5. Some Trace Toxins in Environment: Sources, Health Effects and Treatment Technologies

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Abstract:

Trace toxins in drinking water can pose a pressing public health concern worldwide. Despite stringent regulations, such contaminants continue to infiltrate water sources through domestic and industrial discharges, agricultural runoff, geogenic sources, and urban pollution. Exposure to some toxins such as arsenic, cadmium, chromium, fluoride, nickel, pesticides, etc., has been linked to a number of health issues, including cancer, neurological disorders and reproductive abnormalities. Various technologies such as coagulation, coagulation and flocculation, precipitation, adsorption, electricity and/or membrane-based techniques have been successfully employed worldwide for the removal of such toxins. This paper presents a brief overview of some of the trace toxins present in drinking water and the technologies employed for their removal.

Keywords:

Trace toxins; Drinking water; Arsenic; Fluoride; Pesticide; Coagulation

5.1 Introduction:

Trace toxins are chemicals that are present in food, consumer goods, and the environment at extremely low amounts. Even though they are rare, they have the potential to negatively impact ecosystems, wildlife, and human health. These pollutants may come from a variety of sources, such as routine consumer goods, agricultural practices, and industrial processes. Some of the trace toxins include heavy metals, persistent organic pollutants, volatile organic compounds, phthalates, perfluoroalkyl and poly-fluoroalkyl substances, bisphenol A and chlorinated solvents. However, heavy metals are the most prevalent trace toxins. Heavy metals such as arsenic, cadmium, chromium, mercury, nickel, etc., are found in surface water as well as groundwater (Azimi et al., 2017). While some heavy metals are essential for life in trace amounts (e.g., zinc and copper), excessive exposure to certain metals can lead to severe health complications. Generally, a density of 5 g/cm³ is used to define heavy metals (Koller and Saleh, 2018). However, some elements such as fluoride, which are not heavy metals, are also some of the most prevalent trace toxins. Some of the elemental trace toxins have been discussed below.

• Arsenic (As), the twentieth most abundant element in the earth's crust, has a density of 5.7 g/cm³ at 14°C, is a naturally occurring metalloid and is a major component of more than 200 minerals (Bissen and Frimmel, 2003). Arsenopyrite (FeAsS) is the most common mineral of arsenic. It generally occurs as metal arsenides and is rarely found

as a free element in the environment. Arsenic can exist in an oxidation state from +5 to -3 due to the presence of excess electrons and vacant p-orbitals. Air, food and water are the primary pathways through which humans are exposed to arsenic (Basu et al., 2014). Arsenic contamination has been reported in over 100 countries across the world (Shaji et al., 2021).

- **Cadmium (Cd)** and **mercury (Hg)** belong to Group 12 of the Periodic Table. It has a density of 8.65 g/cm³ (near room temperature) whereas mercury has a density of 13.59 g/cm³.Cadmium is a rare element in the earth's crust but is twice in abundance as compared to mercury. Both of these elements primarily occur in the +2-oxidation state. The most predominant mineral ore for cadmium is greenockite (CdS), whereas mercury is mainly found as a brick-red mineral called cinnabar (HgS). Globally, more than 5 million people are estimated to be at risk due to cadmium pollution (Mohankumar et al., 2024). On the other hand, from small-scale mining alone, mercury poisoning is estimated to affect 12 to 15 million people across the world (UNEP, 2024).
- **Chromium** (**Cr**) is a metallic element with atomic number 24 and is found in the earth's crust. The density of chromium at room temperature is 7.15 g/cm³. It exists in multiple oxidation states, with Cr (III) and Cr (VI) being the most common forms. The only ore of chromium is chromite (FeCr₂O₄).
- **Copper (Cu)** is an extremely ductile metal that belongs to group 11 of the Periodic Table. Its density at room temperature is 8.96 g/cm³. The atomic number of coppers is 29 and generally occurs in +1 and +2 valence states. Chalcopyrite (CuFeS₂) is the most common ore of copper which contains approximately 50% of copper.
- **Fluoride** (**F**⁻) is an ionic form of fluorine. Fluorine, with atomic number 9 and density of 1.505 g/cm³ (in liquid state), belongs to group 17 of the Periodic Table and is the 13th most abundant element in the earth's crust. Fluorine is included among the elements required for normal growth and development (Khairnar et al., 2015). More than 200 million people across 25 nations suffer from fluorosis problems (Mumtaz et al., 2015). Caries of temporary and permanent teeth affect globally 486 million children and 2.4 billion people, respectively (WHO, 2021).
- Lead (Pb) belongs to group 14 of the Periodic Table and mainly occurs in 0, +2, +4 valence states. Density of lead is 11.34 g/cm³ at 20°C. Lead in elemental form is very rare but mainly occurs in the mineral form of galena (PbS). Almost one million people die every year due to lead poisoning (WHO, 2022).
- Zinc (Zn) is a trace mineral with atomic number 30 and a density of 7.134 g/cm³. It predominately exists in the +2 state but, in some cases, has also been found to exist in the +1 state, and the possibility of the +3 state has also been realized (Fang et al., 2021). Calamine or smithsonite (ZnCO₃) is the most common ore of zinc.

Metals such as arsenic, cadmium, lead and mercury tend to accumulate in living organisms over time. Hence, they are also called cumulative trace toxins. Pesticides are also among such cumulative toxins.

They are accredited in agriculture as effective tools for controlling pests and minimizing harm to crop plants and agricultural losses. These toxins can persist for long durations in the environment, and bioaccumulate into food chains consequently resulting in biomagnification in the food web with increased concentrations at higher trophic levels.

5.2 Sources:

Pollution of trace toxins in water can be due to either natural or anthropogenic sources. Natural sources include rocks containing mineral ores, volcanic eruptions, wind-blown dust particles, and forest fires. Anthropogenic sources include industrial activities (such as burning fossil fuels), domestic and agricultural activities, mining-related activities and e-waste. Other miscellaneous sources may include incineration of landfills and open dumps, traffic emissions, and biomedical wastes (Bundschuh et al., 2021).

Sources of arsenic include both natural, such as forest fires, volcanic eruptions, dissolution from ores, as well as anthropogenic, including pesticides, herbicides, insecticides, fossil fuels, semi-conductor industries and wood preservatives (Jang et al., 2016). However, the major cause of arsenic toxicity in the world is its elevated levels in drinking water. Cadmium is dispersed in the environment mainly through mining and smelting, but fertilizers, sewage sludge and industries also contribute to cadmium pollution (ATSDR, 2019). Fluoride enters into the environment through both natural and anthropogenic activities. Although natural groundwater beneath the rocks are prime sources, but with growing industrial developments anthropogenic sources must not be ignored. Geogenic sources are the major pathway for natural contamination of fluoride. Fluoride is mainly found as sellaite, fluorspar, fluorapatite and cryolite. Table 5.1 lists the major natural and anthropogenic sources of various trace toxins. Table 5.2 presents the safe limits of drinking water.

Element	Natural	Anthropogenic	Reference
Arsenic		Pesticides, herbicides, insecticides, fossil fuels, semi-conductor industries, mining, smelting and wood preservatives	(Singh et al., 2021)
Cadmium	Weathering of rocks, volcanic eruptions, windblown silica dust, forest fires	Mining, smelting, sewage sludge, fertilizers, industrial wastes, petrochemicals	(Khanna et al., 2022)
volcanic activities,		Solid waste, sewage, mining, coal- fired power plants, fertilizers, smelting,	(Ali et al., 2023)
Copper Volcanic eruptions, windblown dust, forest fires		Mining and smelting, fertilizers, vehicular emissions, agrochemicals	(Mir et al., 2021)
minerals		Motorization, industrialization, and fluoride containing pesticides, fluoridation of drinking water supplies, fire extinguishers, refrigerants, and dental products	(Mohan et al., 2023; Solanki et al., 2022)

Element	Natural	Anthropogenic	Reference
Lead	geothermal activities,	Metal plating, mining, batteries, automobile exhaust, fertilizers, biomass burning, paints	(Eijsackers et al., 2020)
Mercury	Volcanic and geothermal activities, erosion, forest fires Fossil fuel burning, mining and smelting, oil refineries, cement production, biomass burning, indust activities		(Kumari et al., 2015; Tanwer et al., 2022)
Nickel	^	Petroleum and coal combustion, industrial waste, fertilizers, pesticides	(Mustafa et al., 2023)

Contaminant	Recommended limit by WHO (mg/L)	Recommended limit by Bureau of Indian Standards (mg/L)
Arsenic	< 0.01	<0.01
Cadmium	0.003-0.005	<0.003
Chromium	< 0.05	<0.05
Copper	< 2.0	0.05 - 1.5
Fluoride	0.5 - 1.5	1.0 - 1.5
Lead	< 0.01	<0.01
Mercury	< 0.006	<0.001
Nickel	0.02–0.07	<0.02

< 3.0

All elemental trace toxins have natural as well as anthropogenic sources. Pesticides, on the other hand, have only anthropogenic sources. Only around 0.1% of the total amount of pesticides applied reaches the target organism. The remaining chemicals seep into the environment and disrupt the ecological balance (Bhende et al., 2023). Approximately 95% of applied herbicides and 98% of applied insecticides reach non-target soil microorganisms rather than their target pest since pesticides are sprayed proportionately throughout the entire field, regardless of the affected areas (Meena et al., 2020). The physical and chemical properties of pesticides significantly impact their persistence in the soil. The soil sorption processes that regulate pesticide transfer and bioavailability also play a significant role in determining the fate of pesticides in the environment.

5.0 - 15.0

5.3 Environmental Health Impacts:

Zinc

Arsenic is known to severely affect humans and environment. Acute and chronic arsenic toxicity occurs due to ingestion of large quantities of arsenic over short duration and consumption of arsenic contaminated water for a long time period respectively. Humans can get exposed to arsenic through multiple pathways including air, water and food. Arsenic

contamination in drinking water is one of the major causes of cancer in the world (Chung et al., 2014). Arsenic is a potent carcinogen which may lead to skin, liver, bladder and lung cancers. Arsenic is also known to induce epidemiological toxicity (Kushwaha et al., 2023a, 2023b: Mohan et al., 2022, 2023). Excess arsenic also causes cytotoxicity (Chen et al., 2007; Kapadia et al., 2021). Smoking is another route for arsenic exposure. Smoking along with ingestion of arsenic contaminated water has been known to have a synergistic effect (Chung et al., 2014). Food crops grown in arsenic contaminated water allows arsenic to enter into the food chain. Cosmetics are yet another pathway for arsenic exposure. Currently, no international standard for heavy metal in cosmetics has been defined (Chung et al., 2014). Furthermore, chronic exposure to arsenic can lead to arsenicosis, including skin lesions, peripheral vascular disease, black foot disease, and cancers (Fig. 5.1) (Kapadia et al., 2021). In plants, it inhibits growth and interferes with photosynthesis whereas in animals it can affect the embryonic growth in mammals. Apart from its carcinogenic property, arsenic has also been known to have treatment properties. Arsenical pastes have been used for treatment of skin and breast cancers, and also in treatment of leukemia (Hughes et al., 2011). Solution of arsenic has also been recommended for aliments such as malaria, cholera and syphilis (Sambu and Wilson, 2008).

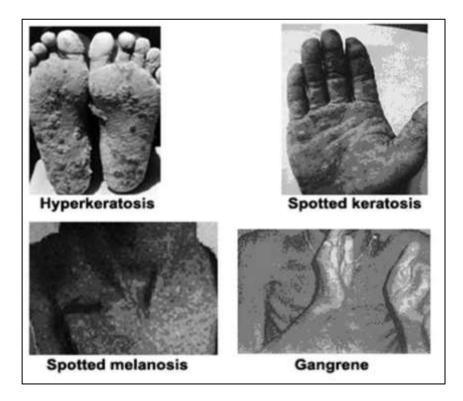


Figure 5.1: Dermatologic effects due to high concentration of arsenic in drinking water (Tareq et al., 2010)

Depending on the uptake concentration and duration, fluoride can have either detrimental or beneficiary effect on human health. Fluoride between 1-1.5 mg/L is essential for the development of bones and teeth and for preventing dental caries among children (Figure 5.2) (Dhar and Bhatnagar, 2009). Ingestion at higher concentrations can lead to dental and

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skeletal fluorosis, which is preceded by mottled teeth in mild cases and neurological complications and brittle bones in severe cases. Fluoride consumption at higher levels (3-6 mg/L) can result in crippling skeletal failure (Rao, 2003). Increased rates of kidney stones, decreased birth rate and impaired thyroid function have also been linked with chronic exposure to fluoride (Dey et al., 2016).



Figure 5.2: Dental and skeletal fluorosis caused due to fluoride in drinking water [Sources: (A) https://fluoridealert.org/issues/fluorosis/; (B) https://fluoridealert.org/news/how-fluorosis-is-crippling-india-and-needs-urgentattention/; (C) https://www.thehansindia.com/posts/index/Hans-Classroom/2018-03-07/Fluorosis/364047; (D) https://en.wikipedia.org/wiki/Skeletal_fluorosis]

Many other trace toxins have also been observed in groundwater as well as in surface water in areas undergoing intensive mining and related activities, and a number of such materials are reported to cause mild to severe adverse effects on plants, animals, and human health. Aluminum toxicity results in liver stenosis and nephrotic syndrome. Its effects on bone marrow leads to the formation of abnormal red blood cells. Osteoporosis and osteomalacia are also the result of the effect of aluminum on the musculoskeletal system. Cadmium has respiratory and cardiovascular effects. It also causes a risk of cancer, bone softening (known as Itai-Itai disease) and also affects reproductive health. Exposure to copper has been linked to cellular damage, which ultimately results in Wilson's disease leading to copper accumulation in the liver, brain, and other vital organs.

Chromium, when consumed in excess, can result in lung cancer, liver damage, and reproductive and neurological problems. Mercury is a cumulative elemental toxin and can result in problems related to the skin and lungs and the deterioration of the nervous system.

Excess of iron and manganese can lead to the formation of precipitates of red and brown colors, posing aesthetic as well as environmental problems. Exposure to nickel leads to skin irritation and can harm the lungs, kidneys and stomach. It can also result in cancer of the skin and other organs (Alka et al., 2021; Azimi et al., 2017). Exposure to pesticides can result in neurological disorders, reproductive problems, skin problems, developmental delays, immune system dysfunction, endocrine disruption, and cancer. Figure 5.3 represents health effects due to exposure to some trace toxins.

A large portion of the pesticide applied gets released into the environment, leading to serious issues such as accumulation and toxicity to non-target organisms. Pesticides can have negative impacts on the environment, including soil contamination, water pollution, harm to non-target species, pesticide resistance, pesticide drift, and bioaccumulation (Kalyabina et al., 2021). They can contaminate both surface and ground water through leaching and thereby accumulate in the food chain (Odukkathil and Vasudevan, 2013). They contaminate soil and reduce soil quality. Its overuse can decrease the diversity of microorganisms in the soil, indirectly impacting soil fertility (Mahmood et al., 2016). Some of the chronic and acute toxicological effects of pesticides are endocrine and reproductive disorders, chronic liver damage, genetic mutations, inhibition of choline esterases, Burkitt's lymphoma, leukemia, Parkinson's and Alzheimer's diseases, etc. (Mostafalou and Abdollahi, 2013). Pregnant women and children are particularly vulnerable to the effects of pesticides, as exposure to these chemicals can interfere with fetal development and cause neurodevelopmental effects in children. Chronic exposure to pesticides has been linked to an increased risk of certain types of cancer, including non-Hodgkin lymphoma, prostate cancer, and childhood leukemia (Lushchak et al., 2018).



Figure 5.3: Human health effects of (A) Cadmium (Dokmeci et al., 2009) (B) Pesticides

(https://serc.carleton.edu/NAGTWorkshops/health/case_studies/pesticides.html) (C) Mercury (https://www.thehansindia.com/posts/index/Hans/2016-11-30/Themercurial-mishap-at-Minamata/266272) (D) Nickel (https://health.howstuffworks.com/skin-care/problems/medical/5-skin-disordersmistaken-for-hives.htm)

5.4 Treatment Technologies:

There are a number of methodologies developed for the removal of such high-potential toxins and more specifically for arsenic, which is the most poisonous among all these. The technologies studied and reported to show efficient removal are adsorption, reverse osmosis, precipitation, etc., to name a few.

However, all of these suffer from one or more demerits, which make them not appropriately suitable for application in a large number of remote pockets in mining-related regions.

Some of the techniques commonly employed in practice may be broadly classified as coagulation and precipitation, adsorption, ion exchange, electrochemical and membranebased processes. Ion exchange is the process of exchanging ions in solution with ions of heavy metals by using zeolites or ion-exchange resins.

This method works well for cleaning wastewater and water, and it's especially helpful for getting rid of cations like mercury, cadmium, and lead. Semipermeable membranes are used in membrane technologies, such as ultrafiltration and reverse osmosis, to extract heavy metal ions from water. Both contaminated groundwater and industrial effluents can be effectively treated using these techniques (Alka et al., 2022).

Bioremediation uses microorganisms such as bacteria, fungi, and algae to reduce the concentrations of heavy metals in the environment. In order to change the metals into less hazardous forms, microorganisms can aid in processes like bioaccumulation, biosorption, and microbial transformation (Kushwaha et al., 2023a). The advantages and disadvantages of various treatment technologies have been discussed in Table 5.3.

Technology	Advantages	Disadvantages
Adsorption	Easy operation; High efficiency; Cost-effective	Low selectivity; Waste production; Requires regeneration of adsorbents
Biosorption	Simple operation; No additional nutrients required; Lesser sludge production; Low operational cost; High efficiency	Highly dependent on pH, temperature, type of bio- adsorbent used, reactive sites
Bioremediation	Environment-friendly; Cost- effective	Time taking; Dependent on environmental conditions
Chemical precipitation	Inexpensive; Simple operation; Multiple metals can be removed	Sludge production
Coagulation/Flocculation	Dewatering qualities; Cost- effective	Sludge generation; Chemical intensive

Table 5.3: Treatment technologies for removal of trace toxins (Carolin et al., 2017;Mohan and Sonam, 2018; Saleh et al., 2022; Shrestha et al., 2021)

Technology	Advantages	Disadvantages
Electrochemical treatment	Metal selective; No chemicals required; Pure metals can be obtained	Cost intensive
Hydrogels	Easy operability; Cost effective; High efficiency; Biodegradable; Reusable and recyclable	Highly dependent on pH, temperature, metal concentration and type of material used for hydrogels
Ion exchange	Metal selective, High revival of materials	Less number of metal ions removed; High cost
Nanofiltration	Selective filtration; Low operating pressure; High efficiency	High operational cost; Requires pre-treatment
Oxidation	No need of electricity	Rusting occurs in the system due to the usage of oxidation
Ultrafiltration	High efficiency; Selective filtration	Energy and cost-intensive; Membrane fouling
Reverse Osmosis	Metal selective; High efficiency; Improved taste and odor	High power consumption; pH sensitive; Membrane fouling

Several new technologies have emerged in the last few decades for arsenic treatment. Techniques such as SONO-Filter have failed to establish itself as a successful technology whereas techniques like ARSIRON Nilogon and AMRIT (Arsenic and Metal Removal by Indian Technology) are still in the field-testing stage.

Solar Oxidation and Removal of Arsenic (SORAS) shows the potential for a better alternative option for lower arsenic concentration due to its vast advantage as compared to other techniques. SORAS is one of the least expensive and simple arsenic removal methods that can be performed even at the household level to treat small quantities of drinking water, and it is also known as Do-It-Yourself (DIY) technique. SORAS was first used for the treatment of effluent from mines and was later put to field test by Wegelin et al. (2000) in Bangladesh. The method uses sunlight irradiation of water in PET- or other UV-A colorless, transparent bottles to reduce arsenic levels. SORAS involves the photochemical oxidation of as (III) to as (V) and its subsequent precipitation by adsorption on Fe (III) oxides (Wegelin et al., 2000).

Citric Acid (lemons, tomatoes, etc.) are used as photo-catalysts, alum is used as a coagulant, ferric chloride (FeCl₃.6H₂O) is also used as a coagulant as well as adds iron to provide adsorption sites to arsenate, sodium hydroxide (NaOH) and hydrochloric acid (HCl) are used to regulate pH of the solution (Gill and O'Farrell, 2015). The method utilizing solar oxidation was employed at the Indian Institute of Technology (Banaras Hindu University) in Varanasi for removing arsenic from synthetic water samples. The organoleptic, physical, and chemical water quality characteristics of the raw water was as detailed in Table 5.4. Arsenic removal generally ranged from 50% to 80%. However, in certain instances, the removal efficiency reached as high as 94% (Mohan, 2022).

Table 5.4: Important water quality parameters of water used for arsenic removal
using SORAS (Mohan, 2023)

Sr. No.	Parameters	Observed Values	Acceptable Limit	Permissible Limit	Reference	
	Organoleptic and Physical Water Quality Parameters					
1	Colour (Hazen Units)	Not Detectable Visibly (< 5 TCU)	5	15	(IS 10500, 2012)	
2	Odour	Not Detectable	Agreeable	Agreeable		
3	pН	6.1 - 8.4	6.5	8.5		
4	Taste	Not Detectable	Agreeable	Agreeable		
5	Total Dissolved Solids (mg/L)	266 - 1496	500	2000		
6	Turbidity (NTU)	Not Detectable Visibly (< 1 NTU)	1	5		
		Chemical Water	Quality Parame	eters		
1	Acidity (mg/L as CaCO ₃)	7 - 60	Not specified in IS10500	Not specified in IS10500	(IS 10500, 2012)	
2	Alkalinity (mg/L as CaCO ₃)	46 - 485	200	600		
3	Hardness (mg/L as CaCO ₃)	172 - 240	200	600		
4	Chloride (mg/L)	5 - 30	250	1000		
5	Sulphate (mg/L)	4 - 25	200	400		

Solar Oxidation can effectively be used for the removal of other elements such as cadmium, chromium, mercury, etc. from contaminated water.

Strong oxidizing radicals (UV-A) produced in the presence of sunlight cause the elements to oxidize from lower oxidation states to higher oxidation states, making them less soluble and, therefore, more precipitable. Its solubility is reduced by the increased electrostatic attraction caused by the higher oxidation state.

The process of solar oxidation was used to remove other elemental trace toxins from polluted water (prepared synthetically in the Environmental Engineering Laboratory) using solar oxidation.

The concentrations used for various soluble compounds related to different elemental trace toxins were approximately 10^{-2} mM. Each transparent and colorless PET bottle received 1 mL of a 10% ferrous alum solution.

Following this, organic acids of vegetable origin were introduced by adding seven to eight drops of lime juice to each bottle, which was then manually shaken for 30 to 45 seconds. The experiments took place on sunny days in April and May 2022, conducted outdoors under field conditions.

The removal percentages observed for the various trace toxins ranged from 50% to 90% (Mohan, 2023). Figure 5.4 presents procedure for removal of elemental trace toxin using solar oxidation and in combination with other treatment methods. SORX stands for Solar Oxidation and Removal of X, where X is an elemental trace toxin such as aluminium, arsenic, cadmium, chromium, cobalt copper, lead, mercury, nickel, zinc, etc.

Various physicochemical techniques, such as Fenton oxidation, adsorption, flocculation, hydrolysis, ultrasound, illumination, etc., have been developed for the removal of pesticides (Pang et al. 2020).

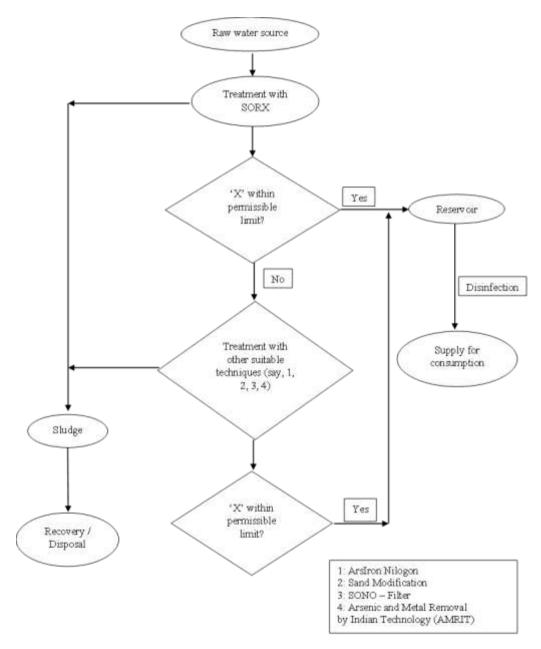
Research have also been focused on safer methods, such as photolysis-based physiochemical approaches and biological methods for a wide range of recalcitrant pesticide residues (Gupta et al., 2016).

Microorganisms with effective degradation capabilities are also being investigated as one of the biological approaches for treatment of such trace toxins. Microorganisms play an important role in the removal of toxic substances from the environment because they contain enzymes that allow them to metabolize environmental contaminants as nutrients for their growth (Shahid et al., 2023).

Bioremediation involves the complete removal of organic toxic pollutants into innocuous or naturally occurring compounds, such as carbon dioxide, water, and inorganic compounds that are safe for terrestrial and aquatic life (Abatenh et al., 2017).

Use of organisms such as bacteria, algae, fungi and yeast have shown potential for removal of toxic substances. Plants have also been employed for removal of trace toxins from the environment.

Use of plants for remediation is termed as phytoremediation. Bioremediation has also emerged as one of the environmentally friendly and promising technique for removal of pollutants from environment.



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Figure 5.4: Procedure for removal of elemental trace toxin using solar oxidation in combination with other treatment methods

5.5 Concluding Remarks:

Certain toxins, even at trace levels in concentrations in drinking water, can present serious health hazards that therefore, cannot be ignored because of their very limited presence. In certain cases, cumulative effects and persistence of such toxins pose quite serious risks to human as well as environmental health. Several technologies exist for the removal of the toxins described above. However, they have certain restrictions on account of the related costs and applicability. SORAS and other similar approaches has shown a potential for removal of a number of above-cited trace toxins and these are not observed to show any major disadvantage. These are the easiest to perform, most economical as well as environment-friendly methods. However, investing in other cutting-edge technologies, enforcing strict laws, and raising public awareness are all crucial to guaranteeing the security of drinking water.

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