**Chromium Contaminated Soil-Groundwater Systems at COPR Site in Rania and Khan Chandpur Villages, Kanpur Dehat, India**

**1. INTRODUCTION**

Observing the increasing concern over groundwater contamination and deteriorating soil-water quality, we moved to Rania and Khan Chandpur villages in Kanpur Dehat district in Uttar Pradesh. Rania-Khan Chandpur site is one of the highly contaminated sites in India (Prakash et al. 2011; CPCB, 2023) due to Chromite Ore Processing Residue (COPR), which is a hazardous (waste) remnant of the chromate (CrO42-) extraction roasting process (Földi et al. 2013; Matern et al. 2017; 2020). As per report of the oversight committee, Hon’ble NGT, U.P. Lucknow, there is an estimated volume of 1,22,800 m3 COPR at Rania site (which has recently relocated to the treatment, storage, and disposal facility (TSDF) located 25Km from this site near Akbarpur, Kanpur Dehat). Both the villages are settled in the vicinity of the leather processing clusters and COPR waste from these tanneries and related industries has severely contaminated soils, the surface-water, and the groundwater. The residents are drinking Cr-containing groundwater and are continuously at risk through the poisonous intake either through groundwater or locally grown vegetables or other sources (Gupta et al. In Preparation). Regardless of this situation, the remediation practices of Cr-contaminated soil-water systems remain unattempted at the Rania-Khan Chandpur, this is because the site-scale Cr fate and mobility in the subsurface is still less investigated.

Cr leachate from the COPR can infiltrate in the vadose zone and ultimately reach the (shallow-) groundwater which can lead to huge Cr contamination in the subsurface. Our initial (Gupta et al. 2023a; Deoli et al. 2023) and other’s works (Singh et. al., 2009; Matern et. al., 2017) have found that groundwater, surface-water, and soil samples from t**he past** have shown signs of a Cr emanating from the COPR dump site in and around Rania-Khan Chandpur villages. In the subsurface, Cr can be in the form of Cr (III) or Cr (VI), the mechanisms and kinetics of Cr release are obscure (Bhattacharya et. al., 2019). The release of Cr from the COPR dump site can be influenced by factors such as the pH of the water/soil, the presence of other chemicals or ions, the hydrogeology and hydrology of the site, the above and below-ground ecology and microbial community dynamics, and so on. Further, climate change may influence the fate and mobility of the Cr by altering the hydro-metrological and subsurface conditions. A better understanding is needed to improve remediation practices including evaluation of potential Cr transport pathways and rates, and more efficient clean-up strategies. However, there remains a dearth of knowledge on Cr fate, transport, and remediation in the soil-water system.

Further, vegetation and microbial communities were identified that can thrive in Cr stress conditions. Plant-bacterial relationships can adsorb, decrease, and precipitate Cr, especially when it comes to Cr (III) and Cr (VI) forms (Thatoi et al. 2014). These plants exhibit strong potential for stabilizing and detoxifying contaminated soils because of their inherent resistance mechanisms and high metal-uptake capacities (Antoniadis et al. 2017). In addition to these plants, several microbes exhibit remarkable abilities to reduce Cr concentrations via the sulphate transport pathway, passive transport, and chromium accumulation pathways (Wang et al. 2015). Among the widely used techniques is the sulphate transport system, which is found in many bacteria, including *Salmonella typhimurium*, *Bacillus subtilis*, *Escherichia coli*, *Pseudomonas fluorescens*, and *Alcaligenes eutrophus* (Su et al. 2023). The function of sulphate transporters is essential for Cr (VI) tolerance because they control both sulphur availability and chromium uptake. This is because CrO42- and sulphate (SO42-) have similar chemical makeups and can compete for the same transporters (Takahashi et al. 2012). Hence, the most effective method for removing Cr (VI) from the hydrogeological matrix is the reduction of Cr (VI) to Cr (III) followed by its adsorption (Fan et al. 2019).

Critical levels of Cr contamination have been found in the groundwater of Rania-Khan Chandpur villages. This contamination primarily results from the improper disposal of tannery waste, including Basic Chrome Sulphate (BCS) sludge. Groundwater has been reported to contain Cr(VI) concentrations as high as 34.8 mg L⁻¹ (Matern et al. 2017). and total chromium levels as high as 40 mg L-1 (Gupta et al. 2024), far surpassing the 0.05 mg L-1 Bureau of Indian Standards (BIS) permitted limit for drinking water. Significant groundwater pollution is additionally indicated by the high levels of electrical conductivity (2243 µS cm-1), sulphate (385 mg L-1), and fluoride up to 4.02 mg L-1 (Srivastava et al. 2013). According to health risk assessments, children's non-carcinogenic Hazard Index (HI) can be as high as 5.214, which is far higher than the safe threshold (HI > 1) and indicates negative health impacts. Furthermore, all receptors have a carcinogenic risk for Cr (VI) greater than 1 × 10⁻⁶, and children are at risk for cancer almost 8.6 times higher than adults (Guleria et al. 2022).

A comprehensive analysis of soil samples from contaminated areas can reveal a diverse array of bacterial communities in both the soil and COPR samples. These findings can offer valuable insights into the microbial dynamics of subsurfaces affected by Cr contamination and underscore the significant Cr retention potential of bacteria (Tripathi et al. 2022). A better understanding of native plants and microbes will help to design bioremediation of such a highly contaminated site. This integrated approach of using both native plants and microbes holds promise for sustainable and effective bioremediation strategies. But to provide optimal hydrogeological conditions for remediation is equally important.

Cr contamination, particularly from COPR, has caused significant environmental damage, especially in places like the Rania-Khan Chandpur. The vadose zone and groundwater have been exposed to chromium, mostly in Cr (VI), which has leached from COPR disposal sites and resulted in higher than usual amounts of this hazardous metal in water sources. The region’s humid subtropical climate enhances the mobility of Cr(VI), thereby increasing contamination levels and posing serious risks to human health, plant life, and soil microbial communities. A comprehensive analysis of soil samples from contaminated areas can reveal a diverse array of bacterial communities in both the soil and COPR samples. These findings can offer valuable insights into the microbial dynamics of the subsurface affected by Cr contamination and underscore bacteria's significant Cr retention potential. A better understanding of native plants and microbes will help to design Cr-bioremediation for such a highly contaminated site. This integrated approach of using native plants and microbes holds promise for sustainable and effective bioremediation strategies. However, to provide optimal hydrogeological conditions for remediation is equally important. Previous studies have often lacked the use of UAV surveys to accurately map contaminated zones and assess the land-use changes caused by Cr contamination. This paper integrates UAV surveys with groundwater and soil data for a more comprehensive understanding of contamination spread and provides insights into the spatial extent of chromium distribution.

Previous studies have found that the use of UAV surveys to accurately map contaminated areas and assess changes in land use caused by chromium pollution has often been overlooked (Khosravi et al. 2021; Capolupo et al. 2015). This research has provided valuable information about the extent of Cr distribution in space and has integrated UAV surveys with groundwater and soil data to gain a more comprehensive understanding of the contaminated areas. To gain a more comprehensive understanding of contamination spread, this work will integrate UAV surveys with groundwater and soil data. Furthermore, it will provide insight into the spatial extent of Cr distribution.

Considering the research gaps prior to the implementation of this research work, a series of investigations has been initiated to generate baseline data of soil-water quality at the Rania-Khan Chandpur site. This has resulted in basic knowledge of the initial site conditions and profusion of excellent baseline data facilitating a better understanding of the soil-water system at this site. In this research work, the fate and mobility of Cr in the subsurface under varying hydrogeological conditions will be investigated first. Thereafter, the performance of the remediation techniques will be evaluated for restoration of Cr-contaminated soil-water systems at a demonstrative site in Rania-Khand Chandpur villages. This project will provide very accurate, multimethod techniques for the forecasting of the Cr mobility in the subsurface, which can assist the site managers/stakeholders for the future site scale planning. Further, this project will not only improve our understanding to manage a highly contaminated site in India, but also help in the management of such contaminated sites in other parts of the globe.

Further, the presence of naturally resistant microbial communities makes it difficult to develop effective remediation strategies for Cr contamination. Although some data exists, there is inadequate documentation of the distribution and concentration of both Cr (III) and Cr (VI) in various environmental media such as soil and groundwater. Despite awareness of the contamination, there has been limited initiation and study of active remediation in soil-water systems. In the present study our objectives are: (1) To measure Cr contamination in soil and groundwater, using UAV surveys to map and prioritize remediation areas., (2) To identify native plants and microbes for bioremediation, and implement a pilot project to test their effectiveness. (3) To integrate hydrogeological and microbial data into a framework for long term Cr management.

**2. Cr Global and National Distribution**

**2.1 Global Sites**

About ten million tons of chromium are produced globally each year. South Africa, Turkey, China, India, and Kazakhstan are the top five countries for chromium production in the world from which South Africa produces almost two-fifths of the chromite ores and concentrates. (Mohanty et al., 2011; Mishra and Bharagave 2016). Oruko et al. (20121) investigated two industrial sites Dongo Bonde Ltd. in Kenya and Bath Ore in South Africa. They found the mean Cr (VI) concentration in treated effluent were 1.82 ppm and 7.9 ppm respectively. In California, the Cr concentration levels in soil samples have varied between 140 to 2220 mg/kg soil (Mills et al., 2011) and in groundwater samples the maximum Cr concentration level has been reported 50 μg/l (Izbicki et al., 2018). Approximately 40% of water resources are polluted with Cr (VI) in California (Sedman et al., 2006). In the Sarigkiol Basin of Greece, up to 120 μg/l of Cr (VI) has been observed in groundwater and the Cr (VI) level varied from 20 – 55 μg/l in spring water (Kazakis et al., 2017). In Sohag Governorate, Egypt, the total Cr concentration level has been reported to be up to 260.6 μg/l which is very higher than the preferred limit of 50 μg/l, set by WHO 2011. The Cr (VI) variation in that area varies between 12 to 58 μg/l (Salman et al., 2020). In Aosta Italy, the Cr (VI) in groundwater varies maximum up to 165 μg/l from minimum value of 0.09 μg/l.

Countries like USA, Argentina, Pakistan, Bangladesh, Germany, Indonesia have suffered from Cr concentration in groundwater (Table 1; Figure 1) (Coyate et al., 2020; Ali et al., 2022; Khan et al., 2022; Vainshtein et al., 2003; Astuti et al., 2023). As per the study conducted in Henan Province (Chen et al., 2021), the concentration of Cr (VI) was maximum up to 299.99 mg/l in shallow groundwater samples and in deep groundwater samples it varies up to 56.30 mg/l. High concentrations of Cr and Cr (VI) have also been reported in some belts of Turkey, Brazil, Morocco (Tokatli, 2021; Hirata et al., 2007; Lotfi et al., 2020). Due to Cr concentration is soil-water system, stomach and lung cancer have been reported in Jin Zhou, China (Zhang and Li, 1987).

**2.2 Indian Sites**

In India, there are more than 18 chromium contaminanted sites and total of 111 probably Cr contaminated sites including Rania-Khan Chandpur (Kanpur, Uttar Pradesh), Sukinda Valley (Odisha) and Ranipat (Tamil Nadu) are the worst-hit states with a high abundance of Cr in soil-water system (CPCB, 2023) (Table 2; Figure 2). In many other states, the levels of Cr have exceeded the permissible limit which creates the consequences. The highest concentration of Cr and Cr (VI) have been reported in Sukinda Valley with values of 48.7–250.2 and 21.4–115.2 μg/l respectively (Naz et al., 2016). In Rania-Khan Chandpur Villages of Kanpur Dehat, Uttar Pradesh The maximum value of Cr in groundwater reported as 33.88 mg/l (Singh et al., 2012). Matern et. al. (2017) found the maximum Cr concentration in Rania and Chhiwali (Kanpur Dehat Uttar Pradesh) maximum up to 34.8 mg/l and 115 mg/l respectively. In Bangalore India, the Cr (III) concentration in surface soils very from 14.9 mg/kg to 718.1 mg/kg whereas in the deep soil 15.1 to 116.1 mg/kg which is showing the surface Cr pollution load is more due to the COPR dumping (Ratnalu ei al., 2021). Previously, similar study has been carried out by Paul et al. (2014) for Jajmau India for agriculture soil, which contains 40,500 mg/kg Cr and 1,400 mg/kg Cr (VI). The groundwater table of Punjab, Rajasthan, New Delhi have also been reported to Cr contaminated.

A map of the world

Description automatically generatedFigure 1: Cr contaminated sites of World

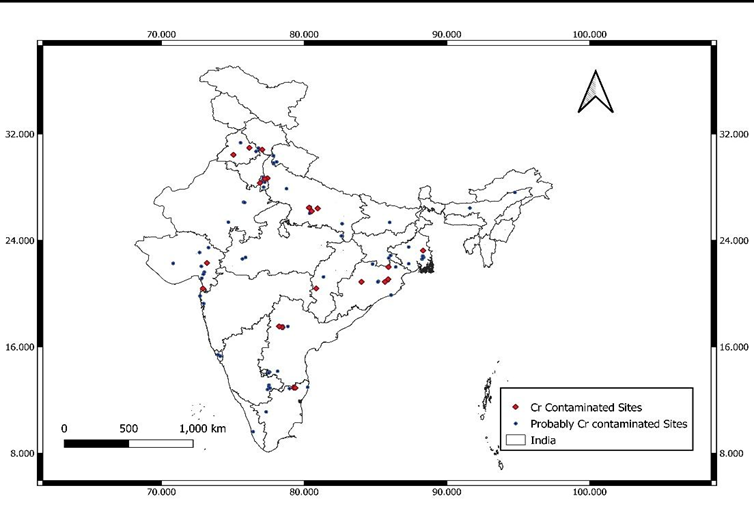


Figure 2: Cr contaminated and probably Cr contaminated sites of India

**Table 1: Global distribution of Cr in different subsurface soil conditions, Vadose Zone and in groundwater systems**

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| --- | --- | --- | --- | --- | --- |
| **Citation** | **Lat/long** | **Scale of Study** | **Samples/Environmental Conditions** | **Methods** | **Key Observations** |
| Szecsody et al. (2019) | Hanford (36.327728N, 119.645912W) | Lab Scale | Cr contaminated sediment collected from vadose zone | * 1D leaching experiment in 2.35 cm diameter and 15-20 cm long column. * Cr (VI) was measured via a spectrophotometer at 540 nm. * EDS was analyzed for Cr in sediment. * Batch Experiment | * Columns with high concentrations of Cr (VI) (up to 187 mg/l Cr (VI)) rapidly leached more than 90% of the Cr (VI) in the vadose zone. * In natural groundwater Barium was not present above the detection limit for the studied area. * A significant amount of Cr was found in the surface phase identification of vadose zone sediments |
| Ballesteros et al. (2017) | Ltitlan (21.127800 N, 98.650787W) | Lab Scale | Soil, Slag and Demolition residues chromates samples were collected from the dumping site. | * XRF, atomic absorption ICP and C and S combustion were used for chemical characterization. * TCLP was used for the lixiviation of the toxic substance. | * All Cr (VI) were reduced to Cr (III) in the residual glass network. * The Cr (VI) in the glass ceramics was low (<0.22 mg/kg). * The final ceramics showed adequate mechanical properties. |
| Broadway et al. (2010) | Glassgow (55.8617° N, 4.2583° W) | Lab Scale | * 27 soil samples collected. | * Chromium was determined by ICP-OES. * UBM and Gamble’s solution used for speciation of Cr. | * Total Cr and Cr (VI) in the soil were 3680 mg/kg and 1485 mg/kg respectively. * In a lung inhalation simulation, it was observed that the fine fraction of soil (with particles smaller than 10 μm) from specific Cr (VI)-contaminated sites contained bioaccessible forms of chromium. |
| Ceballos et al. (2023) | Glassgow (55.8617° N, 4.2583° W) | Lab Scale | 16 soil samples were collected | * Sequential extraction process (SEP) used for characterizing the total Cr. * Flow through experiment and 1 column experiment were performed. The diameter and length of the column were 2 cm and 3 cm respectively. * (1D) reactive transport modelling using the CrunchFlow code. | * Cr (VI) was released from dissolving Cr (VI)-rich phases of the solid waste layer. * The soil profile, Cr predominantly exists in association with S, Fe, K, and Al, forming components such as Cr (VI)-rich jarosite, Cr (VI)-rich ettringite, and Cr (VI)-bearing hydrocalumite. |
| Panagiotakis et al. (2015) | Thiva Greece (38.3226° N, 23.3204° E) | Lab scale | 61 water samples were collected from wells.  14 samples were collected. | * Water quality tests have been done by standard method. * XRD has been used for mineralogical analysis. * Two samples were analyzed for XANES. | * Cr is present in topsoil of both areas due to the ultramafic geologic background of the entire region. * The origin of Cr (VI) detected in groundwater of the wider area of Thiva is primarily of geogenic origin. * The Cr Vi in tested two groundwater samples were Cr (VI) groundwater plumes of 160 µ g/L and 75 µ g/L. |
| Yan et al. (2022) | Shaanxi (34.2649° N, 108.9542° E) | Lab Scale | A total of 75 groundwater samples collected.  265 sediment samples collected. | * Standard water quality methods have been used for chemical analysis of water. * ICP-AES has been utilized for major cations and ICP-MS was used for trace elements. * XRF was used for solid samples analyzed. | * Deep aquifer groundwater had a relatively high median Cr concentration of 142 μg/L, whereas shallow groundwater exhibited a lower median Cr concentration of 33.8 μg/L. * In deep aquifers had anomalously high contents of total Cr (average 115 mg/kg). * Relatively high pH and ionic strength mobilized the adsorbed Cr (VI) into * groundwater. * Manganese oxides were the main oxidant for * Cr (III) oxidation into Cr (VI) in the aquifers. |
| Ceballos and Bea (2018) | Aguel (13.3319° N, 39.5139° E) | Field and Lab Scale | * 7 Groundwater samples have been collected. * Average rainfall recorded was 1008 mm/year. * Average annual recharge * is 133 mm/year. | * Standard water quality methods have been used for chemical analysis of water. * Reactive transport modelling by the MIN3P * UQ analysis | * The concentrations of Cr (VI) in both aquifers are influenced by their hydraulic connectivity. * The Cr concentration varies between 0.001 to 5.63. * A surface-based chromium (Cr) source term is the most realistic scenario to account for observed Cr concentrations. * Cr (VI) concentrations in the PUAQ are sensitive to organic matter contents. |
| Homa et al. (2016) | Ethiopia Tannery Share Company (8027.154’ N and 39+03.894’ E | Lab Scale | * Water samples, Vegetable (cabbage, green pepper, tomatoes, and onions) samples and soil samples. * Average annual rainfall of 800 mm, and minimum and maximum temperature of 17.50C and 260C | * Cr determination has been done using AAS. * One way ANOVA has been used for statical analysis. | * The total chromium concentrations vary, ranging from 10.85 ± 0.885 mg/L to 39.696 ± 0.326 mg/L in water, 16.225 ± 0.12 mg/Kg to 1581.667 ± 0.122 mg/Kg in agricultural soil, and 1.0758 ± 0.05348 mg/Kg to 11.75 ± 0.206 mg/Kg in vegetable samples. * The highest levels of chromium (VI) found from the speciation study were 2.23 ± 0.032 mg/Kg and 0.322 ± 0.07mg/L in soil and water. * The highest concentration of Cr (VI) was detected in onion root (0.048±0.065 mg/Kg) among vegetables. |

**Table 2: Cr distribution across different Indian states.**

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| --- | --- | --- | --- | --- | --- | --- |
| S. No. | State | Place | Type of Samples | Min Value (mg/l) | Max value (mg/l) | References |
| 1 | Uttar Pradesh | Rania-Khan Chandpur | Groundwater | 4.65 | 33.88 | Singh et al. (2012) |
| 2 | Tamil Nadu | Ranipat | Borewells, open wells and handpumps | 0.01 | 40.52 | Vijayakumar et al. (2022) |
| 3 | Tamil Nadu | Vellore | Groundwater | 0 | 0.0286 | Venkatesan et al. (2020) |
| 4 | Tamil Nadu | Vellore | Vegetation | 0.02 | 0.70 | Venkatesan et al. (2020) |
| 5 | Tamil Nadu | Chromepet, Chennai | Groundwater | 0.004 | 0.99 | Brindha and Elango (2012) |
| 6 | Arunachal Pradesh | Papum Pare | Tube wells | 0.14 | 0.18 | Goswami et al. (2023) |
| 7 | Orrisa | Sukinda | Mine water, groundwater, and surface water | 0.04 | 5.2 | Equeenuddin et al. (2020) |
| 8 | Punjab | Sutlej River sub-basin | Groundwater and surface water | 0 | 85.2 | Krishan et al. (2021) |
| 9 | Rajasthan | Bhiwadi | Groundwater | 0.001 | 0.021 | Rajput et al. (2020) |
| 10 | Assam | Dhemaji | tubewells and ringwells | 0 | 0.31 | Buragohain et al. (2009) |
| 11 | Tamil Nadu | Kancheepuram | Open wells and Bore wells | 0.25 | 0.9 | Balakrishnan et al. (2008) |
| 12 | Chhattisgarh | Nadini-Khundini  village of the Durg district | Groundwater | 0 | 22 | Banchhor et al., (2020) |
| 13 | Punjab | Malwa | Groundwater | 0.001 | 3.6 | Sharma and Dutta (2017) |
| 14 | Chhattisgarh | Bhilai-Durg | Bore wells | 0 | 12.3 | Banchhor et al., (2020) |
| 15 | Uttar Pradesh | Jhansi | Groundwater | 0.042 | 0.061 | Verma et al. (2016) |
| 16 | Uttar Pradesh | Jajmu | Soil | 3.4 mg/kg | 40529 | Paul et al. (2015) |
| 17 | Karnataka | Peenya industrial area, Bengaluru | Soil | 14.9 | 718.1 | Ratnalu et al. (2021) |
| 18 | Orissa | Jajpur | Tube well and surface water | 0 | 2.48 | Naz et al. (2016) |
| 19 | Himachal Pradesh | Solan | Hand Pumps and Biwadi | 0.61 | 1.07 | Singh and Sharma (2020) |
| 20 | Gujrat | Surat | Soil samples | 100.4 | 305.2 | Krishna and Govil (2004) |
| 21 | Telangana | Nirmal Province | Soil | 55.9 | 135.8 | Adimalla et al. (2021) |
| 22 | Uttar Pradesh | Ghaziabad | Soil | 356 | 2300 | Chabukdhara, and Nema (2013) |
| 23 | West Bengal | Ranaghat–Fulia | Sediment soil | 1.5 | 451 | Sanyal et al. (2015) |
| 24 | Assam | Guwahati | Soil | 60.1 | 730.7 | Mahanta and Bhattacharyya (2011) |

**3. Hydrogeological Perspectives of Chromium Contamination**

**3.1 Adsorption**

The adsorption of a solute onto any aquifer material results in a reduction of concentration in the aqueous phase and also a retardation of the velocity of contaminant movement. Adsorption is a phenomenon where the accumulation and concentration of molecules at the interface of a sorbent material (Toth 2002). During adsorption, molecules move from the bulk phase and adhere to the porous surface in a semi-liquid state, and this process is primarily driven by the concentration-to-solubility ratio of the compound. The adsorption behaviour of Cr, including its prevalent oxidation states, Cr (III) and Cr (VI), is influenced by soil-groundwater parameters, such as pH, texture, temperature, moisture content, organic matter content, mineralogy, and cation exchange capacity (Suzuki, 1990).

Adsorption kinetics, isotherms, and thermodynamics are three fundamental components of adsorption experiments, important for understanding the removal of Cr from soil-groundwater systems (Table 3). The kinetic study of the adsorption process focuses on elucidating the adsorption rate of Cr (VI) by the adsorbent, including the study of different mechanisms and factors governing the rate at which chromium ions adhere to the solid phase. In the adsorption of Cr, an initial fast adsorption rate is observed, but it gradually decreases over time until it achieves equilibrium.

To understand and analyse the adsorption process of Cr (VI), the adsorption kinetic models, Boyd external diffusion, pseudo–first order (PFO), Weber and Morris internal diffusion, pseudo–second order (PSO), second-order rate equation and Elovich kinetic models have been widely used (Chien et al., 1980; Gupta and Bhattacharyya et al., 2011; Mohan et al., 2006; Xie et al., 2019). The adsorption isotherm is a curve that reveals the equilibrium relationship between the concentration of solute molecules in two phases at a particular temperature when the adsorption process is complete at the interface of these phases. An accurate mathematical model for the adsorption isotherm can simplify the properties of adsorbents and the adsorption capacity of Cr (VI), as well as help in the removal mechanism between adsorbents and Cr (VI). Brunauer–Emmett–Teller adsorption isotherm, Dubinin–Radushkevich equation, Langmuir, Freundlich, Temkin, Redlich–Peterson, Kelvin equation, Toth and Sip model have been used as adsorption isotherm models (Villarroel Rocha et al., 2011; Saadi et al, 2015; Tran et al., 2017). The study of adsorption thermodynamics allows for an understanding of the extent and driving factors behind the removal of Cr (VI), as well as an in-depth analysis of the diverse influences of various factors on the adsorption process. The enthalpy change (ΔH0) is determined using the Claudius–Clapeyron equation, while the Gibbs free energy change (ΔG0) and the entropy change (ΔS0) of the adsorption process are computed through pertinent statistical thermodynamic formulas and the Gibbs–Helmholtz equation once adsorption reaches equilibrium.

Hassan and Garrison (1996) collected three soil samples (glacially derived soil, loose soil sample, and clay soil) to identify the influencing, partitioning, and interconversion process. Absorption isotherms measured have been used to calculate Kd for each of the soil samples for Cr (III) and Cr (VI). The equilibrium constant (Kd) values, obtained under natural soil-groundwater systems with a consistent equilibration time, exhibit significantly lower magnitudes for Cr (VI), falling within the range of <1 to ~50 l/kg across the three soils examined. In contrast, for Cr (III), the Kd values range from approximately 850 to 5,600 l/kg. Notably, the total organic carbon (TOC) concentration in the soil exerts a significant influence on the Kd values for both Cr (III) and Cr (VI) as the highest value of Kd found in the clay soil which has the maximum TOC contain.

McBride et al. (1997) found if the Kd value will be high for Cr, with a very high Kd value, then it will be the least mobile element. This observation reinforced their initial choice of using Cr as the reference element in soil. This reference element, with its high Kd value, served as an indicator for assessing the leaching potential of other elements in the soil. Moreover, Gao et al. found that Cr as CrO4 2− instead of Cr3+ was the last element in the sequence of adsorption with the lowest Kd value. Ramnani and Sabharwal (2005) found that the adsorption of Cr (VI) was maximum at pH 3 on cross-linked chitosan. Equilibrium adsorption studies done using Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) models to analyse results and evaluate model parameters.

Castr-Rodriguez et al. (2015) analysed the adsorption capacity of the soils through adsorption isotherms, enabling the determination of soil particle charge and the Gibbes free energy. They collected a total of 3 soil samples for analysis. The mean concentration of total Cr was 43.5 mg/kg, whereas the average concentration of Cr (VI)was 4.37 mg/kg. Adsorption isotherms were used, and the linear, Langmuir, and Freundlich models were employed for analysis. The Freundlich model exhibited the best fit for two soil samples, while the linear model provided the best fit for another soil. For a sample which contains fine-grained sand, sandy silt the adsorption level was lowest (Kd = 0.0049 ml/g) whereas soil samples which contain a high clay the highest value (Kd = 0.7 ml/g) was obtained. The average adsorption of Cr (VI) was 0.34 ml/g.

Zhang et al. (2019) studied adsorption/reduction of Cr (VI) by a black soil. This study focused on examining the adsorption and reduction kinetics of Cr (VI) using a representative black soil. The research explores different initial Cr (VI) concentrations (ranging from 40 to 400 mg/l), and pH varies between 3.5 to 7.0. At pH 5.7, a nearly linear partition relationship was observed between the adsorbed Cr (VI) content and the remaining Cr (VI) concentration in the solution. This relationship showed a good fit curve with both the linear model (R2 = 0.98) and the Freundlich model (R2 = 0.99). As the pH decreased, the partition behaviour exhibited a non-linear pattern, and the Freundlich model provided a better description of non-linearity.

He et al. (2022) simulated the migration as well as transformation of Cr (VI) from a contaminated site by ferroalloy factory. The experimental data indicates that the Cr (VI) adsorption by silty clay is well-fitted by the Langmuir isotherm model. The maximum adsorption capacity of silty clay for Cr (VI) is 466.6 mg/kg. The hydraulic conductivity of silty clay, when subjected to infiltration by distilled water and a 160 mg/l Cr (VI) solution, ranged between 6.5×10–7 and 6.7×10–7 cm/s. The hydrodynamic dispersion coefficient (D) for silty clay was determined to be 1.4×10–4 m2/d. The retardation factor (R) was found to be in the range of 4.2 to 10.

Cao et al. (2021) investigated the adsorption mechanism of Cr (VI) in sediments with different properties to identify the controlling factors involved in the process. The research involved the evaluation of Cr (VI) adsorption on six natural unconsolidated sediments, including two loamy sands, two sandy loams, one loam, and one silty loam clay which were collected from a fluvial aquifer located in Qiqihar, China. The study evaluated adsorption kinetics with Elovich, pseudo first- and second-order models and equilibrium properties using Henry, Freundlich, and Langmuir isotherms. Higher solution pH and solid-to-solution ratios reduced Cr (VI) adsorption. Authors reported that sediment properties, especially grain size and clay mineral content, were key factors. Smaller grain sizes and higher clay mineral content have more adsorption capacity and slower adsorption rates.

Ye et al. (2019) collected 6 soil samples from chromium-containing slag from Xiangxiang, China and performed batch and column experiments for adsorption of Cr (VI) in soil. To investigate the absorption mechanism kinetic models namely pseudo-first order and pseudo-second order have been tested and the results shows that the pseudo- second order kinetic model fits very well for adsorption of Cr (VI).

**Table 3: Summary of studies performed to investigate Cr adsorption in soil.**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Citation** | **Objectives** | **Study Area** | **Experimental Conditions and Methods** | **Adsorption Coff value** | **Key Observation** |
| Ye et al. (2019) | Investigate soil Cr (VI) adsorption, develop adsorption models, explore Cr (VI) transport behavior, and predict Cr(VI) leaching from chromium-containing slag in soil via mathematical modeling. | Xiangxiang city (112°28′42.91″N, 27°44′50.96″E) | Scale: Batch scale and column experiment (40 cm hight and 7 cm diameter)  Models: Kinetic models of adsorption, Isotherm models of adsorption, Theoretical modelling of transport | Kd = 1.17 cm3/g  Rd = 10.6 | The concentration  levels of Cr (VI) in the soil-leaching solution attained 905 mg/L.  The pseudo-second-  order kinetic model fits very well with the dynamical  adsorption behavior of Cr (VI).  Langmuir isotherm better  fit the equilibrium data for Cr(VI) adsorption. |
| Khan et al. (2010) | Develop models to understand hexavalent chromium sorption and transport in soil media. |  | Scale: Column experiment  Analytical Method: UV spectrophotometer | Kd = 0.0115 cm3/g  Rd = 2 | The initial concentration of Cr (VI) in the solution remarkably  influenced the equilibrium Cr (VI) uptake.  The periodic movement of the inorganic contaminant concentration  front ultimately reaching quite low concentration at the  end of the cycles. |
| Wu et al. (2022) | To develop a mathematical model for quantitatively estimating and effectively predicting Cr pollution in the "slag-soil-groundwater" system by integrating Cr (VI) migration and leaching transport data. | Xiangxiang City, China | Scale: Column experiment (height 81 cm) | Kd = 0.0542 cm3/g  Rd = 1.17 | The total amount of leached Cr (VI) and the concentration  of Cr (VI) slag present a rising trend.  Measured and simulated values exhibited correspondence, with a maximum RE of 31%, a minimum RE of 12%, a ME of 0.221, and an RMSE of 0.430. |
| Ektre et al. (2007) | to comprehend the migration of Cr in diverse soil types and to create models for this purpose. | Guangxi Province, China | Scale: Batch scale  Analytical Method: UV spectrophotometer  Models: Kinetic models of adsorption, Langmuir isotherm | Kd = 0.234 cm2/g  Rd = 2.21 | the results of the  adsorption experiment indicates that Langmuir isotherm better fit the equilibrium data for Cr (VI) adsorption |
| Yan et al. (2023) | To understand Cr migration and its interaction with different soil types, and the associated long-term risks in studied sites. | Shijiazhuang (38˚02'33"N and 114˚30'51"E), Zhuzhou (27˚49'40"N and 113˚08'02"E) and Guangzhou (23˚07'45"N and 113˚15'22"E),  China | Scale: Column experiment (1.2 cm diameter and 8 cm hight)  Analytical Method: UV spectrophotometer | Kd = 0.84 cm2/g  Rd = 1.43 | The soil of Zhuzhou had the maximum adsorption capacity for Cr (VI) (0.225mol/kg).  Rainfall intensity impacted Cr (VI): heavy rain increased vertical risk; light rain aided reduction. |
| Arthur et al. (2017) | Examine DNAN fate in soils, quantify reversible adsorption, assess mass loss, and analyze DNAN-soil property relationships. | Entisols, Inceptisols, Mollisols, Aridisols, and Ultisols in USA | Scale: Batch adsorption  Analytical method: high performance liquid chromatograph (HPLC)  Models: Freundkich and linear isotherms | Kd = 0.6 to  6.3 L/kg  Rd = 3.5 to 27.5 | The equilibrium adsorption data were fitted to Freundlich and linear isotherms with the Freundlich isotherm resulting in slightly better fit on average. |
| Jardine et al (2011) | To investigate the fate and transport of Cr (III) and Cr (VI) in three different soil types | Oak Ridge National Laboratory  (ORNL) eastern Tennessee; Savannah River National  Laboratory (SRL) South Carolina and Hanford facility Washington | Scale: Batch scale and column experiment  Model: Freundkich isotherms | Kd = 0.2 cm3/g (Hanford soil), 14 cm3/g (ORNL) and 5 cm3/g (SRL) | The transportation of contaminants in the environment is determined by whether the sorption processes are linear or nonlinear, and whether they are kinetically controlled or in equilibrium with the soil solution.  Soil chemical and mineralogical properties exert significant control on time-dependent Cr–solid phase interactions, influencing reactive processes. |
| Cao et al. (2021) | to evaluate the adsorption and transport of Cr (VI) on several natural sediments | West of Songnen Plain, China | Scale: Batch scale and column experiment  Models: Kinetic models and Equilibrium adsorption isotherms | Kd = 0.897 to 6.430 L/kg  Rd = 2.86 to 71 | The order of adsorption capacity in different soil was loam, silty loam clay, sandy loam, and loamy sand, respectively.  The adsorption of Cr (VI) decreases with increase of the pH and solid/solution ratio. |
| Liu et al. (2019) | To explore the adsorption characteristics of Cr (VI) in different aquifers and seeking insights into the underlying mechanisms governing Cr (VI) adsorption. | Tianjin Tongsheng Chemical Factory, Tianjin, China (39°14′21.4″N and 117°06′28.3″E). | Scale: Batch scale and column scale  Models: Langmuir model and Freundlich mode | Kd = 0.052 L/kg to 2.230 L/kg | The adsorption capacities of Cr (VI) on three aquifers followed the order as clay > silty clay > silt.  Cr (VI) is not easily adsorbed by the aquifer mediums but transports with groundwater. |

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| --- | --- | --- | --- | --- | --- |
| Hellerich and Nikolaidis (2005) | To define and quantify the capacity and kinetics of the Cr (VI) attenuation processes in the environment | Connecticut US state | Scale: Batch scale, | Kd = 1.1ml/g to 4467 ml/g | Chromium attenuation took place quickly in wetlands soils. The elimination of aqueous phase Cr (VI) from aqueous, soil slurries was obtained in moments at lower pH's.  Elevated Kd's (more than 250 mL/g) noted at environmentally relevant pHs of 6-6.5 suggest that Cr(VI) is being reduced to Cr(III), followed by precipitation or complexation with SOM functional groups. |
| Yolcubal and Akyol  (2007) | to investigate Cr (VI) sorption and transport in a high alkaline and calcareous soil under varied saturated flow conditions | Karstic Travertine Plateau, Antalya Turkish Mediterranean | Scale: Batch Scale, Column experiment  Models: deterministic equilibrium and physical  nonequilibrium (two region) solute transport models | Kd = 0.097 L/kg (from saturated column experiment) and 0.53 L/kg (from batch experiment experiment)  Rd = 1.34 and 1.07 | At both saturated and unsaturated flow conditions, Cr (VI) transport was slightly delayed compared to non-reactive tracers.  Column experiments with low retardation factors and Kd values indicate that Cr (VI) species are relatively mobile and bioavailable in highly calcareous soil conditions. |
| Khan et al. (2010) | To investigate the adsorption of Cr(VI) from aqueous solution by soil in batch and continuous mode of operations |  | Scale: Batch Scale  Analytical method: UV–vis spectrophotometer  Models: Freundlich isotherm, Langmuir isotherm | Kd = 0.0115 to 0.0087 mg/g | Simulated soil redemption cycles show periodic chromium concentration fluctuations, reaching low levels by the cycle's end.  The concentration of contaminants reaching the ground water table becomes quite low. |

**3.2 Precipitation**

The precipitation of Cr is a critical aspect of Cr chemistry, involving the controlled conversion of soluble Cr in aqueous solutions into solid, typically crystalline, phases, with significant implications for environmental remediation applications. Chromium can precipitate in response to changing environmental conditions in the soil-groundwater system (Bodek et al.,1988). The most used method for removing Cr (VI) involves its reduction to Cr (III)) and the subsequent precipitation of Cr (III) as chromium hydroxide, a process often achieved using sulfur compounds like sulfur dioxide (SO2) and sodium bisulfite (NaHSO3) (Barrera-Diaz et al., 2012). The parameters influencing the precipitation process include the precipitation agent, pH level, agitation intensity or speed, and the presence of complexing agents (Abdulla et al., 2010). Traditional chemical precipitation methods involve the use of sulfide precipitants and hydroxide precipitants (USEPA 2000). Chromium is often precipitated by compounds like calcium hydroxide [Ca (OH)2], sodium hydroxide (NaOH), magnesium oxide (MgO), and calcium magnesium carbonate [Ca-Mg (CO3)2] (Hintermeyer et al., 2008).

In their study, experimental data detailing the kinetics of chromium precipitation from chromium (III) acetate solutions was presented by Jou et al. (2000). Precipitation occurs by the rise in solution pH resulting from fluid-rock interactions, predominantly in carbonate rocks. This study was carried out on pH ranging between 7 to 10 and the temperature varies between 25 to 45 C. Elevated temperature, salinity, and higher divalent ion concentration increase precipitation rates and can make the sub-surface placement of chromium acetate-polyacrylamide gels in carbonate matrix rock less effective. Tingting (2021) studied the effect of temperature on precipitation of Cr. The precipitation of Cr has been studied on temperature 20, 40 and 60 C. The finding of the study shows that the maximum precipitation rate was 60 C whereas the minimum precipitation occurs at 20 C which concluded that the precipitation of Cr increased with increase in temperature. Dutrizac and Chen studied Cr (III) precipitation in jarosite compounds. Formation of the Cr (III) analogue of potassium jarosite at 98°C failed, resulting in an amorphous phase with low K content. These analogues were not formed at temperatures below 100°C. However, successful Cr (III) substitution for Fe (III) in potassium jarosite and sodium jarosite occurred. The Cr (III) analogue of potassium jarosite (KCr3(SO4)2(OH)6) was precipitated at 200°C. To comprehend the fate and transport of Cr (III), it is essential to differentiate between homogeneous and heterogeneous precipitation, quantify the volume of precipitates, and elucidate the mechanisms responsible for Cr(III) sequestration within precipitates (Dai et al., 2016). Aqueous Cr (III)/Fe (III) ratios were found to determine the homogeneous and heterogeneous precipitation rates of (Fex, Cr1−x) (OH)3 and affect the mechanisms of Cr (III) sequestration in the (Fex, Cr1−x) (OH)3 precipitates.

**3.3 Dissolution**

The Cr dissolution in soil-groundwater is a process governed by various physicochemical factors such as pH, temperature, redox and involves the interplay of different oxidation states of chromium. Low pH and reducing conditions favour the dissolution of Cr (III) from solid phases, while Cr (VI) solubility is higher under alkaline conditions (Richard and Bourg, 1991). Organic matter and complexing ligands in groundwater can further affect the solubility of both Cr (III) and Cr (VI). Cr (VI) is normally soluble and rarely forms precipitates; nevertheless, it can become integrated into specific solid phases by substituting oxyanions, particularly due to sulphates and carbonates (Baron and Palmer, 1996). Eary and Zachara (1989) highlighted the importance of thermochemical data on Cr (III) and Cr (VI) solid phases with fast dissolution kinetics and low solubility. This data is crucial for comprehending the nature of Cr in natural environments and managing Cr contamination in soil-groundwater systems. Pettine and Capri (2005) analysed the kinetic and thermodynamic characteristics of reactions involving the dissolution of Cr (VI) indicate that at higher pH levels (>10), there is a lower risk of Cr (VI) reduction. The faster reaction kinetics of oxygen divert the reductants away from Cr (VI), reducing the likelihood of its conversion to more toxic Cr (III) forms. Shi et al. (2021) investigated the photo-reductive dissolution of Cr (VI) in the presence of tartaric acid, exploring various influencing factors, such as pH, TA concentrations, in the presence of coexisting ions including Al3+, Ca2+, K+, and CO32-. The results showed that the combination of TA and simulated solar radiation significantly enhanced the release of TFe from the solid phase containing Cr (VI) in the study (SCHeCr (VI)). The produced Cr (III) either adheres to the mineral surface or combines with dissolved Fe (III) to form FeCr (OH)6 precipitates. Lower pH conditions facilitate the release of both TFe and total Cr, while potassium (K+) and calcium (Ca2+) ions had negligible effects on their liberation. Chrysochoou et al. (2016) found that Cr emitting into groundwater involves the dissolution of Cr (III) from minerals, followed by its sorption onto high-valence Mn oxides and oxidation to mobile Cr (VI) under alkaline pH.

**3.4 Leachability**

Leachabilityof contaminants is the process by which pollutants migrate through soil downward, assisted by water seeping through. Typically, more precipitation increases the likelihood of contaminants leaching, which is concerning because these contaminants could seep into the soil-groundwater system (Table 4). The chromium compounds (Cr3+ and Cr6+) that leach through groundwater are dependent upon the effluent's presence, gradient flow direction, and beginning concentration. The main forms of Cr (VI) are bichromate (HCrO-4) and chromate (CrO2-4), which are highly soluble in most environmental pH ranges of 6.5 to 7.5. Even at quantities lower than 50 μg/kg, CrO2-4 is poisonous to a wide range of plants and animals, oxidant, mutagenic, and carcinogenic. At pH levels above circumneutral, Cr (III) is comparatively non-toxic and sparingly soluble in hydroxide, forming mixed hydroxide precipitates with Fe and Cr. Because of its low solubility, it is only weakly mobile in groundwater, and the precipitated Cr (OH)3 interacts slowly with molecular oxygen (Tripathi and Chaurasia, 2020).

The chemical speciation of Cr is important for determining the leachability linked with Cr contaminated soil (Hu et al., 2016). The stability and leachability of Cr (VI) and Cr are important elements impacting the effectiveness of stabilized Cr (VI)-contaminated soil. (Jacobs et al. 2005) found that redox potential, soil pH, and solution pH had a significant impact on Cr (III) leachability. As amorphous Cr (OH)3 degraded into soluble chromium hydroxide cations at low pH (below 6), the solubility of Cr increased. The lowest leachability occurred between pH 6 and 11. Around pH 8.0, insoluble Cr (OH)3 was seen as the circumstances were reducing. Kanchinadham et al. (2013) conducted a leachability study of Cr and Cr (VI) for COPR and soil samples using acetic acid and water as leaching medium. Authors found that, Cr (III) only leached in acetic acid because it was insoluble at pH > 6, Cr (VI) leached out in both media. Zhang et al. (2021) studied leachability of Cr in different grain size of contaminated soil. The contaminated soil was divided into bulk soil, coarse soil, medium sand, fine sand and silt-clay. The proportions of fine sand (43.25%) and silt clay (43.26%) exhibited greater leachability of chromium compared to bulk soil (32.04%). Furthermore, compared to bulk soil (68.77%), the leachability of Cr (VI) was higher in silt-clay (85.72%) and fine sand (75.19%). Hence, as the particle size decreased, the concentrations of Cr and Cr(VI) in the leachate increased.

**Table 4: Summary of studies performed to investigate Leachability Index**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Citation** | **Objectives** | **Study Area** | **Experimental Conditions and Methods** | **Leachability Index** | **Key Observation** |
| Kameswari et al. (2015) | to develop a treatment procedure for the solidification and stabilization (S/S) of CCS caused by Cr (VI) leaching from COPR | Ranipat Tamil Nadu | Leachability test, Compressive strength test | LI = 7.99 – 9.01 | Cr (VI) and total chromium contents in the contaminated soil were as high as 18,770 mg/kg and 44,615 mg/kg, respectively.  LI was mostly between 8 and 9, showing that FA is a good treatment for CCS disposal into secured landfills. |
| Zhang and Lin (2020) | To investigate the influence of redox conditions for Cr release from Cr contaminated soil | Shanghai, China | Semi-dynamic leaching test, TCLP test, Sequential chemical extraction test | LI = 8.52 – 10.27 | Maximum amount of Cr leached on strong oxidation condition (Eh = 400 mV).  Cr leaching was strongly dependent on EH. |
| Sophia and Swaminathan (2005) | to use Portland cement and fly ash as hydraulic binders for solidifying electroplating waste sludge with high chromium and metal concentrations, with various tests to assess post-solidification leaching potential. | Tamil Nadu | TCLP Test, Spectroscopy, | LI = 15.2 – 16.9 | TCLP concentration of Cr in the leachate was lesser than the USEPA regulatory limit.  Diffusion controls the leaching mechanism of the waste. |
| Panda et al. (2022) | To determine the chromium immobilization and resultant leaching from unbonded and concrete bonded ferrochromium slag. | Kalinga Nagar, India | XRF, XRD, SEM, TCLP | LI = 14.6 – 15.2 | As per the comprehensive leaching investigation, the release of Cr from unbound slag frequently exceeds the Indian regulatory discharge norms for Cr (VI). |
| Liu et al. (2018) | to investigate the leachability of PTMs Pb, Zn, Cd, Co, Cr, Cu, and Ni from zinc smelting slag materials-amended acidic soils under acid deposition conditions, and to simulate the probable chemical species of PTMs in the leachate. | Guizhou, China | Column leaching experiment, Leaching Index | LI = 7.1 - 11 | The leaching process was affected by the content of the leachate as well as the geochemical features of PTM-associated minerals.  The primary PTM speciation in leachate was free metallic ions, while metallic sulphate complex factored in as SSM amendment ratios increased in soils. |
| Taghipour and Jalali (2023) | To investigate the leaching behaviour of Cr, Cu, Ni and Zn in four different industrial solid waste. | Hamadan, Iran | Column leaching experiment | LI = 0 – 62.52 | The highest cumulative amount of Cr leaching was made from the Ceramic factory waste and Leather factory waste. |
| Tomasevic et al. (2014) | to evaluate stabilization treatments in landfill-like circumstances, identify As, Pb, and Zn leaching mechanisms, estimate environmental damage through various leaching procedures, and evaluate the efficacy of bentonite- and kaolinite-nZVI for immobilization. | Nadela river basin, Vojvodina, Serbia | Microwave-assisted sequential extraction, ANS method, TCLP test, Synthetic precipitation leaching procedure (SPLP test), Waste extraction test (WET test) | LI = 7.46 – 10.67 | Making LI values, diffusion coefficients, and single leach test results into account, the applied treatments demonstrate efficacy in immobilizing variously distributed metals, providing an economic justification for implementing costly remediation procedures, especially for materials containing a mixture of pollutants. |
| Wang et al. (2022) | to validate the environmental safety of Cr in established material using several static batch leaching experiments, and to assess the release mechanisms of Cr in solidified material using long-term mass transport-based leaching tests and dynamic droplet leaching experiments | Beijing, China | Leaching test | LI = 11.52 – 12.08 | The mechanism of  Cr leached from the solidified material was mainly diffusion.  Because the mean leaching index values were larger than 9, the treatment of contaminants is regarded effective, and the waste-containing material can be used for various building purposes. |

**3.5 Transport of Chromium**

The chromium, which primarily occurs as Cr (III) and Cr (VI), exhibit different transport behaviours. Cr (III) has a propensity to adhere firmly to soil particles and create insoluble precipitates, which reduces its mobility. The pH, organic matter content, and mineral composition of the soil are important factors that affect Cr (III) transport. On the other hand, Cr (VI), which is more soluble, is vulnerable to redox changes, and the pH and prevailing redox conditions have an impact on its mobility. Advection, dispersion, sorption, and degradation are some of the physical and biological mechanisms that cause chromium to migrate through soil. The two primary mechanisms that allow Cr (VI) to transport from the subsurface to the ground surface are capillary rise and evaporative enrichment, and evaporative enrichment (Henry et al., 2007). Contaminants may rise to the surface through capillary action when the capillary rise is higher than the distance between the water table and the surface (Henry et al., 2007; Hillel, 1998).

**3.5.1 Advection**

Advection is the movement of dissolved Cr with soil-groundwater systems. The amount of Cr being transported is a function of its concentration in the groundwater and the quantity of groundwater flowing. Advection, as it relates to chromium transport, is the convective flow of chromium species in a soil-groundwater system. Advection of chromium, for example, occurs in the soil-water system when chromium (III) and chromium (VI) species are displaced by the moving water phase. The behaviour of chromium during advection is influenced by its speciation, with hexavalent chromium exhibiting higher mobility due to its lower propensity for adsorption to soil particles compared to trivalent chromium. Chen et al. (2021) found that advection is the dominant transport mode that highly controls the Cr transport. Soils with lower permeability, including montmorillonite and kaolinite, show significant delays in the transfer of Cr. High montmorillonite content causes the slowest Cr movement and the lowest peak concentration in simulations, as it does in natural clay and montmorillonite soils.

**3.5.2 Diffusion**

Diffusion is the movement of Cr in water from an area of higher concentration to an area of lower concentration (Agah et al., 2017). Even in the absence of fluid movement, diffusion will take place as long as there is a concentration gradient, which means that a contaminant may diffuse outward from the site of injection into a porous medium. If each adjacent stratum has the necessary porosity, diffusion can also occur when a contaminant's concentration is higher in one stratum than in another. The rate of diffusion (Qd) at rest is given by Fick's Law:

Where De (m2s-1) is the coefficient of diffusion and C (kg m-3) is solute concentration in soil-groundwater system. The minus sign shows the direction of diffusion is opposite to the direction of increasing concentration. Diffusion coefficient in soil-groundwater system is determined by mathematical analysis as a function of position or time.

**3.5.3 Dispersion**

Dispersion in the soil-groundwater system refers to the process by which solutes put into the soil are disseminated or distributed in the groundwater as it moves through the subsurface. Differences in the flow velocities due to the different pore size and shape (area and volume of the solute) cause solute transport at different rates and thus lead to dispersion or mixing of an incoming solution. Furthermore, the dispersion may occur in soil-groundwater system due to the development of a velocity profile within an individual pore such as the highest velocity occurs in centre and no flow or negligible flow at the walls, different mean velocities of different size of pore, the mean water flow direction being different from the actual streamlines in the soil-groundwater system and solute particles diverging or conversing from the same pore.

The solute flux is given by an equation below.

Where qh (m/s) is the solute dispersive flux Dh dispersion coefficient (m2 s-1), C (kgm-3) is solute concentration in soil-groundwater system (Table 5).

**Table 5: Summary of studies performed to investigate Dispersion Coefficient**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Citation** | **Objectives** | **Study Area** | **Experimental Conditions and Methods** | **Dispersion Coff value** | **Key Observation** |
| Yan et al. (2023) | to study the  fate and transport of Cr in soil and assess the risks associated with longterm vertical transport of Cr | Shijiazhuang, Zhuzhou and Guangzhou, (China) | Scale: Column experiment  Model: Saturated water flow model, Solute transport model, | D = 7.84 cm2/h | the horizontal transport of pollutants caused by groundwater will also lead to the diffusion of heavy metal. |
| Trento and Alvarez (2011) | to build and utilize an Eulerian numerical model to simulate non-steady chromium transport in water, bed sediments, and fine sediments suspended in a stream |  | Scale: Column  Models: Mathematical model, Numerical model | D = 10.6 m2/cm | The Salado River is fully affected by Chromium.  An accurate approximation of chromium concentrations in water and bed sediments. |
| Khan et al. (2010) | To model the transport of Cr (VI) through soil and estimated the time for reaching the contaminant in layers of aquifers |  | Scale: Column experiment  Analytical Method: UV spectrophotometer  Models: Adsorption isotherm, Freundlich isotherm, Langmuir adsorption isotherm | D = 0.00475 cm2/h, 0.00732 cm2/h and 0.00768 at 1.2 ml/min, 1.0 ml/min and 0.8 ml/min flow rate respectively. | The initial concentration of Cr (VI) in the solution remarkably influenced the equilibrium Cr (VI) uptake.  The periodic movement of the inorganic contaminant concentration front ultimately reaching quite low concentration at the end of the cycles. |
| Selim et al. (1989) | To investigate the mobility of Cr (VI) in six soils with different properties and develop a transport model for the Cr (VI) interactions and movement in soil |  | Models: Kinetic model, Convective-dispersive transport equation, | D = 0.0001296 to 0.0004464 m2/d | The model provided inadequate ETC predictions for the highly reactive soils.  When model parameters were produced using a nonlinear least square (best-fit) parameter optimization approach, the model could provide a good description of Cr BTCs for all soils. |
| Boupha et al. (2004) | To develop a software library and user interface that provide solutions to contaminant transport equations to invert Laplace transforms |  | Models: Laplace transforms, The De Hoog algorithm | D = 0.2 m2/day | The purpose of the program is to readily provide solutions to encourage a better understanding of factors affecting the fate and transport of groundwater contaminants. |
| Yolcubal and Akyol (2007) | To determine the sorption & transport of Cr (VI) in a high alkaline and calcareous soil. | Antalya, Turkish Mediterranean coast | Scale: Batch experiment and Column experiment | D = 44.7 cm2/hr (saturated experiment) and 0.3 cm2/hr in unsaturated condition | The outcomes of the column experiments revealed that Cr (VI) transport was marginally delayed compared to nonreactive tracer at both saturated and The high mobility of Cr (VI) enhances the rate of pollutant distribution and the potential for groundwater contamination flow conditions. |
| Al-Rahman et al. (2006) | To study the different transport mechanisms and soil interaction on the transport of Cr (VI) in groundwater. | Liwa | Scale: Batch experiment, Column experiment  Model: CXTFIT2 | D = 0.93 cm2/hr, 2.72 cm2/hr and 2.75 cm2/hr | The capacity of Liwa sand to absorb Cr (VI) is minimal, whereas its ability to remove Cr (III) from the solution is significant.  The dispersivity of columns packed with Liwa sand averages 0.4 cm. |
| Qiu et al. (2012) | To develop a 1-D mathematical  model basing on advection–diffusion equation, to describe the fate of contaminant in the river. |  | Scale: Laboratory scale  Model: Transport-dynamic model | D = 0.00096 to 0.0088 m2/min | The fate of Cr (VI) in the river was well described, by using mathematical model.  Almost no toxicity was detected in the treated solution even after 36 days. |

**4. Role of Aquifer Materials & Dynamics in Fate and Transport**

There are many environmental factors that influence the fate and transport of chromium in groundwater and aquifers. Type of rocks, precipitation, moisture content, hydraulic conductivity, different soil properties and organic matter content and water table fluctuations are the main components which affect the fate and transport in the soil-groundwater system. Particularly in India, the groundwater characteristic is very complicated due to different climate conditions, different geology, litho-logical characteristics, and different hydro-chemical characteristics. The hydrogeological formation of India is divided into the 6 different zone (Kulkarni et al., 2015).

**4.1 Heterogeneity of surface material**

In a heterogeneous system, Cr will undergo various transformations that can alter the fate and transport as well as toxicity. Understanding various factors which affect the environmental dynamics of Cr is essential to know the interactions between the Cr and heterogenous soil-groundwater system. Surface sediments are a heterogeneous and complex material for fate and transport of Cr (Table 5). Dynamics of Cr is important for understanding as the matrix is composed of pore fluids, inorganic solid particles, organic matter, and living organisms in which various transfers between phases can occur. Although the sediment compartment can be heterogeneous, spreading punctual characterizations as well as monitoring a specific localization of Cr as a function of time can be difficult. Second, large redox gradients can occur in sediments, particularly in surface sediments where bacterial action mineralizes biodegradable organic materials, including the consumption of dissolved oxygen and other oxidants (Froelich et al., 1979).

Soils and sediments in the vadose zone frequently do not contain enough naturally occurring inorganic reductants to influence the redox state of Cr (VI). Aerobic soils and sediments usually contain significant amounts of natural organic matter, which may accelerate the reduction of Cr (VI) to the less soluble, less mobile Cr (III) species (Jardine et al., 1999). Xu et al. (2020) revealed that the behaviour of metal (Cr) in heterogeneous systems is different from the behaviour in homogeneous systems especially in the soil media. They studied the effect of soil pH on the transport, fractionation, and oxidation of Cr (III). The results showed that alkaline soil retards the transport of Cr (III) whereas in acidic soil transport of Cr (III) easily occurs. Moreover, the high retention of Cr (III) was mainly attributed to the precipitate at pH 8.0 soil. Yan et al. (2023) studied migration and transformation of Cr in the heterogeneous soil by collecting soil from various depths in Shijiazhuang, Zhuzhou, and Guangzhou in China. They observed the Ch has greater mobility in the soil collected from Shijiazhuang which may be an alkaline soil. Cr (VI) was faster transport in the upper soil of Guangzhou while subsoil has a strong retarding ability owing to high Fe and TOC content. Kantar et al. (2008) conducted a study to determine the effects of exopolymeric substances (EPS) on Cr (VI) transportation and stabilization in heterogeneous soil systems. The presence of organic matter increases Cr (VI) uptake by soil surfaces under acidic to slightly alkaline pH conditions, depending on the concentration of organic ligands and pH. Fendorf et al. (2000) also concluded that due to the heterogeneous and complex nature of soils and surface water, Cr fate determination is a most difficult task.

**4. 2 Effect of Groundwater Table**

The groundwater table and its associated capillary fringe function as a transition zone between unsaturated and saturated zones in shallow subsurface situations. Natural processes such as seasonal rain and being dried, groundwater-surface water interaction, and tidal processes cause groundwater table fluctuations (Duan et al., 2015). Rainfall infiltration has a great effect on the groundwater table fluctuation (GTF) which linearly depends on the effective accumulated rainfall amount (Jan et al. 2007). Human activities such as groundwater extraction for drinking and irrigation, water conservation initiatives, and artificial groundwater replenishment can all contribute to the variation (Deng et al., 2016). The fluctuation in groundwater table is not only the process by which water exchanges between unsaturated and saturated aquifers, but it is also the main interface via which contaminants migrate from the surface into saturated aquifers (Sreedevi, 2002). The groundwater table variation affects the redox environment and leads to the hydrogeochemical components change. The change in the water content of the unsaturated zone during fluctuation caused by rainfall affects the redox environment. Using a two-dimensional sand tank (Gupta et al., 2019) and three-dimensional tank (Gupta and Yadav 2020), found the fate and transit of toluene in the subsurface region under dynamic groundwater table conditions.

Wei et al. (2021) investigated Cr (VI) migration and transformation in the unsaturated zone by water table fluctuation. Infiltration and groundwater drainage were the two main elements which influence water content, and water level in the unsaturated zone. Water table fluctuations caused Cr (VI) to migrate downwards and reduce. Wei et al. (2023) provided a colloid-facilitated Cr transport model taking variable density flow during groundwater table fluctuations into freshwater and seawater. The study revealed that the fluctuation may affect the migration and transportation of Cr contaminants.

**4. 3 Hydrology of Sites**

Climate change is predicted to affect precipitation, evapotranspiration, and runoff rates, and the dynamics of hydrogeological processes, as well as the quantity and quality of water in aquifers (Narula and Gosain, 2013 and Ercan, 2020). The groundwater-soil system is very complicated, and groundwater table always rise with precipitation and river feeding which lead to the changing of soil properties, and then change the migration and transformation of Cr. The chemistry of the subsurface environment, which is governed by the hydrology and composition of the aquifer substrates, governs the discharge of geogenic contaminants into groundwater (Peel et al., 2022). Cr tend to travel vertically to deeper layers rather than being retained in topsoil due to solid residue percolation, and surface runoff from rainfall. The thickness of the mixing layer determines the instantaneous mixing of soil water and surface runoff, as well as the complete or incomplete adaptation of precipitation in a shallow layer below the soil surface, impacting total solute transfer into surface runoff. The random disposal of Cr (VI) wastes formed chromium-containing slag, and the rainfall causes their movement (Ye et al., 2019). Rainfall intensity significantly affected the migration and diffusion behaviour of Cr (VI). Heavy rainfall would bring greater vertical transport risk, while weak rainfall conditions were more conducive to the reduction of Cr (VI). The infiltration of rainwater through COPR sites, landfills and other waste sites containing Cr, result in the infiltration of Cr leachate into the aquifers. If further disposal of Cr in dump sites is stopped after initial dumping but due to the periodic rainfall the infiltration of Cr contamination is continuous through the soil-groundwater system. The Cr moves from the upper layer to the subsequent lower layer as a result, concentration of contaminants decrease in the top layer but increase in the downward direction.

Zhang et al. (2022) studied effects of simulated acid rain and colloidal on fate and transport of Cr in vadose zone. Chromium transport in vadose zone soils (humic acid + cinnamon, montmorillonite + silt) during acid rain simulated in column experiments. Results indicate minimal Mt colloid impact on Cr; predominant Cr fixation in cinnamon soil with HA boosts adsorption by 12.8%. In the HA-Cr system, SO42− inhibits adsorption, lowering efficiency from 31.4% to 24.4%. Guo et al. (2021) found that the combined effect of dispersion and rainfall caused the Cr concentration. Cr (III) and Cr (VI) temporal and spatial distributions are regulated by anthropogenic (location and emissions) and hydrologic factors such as water flow and particle transport. (Szalinska et al., 2010). Wu et al. (2022) studied the Cr (VI) transfer to the surface runoff from the soil. The soil adsorption properties and the θ0 had the minimum effects on runoff Cr (VI). Results suggest that focusing on the analysis of precipitation conditions and soil parameters that determine the thickness of the mixing layer and the degree of mixing is critical for reducing pollution migration in surface runoff.

**5. Remedial Techniques for Chromium**

Soil-water systems can potentially contain elevated concentrations of chromium (Cr), which can manifest as a significant threat due to its ability for inducing severe toxicity in humans, plants, and animals (Escudero et al. 2017). Therefore, the remediation of soil contaminated with Cr represents a critical research priority. Numerous remediation strategies have been developed with the primary objective of mitigating chromium (Cr) contamination risks, diminishing land fragmentation, facilitating land reclamation, and thereby fostering the expansion of agricultural land to ensure long-term sustainability. Our present review focuses on the best demonstrated available technologies which include bioremediation, phytoremediation, and physical remediation.

**5.1 Chemical Remediation of Chromium**

Numerous reducing agents, typically employed in acidic environments, have been utilized for the remediation of Cr (VI)-contaminated soil-water systems, facilitating the conversion of Cr (VI) to the Cr (III) state. In the remediation process of Cr (VI)-contaminated soil-water by nanoscale zero-valent iron (nZVI), various modified materials such as CMC-stabilized nZVI, nZVI@VR, and nZVI–RBC are commonly employed to prevent iron agglomeration and enhance the efficiency of remediation. Cr (VI) adsorbs onto nZVI via surface pores and oxygen-containing groups, leading to a direct reaction on the surface and reduced to Cr (III), while concurrently nZVI undergoes oxidation to Fe2+ and indirect reduction of Cr (VI) occurs (Liu et al., 2020). Katsoyannis et al. (2020) indicated the presence of an autocatalytic effect, where the concentration of Cr (VI) influences its own reduction by ferrous iron (Fe (II)). Furthermore, the experiment suggested that multiple additions of Fe (II) into Cr (VI)-spiked water are more effective in facilitating the reduction process compared to adding all the required Fe (II) at once. In the study by Wazne et al. (2007), the remediation of COPR involved the use of ferrous sulfate and calcium polysulfide. The findings revealed that to meet the regulatory limits set by NJDEP (240 mg/kg for Cr (VI)) and EPA TCLP (5 mg/L for Cr) after one month of curing. Fu et al. (2021), developed a remediation method using chemical reduction with calcium polysulfide combined with microbial stabilization to address elevated levels of Cr (VI), and reported 97% conversion rate of Cr (VI) to Cr (III).

**5.2 Bioremediation of Chromium**

Bioremediation of Cr remediation are found to be more prominent, which involve the use of different biological mechanisms and processes. Bioremediation, the process by which living organisms are either wholly or partially employed for the treatment of pollutants, represents a pivotal approach in controlling environmental pollution caused by heavy metals like Cr (Elahi and Rehman, 2019). Bioremediation technology offers several advantages over other treatment processes, particularly when implemented on a large scale. These advantages include enhanced efficiency, specificity, and environmental compatibility (Banerjee et al., 2019). Different species of microorganisms may have distinct mechanisms for the removal and immobilization of Cr (VI). In particular, Fungi can mitigate the harmful effects of biologically active, free potentially toxic elements (PTE) through in vivo metal binding characterized by both high specificity and affinity (Herath et al., 2014). Bacteria possess the capacity to alter the valence state of chromium from Cr (VI) to mitigate its ecological toxicity (Elangovan et al., 2010).

Long et al. (2023) used *Penicillium oxalicum SL2* for bioremediation of Cr (VI) contaminated soil. Authors conducted batch experiments with Penicillium *oxalicum SL2*, finding that oxalic acid altered pH, favoring SL2 growth for Cr (VI) bioremediation in alkaline soil. The results indicate oxalic acid enhances strain SL2's bioremediation efficiency by promoting chromium bioleaching from soil and enhancing Cr (VI) removal in the leachate. Li et al. (2020) utilized goethite (FeOOH) in conjunction with Pseudomonas aeruginosa (P. aeruginosa) for the Cr (VI) bioremediation. Cr adsorption by FeOOH and FeOOH P. was monolayer. Extracellular polymeric substances (EPS) produced by the bacterial strain and the leaching of Fe (II) from goethite are essential contributors to the reduction of Cr (VI). Bansal et al. (2019) investigated the dominance of Pseudomonas aeruginosa, Serratia marescens, Alcaligenes faecal, and Klebsiella oxytoca in aerobic and anaerobic microbial cultures. They observed that they can reduce Cr (VI) at concentrations of up to 50 mg/L in 6 hours under aerobic situations and 24 hours under anaerobic situations. Both under aerobic and anaerobic conditions, the presence of Fe (III) had no effect on the reduction of Cr (VI). Raman et al. (2017) suggested that S. maltophilia SRS05 can be used for bioremediation of Cr as a promising agent. Jeyasingh and Philip (2005) investigated Cr (VI) soil bioremediation by an unidentified bacterial strain, achieving complete reduction of 1100 mg/kg Cr (VI) in 20 days.

**Algae: Depending on the joining characteristics of the functional category and the character of the operating conditions, several strategies for the minimization and elimination of Cr (VI) through microalgae have been proposed. Biosorption of Cr (VI) onto extracellular polymeric substances is the major mechanism responsible for chromium bioremediation by Phaeodactylum tricornutum and Navicula pelliculosa (Hedayatkhah et al.2018).** The majority of Cr (VI) was collected in the cytoplasm, organelles, granules, heat-stable peptides, and proteins of microalgal cells (Aharchaou et al., 2017). Furthermore, Leong et al. (2020) proposed that microalgae strains possess bioaccumulation capabilities, engaging various mechanisms including extracellular adsorption, reduction, volatilization, complex formation, ion exchange, intracellular accumulation, chelation, and bio-methylation in the process of bioremediation.

Many microalgae species exhibit tolerance to and the ability to accumulate high concentrations of Cr(VI). Durvillaea antarctica can remove 102.72 mg/g of Cr after 7 hours of contact time. (Guarín-Romero et al. 2019). Enteromorpha intestinalis can remove up to 93.38 % of Cr in 38.5 minutes by biosorption mechanism (Hamouda et al., 2020). Pseudochlorella pringsheimii and Chlorella vulgaris can remediate 80% of Cr contamination in 1 day by Bioaccumulation mechanism (Saranya and Shanthakumar, 2019). Chlorella sorokiniana demonstrates the ability to withstand concentrations of up to 100 ppm Cr (VI) for three days, achieving removal efficiency of up to 99.7% within 24 hours of contact time. Pediastrum duplex and pseudoanabeane mucicola have respective tolerance limits for Cr (VI) of 1.936 and 0.224 g/L, while the former has a removal efficiency for Cr of 71% (Dao and Vo, 2018).

**Fungi: Fungi are employed as highly adaptable biosorbents for Cr (VI) due to their versatility, resilience in hostile conditions, and capacity to endure Cr (VI) concentrations exceeding 10,000 mg/L (Vendruscolo et al, 2017). Fungal species typically exhibit resistance to high metal ion concentrations (Bolisetty et al. 2019).** Fungi such as Aspergillus oryzae, Rhizomucor sp., Aspergillus niger, Aspergillus carbonarius, Candida tropicalis, Trichoderma sp., Fusarium oxysporum and Penicillium chrysogenum (Ashe and Duvnjak 1995; Igwe and Abia 2006; Srivastava and Thakur 2006; Vankar and Bajpai 2008; Elahi and Rehman 2017) have demonstrated highly efficient biosorption capabilities for Cr(VI).For bioremediation of Cr (VI), Bibi et al. (2108) analyzed endophytic fungi with four isolated strains namely *Aspergillus fumigatus, Rhizopus sp., Penicillium radicum and Fusarium proliferatum*. It effectively detoxified up to 95% of Cr extracellularly. Kumar and Dwivedi (2019) demonstrated the effectiveness of the fungus *Trichoderma lixii CR700* in bioremediating Cr (VI), achieving a remarkable 99.4% reduction within 120 hours at a concentration of 50 mg/L of Cr (VI). Sanchez et al. (2019) conducted batch experiments using fungal biomass of Rhizopus sp. to remove Cr (VI) ions from aqueous solutions, finding that the maximum Cr (VI) uptake (99%) occurred at pH 2.0, demonstrating its optimal conditions for Cr (VI) removal.

**5.3 Phytoremediation of Chromium**

Phytoremediation, a cost-effective and environmentally friendly technique, utilizes plants and associated microorganisms to in-situ degrade or reduce the concentration of contaminants in soil-water system, effectively addressing concentration of the toxic effects of contaminants (Mohanty and Patra, 2012; Ali et. al., 2012; Yang et al., 2022; Ullah et al., 2023). The method is energy-efficient, economical, ecofriendly, and it may be used with other remedial methods (Suresh, Avishankar, 2004 and Ali and Sajid, 2012). Phytoremediation stands as an advancing technology in the domain of soil-water remediation, with multiple advantageous attributes and sustained applicability (Kassaye et al., 2017). Jia et al. (2022) developed an improved indicator system for phytoremediator screening strategy and identified Pennisetum is an effective phytoremediator for Cr. The author's belief is that Pennisetum holds significant promise for extensive utilization in the remediation of chromium (Cr)-contaminated soils in the foreseeable future. Sajad et al. (2020) analyzed 61 plants from 30 different families for concentration of Cr. The Bioconcentration Factor (BCF), Translocation Factor (TF), and Biological Accumulation Coefficient (BAC) were used to assess the plants' phytoremediation potential. Based on BCF value, 38 plant species show viability for the phyto-stabilization of Cr excluders. As indicated by Saravanan et al. (2019), this method stands out as one of the best approaches compared to conventional methods for remediating contaminated sites, as it leverages a diverse range of plant species for effective treatment.

Phytoremediation encompasses distinct mechanisms contingent upon the nature of contaminants (Foadi, 2020). Phyto-filtration (Hanus-Fajerska, 2016); phytoextraction (Bhargava, 2012); phytovolatilization (Jhilta et al., 2022); phytodegradation (Vishnoi and Srivastava, 2008); phytodesalination (Vaudry et al., 2023); rhizodegradation (Sharma et al., 2022) and phytodesalination (Zorrig et al., 2012). For phytoremediation nearly 500 plant species belonging to more than 45 families have been identified till now (Srivastava et al., 2021). Most of the tolerant hyper-accumulator plants changed hazardous metals into less hazardous and immobile forms (Cervantes et al., 2001). Several plants such as Lonicera japonica Thunb (Meng et al., 2019); macrophyte Callitriche cophocarpa (Kyzioł-Komosi´ et al., 2018), Vigna unguiculata (Eze et al., 2018), Spirodela polyrrhiza (Singh and Malviya, 2019), Cajanus cajan (Jerez et al., 2016), Canna indica L., Typha angustifolia L. (Taufikurahman et al., 2019).

**5.4 Permeable Reactive Barrier**

PRBs have rapidly developed in the past decade and are considered a highly promising in-situ remediation technology. This is primarily because of their cost-effectiveness and their ability to effectively immobilize various contaminants, making them suitable for a wide range of applications. McMurtry and Elton (1985) gave the very first conceptual idea about PRB which revolved around three main constituents including treatment methodology, the hydraulic data and the geotechnical designs. After that it was first implemented in 1994 as a passive groundwater remediation method for contamination of chlorinated ethylene in Base Borden, Ontario (Powell et al., 1998). PRBs consist of filled materials like adsorbents and reducing agents, strategically placed across contaminant plume flow paths. These barriers intercept and degrade various contaminants while allowing groundwater to pass through. When considering the reactive media for PRBs, it is important to consider their ability to immobilize contaminants as well as permeability. Adsorbents are the preferred selection for PRBs due to their high adsorption capacity, chemical stability, diverse pore structure, and the absence of secondary pollution.

The primary advantage of PRBs over traditional Pump and Treat (P&T) systems is it reduced demand for labour and energy during treatment. To design PRBs effectively, it is important to understand the remediation mechanism. This mechanism involves the transport of Cr contaminants through the barrier via advection, diffusion, and dispersion processes. Advection is an important component of hydrological systems, while Darcy's law describes the horizontal migration of pollutants in the direction of water flow through porous media. Fick's law governs the diffusion of pollutants from areas of high concentration to low concentration, with contaminant-porous media interactions playing a role in limiting diffusion (Vukojević Medvidović et al., 2018).

A PRB operates based on two fundamental treatment principles: immobilization and transformation. In the immobilization process, Cr contaminants either adhere to or form solid precipitates within the reactive zone without any change in their chemical state. This adherence or sorption occurs on the surface of the reactive materials, as adsorbents. Further, Cr contaminants may precipitate by converting substances from a dissolved state into a solid state in the contaminated solution (Scherer et al., 2020). The transformation process involves chemical reactions that degrade the Cr contaminants into a non-harmful substance. The advantage of a transformation process is that it eliminates the need for a comprehensive remediation of pollutants (Thakur et al., 2020).

**6. Case Study of Cr Contaminated Rania and Khan Chandpur Villages**

**6.1 Study Area**

The study was conducted in Rania-Khan Chandpur villages, situated within Akbarpur Tahsil of Kanpur Dehat District, Uttar Pradesh State, India, approximately 30 Km away from Kanpur city (Fig. 3). These villages are located near the NH-2 toll plaza, which is around 10 Km from the main nearby city, Akbarpur. This region has humid subtropical climate conditions with an average rainfall of 782.8 mm (Srivastava et al. 2013) from which about 70–80% of the total precipitation occurs in July, August, and September during the monsoon season (Matern et al. 2017). In Rania, two COPR dump sites, totalling between 30,000 to 35,000 metric tons, were identified by the Central Pollution Control Board. These sites served as repositories for COPR between 1980 and 2005, remaining uncovered and exposed to the atmosphere until October 2022. The COPR sites in Rania underwent capping, however, the COPR is continually leaching from that site to the adjacent landscape. In this study COPR#1 is used for large COPR dumpsite and COPR#2 is used for a compatible COPR dumpsite.

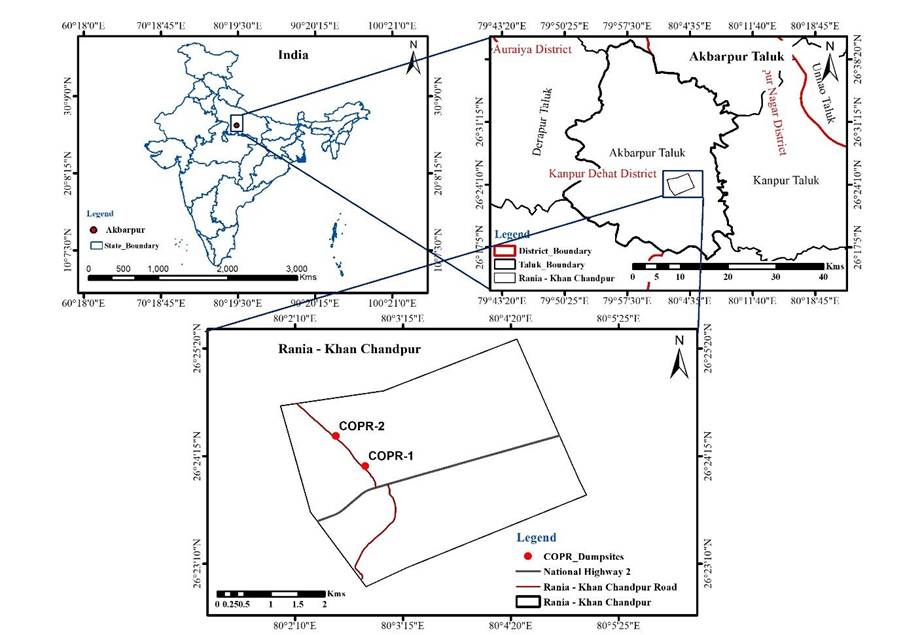
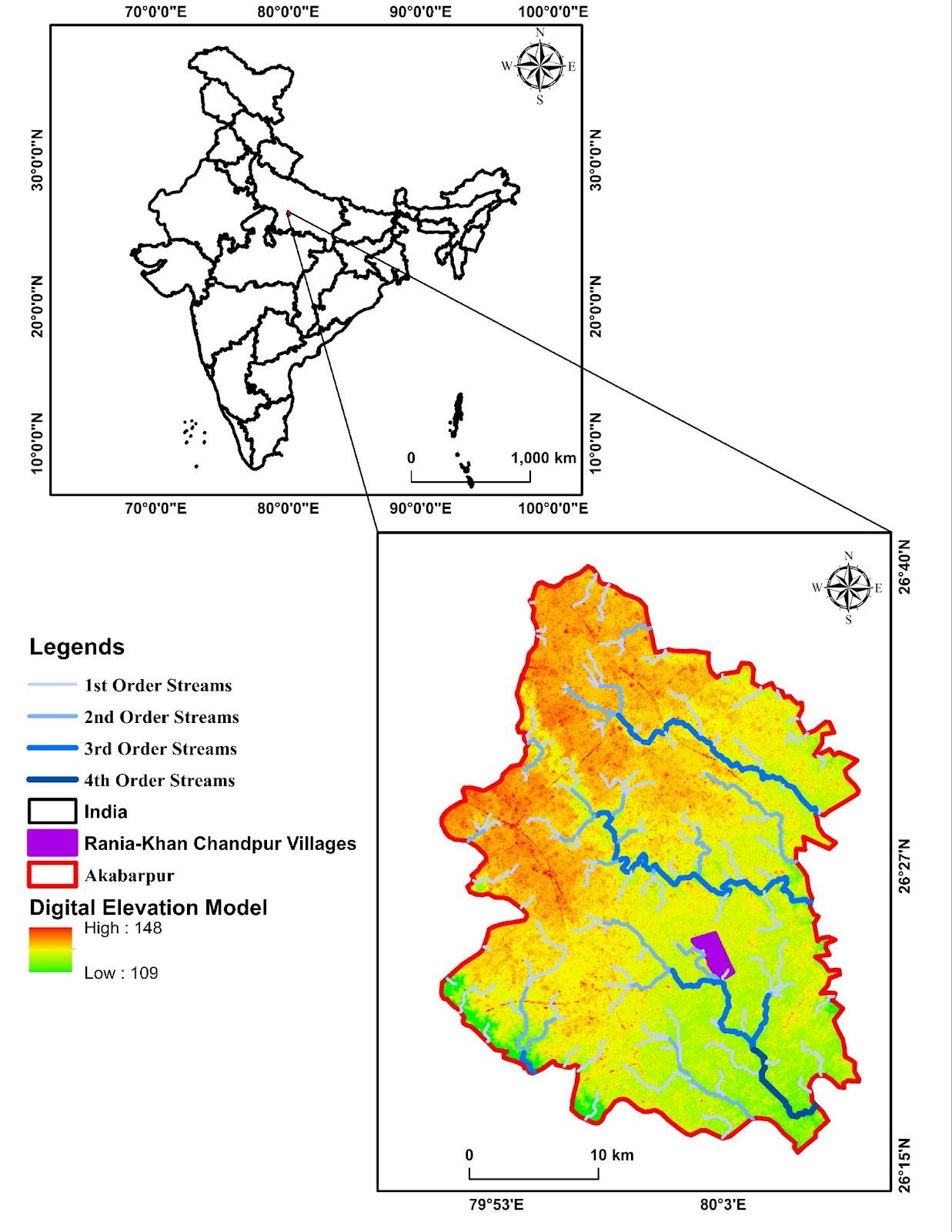
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Figure 3: India map showing the location of Kanpur Dehat which extend the Akbarpur Tahsil with a focus on the Rania-Khan Chandpur Villages. Within this area the map indicates the location of two COPR dump sites COPR-1 and COPR-2, positioned near Rania adjacent to the Rania-Khan Chandpur Road.



(a)

|  |  |
| --- | --- |
| (b) | (c) |
| (d) | |
| (e) | (f) |

Figure 4. (a) Digital elevation model (b) Drainage map of Akbarpur, Kanpur Dehat (c) Drainage map of the study area (d) Groundwater table depth of Akbarpur, Khan Chandpur area (e) Digital elevation model of Akbarpur (f) Digital elevation model of Rania Khan Chandpur.

**6. 2 Research Gaps**

Cr leachate from the COPR can infiltrate in the vadose zone and ultimately meet the (shallow-) groundwater which can result as huge Cr contamination in the subsurface. Our initial (Gupta et al. 2023a; Deoli et al. 2023) and other’s works (Singh et. al., 2009; Matern et. al., 2017) have found that groundwater, surface-water, and soil samples from the past have shown signs of a Cr emanating from the COPR dump site in and around Rania-Khan Chandpur villages. In the subsurface, Cr can be in the form of Cr (III) or Cr (VI), the mechanisms and kinetics of Cr release are obscure (Bhattacharya et. al., 2019). The release of Cr from the COPR dump site can be influenced by factors such as the pH of the water/soil, the presence of other chemicals or ions, the hydrogeology and hydrology of the site, the above and below-ground ecology and microbial community dynamics, and so on. Further, climate change may influence the fate and mobility of the Cr by altering the hydro-metrological and subsurface conditions. A better understanding is needed to improve remediation practices including evaluation of potential Cr transport pathways and rates, and more efficient clean-up strategies. However, there remains a dearth of knowledge on Cr fate, transport, and remediation in the soil-water system (Table 6).

Considering the research gaps prior to the implementation of this research work, a series of investigations has been initiated to generate baseline data of soil-water quality at the Rania-Khan Chandpur site. This has resulted in basic knowledge of the initial site conditions and profusion of excellent baseline data facilitating a better understanding of the soil-water system at this site.Photogrammetric approaches based on UAV surveys have seen significant developments throughout the past decade. Aerial imaging was performed at Rania-Khan Chandpur site in November 2022. The camera model ILCE-5100 has been used in UAV surveys with resolution of 6000 × 4000, 16 mm focal length and 4 × 4 μm pixel size. A total of 2908 images have been taken from the flying altitude of 126 m. The ground resolution was 2.79 cm pixel-1and the total coverage area was 4.69 km2.The DEM and other maps have been shown in Figure 4. Drone images often have distortions due to the drone tilting from wind or movement, as well as issues from the camera and lens used. Therefore, these images need to be corrected to fix these distortions. In this study, the projection was 24363038 and the reprojection error was 1.37 pixel.

Table 6: Summary of Studies performed to investigate Cr contamination in Rania-Khan Chandpur Villages

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| --- | --- | --- | --- | --- | --- |
| **Citation** | **Lat/long** | **Scale of Study** | **Samples/Environmental Conditions** | **Methods** | **Key Observations** |
| Singh et al. (2012) | Rania (26024’12.4” N, 80002’51.2” E) | Lab Scale | 27 soil samples were collected from different depths varying from 0 to 40 feet. | nZVI used in this study was synthesized in the laboratory by the reduction of FeCl3 with NaBH4.  Metal analysis and batch experiments. | five samples  had shown significant level of Cr (VI) with an average concentration of 15.84 mg Kg-1. |
| Foldi et al. (2013) | Rania (26024’12.4” N, 80002’51.2” E) | Lab Scale | Total 21 soil samples were collected from 0 to cm below the surface. | * C, N and S were determined by elemental analyzer. * Other elements were analyzed by XRF. * X-ray diffraction is used for mineralogical composition. * Batch experiment has been performed to know the Cr (VI) solubility and deduce processes of solubility-controlling. | * The COPR displays high Fe and low Mg contain which can be referred as ferro chromite or (high-)ferric (magnesio-) chromite. * Total Cr contents of highly contaminated material ranging from 65.7 to 110 g/kg. * Dissolution was responsible for regulating the Cr (VI) concentrations in the eluates. * With over 1400 mm (90%) of rainfall occurring during the monsoon season, there is a higher chance of increased mobilization of Cr (VI) due to a wider ratio of COPR to percolating rainwater. |
| Prakash et al. (2011) | Rania (26022’00” N to 26025’00” N and 79058’ 00” E to 800 07’ 00” E) | Lab Scale | * A total of 20 water samples were collected. * The elevation of the land surface varies from 117 m to 139 m. * The average annual rainfall of the district was 782.8 mm. | * All the heavy metals were tested by standard water quality method. | * Cr in collected groundwater samples found up to 42.45 mg/l. * Iron concentration in collected samples was also more than the permissible limit up to 2.629 mg/l. * Periodic monitoring of water quality mainly for Cr is very essential for Rania, Kanpur. |
| Matern et. al. (2016) | Rania (26024’12.4” N, 80002’51.2” E) | Field and Lab Scale | * 57 groundwater samples were in pre monsoon and 70 after monsoon. * Rainfall: 681 mm average rainfall from 2009 to 2013. * Aquifer system:   Phreatic zone depth: 25 to 130 m.  Middle aquifer: 90 to 240 m.  Lower aquifer: 180 to 450 m. | * Standard Water Quality Analysis Methods. * IBM SPSS Statistics was used for statical data analysis. | * Cr (VI) concentration in groundwater were <0.005 to 34.8 mg/l for Rania, <0.005 mg/l to 115 mg/l for Chhiwali and <0.005 to 2.0 mg/l for Godhrauli. * 95% of the groundwater samples are unsafe for drinking. * COPR dumps are the main source of Cr (VI) in groundwater. * Urgent need of remediation for COPR |
| Matern et al. (2016) | Rania (26024’12.4” N, 80002’51.2” E) and Chhiwali (26011’45.8” N, 80032’21.3” E), Kanpur India | Lab Scale | COPR Samples | * Lasere particle analyzer was used for particle size distribution. * Total C, N and S were determined by CNS analyzer. * Mineralogical composition was analyzed by DEM analyses. | * both samples had a pH of 12.4, which is due to lime (CaO) during the roasting process. * The two COPR samples had total Cr levels of 81 and 74 g/kg. where 80 to 87% of the Cr was found as Cr (III). * Two new minerals in Indian COPR i.e., voltaite and grimaldiite. |
| Matern et al. (2020) | Rania (26024’12.4” N, 80002’51.2” E) and Chhiwali (26011’45.8” N, 80032’21.3” E), Kanpur India | Lab Scale | COPR samples collected after monsoon | * Column experiment performed by a column of 20 cm long and 4 cm inner diameter. * Cr (VI) concentration was determined by spectrophotometer at 540 nm. * Geochemical modelling done by Visual Minteq 3.0. | * Cr (VI) in both COPR sites is highly soluble and is a major component of leachate. * Cr (VI) will continue to be reached from the COPR dumpsites. * During the column experiment, the ratio of Cr (VI) to total Cr decreased over time. |
| Kumar et al. (2023) | Rania (26024’57” N, 800 3’ 28” E) | Lab ad Field Scale | * 54 BCS sludge samples were collected from 15 different locations during ore and post monsoon season. * The samples were collected from 3 different depth: Top surface (0-15 cm), subsurface layer (15-75 cm) and bottom layer (75-150 cm). | * Toxicity characteristic leaching procedure (TCLP) based concentration of Cr were assessed. * Cr-VI concentrations using spectrophotometrically at 540 nm. * pH, EC, and TDS using standard methods. * Organic matter by Walkley-Black procedures. | * Concentration of total and TCLP based Cr and Cr (VI) increase with increase in sample depth. * Highly leaching tendency of sludge during both seasons. * Illegally dumped require proper treatment, storage, and disposal facilities. * The leaching characteristic of salts tends to increase as the depth level of the dumpsite increases. |

**6.3 Cr in Soil Samples**

For sampling of soil and COPR from hazardous waste, the standard method was followed by CPCB 2011. The samples were collected in zipper polyethene bags which were air dried in the laboratory. All samples were air-dried, and the concentrations of total chromium. Collected samples were digested in Aqua regia solution (3:1: hydrochloric acid: nitric acid) and filtered using 0.2µ syringe filters (Axiva, Cat No. SFNY25RB) and stored in the cold containers in the laboratory. All samples were analysed for Cr using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) with equipment from Agilent Technologies, Singapore, specifically the ICP-MS 7900 model within 72 hours.

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Figure 5: Cr contamination in Soil and COPR samples at different depths

Total Cr concentration in soil and COPR samples increases with an increase in depth. The top layer (0–5 cm bgl) was 12373, 7000, and 2134 mg kg−1 in cores collected from the northern boundary of main dump site (COPR#1), middle of the main dump site (COPR#2) and small dump site (COPR#3) respectively, which was increased to 21996, 10786 and 12789 mg kg−1 in samples collected from 50-55cm bgl in the northern boundary of the main dump site, middle of the main dump site and small dump site, respectively. The total Cr concentrations were further increased at 100–105 cm depth as 23958, 12591, and 15930 mg kg−1 in the northern boundary of the main dump site, middle of the main dump site and small dump site respectively. The total Cr concentrations were highest in the bottom layer of cores, 150-155 cm bgl, as 48330, 41274, and 19930 mg kg−1 in main Cr sites, middle of main COPR sites, and small dump sites samples, respectively, which was quite close to the values reported by Kumar et al. (2023) for 75-150cm bgl. Total Cr concentrations were increased with depth in COPR cores collected from three locations. Similar trends of total Cr concentrations were observed in the soil cores as well in which concentrations of total Cr were also increased with depth, but the ranges of total Cr concentrations (33.3-2918.8 mg kg−1) in soils were much lower than whatever was observed in the COPR (2134-48330 mg kg−1). The total Cr concentrations in soil cores were 590, 33, and 72 mg kg−1 in top layer samples (0–5 cm bgl) from SOIL#1, SOIL#2, and SOIL#3, respectively. The highest total Cr concentrations were 2918, 695, and 618 mg kg−1in bottom layer samples (150–155 cm bgl) from SOIL#1, SOIL#2, and SOIL#3, respectively.

**6.4 Cr in Groundwater Samples**

Total 78 groundwater samples were collected in October 2022 to know the status of Cr in and around COPR sites in Rania and Khan Chandpur villages. The samples were collected from hand pumps and each sample was collected after approximately 20 L of water was flushed out from this. The samples were immediately kept in the cool box during transportation to the laboratory. All samples were filtered by 0.45 µsyringe filters (Axiva, Cat No. SFNY13X). The analysis has been done using ICP-MS (Agilent Technologies, Singapore, Model: ICP-MS 7900).

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