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Review Paper

A review of hexavalent chromium contamination in India

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Abstract

Risk from the Hexavalent Chromium has become a worldwide concern. The use of chromium compounds is the greatest chemical problem in the developing countries. The concentration of chromium in drinking water as per World Health Organization (WHO), Unites States Environmental Protection Agency (USEPA) should have less than 0.05 mg/L. Central Pollution Control Board (CPCB), 2012 gave the permissible limit of chromium(VI) for industrial discharge water as 0.1ppm. Chromium causes adverse impact on human health. Due to chromium contamination various health impacts has been reported in Tamil Nadu, Kanpur, Manaliand Balanagar. The present review study deals with the Chromium problems in groundwater, its source, occurrence and case study with special reference to Sukinda Mines, Orissa; Tanneries of Vellore, Tamil Nadu, Kanpur; and from other industrial activities . Sources of chromium are well known. In India Chromites ore mining in Sukinda Valley Orissa and the tannery Industry in Vellore Tamil Nadu and Kanpur is the Main source contributing to come India in the Blacksmith Institute's "worst polluted countries" list. Ganga River is at high risk due to the tanneries of Kanpur. This review paper provides social awareness among the public.

Keywords: Hexavalent Chromium, Toxicity, Mining, Tanneries.

Introduction

Chromium is considered to be an environmentally hazardous element and classified as class-A human carcinogen. Large quantities of chromium in nature exist in the form of chromite mineral, the main source of this metal. The use of chromium and chromium compounds are increased due to rapid industrialization. In metallurgical industry, it is used for the manufacture of various alloys and steel. Chromate ore is also extensively used in making refractory materials like bricks. Chromate is used in chemical industry to make a number of chromium containing chemicals. Chromium compounds are used in electroplating, tanneries, catalysts, pigments, wood preservatives and corrosion inhibitors[1].

All these wide ranging applications of chromium may be the source of contamination in environmental matrices. Chromium exhibits varying oxidation state of 0 to 6. The oxidation states mostly found are chromium(0), trivalent and hexavalent[2]. Naturally trivalent chromium is present in environment. Various foods contain trivalent chromium. The intake of trivalent of chromium is essential for the human body as it promote the action o insulin. Hexavalent and zero-valent chromium are introduced into the environment due to various industrial processes. Sources and forms of chromium liberated through various industries are listed in Table-1.

Toxicity of chromium varies with the oxidation state of metal and species involved. Cr(III) is an important part of most of the biological tissues and is non toxic whereas Cr(VI) is toxic in nature. This paper reviews the fate, mobilization and environmental impact of chromium, further the extent of chromium contamination at various sites generating chromium waste in India[3].

Table-1: Sources of Cr(III) and Cr(VI).

Sources	Chemical Forms of chromium	Environmental matrices
Emission from burning of coal and oil, steel production	Cr(III)	Air
Welding of Stainless steel, Manufacturing of Chemicals, Use of chromium containing compounds	Cr(VI)	Air
Waste stream from electroplating	Cr(VI)	Water
Leather tanning, Textile Industries, Dyes and Pigments Industry	Cr(VI) and Cr(III)	Water
Disposal of waste containing Cr from industries and coal ash from electric utilities	Cr(III) and Cr(VI)	Soil

Fate of chromium in abiotic environment

Chromium enters in to various environmental matrices mostly in Cr(III) and Cr(VI) form.

The behavior of chromium in environmental system is affected by partitioning behavior, reducing/oxidizing system in the environment and the rate of flow of the aqueous phase[4].

Cr(III) is stable and immobile, hence its bioavailability decreases. Literature reports the presence of inorganic species of chromium in both oxidizing and reducing environment at different pH (Table-2).

The type and condition of the soil is responsible for the dynamic exchange of chromium forms, like pH and Eh, presence of organic matter, micro-organism, Fe(III) and Mn oxides in the soil horizon[3]. The solubility of chromium is largely depended upon the pH of the environmental system. Cifuentes et al reported that above pH 7, chromium oxides (Cr_2O_3) and hydroxides ($Cr(OH)_3$) are formed which settles down as insoluble precipitates and hinder the mobility of Cr(III) $CrOH^{2+}$ and $Cr(OH)_2^+$ may exists in the soluble form[5,6].

Electron donor organic matter may form complex with Cr(III) even in acidic environment and alter the solubility of Cr(III). These complexes is considered to be insoluble in terms of its bioavailability[7,8]. Although the complexes themselves are soluble at acidic to circum neutral pH[9]. In aerobic condition oxidation/reduction cycling of Fe and sulfur is driven by microbial respiration, and can lead to chromate reduction $Cr_{1-x}Fe_x(OH)_3 \cdot {}_nH_2O$ precipitates[10].

Major environmental consequences of chromium is the solubility, mobility, bioavailability and toxicity of Cr(VI) species. Manganese oxide present in soil is the only oxidant of Cr(III)[3]. Yuanzhi Tang, reported the presence of photochemical carbon for the sustained oxidation of Cr(III) mediated by manganese oxide. However, a large concentration of chromium in soil is not oxidized to Cr(VI) due to the lack of availability of mobile Cr(III) even in the presence of manganese oxide and favorable condition[11].

The soil with high Mn(VI) oxides and low organic matter showed oxidation of Cr(III) to Cr(VI) which is facilitated only when the concentration exceeds both the adsorbing and the reducing capacities of the soil and water system. Oxidation also occurs by low oxizidisable organic matter, oxygen, manganese dioxide and moisture. Oxidation is also enhanced at elevated temperatures[12].

Stability of Cr(III) is due to the various physio-chemical reaction in soil which is governed by the type and condition of soil environment. With the increase in pH, thermodynamically stable form of chromium is +3 and +6. Cationic trivalent chromium form is immobile and less toxic as it is retained in the soil particles through the process of adsorption, complexation with soil organics, formation of oxides and hydroxide and other mineral compounds[13].

The common cationic species of Cr(III) in aquatic environment are Cr_3^+, $Cr(OH)_2^+$, $Cr_2(OH)_2^{4+}$ and $Cr_3(OH)_6^+$. Cr(III) is precipitated as chromium hydroxide {$Cr(OH)_3$} or chromium oxide Cr_2O_3 at pH >5.5. Cr(VI) occurs as chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$). Land disposal wastes containing chromium comes in contact with oxidant and reductant in soil. The redox reactions results from the contact may enhance or reduce the risk and rate of subsequent toxicity and mobility[3].

Toxicity

Chromate CrO_4^{2-} predominates in basic pH value whereas dichromate ion $Cr_2O_7^-$ is favored under acidic conditions[3]. Both ions are strong oxidizing agent and are known to cross the cell membranes and thus can target genes causing genotoxic effects. According to literature genotoxicity is associated with laboratory compounds of chromium, tannings used in leather industry, volatile chromyl chloride used in variety of process fume particles emitted during welding process, and pigments used in paints. Soluble Cr(VI) compounds are the most active mutagens in short-term tests, whereas poorly soluble Cr(VI) compounds are most powerful carcinogens in long-term assays on mammals[14].

Mining of Chromite ore

Chromite ore is the principle ore of the element chromium. According to the annual report submitted by the "ministry of mines"- government of India showed that India's ranking in 2012 was 3rd in chromite ore production. Orissa reported almost entire output of chromite (96- 99%) in the country.

Sukinda valley situated in Dhenkaanal and Jajpur district of Orissa containing about 98 % of chrome ore reserves. Jajpur district is known as chromite hub as the chromite ore in sukinda mines are spreaded over 200 sq.km[15]. The open cast mining for chromium is being carried out since 1950 and there are 20 open cast mines and 2 underground mines.

Table-2: Aqueous species of chromium in different pH.

pH 4		pH7		pH10	
Oxidizing Environment	Reducing Environment	Oxidizing environment	Reducing environment	Oxidizing environment	Reducing environment
$HCrO_4^-$	$CrOH^{2+}$	$HCrO_4^-$, CrO_4^{2-}	$CrOH^{2+}$, $Cr(OH)_2^+$	CrO_4^{2-}	$Cr(OH)_4^-$

Source: Environmental Chemistry, Gary W. Vanloon and Stephen J. Duffy[4]

The open cast mining generates lots of over burden which results in leaching of the Cr(VI) to groundwater regime. Ground water in the Sukinda valley is found at a shallow depth[16]. According to the report, it was found that twelve mines continue to operate without any management plans and over surrounding and at the bank of Brahmani river more than 30 million tons of waste rocks Around 7.6 million tons of solid wastes which have been generated as rejected minerals, over burden material/waste rock and sub-grade ore results in environmental degradation and it is mainly causing lowering in the water table as well as deterioration in water quality of surface and ground water[17]. Most of the mines causes seepage as it is situated at the upstream of the Dhamasala Nala. The seepage water contains water with heavy metals such as hexavalent chromium[18]. Das et al reported that the alkaline pore water is being generated due to lateralization process which mainly involves oxidation and alteration of the serpentines. This alkaline pore water facilitates the generation of Cr(VI) from inert chromites and causes the water to be polluted by hazardous chromium. The ground water and the chrome ore together when come in contact with the atmospheric air, it gets contaminated with Cr(VI) beyond permissible limits[19]. The survey data from the Odisha Voluntary Health Association (OVHA) (1995) reported more than 85% deaths in the mining areas, and 86% deaths in the nearby villages which occurred due to diseases caused by hexavalent chromium polluted water[20]. However, till now there is virtually no management plans to reduce and remove this contamination. There are many local organizations which are protesting against the mining activities. The Sukinda valley in Odisha has made its place in list of top ten of the world's 30 most polluted places[21].

Leather industry

Tanning industries in India is contributing high Cr contamination to the environment. These industries of India alone contributes about 2000-3000 tons of Cr contamination to the environment in which Cr concentration ranges from 2000-5000 mg/L in the aqueous effluent[22]. Of the several different process involved in leather manufacturing, tanning of raw hides is one of the important process. In this process chromium compounds are most widely used and the indiscriminate disposal of tannery waste is resulting in widespread Cr contamination of both soil and groundwater in the area[21].

More than 60% of Indian tanneries are in Vellore district. More than 500,000 hectare productive lands have been contaminated by Cr(VI) which shows Cr(VI) contamination >200 mg/L in the year 2011-2012. As the soil samples were collected from more than 65 hot-spots and the wide variations of Cr(VI) concentration from trace to 1646 was shown[21,23,24]. As Cr can seep into the soil and contaminate ground water system, the above data really shows that the soil close to tanneries is severely contaminated with Cr. Sundar et. al reported severe contamination of soil due to Cr from tannery wastes in Vellore.[25] Water contamination is limited to surface water and because of the reason that Cr strongly attaches to the soil within the slit layer it contaminates the ground water little less. The soil Cr concentration was increased due to leaching process. Reason why it happens is the reduction in soil Cr might be due to oxidation of Cr(III) to Cr(VI), which dissolve in water leached down in the soil profile and reached the ground water[25]. This is how the area nearer to the effluent contaminated with Cr(VI) tanneries are getting contaminated. In Erode district of Tamil Nadu, there is high protest from the farmer against the effluents form the tannery industries to protect the Kalingarayan canal. The 91-kilometre Kalingarayan canal contains more than 44 tanneries and 532 dyeing units near it. The contaminated effluents from these industries have affected the biota of the surroundings. In the long run, dissolved oxygen in the canal water would get reduced and affect aquatic life in the Bhavani river.

The mushrooming tannery industries of north- India have converted the clean Ganga to a polluted one by dumping wastes into it. As per estimation about 50-70% of the tanneries discharge its effluent in to the environment out of total 80-90% tanneries of Kanpur.

The Cr(VI) was only found to exceed its lowest effect level (LEL) and probable effect level (PEL). Cr(VI) was only found to may cause or contribute sediment toxicity to fresh water ecosystem of the Ganga River. So River Ganga is at high risk of Cr(VI) contamination[26].

Leather complex, situated 20 km away on the southern periphery of Kolkata, is a living hell. Supreme court had ordered 538 polluting tanneries of the city to relocate at the periphery, which was previously situated at the middle of the city. The court also advised to treat the waste according to the guidelines prescribed by it. The Calcutta leather complex (CLC) has shifted to Bantala from Tangra, Topsia and Tiljala in 2005. Surrounding area has high smell of chemicals which are used to treat leather, water canals was found choked by animal's hair and fat. Water in the canal was found to have red which can be either due to blood or due to the dye or chromium. Binay Dutta, chairperson of WBPCB, says, "Surveillance on our part is high. Our teams regularly monitor groundwater". Last year about 18 tanneries got notice by WBPCB as it was violating the pH level, TSS (total suspended solids) and chromium. TSS of the tanneries was found to be 2,400 mg/L whereas the prescribed standard level is 600 mg/L and the chromium level was found to be 190 mg/L in some tanneries. In July 2012 the TSS and the chromium level was found to be as high as 10,820 mg/L and 1,155.3 mg/L respectively. The tanneries of the Kolkata were given notice for closure and the electricity was disconnected but within a month the notice was revoked and the work in industries was resume[27].

Other Contributing Industries

In Balanagar, Hyderabad the average concentration of Cr(VI) was found to be 178.5 mg/kg and much higher concentration was found near the industries as 90.8 mg/kg to 551.6 mg/kg. The source of Cr(VI) was found to be anthropogenic from some industries producing steel, textiles and some chrome plating industries. Inadequate disposal of the effluents were found to contribute towards the high concentration of Cr(VI) in the ground water[28].

The study of heavy metal in soil around Manali industrial area in Chennai, southern India revealed that the area was affected by many heavy metals due to the activities of industries like petrochemicals, refineries and fertilizers. The basis of soil analysis was geo-accumulation, enrichment factor(EF), contamination factor and the degree of contamination. The chromium was reported with elevated concentration (149.8-418 mg/kg with an average of 221.7 mg/kg)[29]. The contaminated site possesses high environmental risk for land and water systems. Ansari et al also reported high chromium contamination (2,000 mg/kg) in industrial area[30]. In India there are many other industries that are contributing to Cr(VI) contamination to the environment. Some of the industries are listed in Table-3.

Table-3: Various Industrial sources of Cr(VI) contamination in India.

Site Location	Polluter	Number of contaminated sites	Main polluter product	Type of waste generated	Quantity of waste	Primary contaminant
Vadodara	Hema chemicals unit-II	1	Basic chrome sulphate(BCS)	Chromium residue	Approx.77000 tonnes of waste	Chromium
Talcher	Orichem Ltd. (closed)	1	Sodium dichromate	Leached residue	60000tonnes of waste	Chromium
Sundargarh	Konarkcrome chemicals & Lotus Chemicals	4	Sodium dichromate	Leached residue	-	Chromium
Mayurbhanj	Kerbs & Cie (closed)	5	Sodium dichromate	Leached residue	15000 MT/ 330 MT/45 MT/225000 MT/1275 Mt of waste at 5 locations	Chromium
Ranipet	Tamil Nadu chromates & chemicals Ltd.	1	Sodium dichromate, BCS	Chromium residue	7.41 acres of contaminated site, 2-4 m Ht. chrome bearing waste. Approx. 2.2 lakh tones of waste.	Chromium
Kanpur Nauraiya, kheda	Ashoka chemicals Pvt. Ltd.(factory dismantled long back)	1	-	Mostly BCS waste containing heavy metals	Area of 6000 sq.ft. approx. size could not be exactly ascertained as many pucca house have been constructed on it. Approx.15000 tonnes of waste.	Chromium
Kanpur juiBaburaiya (rakhimandi)	Kanpur Chemicals (factory dismantled long Back)	1	-	Mostly BCS waste containing chromium	Area of 5-6 acres approx. owners not known. At present area is densely populated with settlement and households. approx. 10000 tonnes of waste.	Chromium
Khanpur village, Kanpurdehat	Cerrelena chemicals, warsi chemicals, chandani chemicals, ameliya textiles, hilger chemicals (all units closed & dismanted long back)	1	-	BCS wsates	Approx. 450000 tonnes of waste	Chromium

Source: List of Hazardous waste contaminated dump sites in the country (as per the information received from SPCBs) http://www.cpcb.nic.in/LIST_OF_HW_CONTAMINATED_SITES.pdf.[31]

Conclusion

This paper establishes a high discharge of Cr(VI) to the environmental matrices from various industries and mining activities and also puts light on the environmental fate and transport of chromium including exposure pathway to human. The population residing near and the workers of the industries may experience various health problems due to the exposure of hexavalent chromium contamination. Due to high mobility of Cr in soil and high solubility in water the concentration of chromium in soil decreases and in water it increases. The reason behind this was leaching of chromium from the wastes. The risk in the contaminated water was also due to salinity and sodicity of chromium compounds. This makes the water unsuitable for drinking and irrigation purpose. A comprehensive health effect and environmental impact assessment in prior to setting up of chromite ore mines or tannery industries and steel industries can review discharges to the environment and potential pathways of exposure for workers and to public. Specific mitigation and control strategies can be employed to ensure that objective related to protection to human and environment are met.

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