, X. (2019). Dynamics and Diagenesis of Trace Metals in Sediments of the Changjiang Estuary. *Science of the Total Environment*, *675*, 247–259.

19. Eggleton, J. & Thomas, V.K. (2004). A Review of Factors Affecting the Release and Bioavailability of Contaminants During Sediment Disturbance Events. *Environment International*, *30*(7), 973–980.

20. EPA. (1996a). *Method 3050B*: *Acid digestion of Sediments, Sludges and Soils by AA-Direct Aspiration.* Revision 2. Washington, DC.

21. EPA. (1996b). Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices. *Office of Solid Waste*, *Method 3052-1:* 1–13.

22. EPA. (2007). Method 3051A: Microwave assisted acid digestion of sediments, sludges, soils, oils. Test Methods for Evaluating Solid Waste, SW846, Revision 4, pp. 1–5.

23. Esmaeili, A., Mobini, M., & Eslami, H. (2019). Removal of Heavy Metals from Acid Mine Drainage by Native Natural Clay Minerals, Batch and Continuous Studies. *Applied Water Science*, 9(97), 1–6.

24. Gale, M.P., Reddy, R.K., & Graetz, A. D. (1992). Mineralization of Sediment Organic Matter under Anoxic Conditions. *Journal of Environmental Quality*, *21*(3), 394–400.

25. Giordano, R., Musmeci, L., Ciaralli, L., Vernillo, I., Chirico, M., Piccioni, A., & Costantini, S. (1992). Total Contents and Sequential Extractions of Mercury, Cadmium, and Lead in Coastal Sediments. *Marine Pollution Bulletin*, 24(7), 351–357,

26. Hudson, L.T., Fox, F.D., & Plumlee, G. S. (1999). *Metal Mining and Environment*. In: American Geological Institute (AGI), Alexandria, VA**,** pp. 20-39.

27. Huseen, M.H. & Mohammed, J. A. (2019). Heavy Metals Causing Toxicity in Fishes. *Journal of Physics*, *062028*(Conf. Ser. 1294), 9.

28. Irshad, M.K., Ibrahim, M., Noman, A., Shang, J., Mahmood, A., Mubashir, M., Kuan Shiong Khoo, K.S., Hui Suan Ng, H.S., & Show, P.L. (2020). Elucidating the Impact of Goethite-Modified Biochar on Arsenic Mobility, Bioaccumulation in Paddy Rice (Oryza sativa L.) Along with Soil Enzyme Activities. *Process Safety and Environmental Protection* 160, 958–967.

29. ISO. (2001). *Soil quality — Dissolution for the determination of total element content —* Part1: Dissolution with hydrofluoric and perchloric acids. First Ed. International Standard.

30. ISO. (2020). *Soil quality, Extraction of Trace Elements Soluble in Aqua Regia. Second Ed. International Standards* (Vol. 357).

31. Jackson, K. S., Jonasson, I. R., & Skippen, G. B. (1978). The Nature of Metals-Sediment-Water Interactions in Freshwater Bodies, with Emphasis on the Role of Organic Matter. *Earth Science Reviews*, *14*(2), 97–146.

32. Jenne, E. A. (1968). Controls on Mn, Fe, Co, Ni, Cu, and Zn Concentrations in Soils and Water: the Significant Role of Hydrous Mn and Fe Oxides. *Adavances in Chemistry*, *73*, 337–387.

33. Jenne, E. A. (1985). Behaviour of Radionuclides Released Into Coastal Waters. In *Literature Review* (pp. 20–47). IAEA-TECDOC-329.

34. Kersten, M. & Förstner, U. (1987). Effect of Sample Pretreatment on the Reliability of Solid Speciation Data of Heavy Metals-Implications for the Study of Early Diagenetic Processes. *Marine Chemistry*, *22(2-4)*, 299–312.

35. Khalid, S., Shahid, M., Niazi, K.N., Murtaza, B., Bibi, I., & Dumat, C. (2017). A Comparison of Technologies for Remediation of Heavy Metal Contaminated Contaminated Soils. *Journal of Geochemical Exploration*, *182*, 247–268.

36. Khan, A.S., Ansari, G.K.M.S., & Lyla, S. P. (2012). Organic Matter Content of Sediments in Continental Shelf Area of Southeast Coast of India. *Environ Monit Assess*, 1–11.

37. Kraus, U. & Wiegand, J. (2006). Long-term Effects of the Aznalcóllar Mine Spill-heavy Metal Content and Mobility in Soils and Sediments of the Guadiamar River Valley (SW Spain). *Science of the Total Environment*, *367*(2–3), 855–871.

38. Levinson, R. (2002). *Atomic absorption spectrometry.* Modern Chemical Techniques (T. R. S. of C. F. C. and M. Group (ed.); 4th ed.). The Royal Society of Chemistry

39. Machowski, R., Rzetala, A.M., Rzetala, M., & Solarski, M. (2019). Anthropogenic Enrichment of the Chemical Composition of Bottom Sediments of Water Bodies in the Neighborhood of a Non-ferrous Metal Smelter (Silesian Upland, Southern Poland). *Scientific Reports*, *9*(1), 1–13.

40. Makuleke, P. & Ngole-Jeme, M. V. (2020). Soil Heavy Metal Distribution with Depth around a Closed Landfill and Their Uptake by Datura stramonium. *Applied and Environmental Soil Science*, 2020, 8872475, 1-14.

41. Malik, D. S. & Maurya, P. K. (2014). Heavy Metal Concentration in Water, Sediment, and Tissues of Fish Species (Heteropneustis fossilis and Puntius ticto) from Kali River, India. *Toxicological and Environmental Chemistry*, *96*(8), 1195–1206.

42. Manahan, S. E. (2000). *"Front Matter" Environmental Chemistry*. Water pollution (7th ed., pp. 200–232). Boca Raton: CRC Press LLC.

43. Martley, E. & Gulson, L. B. (2003). Heavy Metal Partitioning in Soil Profiles in the Vicinity of an Industrial Complex and Potential Health Implication. *J Phys. IV France*, *107*.

44. Muhammed, R. T. (1991). Environmental Impact of Heavy Metal Pollution in Natural Aquatic Systems (pp. 1–171). PhD Thesis, Brunel, the University of West London.

45. Müller, G. (1979). Heavy Metals in Sediments of the Rhine-changes Since 1071 (Schwermetalle in den Sedimenten des Rheins-Veränderungen seit 1971). *A Review in Science and Technology*, *79*, 778–783.

46. Nabulo, G., Origa, O.H., Nasinyama, G.W., & Cole, D. (2008). Assessment of Zn, Cu, Pb and Ni Contamination in Wetland Soils and Plants in the Lake Victoria Basin. *Int. J.*

Environ. Sci. Tech, 5(1), 65–74.

47. Narjala, R.J. (2020). Heavy Metal Sources and Their Effects on Human Health. *IntechOpen*, 12.

48. Nhapi, I. (2011). Assessment of Water Pollution Levels in the Nyabugogo Catchment, Rwanda. *The Open Environmental Engineering Journal*, 4(1), 40–53.

49. Nijeje, E., Senyonjo, A., Sahan, S.J., Byamugisha, D. & Ntambi, E. (2023). Speciation of Selected Heavy Metals in Bottom Sediments of River Rwizi , Mbarara City , Uganda. *Water Air Soil Pollution*, 234(198), 1–18.

50. Ochieng, M. O. (2013). Assessment of Heavy Metal Pollution in Pece Channelized Stream Water Gulu town, Northern-Uganda. Makerere University. 14-44.

51. Olsen, M., Petersen, K., Lehoux A.P., Leppänen, M., Schaanning M., Snowball, I., Øxnevad, S., & Lund, E. (2019). Contaminated Sediments : *Review of solutions for protecting aquatic environment*, 33-54.

52. Olutona, O.G., Aribisala, O.G., & Akintunde, E. A. (2012). A Study of Chemical Speciation of Metals in Aquatic Bottom Sediment of Aiba Reservoir, Iwo, Nigeria. *African Journal of Environmental Science and Technology*, 6(8), 312–321.

53. Osakwe, S. A. (2011). Chemical Speciation and Mobility of Some Heavy Metals in Soils around Automobile Waste Dumpsites in Northern Part of Niger Delta, South Central Nigeria. *Journal of Applied Sciences and Environmental Management*, 14(4), 123–130.

54. Peña-icart, M., Tagle Margarita Villanueva, E., Hernández, A.C., Hernández, R.J., Behar, M., & Alfonso Mario Pomares, S. (2012). Comparative Study of Digestion Methods EPA 3050B (HNO-HO-HCl) and ISO 11466 . 3 (aqua regia) for Cu , Ni and Pb Contamination Assessment in Marine Sediments. *Marine Environmental Research*, 72(1–2), 60.

55. Peng, J., Song, Y., Yuan, P., Cui, X., & Qiu, G. (2009). The Remediation of Heavy Metals Contaminated Sediment. *Journal of Hazardous Materials*, 161, 633–640.

56. PerkinElmer. (2018). *Atomic Spectroscopy. A Guide to Selecting the Appropriate Technique and System. Waltham, MA 02451 USA, p. 2-12*.

57. Pueyo, M., Rauret, G., Lück, D., Yli-Halla, M., Muntau, H., Quevauviller, P., & López-Sánchez, J. F. (2001). Certification of the Extractable Contents of Cd , Cr , Cu , Ni , Pb and Zn in a Freshwater Sediment Following a Collaboratively Tested and Optimised Three- step Sequential Extraction Procedure. *J. Environ. Monit.*, 3, 243–250.

58. Saleem, M., Iqbal, J., & Shah, H. M. (2015). Geochemical Speciation, Anthropogenic Contamination, Risk Assessment and Source Identification of Selected Metals in Freshwater Sediments - A case Study from Mangla Lake, Pakistan. *Environmental Nanotechnology, Monitoring and Management*, 4, 27–36.

59. Schiff, C.K. & Weisberg, B.S. (1999). Iron as a Reference Element for Determining Trace Metal Enrichment in Southern California Coastal Shelf Sediments. *Marine Environmental Research*, 48(2), 161–176.

60. Sekabira, K., Origa, O.H., Mutumba, G., Kakudidi, E., & Basamba, A. T. (2010). Heavy Metal Phytoremediation by Commelina benghalensis (L) and Cynodon dactylon (L) growing in Urban Stream Sediments. *International Journal of Plant Physiology and Biochemistry*, 7, 759–770.

61. Sekomo, B.C., Nkuranga, E., Rousseau, D.P.L., & Lens, P. N. L. (2011). Fate of Heavy Metals in an Urban Natural Wetland: The Nyabugogo Swamp (Rwanda). *Water, Air, and Soil Pollution*, 214(1–4), 321–333.

62. Sekomo, C.B., Rousseau, D. P. L., & Lens, P. N. L. (2012). Use of Gisenyi Volcanic Rock for Adsorptive Removal of Cd (II), Cu (II), Pb (II), and Zn (II) from Wastewater. *Water Air Soil Pollution*, 223, 533–547.

63. Sibomana, J.B., Habinshuti, J., Muhizi, T., Safari, J.C., & Mukarunyana, B. (2019). A Chemical Speciation Study of Selected Heavy Metals in Aquatic Bottom Sediment Samples from Mpenge Stream, Musanze District, Rwanda. *African Journal of Environmental Science and Technology*, 13(11), 450–455.

64. Slavko, S., Neda, T.T., Mitar, P., Ljubica, V., & Svetlana, P. (2019). The Main Sources of Heavy Metals in the Soil. *VI International Congress Engineering, Environment and Materials in Processing Industry*, 453–465.

65. Tangahu, V.B., Siti, R.S.A., Basri, H., Idris, M., Anuar, N., & Mukhlisin, M. (2011). A Review on Heavy Metals (As , Pb , and Hg) Uptake by Plants through Phytoremediation. *International Journal of Chemical Engineering*, 31.

66. Tessier, A., Campbell, P.G., & Bisson, M. (1979). Sequential Extraction Procedure for the Speciation of Particulate Trace Metals. *Analytical Chemistry*, 51, (7), 844–851.

67. Turekian, K.K., & Wedepohl, H.K. (1961). Distribution of the Elements in Some Major Units of the Earth's Crust. *Geological Society of America Bulletin*, 72 (2), 175–192.

68. Uddin Helal, A.B.M., Khalid, S. R., Alaama, M., Abdualkader, M.A., & Kasmuri, A. (2016). Comparative Study of Three Digestion Methods for Elemental Analysis in Traditional Medicine Products Using Atomic Absorption Spectrometry. *Journal of Analytical Science and Technology*, 7(6), 7.

69. UN-Water. (2010). World Water Quality Facts and Statistics, World Water Day. *Clean Water for Health World*, 1-4.

70. Uwamariya, V. (2013). *Adsorptive Removal of Heavy Metals from Groundwater by Iron Oxide based adsorbents*. Delft University of Technology.

71. Virtanen, S., Simojoki, A., Hartikainen, H., & Yli-Halla, M. (2015). *Redox reactions and water quality in cultivated boreal acid sulphate soils in relation to water management*.

72. WHO. (2008). Guidelines for Drinking-water Quality. In *incorporating 1st and 2nd addenda,Vol.1, Recommendations,* 3, pp. 390–587.

73. WHO. (2020). WHO Recommended Classification of Pesticides by Hazard and Guidelines to Classification, 2019th Edition. Geneva: *World Health Organization*. Licence: CC BY-NC-SA 3.0 IGO.

74. WWAP. (2021). The United Nations World Water Development Report. *Water Politics*.

75. Zang, F., Wang, S., Nan, Z., Ma, J., Wang, Y., Chen, Y., Zhang, Q., & Li, Y. (2017). Influence of pH on the Release and Chemical Fractionation of Heavy Metals in Sediment from a Suburban Drainage Stream in an Arid mine-based Oasis. *Journal of Soils and Sediments*, 17(10), 2524–2536.