



Electrokinetic remediation of chromium contaminated soil: Impact of particle size on treatment efficiency and bioavailability

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ABSTRACT

The electrokinetic remediation (EKR) is a potential method employed for removal and recovery of heavy metals from soil and various waste materials. However, it demonstrated promising efficacy in laboratory settings, diminished in practical implementations as a result of insufficient comprehension of in-situ conditions. In this study, experimental investigations were conducted to determine the effect of soil particle size on the performance of EKR. Four distinct soil particle sizes were utilized i.e., retained on 1.18 mm (EKR-A), 300 μm (EKR-B), 150 μm (EKR-C), and passing through 150 μm (EKR-D). The alteration in bioavailability as well as physiochemical properties of Chromium (Cr) was investigated through sequential extraction process (SEP) along with soil characterization techniques such as FE-SEM-EDX, XRD, FT-IR. Studies of soil particle size, composition and morphology indicate that as particle size decreases, pollutant concentration increases. Consensus was reached through the research that the treatment efficiency is substantially impacted by the particle size of the soil; in other words, smaller particle sizes led to diminished efficacy. The cumulative Cr removal percentages for EKR-A, EKR-B, EKR-C, and EKR-D were achieved as 27 %, 19 %, 10 %, and 7 %, respectively. The SEP study revealed that the initial soil Cr-concentration was predominated with oxidizable fraction (63–81 %) and the EKR facilitates the extraction of pollutants from the soil matrix by increasing their leachability from 1 % to 30 %, thus providing both removal and recovery of Cr as a feasible option.

1. Introduction

Several soil sites and water reservoirs have been contaminated as a result of the massive usage of anthropogenic chemicals, often with heedless control. It is reported that, over five million sites are contaminated with the hazardous heavy metals worldwide (Khan et al., 2021). Once this pollutant is released into the environment, can stay unchanged in the soil for a long period and potentially contaminate other parts of the ecosystem (Li et al., 2020). For instance, Chromium (Cr), a hazardous metal, is extensively utilized in industrial applications, such as electroplating, mining, leather tanning, dye, and pigment manufacturing, stainless steel production, etc. (H. Xu et al., 2022a). One such example is the Cr-mining in Sukinda valley in Odisha, India which releases about 11.73 tons of Cr(VI) (Nayak et al., 2020) whereas tanning process generates around 600,000 tons of Cr wastes into the environment annually (Princy et al., 2020). The inappropriate storage and

disposal of the Cr byproducts generated from these activities have resulted in extensive soil and groundwater contamination worldwide. The two most stable oxidation states of Cr in the environment are trivalent (Cr(III)) and hexavalent (Cr(VI)) chromium (Zheng et al., 2021). The Cr(III) typically exists as cationic species such as Cr^{3+} , $\text{Cr}_3(\text{OH})_4^{5+}$, CrOH^{2+} , and $\text{Cr}(\text{OH})_2^+$ that are less mobile, least soluble, and less toxic. Whereas Cr(VI) exists as $\text{Cr}_2\text{O}_7^{2-}$ (dichromate), HCrO_4^- (hydro-chromate), and CrO_4^{2-} (chromate), which are highly mobile, carcinogenic, and extremely toxic (Nasiri et al., 2020).

In the interest of environmental protection and restoration, many developed nations prioritize the remediation and management of Cr-contaminated soils (Y. Xu et al., 2022). These soils can be treated mainly by two approaches: 1. by converting Cr(VI) to Cr(III) which is less mobile and less toxic; this includes techniques such as the use of reducing agents e.g., zero valent ion, oxalic acid, ascorbic acid, etc. (Wang et al., 2021), microorganisms (Selvi et al., 2021), etc. 2. by

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removing Cr from the soil which includes techniques such as bioremediation, phytoremediation, soil washing, chemical leaching, electrokinetic remediation (EKR), etc. (Akansha et al., 2024). The Cr can either be removed and/or recovered from the soil matrix by combining these techniques (B. Wu et al., 2020). In case of closed-loop process, recovery is desirable over removal whereas in remediation process, removal is preferred (Ding et al., 2024). Furthermore, immobilizing Cr in contaminated site by converting it to Cr(III) is effective, but the potential risks associated with the inter-transformation due to altered soil conditions cannot be neglected. In comparison to immobilization or passivation of Cr in the soil, the methods for extracting or eliminating Cr from the soil matrix are more desirable and controlled remediation processes (Gao et al., 2020).

The EKR is often preferred over other methods because of its greater efficacy, economic feasibility, minimal environmental imprint, and applicability in treating a broad spectrum of contaminants, either organic pollutants or hazardous heavy metals (Sun et al., 2021; Yu et al., 2022). This technique is applied for the removal or recovery of heavy metals from soils as well as industrial wastes (Peppicelli et al., 2018; J. Wu et al., 2020). For this, EKR applies either a low direct electric current (DC) or a low direct electric voltage gradient through the electrodes (Zheng et al., 2021). Its functioning mainly depends on four key mechanisms: electromigration (EM), electroosmosis (EO), electrophoresis (EP), and electrolysis (EL). In particular, metal ions are mostly transported in the direction of an electrode with an opposing charge due to the EM phenomena (H. Xu et al., 2022b; Yu et al., 2022). Numerous studies have revealed the relevance of EKR for the remediation of soil contaminated with Cr. However, few studies have also reported lower Cr removal by the conventional EKR process (Gao et al., 2020; Zhao et al., 2021), owing to the fact that, effectiveness of the EKR process is intricately affected by a multitude of variables. These factors encompass the electrical field parameters (Yan et al., 2019), the nature of the contaminants, composition of the electrolyte solution, configuration of the electrodes etc. are significant determinants (Kumar et al., 2023; Zhang and Li, 2019). Treatment duration, temperature, hydraulic conditions are also noteworthy variables. Furthermore, soil properties, including pH and soil composition (such as particle size, texture, mineral content, and organic matter), all have a direct impact on the efficiency of the EKR process (Karami et al., 2021; Wu et al., 2016).

This study involved the utilization of real contaminated soil sourced from the Puliyanthangal Lake in the Ranipet district of Tamil Nadu. Previous studies have consistently revealed alarming levels of contamination in the soil, surface water, and groundwater in and around the Ranipet (Arivoli et al., 2021; Sathish et al., 2022; Vidhya et al., 2023; Vijayakumar et al., 2022). The underlying cause of this contamination has been traced back to the discharge of industrial effluents into the environment. Consequently, there is a pressing need to develop an efficient, environmentally friendly, and cost-effective approach to remediate such severely contaminated soil, and one promising technique for this purpose is EKR.

While numerous researchers have previously focused on bulk soil sizes lesser than 2 mm in the context of EKR studies (Fagerlund et al., 2022; Rocha et al., 2019; Wen et al., 2022), it is noteworthy that no prior studies have explored the potential impact of soil particle size on the performance of EKR and bioavailability of Cr post treatment. However, it is a well established fact that soil particle size influences the adsorption, distribution, migration of heavy metals in soil (Huand B, Yuan Z, Li D, Zheng M, Nie X, 2020). It can also greatly affect the electrokinetic phenomenon taking place during EKR process. Thus, based on this hypothesis, in this current research endeavor, an EKR study was conducted on representative samples with four distinct size ranges of Cr-contaminated soil. Typically, the total metal concentration is employed as an indicator of soil contamination. Nevertheless, it does not furnish insights regarding the toxicity level, bioavailability, mobility, or distribution of metals in soils. Thus, in addition to the EKR treatment, the Commission of the European Communities Bureau of Reference

(BCR), a four-step sequential extraction procedure (SEP) (Hagarov and Bartekov, 2006; Hsueh et al., 2022) was applied to the soil samples both pre and post EKR treatment to get insights into the speciation of Cr in the soil samples. Few analytical techniques were also employed to study the composition and morphology of the soil. This was done to investigate the alterations in the geochemical fractions of Cr metal post treatment and gain a comprehensive understanding of its behavior in the soil matrix. This study would help in designing efficient soil remediation technique for metal removal or recovery.

2. Materials and methods

2.1. Study area

The soil from the bed of Puliyanthangal Lake (Latitude 12° 57' 53.12", Longitude 79° 17' 36.99") situated in Puliyanthangal village, Ranipet, Tamil Nadu, India was considered for this study Fig. 1. Ranipet is renowned for its extensive industrial presence, encompassing various sectors including ceramics, pharmaceuticals, refractories, paints and pigments, and tanneries. It is also home to industrial hubs like the State Industries Promotion Corporation of Tamil Nadu Limited (SIPCOT), Bharat Heavy Electricals Limited (BHEL), and Tamil Nadu Chromate and Chemicals Limited (TCCL). These industries generate extremely hazardous waste, which is often haphazardly dumped onto the land or into neighbouring water bodies without undergoing sufficient pre-treatment. Puliyanthangal Lake stands as a typical illustration, bearing the brunt of industrial effluent discharges and suffering from severe water and soil pollution (Sai Chaithanya et al., 2023; Sathish et al., 2022). The lake has a large, shallow area covering about 29.92 hectares of land. The submerged area of the lake varies from 0.80 ha (pre-monsoon) to 14.70 ha (post-monsoon), whereas the depths range from 1 to 3 m (Sai Chaithanya et al., 2023). Effluents from nearby industries in SIPCOT and untreated sewage from the nearby villages of Puliyanthangal and Periyanthangal all make their way into the lake thus polluting it (Sathish et al., 2022). The unsubmerged area is used as a grazing field by the cattle of the nearby villages.

2.2. Collection of samples and preparation

Representative soil sample from the unsubmerged area of the lake from three different sampling points P1, P2 and P3 near the inlets were collected from a depth of 20 cm below the surface to eliminate any interference from grasses and debris. Subsequently, the samples were transported to the laboratory and subjected to air-drying procedures to eliminate excess moisture, while also removing lumps and debris. The samples were mixed thoroughly to obtain a homogenized composite sample. Then it was sieved through a set of sieves (2.36 mm, 1.18 mm, 300 µm, and 150 µm, 50 µm) to obtain the desired soil particle sizes and securely stored in sealed bags at room temperature in anticipation of the treatment process.

2.3. EKR experimental setup and operational methodology

Lab scale EKR setup was designed for the experimental studies. EKR reactor of dimension (30 cm x 7 cm x 8 cm) made up of an acrylic sheet was used. The reactor was divided into three chambers namely the anode chamber (5 cm x 7 cm x 8 cm), soil chamber (20 cm x 7 cm x 6 cm), and cathode chamber (5 cm x 7 cm x 8 cm), separated with the help of Whatman filter papers Grade 41 sandwiched between two porous acrylic sheets to prevent the mixing of soil and the electrolytes. About 500 gs of well-mixed contaminated soil was taken for each experiment. One number of high-density graphite plate electrode was used as anode and cathode each. Power to the anode and cathode was supplied with the help of a DC power supply unit. Ultrapure water (UPW) and 0.1 M KCl were used as anolyte and catholyte respectively. A voltage gradient of 2 V/cm was maintained for all the experiments. The detailed

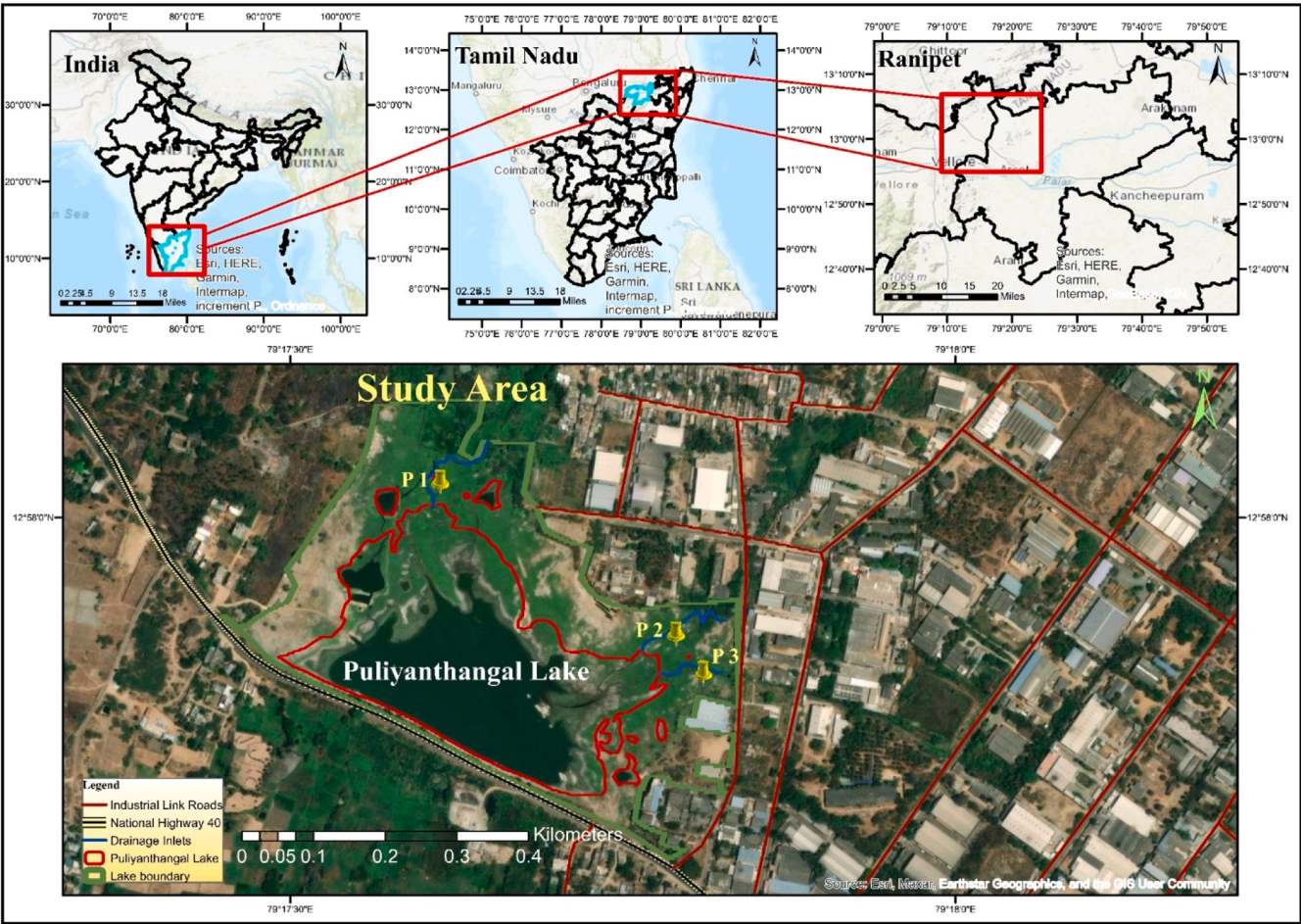


Fig. 1. Location of the study area (Puliyanthangal Lake) along with sampling points.

experimental information is illustrated in Table 1.

Before starting the experiment, the soil sample was thoroughly mixed with UPW to provide the initial moisture content of 40% and left overnight. Then it was placed in the soil compartment with light compaction followed by filling of electrolytes in the respective chambers. Electrodes were submerged into the electrolytes and power was supplied maintaining the required voltage gradient. Both anolyte and catholyte were collected and fresh electrolytes were replaced every 24 h throughout the experimental run. The electroosmotic flow was measured with the difference in the volume of the anolyte and catholyte. Then the collected electrolytes were analyzed for their pH, Total Dissolved Solids (TDS), Electrical Conductivity (EC), and total Cr-concentration. After the experiments, the soil was further divided into five equal sections namely section S1 (0–4 cm), S2 (4–8 cm), S3 (8–12 cm), S4 (12–16 cm), and S5 (16–20 cm) from anode to cathode. A representative sample was collected from each section and was oven-

dried at 105 °C until complete moisture was evaporated and stored in polyethylene covers for further analysis.

2.4. Chemicals and materials

All chemicals used in this study were of analytical grades and used as received. Some of the important chemicals such as potassium chloride (KCl), acetic acid (CH₃COOH), hydrogen peroxide (H₂O₂), ammonium acetate (C₂H₇NO₂) and, hydroxyl ammonium chloride (HONH₂•HCl) were used for catholytes preparation and SEP analysis whereas, nitric acid (HNO₃) and hydrochloric acid (HCl) was used for soil digestion. A set of commercially available high-density graphite plate electrodes, each measuring 5 cm x 5 cm x 1 cm were utilized as both anode and cathode. All the reagents were meticulously prepared in UPW ensuring the highest standard of purity.

2.5. Analysis and quality control

2.5.1. Analysis of physicochemical indicators of Cr-contaminated soil

The soil of Puliyanthangal Lake was analysed for its physicochemical parameters and Cr-concentration. The detailed procedure has been reported in Supplementary file. A concise summary of the characteristics of the Cr-contaminated soil is tabulated in Table 2 and Supplementary Table S1.

2.5.2. Analysis of Cr-concentration in electrolytes and soil

The collected electrolytes underwent a preliminary processing step involving filtration through a 0.45-micron filter membrane.

Table 1
Experimental details.

Experiment	Soil Particle Size	Voltage Gradient	Anolyte	Catholyte	Duration (Days)
EKR-A	2.36 mm - 1.18 mm	2 V/cm	UPW	0.1 M KCl	10
EKR-B	1.18 mm - 300 µm				
EKR-C	300 µm - 150 µm				
EKR-D	150 µm - 50 and less				

Table 2
Physicochemical properties of Puliyanthangal Lake soil.

Parameters	Contents
pH	6.78 ± 0.5
Moisture content (%)	39.78 ± 0.7
Organic content (%)	3.11
Electrical conductivity (dS/m)	0.37
Soil particle sizes	
and (%)	34.06
silt (%)	43.03
clay (%)	22.91
Soil type	loam
Total Cr mass (mg/kg)	
EKR-A	1975
EKR-B	2197
EKR-C	4748
EKR-D	7464

Subsequently, the resulting filtrate was subjected to quantitative analysis for total Cr-concentration using ICP-OES. In the case of soil samples, the determination of Cr-concentration required a well-established and standardized approach involving microwave-assisted digestion. This procedure adhered to the United States Environmental Protection Agency's (USEPA) Method 3051A for Microwave-Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils (United States Environmental Protection Agency, 2007). For this, approximately 0.5 gram of soil was precisely weighed and placed in Teflon vials. Subsequently, 2 mL of HNO_3 and 6 mL of HCl were introduced in a ratio of 1:3 to facilitate the extraction process. The microwave digestion step, lasting 45 min, played a crucial role in solubilizing the Cr from the soil matrix. Following digestion, the sample was allowed to cool to ambient temperature before it was subjected to further filtration through a 0.45-micron filter membrane. This rigorous preparation process was performed both for the initial soil samples and representative soil samples extracted from five distinct sections, post EKR experiments. For assurance of quality, one blank and one sample of certified reference material (SQC001 from Sigma-Aldrich for soil samples) were added after every 10 samples. The analysis of these samples via ICP-OES served to determine the presence

and concentration of total Cr, offering valuable insights into the impact of EKR on the Cr-concentration in the soil samples.

2.5.3. BCR four-step sequential extraction process

Typically, the total metal concentration is employed as a soil pollution indicator. Nevertheless, it does not offer information regarding the toxicity level, distribution, mobility, and/or bioavailability of metals in soils. Assessing this requires understanding of chemical speciation (Zornoza et al., 2019). SEP is a commonly employed technique for evaluating the chemical speciation of heavy metals in environmental samples. The BCR four-step sequential extraction method was adopted to determine the geochemical fraction of Cr pre and post (at five different sections) the EKR process. The four fractions were namely Exchangeable and acid soluble fraction (F1); Reducible fraction- iron/-manganese oxides (F2), Oxidisable fraction- organic matter and sulfides (F3), and Residual fraction (F4). The complete sequential extraction procedure (Ahmadipour et al., 2014) is depicted in Fig. 2. The metals present in the F1, F2, and F3 fractions are deemed more bioavailable and possess potential toxicity compared to those in the F4 fraction (Chanaka et al., 2019).

2.5.4. Morphological and composition study

The microstructural attributes and elemental composition of the soil were meticulously assessed through analytical instrumentations, namely, Field Emission-Scanning Electron Microscopy (FE-SEM, Thermo Fisher, FEI QUANTA 250 FEG) and Energy Dispersive X-ray Spectroscopy (EDX, Oxford INCA x-act), respectively. Furthermore, to elucidate the mineralogical structure of the soil samples, Powder X-ray diffraction (XRD, Bruker D8 Advance, Panalytical X Pert3, Germany, Netherlands) analysis was carried out spanning a 2θ range from 10° to 90° . Simultaneously, the molecular composition and functional group arrangements of the soil samples were probed through Fourier Transform-Infrared Spectroscopy (FT-IR, Shimadzu, Japan, Thermo Fisher Scientific, USA, IRAffinity-1, Thermo Nicolet iS50 with inbuilt ATR). This multifaceted characterization approach offers a comprehensive understanding of the soil's microscale features, elemental constitution, mineral structure, and chemical functionalities.

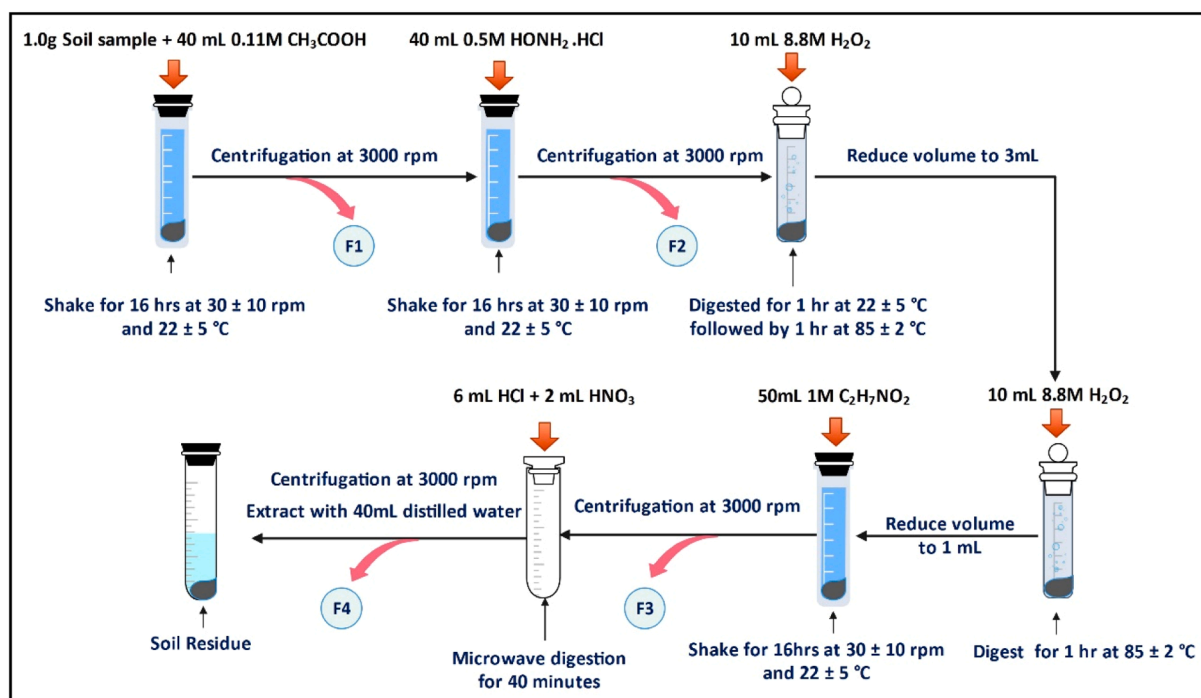
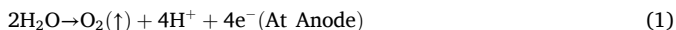


Fig. 2. Four step BCR sequential extraction procedure for heavy metal fractions.

3. Results and discussion

3.1. Change in pH, EC, and TDS of electrolytes

In an EKR system, the electrochemical reactions, transport of target ions, and physicochemical processes are all influenced by the alteration in pH, EC, and TDS of electrolytes (Yan et al., 2023). pH is one of the most influential parameters for metal migration in soil, which controls many geochemical processes including precipitation, dissolution, adsorption, desorption, oxidation, and reduction (Reddy et al., 2001). During the electrolysis of water, the formation of hydrogen (H^+) ions Eq. (1) would reduce the pH at the anode chamber, creating an acidic front, whereas the production of hydroxyl (OH^-) ions Eq. (2) would increase the pH at the cathode chamber and cause alkaline conditions in the surrounding region (Zhang et al., 2017).



Since H^+ ions have 1.75 times higher mobility compared to OH^- ions, the predominance of H^+ ion movement renders the EKR system more acidic (Jadhao et al., 2023). Notably, the lower pH of the soil favors the movement of Cr within the soil matrix as Cr is highly mobile at a pH range below 6, thus favoring the EKR treatment of soil contaminated with Cr (Hu et al., 2022). Fig. 3(a) and (b) illustrates the trends of pH variations in electrolytes over time. The initial pH of UPW (anolyte) and 0.1 M KCl (catholyte) was 6.9 and 5.6 respectively. During the experiments, a discernible rise in pH is observed within the cathodic chamber, attributed to the electrochemical reduction of water (Wu et al., 2016). This pH elevation persists until attaining a steadfast equilibrium at approximately 12–13. Concurrently, within the anodic chamber, a pronounced decrease in pH transpires as a consequence of the oxidation of water (Rocha et al., 2019). The resultant pH in the anodic region descends below the threshold of pH 2. The same trend was observed where the impact of applied voltage was studied on the electroosmotic flow (Cameselle, 2015; Liu et al., 2023; Wu et al., 2016). The pH levels of the electrolytes consistently followed a similar pattern in all four experiments irrespective of the soil particle sizes. From the anode part to the cathode section, the soil pH distribution incessantly increased in all experiments. The pH was lowest in the region close to the anode (S1) and raised steadily to the cathode (S5).

The EC and TDS are interrelated due to the presence of ionic salts which are migrated from soil into the electrolytes (Zhou et al., 2020). Ion leaching and migration are strongly supported by the time-dependent change in the EC of electrolytes during electrokinetic treatment (Tang et al., 2017). According to the experimental data displayed in Fig. 3(c–f), the EC and TDS of electrolytes was considerably raised by the electrolytic reaction and electromigration. The OH^- ions neutralized the H^+ ions generated by electrolysis, resulting in a lower EC in the anode chamber when compared to the cathode chamber (Chen et al., 2023). As the experiment proceeded the EC of the electrolytes also decreased in all the cases. The high EC in the portions near anode and the low EC near cathode sections can be explained by the adsorption and buildup of Cr(VI) oxyanions in an acidic environment and the precipitation of Cr(III) in an alkaline soil, respectively. The EC and TDS of the electrolyte was observed to be higher in case of EKR-A when compared to other experimental runs. This may be due to the higher ions migration due to weaker bonding of the pollutants to the larger soil particles and resulted in attaining maximum pollutant removal. The decrease in ion migration into the electrolytes due to the finer soil particles, is the primary factor that influences the treatment efficiency (Kim et al., 2010). Furthermore, it is noteworthy that the pH, EC and TDS showed substantial change within few hours of experimental run due to the electrokinetic mechanisms taking place in the system. These mechanisms are maximal in the initial hours and slowly retards as the experiment proceeds.

3.2. Cr-migration into the electrolytes

The monitoring of Cr-migration into the electrolytes were conducted systematically and it was observed that negligible amount of Cr moved into the catholyte, thus Cr-migration only to the anolyte was examined throughout the experimental investigation. Analysis of Fig. 4(a) revealed that as the duration of the treatment progresses, the movement of Cr towards the anolyte also decreases in all the experiments. Here electro-osmotic flow (EOF) (Mahmoud et al., 2010), soil mineralogy emerges as a pivotal mechanism in directing ion migration toward the electrolytes (Tang et al., 2020). The electronegativity of soil causes EOF to typically flow from the soil media to the cathode (Chu et al., 2022). Finer soil particle size correlates with a reduction in void ratio and porosity, consequently leading to decreased ion migration under the action of EOF (Sánchez et al., 2019). The experimental outcomes for EKR-A indicate a consistent migration of Cr ions towards the anolyte; however, removal efficiency exhibited a diminishing trend over time. A parallel trend is observed in the case of EKR-B. Conversely, in the case of EKR-C and EKR-D, ion migration into the electrolyte experienced a reduction after the second day of experimentation, directly attributed to EOF dynamics. The cumulative Cr-removal percentages for EKR-A, EKR-B, EKR-C, and EKR-D were determined as 27 %, 19 %, 10 %, and 7 %, respectively. This data has also been represented in statistical plot in supplementary Fig. S2(a). Conspicuously, the significance of soil particle size in the efficacy of the EKR process becomes evident. Larger particle sizes exhibit lower Cr-concentrations due to lesser surface area compared to finer sizes, with removal efficiency proportional to particle size. This establishes a direct relationship between soil particle size, Cr-concentration, and removal efficiency in the context of EKR. It is also noteworthy that, the overall efficiency of removing contaminants is determined by various geochemical reactions, such as oxidation–reduction, adsorption, and precipitation. None of these experiments yielded significant pollutant removal. However, several additional studies have also documented a decrease in the effectiveness of heavy metal removal caused by the precipitation of these metals due to acidic pH levels in the soil proximate to the anode areas (Reddy et al., 2001).

3.3. Distribution of Cr in contaminated soil post EKR treatment

The initial total Cr in the soil subjected to EKR processes denoted as EKR-A, EKR-B, EKR-C, and EKR-D were quantified as 1975, 2197, 4748, and 7464 mg/kg, respectively. Notably, a direct correlation was observed between soil particle fineness and Cr-concentration, wherein finer particles exhibited higher concentrations (Kim et al., 2010; Xu et al., 2014). This phenomenon is attributable to the inverse relationship between particle size and surface area; as particle size decreases, the surface area increases, providing a larger substratum for ion adhesion (Huand B, Yuan Z, Li D, Zheng M, Nie X, 2020). The resultant Cr-concentrations across five distinct soil sections post-EKR experimentation are graphically illustrated in Fig. 4(b). Also, it has been depicted statistically in supplementary Fig. S2(b). Analysis of the Fig. 4 (b) reveals maximal Cr content at mid-sections (S2–S4), indicating ion migration toward the anode but subsequent precipitation at these locations, leading to reduced Cr removal via the EM process. The precipitation of Cr ions is postulated to be influenced by changes in soil pH, with observed acidity contributing to ion precipitation (Reddy et al., 2001). Furthermore, a decline in EOF a few days into the experiment is identified as a potential governing factor for Cr precipitation within the soil matrix (Liu et al., 2024). The applied voltage gradient emerges as a critical determinant in ion migration, with literature corroborating the necessity of higher voltage gradients for efficient pollutant extraction at elevated concentrations. In this context, it is asserted that the provided 2 V/cm voltage gradient may be insufficient for the effective mobilization of Cr ions into the electrolytes during the EKR process. Nevertheless, an increased voltage gradient would impact the cost efficiency of the

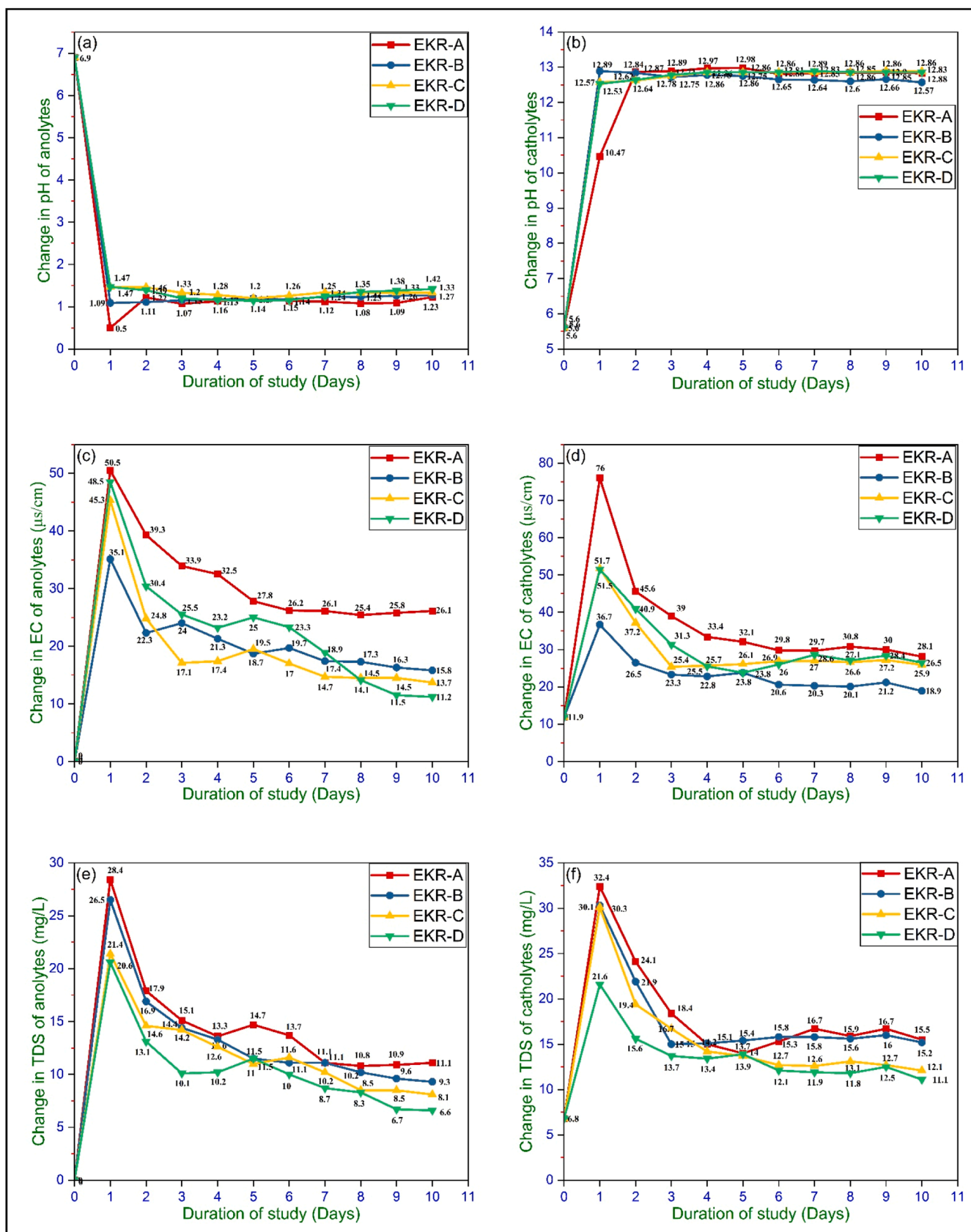


Fig. 3. Variation in (a) pH of anolyte, (b) pH of catholyte, (c) EC of anolyte, (d) EC of catholyte, (e) TDS of anolyte, (f) TDS of catholyte.

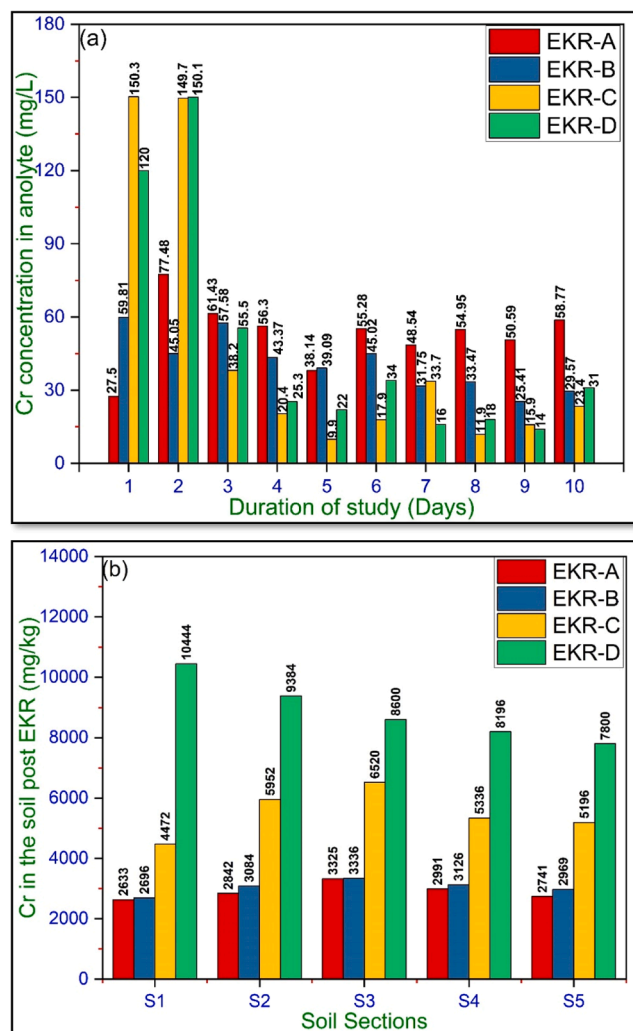


Fig. 4. (a) Cr migration into electrolyte, (b) Cr distribution in different soil sections post EKR.

remediation procedure.

3.4. Changes in soil metal fractionations

Along with the remediation technique, pre and post speciation study is essential to gain insights into the changes taking place in the system during remediation (Hsueh et al., 2022). The alterations in chemical fractionations of Cr metal were assessed through four step BCR sequential extraction method on the initial soil samples and those procured from diverse sections subsequent to EKR treatments, as elucidated in Fig. 5(a-d). The metals of geogenic origin predominantly associate with the residual fraction. In contrast, metals from anthropogenic sources distribute among various other fractions influenced by soil pH, redox potential, and the concentrations of carbonates, organic matter, Mn/Fe oxides and hydroxides, as well as clay minerals (Ahmadipour et al., 2014). Notably, in case of all four soil particle sizes, the initial soil samples exhibited a preeminence of fraction F3, i.e., oxidizable fraction ranging from 63 to 81 %, which clearly indicates the contamination of soil by the anthropogenic sources. This also indicates the availability of Cr in more labile forms (Alonso-azc et al., 2023). Post EKR experiments, increase in the F3 fraction was noted in case of EKR-A and B, however a discernible reduction in F3 was observed in case of EKR-C and EKR-D due to the concomitant conversion of Cr into either F1, F2, or F4 fractions. This transformation of F3 into F1 or F2, due to the redox reaction

taking place in the system attests to the efficacy of EKR with the use of KCl as catholyte in augmenting the leachability of Cr, enabling the extraction of the pollutant from the soil matrix. The increase in F1 and F2 fractions (i.e., 1 % to 30 %) majorly in sections near to anode in EKR-C and D are also a result of acidic pH of the soil post treatment (Peppicelli et al., 2018). This is due to the fact that soil carbonates are known to have high amounts of trace metals that are very sensitive to pH fluctuations (Ahmadipour et al., 2014). Conversely, the amplification of F4 is particularly advantageous, given its inherent stability and inert nature. This fraction is tightly bound within the mineral structure of the soil. Heavy metals in the residual fraction are generally not readily available, thus reducing the potential environmental impact (Borah et al., 2020). However, reduction in F4 fraction was observed post EKR treatment, thus increasing the bioavailability of Cr. This shift was majorly observed in all the sections in EKR-A and EKR-B, whereas, predominantly in sections S1–S3, in case of EKR-C and EKR-D i.e., proximate to the anode where oxidation takes place. However, a slight escalation in F4 was observed in sections S3–S5 in EKR-C and EKR-D. Although the removal efficiency in EKR-C and EKR-D is relatively low, a notable surge in the conversion of F3 into F1 and F2 is discerned in sections S1–S3. The extraction of F1 and F2 fractions was impeded which may be due to the diminution in EOF after the second day of experimentation.

Furthermore, it is evident that EKR increases the leachability of Cr to facilitate its extraction from the soil, which can be seen in all particle sizes. This is attributed to the chemistry between liquid and solid phase taking place during EKR process. In case of coarser particles, the more labile fraction of Cr is easily removed into the electrolytes by the electrokinetic phenomenon. However, in finer particles, the converted labile fraction is not extracted out efficiently due to the reduction in void ratio of the soil, which ultimately results in the diminution of EM and EO. But, if this labile fraction of Cr is not successfully removed from the soil matrix, it may result in the mobilization of pollutant and extending soil contamination with the alteration in soil conditions. This may lead to further food chain contamination through the water or plants grown on such contaminated soil. To effectively address this issue, EKR can be integrated with complementary soil remediation techniques, such as soil washing or flushing, to enhance the removal or recovery of contaminants. This approach is particularly advantageous for finer soil fractions, which typically exhibit higher pollutant concentration.

3.5. Morphological studies of the soil sample

3.5.1. FE-SEM-EDX analysis

The morphological structure of different soil particle sizes obtained by FE-SEM analysis showed that the soil has prismatic structure with lesser surface area in EKR-A, Fig. 6(a) and EKR-B showed blocky texture, Fig. 6(b). In case of EKR-C, it had mainly granular structure as shown in Fig. 6(c), whereas EKR-D, majorly showed platy structure Fig. 6(d) providing greater surface area for the pollutant to adhere to it (Shober et al., 2009). However, the soil post EKR treatment developed honeycomb structure Fig. 6(e) (Liu et al., 2023). This may be due to the intermolecular reaction taken place by the reaction of electrolyte with the pollutant adhered to the soil surface and also may be due to the alteration in pH condition of soil post treatment. Furthermore, the level of concentration can be observed from the shades of the FE-SEM images (Paramkusam et al., 2011). The image of soil sample of EKR-A has brighter shade whereas that of EKR-D have the darkest shade. Thus, it is conclusive that, as the soil particle size decreases, the concentration of pollutants increases which is confirmed by the FE-SEM images. It is noteworthy that the FE-SEM image of the soil sample post EKR treatment has lighter shade which is due to the elimination of certain pollutants. As depicted in Fig. 6(f-i), the EDX results the elemental composition of soil for various size fractions revealed the predominant presence of Si-O-Al, with secondary constituents such as Fe-Cr-Ti and trace amounts of Cu-Mn-Mg. Notably, the comprehensive FE-SEM+EDX characterization unveiled the substantial occurrence of environmentally

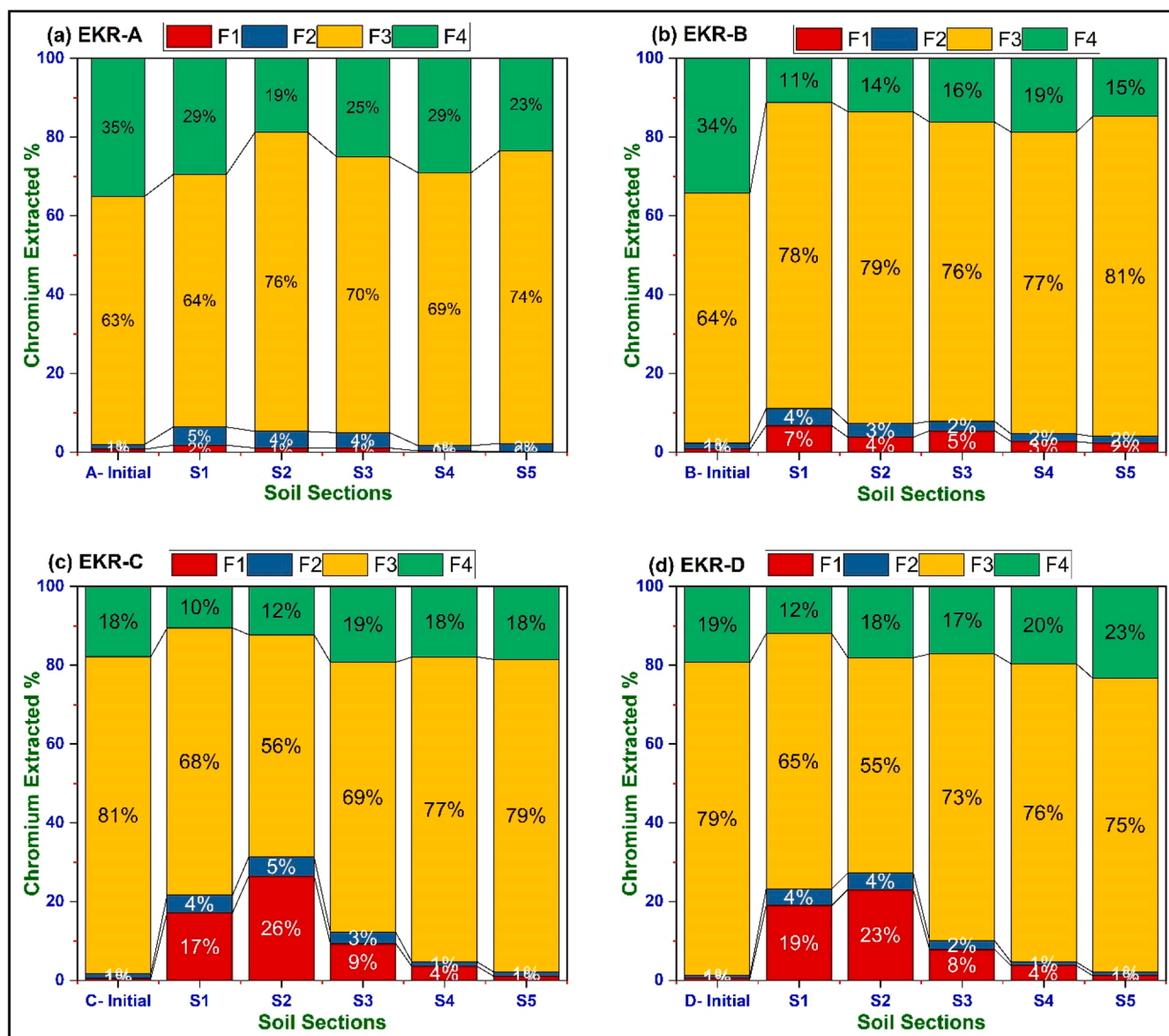


Fig. 5. BCR sequential extraction of Cr metal in the soil pre and post EKR treatment.

deleterious contaminants, including Cr, Cu, Mn, Ti, and others, in the Puliyanthangal Lake soil. These metallic contaminants exhibited robust adhesion to the surface of the soil, resulting in discernible characteristic peak intensities in the EDX profiles. The surface area of soil particles grows inversely proportion to their size, as shown in SEM images; which indicates that there is a greater potential for the pollutant to cling to the finer particles. A decrease in Cr concentration, as shown by EDX mapping of the soil before Fig. 6(f) and after Fig. 6(j) the experiment in case of EKR-A, provides support for the removal effectiveness achieved by the EKR approach.

3.5.2. XRD analysis

From the XRD analysis of the soil samples before and after EKR experiments represented in Fig. 7(a)-(d), it can be seen that certain peaks disappeared whereas few new peaks appeared after the experiments. This is attributed to the intermolecular and intramolecular reaction taking place due to the electrokinetic mechanisms. Majorly the peaks of Strontium Chromium oxide (SrCrO_4) were found in the soil samples followed by Chromium Silicide (CrSi_2), Chromium Carbide (Cr_{23}C_6), Chromium carbide (Cr_3C_2) and traces of Chromium Tungsten Oxide

(Cr_2WO_6), and Chromium Nitride (Cr_2N) which was matched with the hkl values of respective JCPDS files. The presence of all these forms of Cr compounds in the soil of Puliyanthangal Lake is likely to be due to the industrial contamination rather than natural geological processes. In EKR-A, the least distinct peaks could be seen in initial soil sample, however few new peaks of Cr_3C_2 and Cr_2WO_6 appeared in the soils of S2-S4. Whereas in case of EKR-B, new peaks of SrCrO_4 could be seen in S2 and S5. Also, there was a change in peaks of Cr_3C_2 . In EKR-C, the intensity of peaks shown for initial soil sample, decreased in S1-S3. Similar to that of EKR-B, here also new peaks of SrCrO_4 were noted in the soil samples after the test. The same trend was observed in case of EKR-D, also more Cr compounds could be seen in this finer soil fraction. In all the cases, the intensity of peaks of initial soil samples decreased and new peaks appeared. The initial soil sample had peaks of both hexavalent and trivalent oxidation state of Cr, however, the new peaks developed post treatment were majorly of hexavalent state. The XRD result aligns with the results of EDX mapping as the elements such as O, C, Si etc. found by EDX can also be identified in the Cr compounds peaks of the soil obtained through XRD analysis.

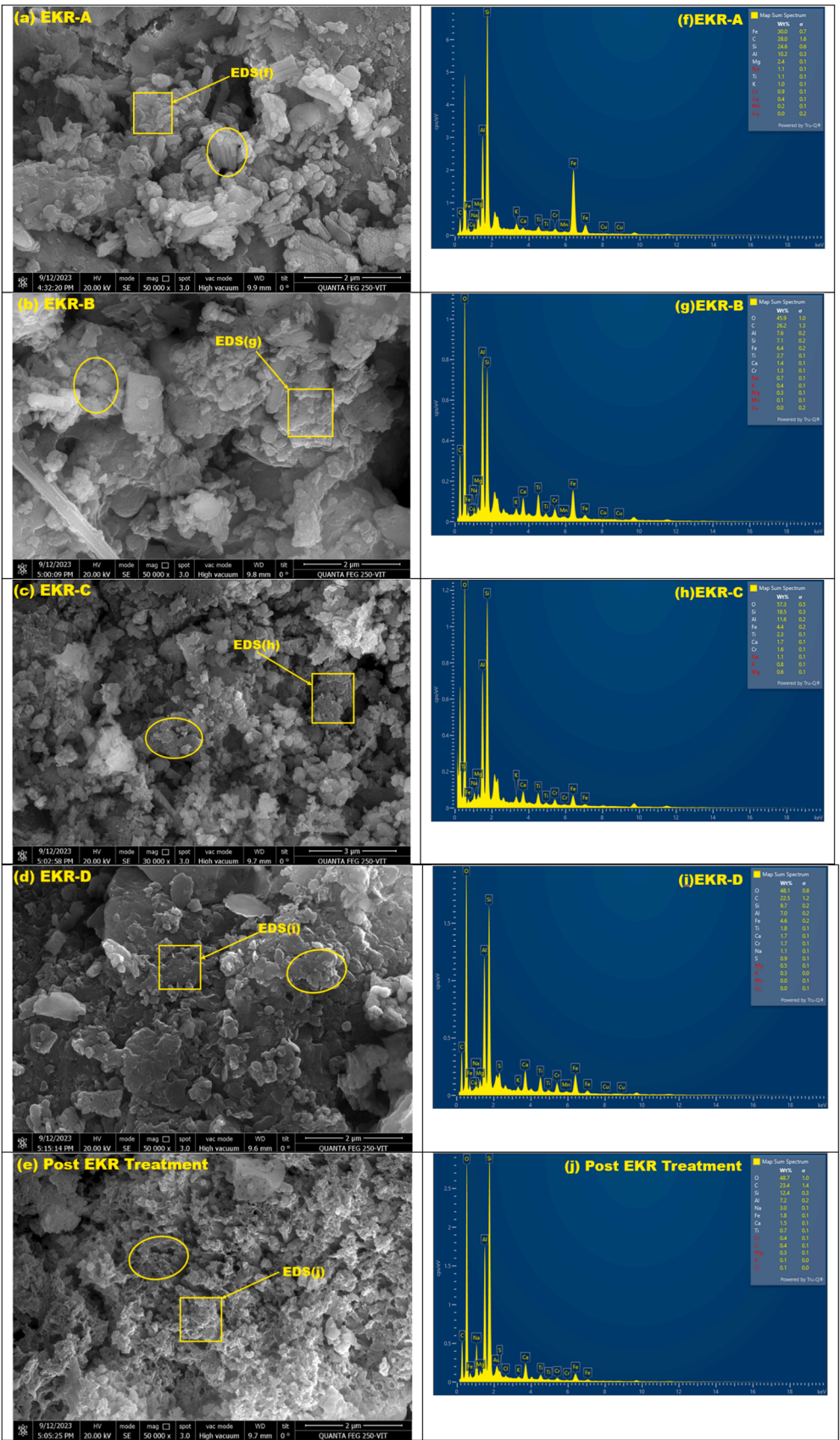


Fig. 6. FE-SEM image (a)-(e) and EDX mapping (f)-(j) of soil pre and post EKR treatment.

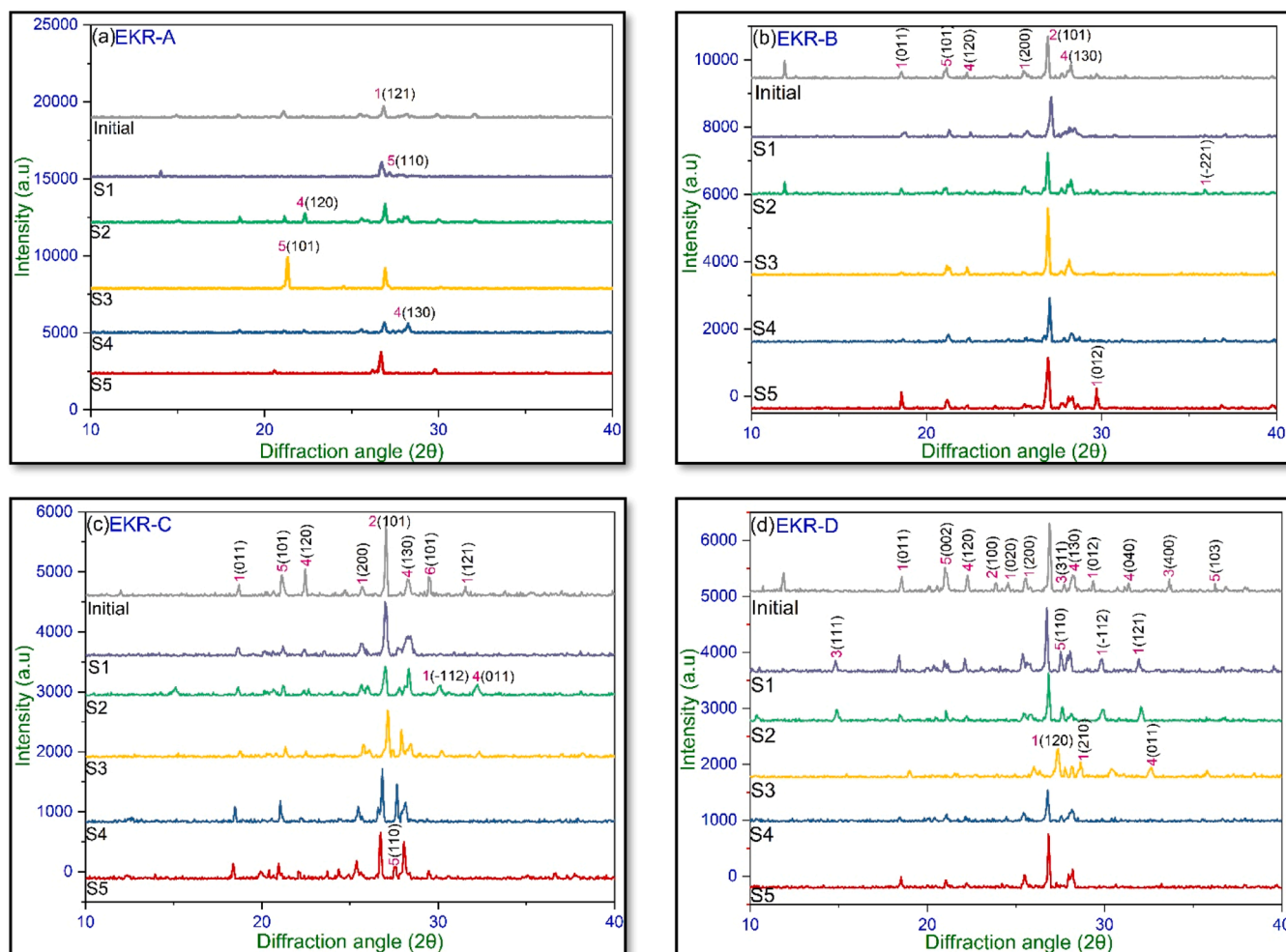


Fig. 7. XRD pattern of the soil for (a) EKR-A, (b) EKR-B, (c) EKR-C, and (d) EKR-D, where the chemical formula and JCPDS file number are: 1- SrCrO_4 (PDF 00-035-0743), 2- CrSi_2 (PDF 03-065-9705), 3- Cr_{23}C_6 (PDF 00-035-0783), 4- Cr_3C_2 (PDF 01-074-7137), 5- Cr_2WO_6 (PDF 00-035-0791), 6- Cr_2N (PDF 00-035-0803).

3.5.3. FT-IR analysis

The FT-IR spectrum has been widely employed for characterizing materials and providing information on their functional properties. It is done to characterize surface functional group of materials. By analyzing the soil sample using FT-IR with fingerprint area between 4000 cm^{-1} to 400 cm^{-1} , we were able to determine its unique functional groups, which align with its physicochemical composition. The broadening and intensification of the peaks after EKR treatment can be observed in all four experiments Fig. 8(a)–(d), which may be due to the intramolecular and intermolecular changes in the soil. The same was noted in case of XRD results. However, no new bonds were formed post treatment. As the size of the soil particle decreases, the number of bonds and functional groups increases.

A strong absorption bands around $900\text{--}1000\text{ cm}^{-1}$ is due to the $\text{Cr}=\text{O}$ stretching vibrations (Ren et al., 2016) which can be seen in all the soil particle sizes but the intensity increases as the soil particle size decreases. The peak ranging between 545 and 750 cm^{-1} attributes to Cr_2O_3 (Madi et al., 2007). Occurrence of such peaks indicates the amorphous nature of soil. The broad but distinguish peaks ranging between 997 and 1030 corresponds to the presence of CrO_2 phase. These peaks attributes to chromyl ($\text{C}=\text{O}$) vibrations (Trivedi, 2015). The broad band from 3200 to 3600 attributed to the stretching vibration of $\text{O}-\text{H}$ bond that can be noted in case of EKR-B, EKR-C and EKR-D. The infrared spectrum analysis indicates the existence of chromate and dichromate species. The presence of chromate can be indicated by peaks

observed at around $850\text{--}855\text{ cm}^{-1}$ and $950\text{--}970\text{ cm}^{-1}$. Dichromates can be distinguished by their characteristic peaks at 729 , 735 , 895 , and 903 cm^{-1} (Hedberg et al., 2021; Hoffmann et al., 2001; Muller et al., 1969). Based on vibrational analysis, it can be inferred that the peaks at 729 and 735 cm^{-1} are indicative of $\text{Cr}-\text{O}-\text{Cr}$ anti-symmetric stretching in dichromates. The peaks at 895 and 903 cm^{-1} correspond to the symmetric stretching vibrations occurring within the CrO_3 groups of the CrO_4 tetrahedra in dichromates (Azeez and Mohammad, 2017). The bridging structure ($\text{O}_3\text{Cr}-\text{O}-\text{CrO}_3$) of dichromates facilitates the vibrations of $\text{Cr}-\text{O}-\text{Cr}$ and internal CrO_4 (H. Stammreich, D. Bassi, O. Sala, 1958). Furthermore, the presence of a peak at 964 cm^{-1} indicates the creation of metastable CrO_3 as a result of $\text{Cr}=\text{O}$ vibrations. Chromium oxides (CrO_x) generally display $\text{Cr}-\text{O}$ vibrations related to Cr_2O_3 at around 770 , 630 , 570 , 450 , and 420 cm^{-1} (Vats et al., 2023). Based on the FT-IR bands, it is evident that Cr is primarily bonded with oxygen, which can also be linked to the SEP results that indicate a higher percentage of oxidizable fraction. Similar results were reported for both the soil samples before and after EKR treatments. Therefore, the effectiveness of EKR can be improved by adding a potent oxidizing agent to the soil. This would aid in removing the oxidizable portion of Cr from the soil matrix.

4. Conclusion

This research endeavour is helpful in designing and execution of

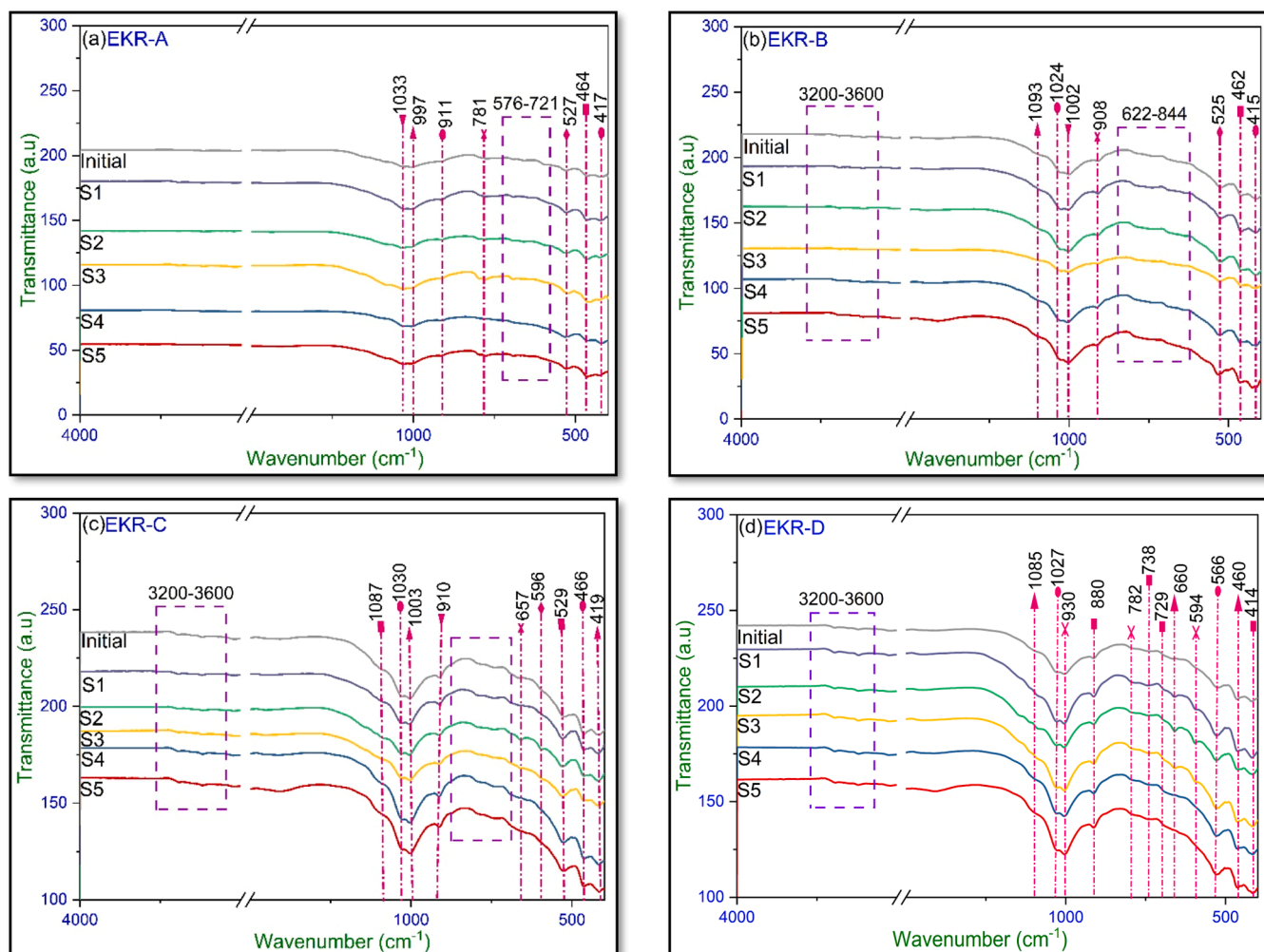


Fig. 8. FT-IR pattern of the soil for (a)EKR-A, (b)EKR-B, (c)EKR-C, and (d)EKR-D.

efficient electrokinetic soil remediation technique based on the following conclusions:

- Initial soil characterization indicated an inverse relationship between pollutant concentration and particle size. Post-treatment analysis revealed that treatment efficiency is significantly depended on particle size; as particle size decreased, removal efficiency also decreased. This is due to the reduction in electroosmotic flow, which hinders pollutant transport into the electrolytes.
- Analytical studies employed for the morphological and composition studies of soil pre and post treatment revealed that notable changes was observed on soil surfaces. The XRD showed decreasing intensity of certain peaks and the emerging of new peaks, likely due to the alteration taking place by the reduction and oxidation of Cr-compounds. The FT-IR analysis indicated no new bond formations; however, peak broadening and intensification suggested intermolecular reactions induced by EKR mechanisms.
- The mobility of heavy metals in soil are mostly determined by the specific types of binding forms they exhibit. The SEP proclaimed that, EKR increased the leachability of pollutants, converting them into more bioavailable forms. Moreover, EKR could easily remove the available Cr out of the soil matrix in case of coarser particle sizes.
- Furthermore, this research underscores the critical need to treat soils with smaller particle sizes, which contain higher pollutant concentrations compared to larger particles. However, desired level of removal was not achieved, thus EKR combined with other methods

such as soil washing/ flushing can be efficient in recovery of Cr. Also, different electrolytes and oxidizing agents can be employed to efficiently recover the heavy metals from finer particle sizes. This can be the scope of future studies.

CRediT authorship contribution statement

J. Akansha: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Bhaskar Das:** Validation, Supervision, Resources, Project administration. **N. Rajasekar:** Validation, Supervision, Resources, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

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Data availability

Data will be made available on request.

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