Toxic Metals in Oil Sands: Review of Human Health Implications, Environmental Impact, and Potential Remediation Using Membrane-based Approach

Odunayo T. Ore [1*] and Adedapo O. Adeola [2,3]
ind
[1] Department of Chemistry, Faculty of Science, Obafemi Awolowo University, Ile-Ife 220005, Nigeria
[2] Department of Chemical Sciences, Adekunle Ajasin University, Akungba-Akoko, Nigeria
[3] Department of Chemistry, Faculty of Natural and Agricultural Sciences, University of Pretoria, Lynnwood Road, Hatfield, Pretoria 0002, South Africa.

* Corresponding author's email address: oreodunayo@yahoo.com; Phone: +2348064251343

Abstract

The upsurge in energy needs is the primary influencing factor for the shift of attention from conventional hydrocarbon resources to unconventional resources. In the process of exploiting unconventional oil resources such as oil sands, priority pollutants such as heavy metals are released into the environment. Thus, there are health and environmental risks associated with exploration and mining practices. This study seeks to present an overview of the health and environmental effects of these toxic metals in oil sands. Predominantly, the sources of these pollutants in oil sands are biogenic processes and weathering of source rocks. The toxicity of metals is dependent upon the nature of the metals as well as its affinity to bond with the silicate matrix. The consumption of plants and water from rivers, lakes, and streams with proximity to oil sand deposits, could pose severe health risks to consumers, as significant amounts of Hg and other toxic metals are leached during oil recovery and other developmental processes. This review pointed to the use of membrane-based processes and other integrated approaches as vital remediation strategies employed for the restoration of resources to their pristine state and metal recovery. It is recommended that exploration practices and technologies should be improved towards the reduction of on-site metal pollution or off-site metallic contamination during refining or waste management.

Keywords: Environment; Health risk; Oil sand; Remediation; Toxic metal

Article Highlights

- Exposure to metals are associated with oil sand exploration
- Metal toxicity depends on its forms, nature, and concentration levels.
- Membrane-based processes are possible remediation strategies

1. Introduction

In the last two decades, researchers have focused on seeking out unconventional oil deposits as an alternative to the dwindling oil resources to satisfy both current and future energy needs. The attention of geologists, geophysicists, petroleum engineers, and petroleum chemists among others, is shifting to unconventional oil resources such as oil shale, tight oil, and oil sands (Al-Marshed et al. 2015; Wang et al. 2014; Zhang et al. 2012). Numerous deposits of oil sand are in several places around the world; however, the biggest oil sand deposits are in Canada, Venezuela, Kazakhstan, and Russia, larger than those discovered in other parts of the world combined. In Canada, the major oil sand deposits are the Peace River oil sand, the Cold Lake oil sand, and Athabasca oil sand as shown in **Figure 1** (Wang et al. 2005). In Africa, Nigeria has large deposits of natural resources such as natural gas, petroleum/crude oil, bitumen agglomerated oil sands, coal deposits, tin, etc. The sand deposits are located within the eastern belt of the Dahomey basin and cut across three major States (Ogun, Ondo, and Edo states) in the South-western and South-southern Nigeria, respectively (Adegoke 2000)**.** Generally, the composition of oil sands includes 68%, 23%, and 9% of sand, bitumen, and water respectively, however, reports suggest that Nigerian oil sand contains an average of 20% of bitumen (Adebiyi and Omode 2007; Fair 2010).

Bitumen is a black viscous mixture of hydrocarbons that can be recovered naturally or as a by-product of petroleum distillation. It is an important resource as it can be upgraded to synthetic crude oil. As defined by the World Energy Council, bitumen refers to “oil having a viscosity greater than 10,000 centipoises under reservoir conditions and API gravity of less than 10° API” (Attanasi and Meyer 2010). A major challenge posed by bitumen to the oil industry has been its transportation to an upgrading location as well as, the potential for environmental contamination by toxic elements. Other technological constraints such as catalytic poisoning/deactivation etc.,

Figure 1: Map of the Canadian Oil Sands (Adapted from Larter et al. 2006)

are associated with bitumen upgrade and refining as a result of the trace elements contained in the oil sands (Hashemi 2013). It is presumed that there are occupational health hazards associated with the exploration of natural resources.

Trace elements, among others, constitute significant problems both in the oil industry and the environment. Elements of relatively high atomic mass, weight, and density relative to that of the earth's crust are known as "heavy metals". Their ability to be transformed from one oxidation state to another confers on them a non-biodegradable property, which makes them toxic (Oyekunle et al. 2020; Turkdogan 2003). Most of the elements classified as "heavy metals" do not have any known biological roles in the human body, however, a few of them such as iron, cobalt, copper, zinc, manganese, etc. are required in trace amounts for the proper functioning of the body (Emsley 2011). The rapid upsurge in the world population places a demand for the development of all industrial sectors, including the oil industry. The resultant effect of this is the contamination of the environment by metals (Sarwar et al. 2016). Naturally, these toxic metals exist in oils, however, an upsurge in their levels can occur during production, refining, and storage (Speight 2001). Some of the metals are simply a reflection of the metals present in source rocks while some were picked up during migration from source rock to reservoir rock (Adebiyi et al. 2020). While these metals are geochemically significant in the understanding of organic matter source and depositional environments of these oils (Akinlua et al. 2007), yet they constitute severe environmental challenges as a result of the indiscriminate release of toxic metals into the ecosystem during exploration and refining processes. The exploration of oil sands, particularly, requires the discharge of its sand fraction after the bitumen fraction has been extracted. The metal levels of these “sand fractions” poses a potential ecological risk to the environment (Adebiyi and Ore 2020).

Table 1: Indices of Corresponding Degrees of Potential Ecological Risk (Hakanson, 1980)

Er value	Grades of ecological risk of single metal	RI value	Grades of potential ecological risk of the environment
Er < 40	Low risk	RI < 150	Low risk
40 ≤ Er < 80	Moderate risk	150 ≤ RI < 300	Moderate risk
80 ≤ Er < 160	Considerable risk	300 ≤ RI < 600	Considerable risk
160 ≤ Er < 320	High risk	RI > 600	Very high risk
Er > 320	Very high risk		

Despite the presence of “heavy metals” on the list of United States Environmental Protection Agency (USEPA) as priority pollutants, much attention has been focused on organic pollutants (Headley and McMartin 2004; Headley et al. 2002; Kelly et al. 2009; Kurek et al. 2013; Nyakas et al. 2013; Pereira et al. 2013).

The objectives of this review are to bridge information gaps towards a comprehensive understanding of the human health and environmental impact of non-target exposures to toxic metals present in oil sands. The need to mitigate pollution risks associated with the development (exploration and refining) of natural resources such as crude oil and application of a membrane-based water treatment approach for metal recovery were also discussed.

2. Sources of Metal Contents of Oil Sands

The types of metals found in oil sands are dependent on the geological environment from which the oil is formed (Adebiyi et al. 2020). The formation of oil sand is brought about by the migration of crude oil into porous sands where biodegradation and water-washing processes cause its alteration. The migrated crude oil contains several metals, hydrocarbon, and sulphur compounds. This results in oil sands with a relatively higher content of the aforementioned compounds than the conventional crude (Adebiyi et al. 2013; Tissot and Welte 1984). Highly influential factors in the formation of oil sands are thermal maturation, bacterial biodegradation, underground water flow, dewaxing, and evaporative transformation (Wenger et al. 2002).

While the metals found in conventional crude oil, oil sands, shale oils, etc., are particularly useful in the understanding of oil-oil source correlation, determination of the age of producing field, and type of source rock, among others (Oluwole et al. 1993), some of them are crustal elements while some are hazardous in certain forms and states. Metals that are predominantly found in oils include vanadium and nickel, among others. Like other environmental compartments, metals are present in oil sands via both natural and anthropogenic sources (He et al. 2013). In addition to the natural levels of metals and metalloids in crude oils, they can also be incorporated into crude oils during production, transportation, and storage. They exist naturally in oils as inorganic salts (majorly as chlorides and sulphates of Na, K, Mg, and Ca) connected with the aqueous phase of crude oil emulsions. They are also present as organometallic compounds of Mg, V, Cu, Fe, Cr, Ni, Ca, Zn, and Ti adsorbed in water-soil interface, functioning as emulsion stabilizers (Speight et al. 2001).

Predominantly, metals that exist in oils are V (II) and Ni (II) porphyrins and nonporphyrins. Several other metal ions present in crude oils include cadmium, titanium, manganese, aluminium, among others. These metals are bound to the porphyrin complexes in oils to form metalloporphyrins. Metalloporphyrins represent one of the first compounds identified and reported to be of biological origin. It was proposed that plant chlorophylls are sometimes transformed into geoporphyrins. A knowledge of the chemistry of metalloporphyrins is critical for an understanding of the depositional environment as well as the origin of crude oils. Diagenesis from organic molecules, biogenic, and abiogenic sources are the other possible natural sources of metals in oils (Onojake et al. 2017).

3. Fate of Toxic Metals in Oil Sands

Speciation is defined as “the oxidation state, concentration and composition of each of the species present in a chemical sample, or the determination of the concentration of the different physicochemical forms of the element, which together make up its total concentration in the sample” (Ebdon et al. 1985; Hersfall et al. 1999; Lynch et al. 1984). The binding ability of metal ions, redox behaviour, the nature of the bond, and desorption potential or release mechanism of trace elements in oil sands have been previously reported (Pillay et al. 2014). The release of chemical species, particularly priority pollutants such as toxic metals, at elevated levels into the environment is hazardous (Pillay et al. 2014). The forms of toxic metals in environmental matrices, determined by sequential extraction techniques, are required in a bid to understanding their bioavailability, pathways, and mobility/transport in several environmental media. This results in the availability of clear and accurate information about the affinities of these metals to various sand components, as well as the strength of complexation (Awan et al. 2003; Oyewole and Adebiyi 2017). The distribution and fate of metals in the ecosystem are predicated upon their speciation. The total elemental concentration of environmental matrices is not a reliable indicator of their fate in the environment (Tessier and Turner 1995).

High mobility factors observed for metals in oil sands are indicative of weak interactive forces between the metals and the mineral matrix of the oil sands. In stark contrast, low mobility factors indicate that strong interaction exists between the metals and silicate matrix of the oil sands. The nature of metals exhibiting weak interactive forces with oil sand-mineral matrix would determine the toxicity of the oil sands.

4. Risk Assessment

Risk assessment is a vital scientific tool that provides the necessary information required by decision-makers in the management of contaminated sites in a sustainable, eco-friendly, and cost-effective manner (Adeola and Forbes 2020; Zhao and Kaluarachchi 2002). Risk assessment is basically employed to estimate the extent of health risks associated with contaminants upon exposure to humans and the environment.

4.1 Human Health Risk Assessment

The processing of oil sand resources is necessary in a bid to meeting ever-increasing energy needs and the world population, nevertheless, it poses a serious health and environmental challenges, in the absence of proper management and best practices. Potential threats emanate from occupational exposures to these toxic metals or the consumption of polluted water and contaminated plants.

The USEPA method is adopted in calculating the exposure risk of adults and children to the concentrations of potentially toxic metals in soils, and by extension, oil sands (Ogunbanjo et al. 2016; Olutona et al. 2017; Tenebe et al. 2018). Three major exposure pathways to potentially toxic metals include dermal, ingestion, and inhalation exposure pathways. The chronic daily intake measures the exposure to the toxic metals.

4.2 Potential Ecological Risk Assessment

The environmental safety of biological organisms inhabiting an ecological habitat is determined by the potential environmental risk index (RI). RI is defined by the sum of potential risk for each metal. It does not take into consideration the combined effects of their mixture. For example, some metals may have their toxicity increased in the presence of other substances. The concentration of the potentially toxic metal, its toxic level, synergy, and ecological sensitivity are considered by this method (Douay et al. 2013).

5. Health Effects on Flora and Fauna

The processing of oil sands and crude oil is accompanied by a direct or indirect release of toxic elements via atmospheric particulate deposition of metals from oil sand upgrading facilities (Kirk et al. 2014), leaching of metals from oil sand deposits into water bodies (Coniy et al. 2007; Gueguen et al. 2011; Kelly et al. 2010), and via run-offs from agricultural farmlands; thus affecting aquatic life and plants in the process (Blum et al. 2012; Graney et al. 2012).

Studies have shown that increased levels of the elements found in oil sands and its deposit areas above threshold levels are unsafe for the aquatic and terrestrial ecosystems (Huang et al. 2016; Oyewole and Adebiyi 2017). The development of natural resources is closely associated with the release of these elements into the environment. Plants, particularly have a well-developed system capable of element uptake. In the course of this uptake, they pick up both the essential and toxic metals, causing several metabolic alterations as they move up the food chain.

Like soils, the metals in the oil sands can be leached via erosion to nearby farmlands and water bodies. A gradual build-up of these metals up the food chain can occur. The development of bitumen deposit has been reported to leach metals into nearby surface and groundwaters (Asubiojo and Adebiyi 2013). Hazardous environmental impacts are associated with the atmospheric deposition of elements by oil sand dust (Gopalapillai et al. 2019). The development of the Athabasca oil sands contributes methyl mercury to neighbouring water bodies (Kirk et al. 2014). The mining and processing of oil sands represent a significant contribution of Pb source signature to epiphytic lichens (Graney et al. 2012). Oil sand exposure to the flow of tributaries significantly raises the levels of metals in sediments and rivers, thus making it unsafe for aquatic life (Conly et al. 2007). However, a notable decline in elemental levels has been reported since the onset of oil sand production in some areas (Skierszkan et al. 2013; Wiklund et al. 2012). Some fish tissues in the Athabasca river were also reported to show a decline in Hg levels (Evans and Talbot 2012). Colonial water-bird eggs with proximity to the oil sand exploration site reveal an upsurge in Hg levels (Hebert et al. 2011; Hebert et al. 2013). These metals are known to affect the defence system of antioxidants, causing interference with the modulation of nonprotein thiols and glutathione. This, in turn, brings about an alteration in the physiological activity of plants (Israr et al. 2006; Sengar et al. 2010). The impairment of growth in plants is caused by Pb toxicity due to the distortion of the ultrastructure of the plant's chloroplast (Islam et al. 2007; Pourrut et al. 2011), the substitution of divalent ions (Cenkci et al. 2010), and obstruction of electron mobility (Qufei and Fashui 2009). The bioavailability of Al, Co, Mo, Be, Pb, Cr, V, and Ni in mussel tissues and aquatic environment of the Fort McMurray area of the Athabasca oil sand region has also been highlighted to pose potential ecological risks to biota and the aquatic environment due to increasing mining activity of oil sands (Pilote et al. 2018). Toxicological data obtained from *in vivo* and *in vitro* exposure to oil sand process-affected water have also indicated that the exposure might bring about a disrupted endocrine system, impaired reproduction, compromised immunological function, etc. (Li et al. 2017).

6. Potential Impact on Humans

Trace metals have been known to be present in oils for many decades. The impact of trace metals on the successful refining and environment is immense. Common metals found in the oil sand deposits are Ni (II) and VO (II) porphyrins and non-porphyrins, others are antimony, uranium, aluminum, tin, barium, gallium, silver, magnesium, sodium, molybdenum, zinc, cadmium, titanium, manganese, chromium, cobalt, arsenic, copper, lead and iron. However, vanadium and nickel metalloporphyrin is most abundant in high molecular weight oils. These metals have been reported to cause several health problems even in minute amounts (**Table 2**) (Babel and Kurniawan 2003).

Table 2: United State Environmental Protection Agency (US EPA) maximum concentration level of some heavy metals present in oil sands

Metals	Health effect	Threshold levels (mg/L)
Arsenic	Skin irritations, visceral cancers, cardiovascular disease	0.05
Cadmium	Kidney damage, renal disorder, human carcinogen	0.01
Chromium	Headache, diarrhea, nausea, vomiting, carcinogenic	0.05
Copper	Liver damage, Wilson disease, insomnia	0.25
Lead	Damage the fetal brain, kidney diseases, circulatory and nervous system failure	0.006
Nickel	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	0.20
Zinc	Depression, lethargy, neurological signs and increased thirst	0.80

6.1 Arsenic

Leaching of arsenic from oil sands onto groundwater and other natural and /or anthropogenic activities puts humans at risk of toxic exposure via water, air, and food sources. Long term and the lower dose of arsenic results in several medical complications called “Arsenicosis” (Kathleen et al. 2011). Arsenic has been attributed to several health complications in human body organ systems: integumentary, respiratory, cardiovascular, nervous, immune, endocrine, hepatic, renal, hematopoietic, reproductive system, and development **(Figure 2)** (Mohammed Abdul et al. 2015; Zheng et al. 2014). Developmental toxicity such as birth defects, child mortality, growth retardation, and cell alteration, are potential health impact of different degree of arsenic exposures (Kwok et al. 2006; Wu et al. 2011).

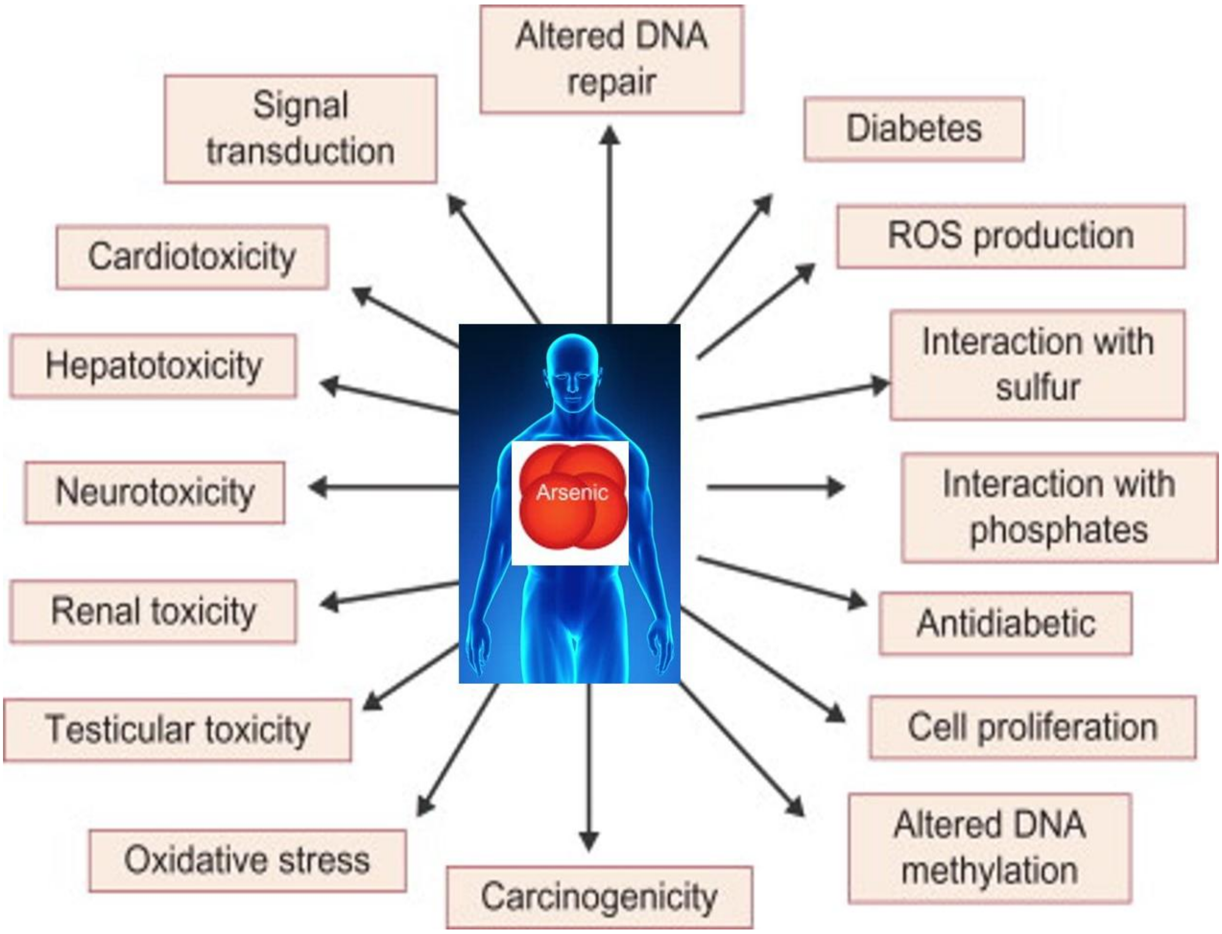

Figure 2: Exposures and health effect of Arsenic on humans (Adapted with permission from Kathleen, M.M., Hoang Thi, H., Kyoung-Woong, K. Reviews on Environmental Health, 26, 71-78. Copyright 2011 De Gruyter.)

6.2 Nickel

Unlike arsenic, exposure to nickel has both positive and negative effects on human health. Particulate and insoluble form of nickel penetrates cells of vertebrates by phagocytosis, while those soluble in lipids, can penetrate the plasma membrane. Calcium and other divalent cation transporters/channels aid the transport of Ni (II) into cells (DMT-1). Transport of nickel in blood plasma is promoted by albumin, amino acids (e.g. histidine), and small peptides. Insoluble nickel compounds are reported to be more carcinogenic than soluble compounds, probably due to their persistence in body tissues than a soluble nickel (Denkhaus and Salnikow 2002). Nickel also damages cell mitochondria via oxidation (Lee et al. 2016) and substitutes cognate metal ions, such as Fe^{2+}, Cu^{2+}, Zn^{2+}, and Ca^{2+} in cellular metabolic pathways especially, in metal-binding proteins regulation (Hu et al. 2016).

6.3 Vanadium

Vanadium exists in a combined state in nature and often found along with earth minerals, coal, and crude oil and is mostly released due to human activities (Zwolak 2020). Burning of fuel contributes to the environmental release of vanadium and large amounts are reported in urban and industrial settlements (Imtiaz et al. 2015). The elemental metallic form of vanadium is regarded as non-toxic but oxides of vanadium which are relatively abundant in oil sand deposits cause irritation of the nose, diarrhea, cytotoxicity, and potential degeneration of the lungs, kidneys, liver, and brain after long term exposure (Xi et al. 2019).

6.4 Lead

Lead is regarded as one of the most toxic heavy metals in the environment and human exposure is majorly occupational and drinking of polluted water sources (Assi et al. 2016). The daily limit for lead intake, set by most pharmaceutical agencies is 1.0 μg/g, however prolonged intake is discouraged as it is deemed hazardous to human beings due to bioaccumulation potential (Shih et al. 2007). Long-time exposure causes anemia and high blood pressure in old and middle-aged people. Several adults and children have suffered brain damage and kidney failure due to exposure to high levels of lead (Ekong et al. 2006). Blood disorders, cancer, and damage to the nervous system have also been attributed to lead. In pregnant women, high exposure to lead may cause birth defects and/or miscarriage, and several reproductive infertilities in males have been attributed to lead poisoning, as well as death (Lin and Huang 1994; Sokol and Berman 1991).

6.5 Other metals present in oil sands

Acute zinc toxicity is rare, as zinc only becomes toxic on exposure to a very high concentration. Chronic and high-dose exposure of zinc interferes with bodily uptake of essential copper; hence, major toxic effects of zinc are essentially due to copper deficiency (Plum et al. 2010). Exposure to soluble silver compounds and zinc dust from crude oil exploration and from oil sands during refining may result in other toxic effects, such as argyria, liver and kidney damage; eyes, skin, respiratory and intestinal tract, irritation and damaging change in blood cells (Drake and Hazelwood 2005; Hadrup et al. 2018).

Although, iron is one of the essential minerals required by humans, especially for blood production. however, iron toxicity occurs at doses above 10 – 20 mg/kg of elemental iron, and iron levels above 350 – 500 µg/dL in the blood are considered toxic. Accidental consumption or exposure to 50 mg/kg of elemental forms of iron are associated with severe toxicity and levels over 1000 µg/dL in human serum is indicative of severe iron poisoning (Anderson 2007). Copper poisoning leads to symptoms such as vomiting, coma, hematemesis (vomiting of blood), hypotension (low blood pressure), melena (black "tarry" feces), coma, jaundice (yellowish pigmentation of the skin), and gastrointestinal discomfort (Gaetke et al. 2014). Chronic or long-term exposure to cadmium through the air, water, soil, and food leads to cancer; skeletal, urinary, reproductive, and cardiovascular problems; central nervous system breakdown and respiratory system (Rafati Rahimzadeh et al. 2017).

Heavy metal pollution has attracted immense scientific interest for several decades and a great deal of environmental research has focused on the subject. Apart from mining and exploration activities, various anthropomorphic activities have contributed to the existing high concentration of metals in different environmental compartments. The characteristic persistence of metals in the natural environment, leading to dangerous health consequences in humans, animals, and plants, requires sustained effort towards the management of this dangerous class of pollutants. Furthermore, the absence or non-enforcement of strict legislation against the indiscriminate release of harmful metals to the environment and not holding stakeholders in the mining sector responsible, when such pollution is detected, are all factors responsible for the ever-increasing metal pollution (Khalid et al. 2017).

7. Membrane-based approach to heavy metal pollution treatment

Several individual strategies have been reported for the remediation of heavy metal pollution from different environmental compartments. But they have drawbacks such as operational cost, generation of sludge or secondary pollutants, time requirement, sustainability, field-scale applicability, etc. Hence, integrated processes have been reported to achieve treatment objectives effectively in various environmental matrices. Integrated processes involve hyphenation of two or more different methods synergistically with the sole aim of optimized treatment performance and heavy metal removal.

Membrane processes have been used for the treatment of metal pollution for several years now. This process which combines mechanisms such as adsorption, size exclusion, and hydrophobic interactions; has been integrated in next-generation reusable and portable water purification technologies (Abdullah et al. 2019). Membranes have the dual function of adsorption and filtration which makes it very effective for the removal of trace amounts of heavy metals (Khulbe and

Matsuura 2018). Other remediation techniques for heavy metal removal include coagulation-flocculation, precipitation, adsorption, electrochemical method, and ion-exchange (Barakat 2011; Fu and Wang 2011). Researchers have reported successes with respect to the removal of heavy metals that could be released from oil sands into water bodies using membranes (**Table 3**), several of which have been commercialized while others are still in the developmental phase. Membrane separation of toxic metals has been carried out using liquid membrane, electrodialysis, complexation-enhanced ultrafiltration, micellar-enhanced ultrafiltration, nanofiltration, ultrafiltration mixed-matrix membrane and forward/reverse osmosis (Abdullah et al. 2019). However, membrane fouling and high operational cost are drawbacks for these methods; although back-wash tends to deal with fouling, membrane performance often diminishes over time.

Furthermore, several factors influence the choice of adsorbent phase for membranes used in the treatment of metal pollution, such as the efficiency of the material, non-toxicity, availability of material, flexibility, robustness, reusability, to mention a few (Adeola and Forbes 2019). Several factors need to be considered in the choice of membrane used for removal of heavy metals present in environmental compartments, they include but not limited to; (1) physicochemical conditions such as organic matter content, temperature, turbidity, pH, nutrients/mineral content, etc.); (2) microbial/biotic community (3) Bioavailable fractions of target metals and co-existing metals/contaminants; (4) cost; and other non-technical factors such as environmental regulations, human resources, infrastructure, etc. (Adeola and Forbes 2020).

Table 3: Membrane-based treatment technologies for metal pollution in water

Membrane	Removal of	Present in	Efficiency (%)	Reference
$ZnA1_2O_4–TiO_2$ UF membranes	Cadmium	Water	>90	(Saffaj et al., 2004)
Polymeric exchanger	Copper and Nickel	Wastewater	>90	(Padmavathi et al., 2014)
Polymeric cation exchanger containing nano Zr $(HPO_3\text{-}S)_2$	Lead, cadmium and zince	Water	84 - 98	(Zhang et al., 2008)
Ceria modified carbon	Arsenic	Drinking water	80 - 93	(Sawana et al., 2017)
Chitosan-coated magnetic nanoparticles modified with α-ketoglutaric acid	Copper	Aqueous solution	>95	(Zhou et al., 2009)
Graphene oxide membrane	Copper	Aqueous solution	90	(Wu et al., 2012)
UF membrane (cellulose acetate, nanochitosan, and polyethylene glycol)	Chromium	Tannery effluent	>90	(Vinodhini and Sudha, 2016)
Polyethylenimine-grafted gelatin sponge	Cadmium and lead	Irrigation wastewater	79.7 – 89.9	(Li et al., 2016)
Polypyrrole (PPy) based	Chromium, zinc, lead	Polluted water	>90	(Muhammad Ekramul Mahmud et al., 2016)
Silicon–nitride–BN nanotubes	Zinc	water	-	(Azamat et al., 2014)
Ceramic UF	Iron, copper, chromium	portable water	99.9	(Khulbe and Matsuura, 2018)
Polystyrene and polyHIPE/iron hydroxides	Arsenic	Polluted water	-	(Katsoyiannis and Zouboulis, 2002)
Polymeric membrane	Iron, copper, zinc, vanadium	Polluted water	>99	(Castro-Muñoz et al., 2020)

8. Conclusion

In this review, research problem that requires the world's attention is extensively discussed, because every entity has the corporate and social responsibility to promote clean water and sanitation, sustainable cities and communities, responsible consumption and production, protection of life on land and sea, as well as promoting good health and well-being, as advocated in the 17 Sustainable Development Goals (SDGs) developed by the United Nations. A background knowledge of the toxic metal type, source, and environmental fate is critical in the understanding of associated potential health and ecological risks. The ecosystem is also at risk of collapse due to the persistence of these priority pollutants (toxic metals) in the environment. Membrane-integrated technologies have been reported to have an optimized treatment performance over other conventional remediation strategies, and highly recommended for field applications. The review manuscript provided pathways through which oil sands potentially contribute to metal pollution and highlighted successful remediation of such pollution by application of the synthetic membrane. These are useful information which exploration geologist and technologist should take note, towards optimizing their operations in an eco-friendly and sustainable way. Furthermore, chemical engineers and water treatment practitioners can also evaluate information on materials that work and seek to improve or develop novel materials for improved performance. However, future research should be directed towards the integration of efficient metal recovery systems to natural resource exploration practices and waste disposal management, in order to ensure the safe, sustainable, and ecofriendly exploration of natural resources.

Conflict of Interest

The authors declare that they have no conflict of interest.

References

Abdullah, N., Yusof, N., Lau, W.J., Jaafar, J., Ismail, A.F., 2019. Recent trends of heavy metal removal from water/wastewater by membrane technologies. J Ind Eng Chem 76, 17-38.

Adebiyi F. M., Omode A. A. 2007. Chemical and elemental characterization of components of Nigerian bituminous sands bitumen. Energy Sources Part A Recovery Util Environ Effects 29(8):669–76

Adebiyi F. M., Ore O. T., Akhigbe G. E., Adegunwa A. O. 2020. Metal fractionation in the soils around a refined petroleum products depot, Environ Forensics, 21:2, 121-131, DOI: 10.1080/15275922.2020.1728432

Adebiyi FM, Obiajunwa EI, Akpan I. 2013. Mineralogy of Nigerian bituminous sands using particle induced X-ray emission (PIXE) spectrometry. J Sustain Energy Eng 1(1):1–13

Adebiyi, F. M., Ore, O. T. 2020. EDXRF analysis and risks assessment of potentially toxic elements in sand fraction (tailing) of Nigerian oil sands. Energ Ecol Environ. doi:10.1007/s40974-020-00175-1

Adegoke, O. S. 2000. Historical perspective of bitumen/tar sand development in Southwestern Nigeria. Proceedings of the 1st International Summit on Bitumen in Nigeria, 14-16.

Adeola, A.O., Forbes, P.B.C., 2019. Optimization of the sorption of selected polycyclic aromatic hydrocarbons by regenerable graphene wool. Water Sci Technol 80, 1931-1943.

Adeola, A.O., Forbes, P.B.C., 2020. Advances in water treatment technologies for removal of polycyclic aromatic hydrocarbons: Existing concepts, emerging trends, and future prospects. Water Environ Res. http://doi.org/10.1002/wer.1420.

Akinlua, A., Torto, N., Ajayi, T.R., Oyekunle, J.A.O., 2007. Trace metals characterization of Niger Delta kerogens. Fuel 86, 1358e1364

Al-Marshed A, Hart A, Leeke G, Greaves M, Wood J. 2015. Effectiveness of different transition metal dispersed catalysts for in situ heavy oil upgrading. Ind Eng Chem Res 54(43):10645–10655

Anderson, G.J., 2007. Mechanisms of iron loading and toxicity. Am J Hematol 82, 1128-1131.

Assi, M.A., Hezmee, M.N.M., Haron, A.W., Sabri, M.Y.M., Rajion, M.A., 2016. The detrimental effects of lead on human and animal health. Vet World 9, 660-671.

Asubiojo, O. I., Adebiyi, F. M. 2013. The Impact of Bitumen Deposits on Groundwater Quality. Energy Sources Part A Recovery Util Environ Effects, 36(4), 445–456. doi:10.1080/15567036.2010.536819

Attanasi, E. D., Meyer, R. F. 2010. "Natural Bitumen and Extra-Heavy Oil"(PDF). Survey of energy resources (22 ed.). World Energy Council. pp. 123–140.

Awan M.A, Qazi I.A, Khalid I, 2003. Removal of heavy metals through adsorption using sand. J Environ Sci (China) 15, 413-416.

Azamat, J., Khataee, A., Joo, S.W., 2014. Separation of a heavy metal from water through a membrane containing boron nitride nanotubes: molecular dynamics simulations. J Mol Model 20, 2468.

Babel, S., Kurniawan, T.A., 2003. Low-cost adsorbents for heavy metals uptake from contaminated water: a review. J Hazard Mater 97, 219-243.

Barakat, M.A., 2011. New trends in removing heavy metals from industrial wastewater. Arab J Chem 4, 361-377.

Blum, J. D., Johnson, M. W., Gleason, J. D., Demers, J. D., Landis, M. S., Krupa, S. 2012. Mercury concentration and isotopic composition of epiphytic tree lichens in the Athabasca Oil Sands Region. In *Developments in Environmental Science*. 11:373-390

Castro-Muñoz, R., Gontarek, E., Figoli, A., 2020. Chapter 7 - Membranes for toxic- and heavy-metal removal, in: Figoli, A., Li, Y., Basile, A. (Eds.), Current Trends and Future Developments on (Bio-) Membranes. Elsevier, pp. 125-149.

Cenkci S, Cigerci IH, Yildiz M, Özay C, Bozdag A, Terzi H. 2010. Lead contamination reduces chlorophyll biosynthesis and genomic template stability in Brassica rapa L. Environ Exp Bot 67(3):467–473

Conly, F.M., Crosley, R.W., Headley, J.V., Quagraine, E.K., 2007. Assessment of metals in bed and suspended sediments in tributaries of the lower Athabasca river. Journal of Environmental Science and Health, Part A 42, 1021–1028.

Denkhaus, E., Salnikow, K., 2002. Nickel essentiality, toxicity, and carcinogenicity. Crit Rev Oncol Hematol 42, 35-56.

Douay, F., Pelfrêne, A., Planque, J., Fourrier, H., Richard, A., Roussel, H., Girondelot, B. 2013. Assessment of potential health risk for inhabitants living near a former lead smelter, Part 1: metal concentrations in soils, agricultural crops, and home- grown vegetables, Environ Monit Assess, 185, 3665–3680, doi:10.1007/s10661-012-2818-3.

Drake, P.L., Hazelwood, K.J., 2005. Exposure-Related Health Effects of Silver and Silver Compounds: A Review. Annals Occup Hyg 49, 575-585.

Ebdon L, Hill SJ, Jones P. 1985. Speciation of tin in natural water using coupled high-performance liquid chromatography flame atomic-absorption spectrometry. Analyst 110:551–17

Ekong, E.B., Jaar, B.G., Weaver, V.M., 2006. Lead-related nephrotoxicity: a review of the epidemiologic evidence. Kidney Int 70, 2074-2084.

Emsley J. 2011. Nature's Building Blocks, new edition, Oxford University Press, Oxford, ISBN 978-0-19-960563-7.

Fair A. 2010. CONRAD - Promoting Innovation in the Oil Sands. Presented at the National Buyer/Seller Forum, Edmonton, Alberta. March 25, 2010.

Fu, F., Wang, Q., 2011. Removal of heavy metal ions from wastewaters: A review. J Environ Manage 92, 407-418.

Gaetke, L.M., Chow-Johnson, H.S., Chow, C.K., 2014. Copper: toxicological relevance and mechanisms. Arch Toxicol 88, 1929-1938.

Gopalapillai, Y., Kirk, J. L., Landis, M. S., Muir, D. C. G., Cooke, C. A., Gleason, A., Ho A., Kelly E., Schindler D., Wang X. and Lawson, G. (2019). Source Analysis of Pollutant Elements in Winter Air Deposition in the Athabasca Oil Sands Region: A Temporal and Spatial Study. ACS Earth Space Chem. doi:10.1021/acsearthspacechem.9b00150

Graney, J. R., Landis, M. S., Krupa, S. 2012. Coupling lead isotopes and element concentrations in epiphytic lichens to track sources of air emissions in the Athabasca Oil Sands Region. In *Developments in Environmental Science*. 11:343-372.

Guéguen, C., Clarisse, O., Perroud, A., McDonald, A. 2011. Chemical speciation and partitioning of trace metals (Cd, Co, Cu, Ni, Pb) in the lower Athabasca river and its tributaries (Alberta, Canada). *Journal of Environmental Monitoring*, *13*(10), 2865-2872.

Hadrup, N., Sharma, A.K., Loeschner, K., 2018. Toxicity of silver ions, metallic silver, and silver nanoparticle materials after in vivo dermal and mucosal surface exposure: A review. Regul Toxicol Pharmacol 98, 257-267.

Hashemi, R. 2013. In-Situ Upgrading and Recovery Enhancement of Athabasca Bitumen by Ultra-Dispersed Nanocatalysts. Unpublished Doctoral Thesis, University of Calgary, Calgary, AB. doi:10.11575/PRISM/26558

He, B., Yun, Z., Shi, J., Jiang, G. 2013. Research progress of heavy metal pollution in China: Sources, analytical methods, status, and toxicity. Chinese Sci. Bull. 58, 134–140.

Headley, J.V., McMartin, D.W., 2004. A review of the occurrence and fate of naphthenic acids in aquatic environments. J. Environ. Sci. Health. Part A Toxic Hazard. Subst. Environ. Eng. 39, 1989e2010.

Headley, J.V., Peru, K.M., McMartin, D.W., Winkler, M., 2002. Determination of dissolved naphthenic acids in natural waters by using negative-ion electrospray mass spectrometry. J. AOAC Int. 85, 182e187.

Hebert, C.E., Campbell, D., Kindopp, R., MacMillan, S., Martin, P., Neugebauer, E., Patterson, L., Shatford, J., 2013. Mercury trends in colonial waterbird eggs downstream of the oil sands region of Alberta, Canada. Environ. Sci. Technol. 47, 11785e11792.

Hebert, C.E., Weseloh, D.V.C., MacMillan, S., Campbell, D., Nordstrom, W., 2011. Metals and polycyclic aromatic hydrocarbons in colonial waterbird eggs from lake Athabasca and the peace-Athabasca delta, Canada. Environ. Toxicol. Chem. 30, 1178e1183.

Hersfall M, Mitlie NH, Spiff AI. 1999. Speciation of heavy metals in inter-trdal sediments in Okrika river system. Bull Chem Soc Ethiop 3(1):1–9

Hu, J., Hu, Z., Zhang, Y., Gou, X., Mu, Y., Wang, L., Xie, X.-Q., 2016. Metal binding mediated conformational change of XPA protein:a potential cytotoxic mechanism of nickel in the nucleotide excision repair. J Mol Model 22, 156.

Huang, R., McPhedran, K. N., Sun, N., Chelme-Ayala, P., El-Din, M. G. 2016. Investigation of the impact of organic solvent type and solution pH on the extraction efficiency of naphthenic acids from oil sands process-affected water. *Chemosphere*, *146*, 472-477.

Imtiaz, M., Rizwan, M.S., Xiong, S., Li, H., Ashraf, M., Shahzad, S.M., Shahzad, M., Rizwan, M., Tu, S., 2015. Vanadium, recent advancements and research prospects: A review. Environ Int 80, 79-88.

Islam E, Yang X, Li T, Liu D, Jin X, Meng F. 2007. Effect of Pb toxicity on root morphology, physiology and ultrastructure in the two ecotypes of Elsholtzia argyi. J Hazard Mater 147(3):806–816

Israr M., Sahi S., Datta R., Sarkar D. 2006. Bioaccumulation and physiological effects of mercury in Sesbania drummondii. Chemosphere, vol. 65, no. 4, pp. 591–598.

Kathleen, M.M., Hoang Thi, H., Kyoung-Woong, K., 2011. Arsenic geochemistry and human health in South East Asia. Rev Environ Health 26, 71-78.

Katsoyiannis, I.A., Zouboulis, A.I., 2002. Removal of arsenic from contaminated water sources by sorption onto iron-oxide-coated polymeric materials. Water Res 36, 5141-5155.

Kelly, E. N., Schindler, D. W., Hodson, P. V., Short, J. W., Radmanovich, R., Nielsen, C. C. 2010. Oil sands development contributes elements toxic at low concentrations to the Athabasca

River and its tributaries. *Proceedings of the National Academy of Sciences*, *107*(37), 16178-16183.

Kelly, E.N., Short, J.W., Schindler, D.W., Hodson, P.V., Ma, M., Kwan, A.K., Fortin, B.L., 2009. Oil sands development contributes polycyclic aromatic compounds to the Athabasca river and its tributaries. Proc. Natl. Acad. Sci. 106, 22346e22351

Khalid, S., Shahid, M., Niazi, N.K., Murtaza, B., Bibi, I., Dumat, C., 2017. A comparison of technologies for remediation of heavy metal contaminated soils. J Geochem Explor 182, 247-268.

Khulbe, K.C., Matsuura, T., 2018. Removal of heavy metals and pollutants by membrane adsorption techniques. Appl Water Sci 8.

Kirk, J. L., Muir, D. C., Gleason, A., Wang, X., Lawson, G., Frank, R. A., Wrona, F. 2014. Atmospheric deposition of mercury and methylmercury to landscapes and waterbodies of the Athabasca oil sands region. *Environmental science & technology*, *48*(13), 7374-7383.

Kurek, J., Kirk, J.L., Muir, D.C.G., Wang, X., Evans, M.S., Smol, J.P., 2013. Legacy of a half century of Athabasca oil sands development recorded by lake ecosystems. Proc. Natl. Acad. Sci. 110, 1761e1765.

Kwok, R.K., Kaufmann, R.B., Jakariya, M., 2006. Arsenic in drinking-water and reproductive health outcomes: A study of participants in the Bangladesh integrated nutrition programme. J Health Popul Nutr 24, 190-205.

Larter, S., Huang, H., Adams, J., Bennett, B., Jokanola, O., Oldenburg, T., Jones, M., Head, I., Riediger, C., Fowler, M. 2006. The controls on the composition of biodegraded oils in the deep subsurface: Part II—Geological controls on subsurface biodegradation fluxes and constraints on reservoir-fluid property prediction. AAPG Bull, 90(6), 921–938. doi:10.1306/01270605130

Lee, Y.J., Lim, S.S., Baek, B.J., An, J.M., Nam, H.S., Woo, K.M., Cho, M.K., Kim, S.H., Lee, S.H., 2016. Nickel(II)-induced nasal epithelial toxicity and oxidative mitochondrial damage. Environ Toxicol Pharmacol 42, 76-84.

Li, B., Zhou, F., Huang, K., Wang, Y., Mei, S., Zhou, Y., Jing, T., 2016. Highly efficient removal of lead and cadmium during wastewater irrigation using a polyethylenimine-grafted gelatin sponge. Sci Rep 6, 33573.

Li, C., Fu, L., Stafford, J., Belosevic, M., Gamal El-Din, M. 2017. The toxicity of oil sands process-affected water (OSPW): A critical review. Sci Total Environ, 601-602, 1785–1802. doi:10.1016/j.scitotenv.2017.06.024

Lin, J.L., Huang, P.T., 1994. Body lead stores and urate excretion in men with chronic renal disease. J Rheumatol 21, 705-709.

Lynch, YP, Kernoghan, NJ, Wilson, JN. 1984. Speciation of metals in solution by flow injection analyses. Part I. sequential spectrophotometric and atomic-adsorption detectors. Analyst 109:839–42

Mohammed Abdul, K.S., Jayasinghe, S.S., Chandana, E.P.S., Jayasumana, C., De Silva, P.M.C.S., 2015. Arsenic and human health effects: A review. Environ Toxicol Pharmacol 40, 828-846.

Muhammad Ekramul Mahmud, H.N., Huq, A.K.O., Yahya, R.b., 2016. The removal of heavy metal ions from wastewater/aqueous solution using polypyrrole-based adsorbents: a review. RSC Adv 6, 14778-14791.

Nyakas, A., Han, J., Peru, K.M., Headley, J.V., Borchers, C.H., 2013. Comprehensive analysis of oil sands processed water by direct-infusion fourier-transform ion cyclotron resonance mass spectrometry with and without offline UHPLC sample prefractionation. Environ. Sci. Technol. 47, 4471e4479

Ogunbanjo O, Onawumi O, Gbadamosi M, Ogunlana A, Anselm O. 2016. Chemical speciation of some heavy metals and human health risk assessment in soil around two municipal dumpsites in Sagamu, Ogun state, Nigeria. Chem Speciation Bioavail 28:142–151

Olutona, G. O., Oyekunle, J. A. O., Dawodu, M. O., Ogunwale, T. O., Kehinde, P. 2017. Physicochemical Characteristics of Soil and Health Risk Assessment of Potentially Toxic Metals in Soil and Vegetables from roadside farmlands in Iwo, South-western Nigeria. Environ Sci Pollut Res, 3(3), 213–218.

Oluwole, A. F., Asubiojo, O. I., Nwachukwu, J. I., Ojo, J. O., Ogunsola, O. J., Adejumo, J. A., Filby, R. H., Fitzgerald, S., Grimm, C. 1993. Neutron activation analysis of Nigeran crude oils. J. Radioanal. Nucl. Chem. 168:145–152.

Onojake, M. C., Osuji, L. C., Ndubuka, C. O. 2017. Characterization of bitumen samples from four deposits in southwest, Nigeria using trace metals. Egypt J Pet, 26(2), 547–552. doi:10.1016/j.ejpe.2016.08.002

Oyekunle, J. A. O., Ore, O. T., Durodola, S. S., Oyinloye, J. A., Oyebode, B. A., & Ajanaku, O. L. 2020. Heavy metal levels and changes in trimethylamine content of smoked fish and meat under different storage conditions. SN Appl Sci, 2(6). doi:10.1007/s42452-020-2844-7

Oyewole F. G., Adebiyi F. M. 2017. Total and speciation analyses of heavy metals in the sand fraction of Nigerian oil sands for human and ecological risk assessment, Hum Ecol Risk Assess, 23:8, 2046-2068, DOI: 10.1080/10807039.2017.1364129

Padmavathi, R., Minnoli, M., Sangeetha, D., 2014. Removal of heavy metal ions from waste water using anion exchange polymer membranes. Int J Plast Technol 18, 88-99.

Pereira, A.S., Bhattacharjee, S., Martin, J.W., 2013. Characterization of oil sands process-affected waters by liquid chromatography orbitrap mass spectrometry. Environ. Sci. Technol. 47, 5504e5513

Pillay, AE, Elkadi M, Stephen S. 2014. Application of a hyphenated facility for simultaneous speciation studies of toxic oxidation states [Cr^{3+}/Cr^{6+}] and [As^{3+}/As^{5+}] in produced water from crude oil. Can J Pure Appl Sci 8(2):2807–12

Pilote, M., André, C., Turcotte, P., Gagné, F., Gagnon, C. 2018. Metal bioaccumulation and biomarkers of effects in caged mussels exposed in the Athabasca oil sands area. Sci Total Environ, 610-611, 377–390. doi:10.1016/j.scitotenv.2017.08.023

Plum, L.M., Rink, L., Haase, H., 2010. The essential toxin: impact of zinc on human health. Int J Environ Res Pub Health 7, 1342-1365.

Pourrut, B., Shahid, M., Dumat, C., Winterton, P., Pinelli, E. 2011. Lead Uptake, Toxicity, and Detoxification in Plants. Rev Environ Contam Toxicol Volume 213, 113–136. doi:10.1007/978-1-4419-9860-6_4.

Qufei L, Fashui H. 2009. Effects of Pb2+ on the Structure and Function of Photosystem II of Spirodela polyrrhiza. Biol Trace Elem Res 129(1):251–260

Rafati Rahimzadeh, M., Rafati Rahimzadeh, M., Kazemi, S., Moghadamnia, A.-A., 2017. Cadmium toxicity and treatment: An update. Caspian J Intern Med 8, 135-145.

Saffaj, N., Loukili, H., Alami, S., Albizane, A., Bouhria, M., Persin, M., Larbot, A., 2004. Filtration of solution containing heavy metals and dyes by means of ultrafiltration membranes deposited on support made of Moroccan clay. Desalination 168, 301-306.

Sarwar, N., Imran, M., Shaheen, M. R., Ishaque, W., Kamran, M. A., Matloob, A., Rehim, A., Hussain, S. 2016. Phytoremediation strategies for soils contaminated with heavy metals: Modifications and future perspectives. Chemosphere. 171, 710–721. doi:10.1016/j.chemosphere.2016.12.116.

Sawana, R., Somasundar, Y., Iyer, V.S., Baruwati, B., 2017. Ceria modified activated carbon: an efficient arsenic removal adsorbent for drinking water purification. Appl Water Sci 7, 1223-1230.

Sengar, R. S., Gautam, M., Sengar, K., Chaudhary, R., & Garg, S. 2010. Physiological and metabolic effect of mercury accumulation in higher plants system. Toxicol Environ Chem, 92(7), 1265–1281. doi:10.1080/02772240903450678

Shih, R.A., Hu, H., Weisskopf, M.G., Schwartz, B.S., 2007. Cumulative lead dose and cognitive function in adults: a review of studies that measured both blood lead and bone lead. Environ Health Perspect 115, 483-492.

Sokol, R.Z., Berman, N., 1991. The effect of age of exposure on lead-induced testicular toxicity. Toxicology 69, 269-278.

Speight, J.G. 2001. Handbook of Petroleum Analysis, John Wiley and Sons Inc. New Jersey, 519.

Tenebe, I. T., Emenike, C. P., Chukwuka, C. D. 2018. Prevalence of heavy metals and computation of its associated risk in surface water consumed in Ado-. Hum Ecol Risk Assess, 1–23. https://doi.org/10.1080/10807039.2018.1454824

Tessier A., Turner D. R. 1995. Metal speciation and bioavailability in aquatic systems. J. Buffle, H. P. VanLeeuwen (Eds), John Wiley and Sons, Chichester. p-679.

Tissot, B. P., Welte, D. H. 1984. Petroleum Formation and Occurrence, 2nd Ed. New York: Berlin Heidelberg, 379–473.

Turkdogan M. K., Kilicel F., Kara K., Tuncer I., Uygan I. 2003. Heavy metals in soils, vegetables and fruits in the endemic upper gastrointestinal cancer region of Turkey. Environ Toxicol Pharmacol. 13:175–179

Vinodhini, P.A., Sudha, P.N., 2016. Removal of heavy metal chromium from tannery effluent using ultrafiltration membrane. Text Cloth Sustain 2, 5. https://doi.org/10.1186/s40689-016-0016-3

Wang L, Zachariah A, Yang S, Prasad V, de Klerk A. 2014. Visbreaking oilsands-derived bitumen in the temperature range of 340–400 C. Energy Fuels 28(8):5014–5022.

Wang S, Axcell E, Bosch R, Little V. 2005. Effects of chemical application on antifouling in steam-assisted gravity drainage operations. Energy Fuels 19, 1425-1429.

Wenger L. M., Davis C. L., Isaksen G. H. 2002. Multiple controls on petroleum biodegradation and impact on oil quality. SPE Reserv Eval Eng. 5: 375-383

Wu, J.B., Fu, H.Q., Huang, L.Z., Liu, A.W., Zhang, J.X., 2011. Effects of siRNA-targeting BMP-2 on the abilities of migration and invasion of human liver cancer SMMC7721 cells and its mechanism. Cancer Gene Ther 18, 20-25.

Wu, W., Yang, Y., Zhou, H., Ye, T., Huang, Z., Liu, R., Kuang, Y., 2012. Highly efficient removal of Cu(II) from aqueous solution by using graphene oxide. Water Air Soil Pollut 224, 1372.

Xi, W.-S., Song, Z.-M., Chen, Z., Chen, N., Yan, G.-H., Gao, Y., Cao, A., Liu, Y., Wang, H., 2019. Short-term and long-term toxicological effects of vanadium dioxide nanoparticles on A549 cells. Environ Sci Nano 6, 565-579.

Zhang HQ, Sarica C, Pereyra E. 2012. Review of high-viscosity oil multiphase pipe flow. Energy Fuel. https://doi.org/10.1021/ef300179s

Zhang, Q., Pan, B., Pan, B., Zhang, W., Jia, K., Zhang, Q., 2008. Selective Sorption of Lead, Cadmium and Zinc Ions by a Polymeric Cation Exchanger Containing Nano-Zr(HPO3S)2. Environ Sci Technol 42, 4140-4145.

Zhao, Q., Kaluarachchi, J. J. 2002. Risk assessment at hazardous waste-contaminated sites with variability of population characteristics. Environ Int, 28(1-2), 41-53.

Zheng, L., Kuo, C.-C., Fadrowski, J., Agnew, J., Weaver, V.M., Navas-Acien, A., 2014. Arsenic and Chronic Kidney Disease: A Systematic Review. Curr Environ Health Rep 1, 192-207.

Zhou, Y.T., Nie, H.L., Branford-White, C., He, Z.Y., Zhu, L.M., 2009. Removal of Cu2+ from aqueous solution by chitosan-coated magnetic nanoparticles modified with alpha-ketoglutaric acid. J Colloid Interface Sci 330, 29-37.

Zwolak, I., 2020. Protective Effects of Dietary Antioxidants against Vanadium-Induced Toxicity: A Review. Oxid Med Cell Longev 2020, 1490316.