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Review article

Technological and economic analysis of electrokinetic remediation of contaminated soil: A global perspective and its application in Indian scenario

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ABSTRACT

Globally million hectares of land annually is getting contaminated by heavy metalloids like As, Cd, Cr, Hg, Pb, Co, Cu, Ni, Zn, and Se, with current concentrations in soil above geo-baseline or regulatory standards. The heavy metals are highly toxic, mobile, and persistent and hence require immediate and effective mitigation. There are many available remediation techniques like surface capping, encapsulation, landfilling, soil flushing, soil washing, electrokinetic extraction, stabilization, solidification, vitrification, phytoremediation, and bioremediation which have been evolved to clean up heavy metal-contaminated sites. Nevertheless, all of the technologies have some applicability and limitations making the soil remediation initiative unsustainable. Among the available technologies, electrokinetic remediation (EKR) has been comparatively recognized to mitigate contaminated sites via both in-situ and ex-situ approaches due to its efficiency, suitability for use in low permeability soil, and requirement of low potential gradient. The work critically analyzes the EKR concerning techno, economic, and sustainability aspect for evaluating its application on various substrates and environmental conditions. The current soil contamination status in India is presented and the application of EKR for the heavy metal remediation from soil has been evaluated. The present work summaries a comprehensive and exhaustive review on EKR technology proving its effectiveness for a country like India where the huge amount of waste generated could not be treated due to lack of infrastructure, technology, and economic constraints.

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1. Introduction

Soil pollution is one of the major environmental concerns in developing countries due to the ungoverned disposal of liquid and solid wastes. Primary pollutants such as metals, organic compounds, pesticides, antibiotics, and even radioactive substances are predominantly toxic in their characteristics [1]. Consequently, they have the potential to directly harm the environment, living organisms, and human health, as well as can impact the economic activities and overall well-being of the society [2]. Therefore, solution that effectively creates a sustainable environment for present and future generations, especially in developing countries like India, where the current rate of decontamination is not sufficient, needed to be addressed with paramount importance [3].

Heavy metals in the environment can be introduced through various natural sources which primarily comprise geological activities like erosion, volcanic eruptions, mineral weathering, and continental dust [4]. On the other hand, concerning anthropogenic activities (e.g., industrial, domestic, and agricultural), improper discharge of toxic metal-rich effluents from tanneries, mining industries, thermal power plants, pharmaceuticals, chemical industries are the major sources of water and soil pollution [5]. Soil and water being essential components of the food chain, these heavy metals tend to easily enter the food chain and cause toxic effects to humans, animals, and plants, which can be as simple as eye irritation to more severe as endocrine disruptions, degenerative diseases and genetic disorders [6].

Soil remediation can be achieved by either engineering, chemical or biological approaches. Engineering technologies include vitrification [7], soil washing [8], solidification/stabilization [9], soil flushing [10], thermal treatment creating a sub-surface barrier to protect groundwater from contamination, excavation, and landfilling [11] and electrokinetic method, etc. [12]. The electrokinetics method stands for a set of well-defined stages when an ionic liquid migrates tangentially to a charged surface [13]. Chemical methods in soil remediation include applications like phosphates [14], liming material such as burnt lime, dolomite, agricultural lime, crushed shells, gypsum etc. [15], Fe/Mn oxyhydroxides, organic materials, zeolites, modified aluminosilicates etc. [16]. Mitigation by microbiological [17] means can be applied in numerous ways, which include contaminant-specific site decontamination by using specialized strains of bacteria [18] known for consuming and degrading contaminants. Engineering methods of decontamination are typically adopted for soils with metal toxicity to prevent contamination of unpolluted areas and ultimately entering food chain [19]. It is more effective in bringing the contamination level down to some acceptable limit while maintaining a short time frame. The cost of implementation of these methods is relatively high, especially in field applications. In view of both the remediation efficiency and cost aspects, EKR has appeared to be a feasible option for the remediation of contaminated soils under ex-situ condition [20]. This approach is also suitable for soils with low-permeability, saturated or unsaturated conditions. Moreover, EKR also helps in the removal of charged particles (anions and metal ions) by the electromigration process [21].

Although increased levels of urbanization have boosted India's economy, the environmental damage that resulted is a major worry. Based on the Comprehensive Environmental Pollution Index (CEPI) ranking, researchers identified critically contaminated industrial locations and clusters, as well as possible effect zones [22]. As the soil contamination issue is critical in India, the potential technology improvements for the elimination of these toxins are urgently needed. If not, it would have devastating effects on local biodiversity and the health of people living in and around the polluted sites [21]. Selection criteria of any method over others depends on many factors like type of soil, level and characteristics of pollutants, available technology and resources, and overall economy. In this regard, the present review work initially attempts to provide a glimpse of the available soil remediation technologies followed by emphasizing on EKR providing a critical analysis of its eco-technological aspects. Later the status of soil contamination with heavy metals in India have been summarized with the applicability and challenges of implementing the EKR technology.

2. Available soil remediation technique

Over the past years, many methods have been developed for the restoration, remediation, excavation, or cleaning of contaminated soil. Based on the nature of the treatment, these methods can be grouped as physical, chemical, electrical, thermal, and biological remediation [23], or they can be divided into three groups: containment-based (e.g., capping/encapsulation), transformation-based (e.g., stabilization/immobilization), and transport-based (e.g., extraction/removal) methods [24]. The remediation techniques can further be grouped as in-situ or ex-situ. In-situ remediation techniques include surface capping, encapsulation, electrokinetic extraction, soil flushing, chemical immobilization, phytoremediation, bioremediation, etc. whereas, ex-situ techniques include landfilling, soil washing, solidification, and vitrification [25,26]. These remediation techniques have been discussed in brief below.

In-situ remediation minimizes soil disturbances, reduces exposure to contaminants, and lowers treatment costs by avoiding excavation and off-site transportation [27]. However, field factors, such as temperature, soil permeability, pollution depth, and probable chemical leaching must be carefully managed [28]. Surface capping, is a technique of creating a stable, protective barrier of waterproof material, that prevents groundwater and surface water penetration, limiting the spread of soil pollutants. However, the capped soil loses its natural habitat, particularly for fostering plant development. The capping materials include biochar, non-contaminated soil, alkali-activated blast-furnace slag, metakaolin geopolymer, exfoliated vermiculite, alum sludge, etc [29]. Another method similar to encapsulation is surface capping, also known as the "barrier wall", or the "cutoff wall" approach. It combines polluted soil with other materials, such as concrete, lime, or asphalt making it immovable [30]. However this method is restricted to shallow, small-area contamination locations, much like surface capping [31]. Another method, electrokinetic extraction uses electrical adsorption; electrokinetic extraction purges heavy metals from polluted soils. When low-density direct current (DC) is provided through electrodes buried in the ground, cations in the contaminated soil solution phase move to the cathode and anions move to the anode due to the attractive force of the established electric field [12]. It is effective on a variety of contaminants, including sludge sediments and heavy metals (Cr, Pb, Cd, As, and Ni) [32].

In continuation with various techniques, soil flushing involves contaminant removal by passing an extraction fluid through the soil. The extraction fluid is then collected, reused, and ultimately treated and disposed of [24]. Solvent flushing, ground water pumping, solvent recovery, and water treatment are few of the operational units involved in this technique. The variable elements like leaching agent, concentration, pH, time, solid-to-liquid ratio needs monitoring during the process [33]. Further, Chemical immobilization is the process of capturing or immobilising pollutants in contaminated soil by adding chemical agents to the initial medium to solidify the soil or change the mobile pollutant fractions into precipitates and/or strongly sorbed moieties [34]. Phytoremediation is a technology used to clean up and re-vegetate contaminated environments. The physical, chemical, and biological quality of contaminated soils are typically improved via phytoremediation, in contrast to physical and chemical treatments that permanently change soil attributes. It

Fig. 1. Different In-Situ soil remediation techniques: **(a)** Surface Capping [25,29]; **(b)** Encapsulation [24,37]; **(c)** Electrokinetic Extraction [38,39]; **(d)** Soil Flushing [10,40]; **(e)** Chemical Immobilization [14,15]; **(f)** Phytoremediation [3,23]; **(g)** Bioremediation [36,41].

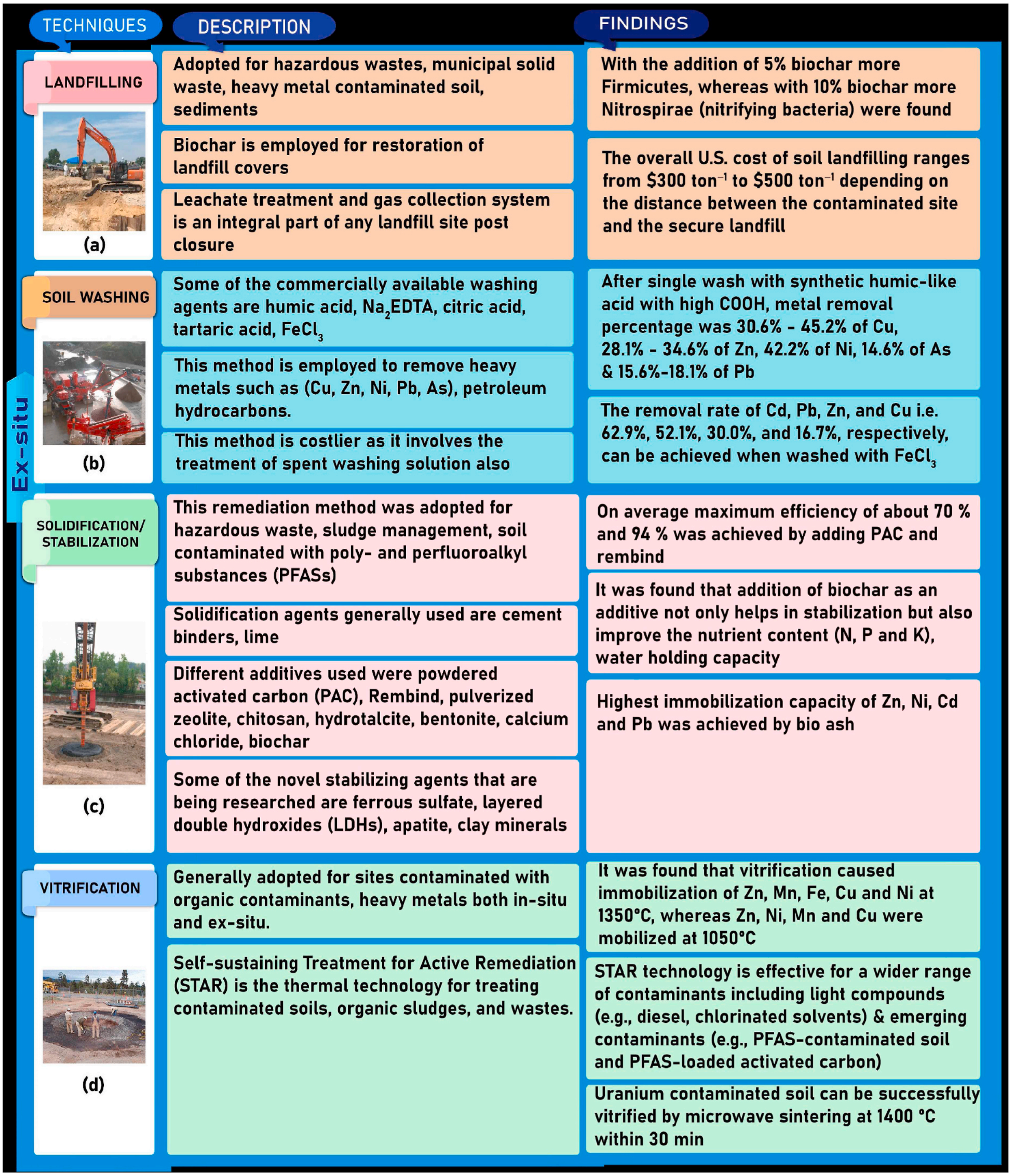

Fig. 2. Different Ex-Situ soil remediation techniques: **(a)** Landfilling [27,45]; **(b)** Soil washing [8,46]; **(c)** Solidification/Stabilization [9,34]; **(d)** Vitrification [7,47].

has been adopted to remediate the soil contaminated with polycyclic aromatic hydrocarbon (PAH), Cr, Cu, Pb, Zn, etc. [3]. Instead of plants, when remediation is done with the help of biological organisms, the technique is called bioremediation [35]. It uses micro-organisms to detoxify or eliminate heavy metals from the soil and also it is cost-effective, non-intrusive, and permanent. It is frequently used in conjunction with other methods, such as soil flushing and phytoextraction, to boost the solubilization of heavy metals prior to extraction. Sites with oil spills, sewage sludge, petroleum hydrocarbons, selenium, and other heavy metal contamination typically use this technique [36]. The implementation of in-situ remediation methods is discussed in (Fig. 1(a–g)).

Ex-situ remediation involves excavating contaminated soil, transferring it to a treatment unit, and treating pollutants at designated locations [32]. This treatment incurs high costs due to soil extraction, storage, disposal, and site refilling, however it allows for controlled and refined remediation, achieving better results in less time [41]. One of the ex-situ methods is landfilling, which is the simplest method for removing contaminated soil from its original location and transporting it to a secure landfill for disposal. Impermeable liners, leachate drains, and dike enclosures are all features of a secure landfill. It is used for sediments, heavy metal-contaminated soil, municipal solid waste, and hazardous waste [42]. Another method is soil washing which involves a physical and chemical procedure that uses ex-situ washing of the soil with specially prepared solutions to remove heavy metals from polluted soil. By modifying the soil's acidity, the solution's ionic strength, redox potential, or complexation, washing solutions are used to mobilise heavy metals. An ideal washing solution should be nontoxic, biodegradable, and greatly increase the solubility and mobility of heavy metal pollutants while interacting minimally with soil components [43]. The method of soil solidification involves removing metal-contaminated soil from the site, moving it to a facility for treatment, screening out coarse debris, and combining it with a binder in an extruder. The binding substance permeates through the soil and creates a water-proof solid entity that encases the contaminants [44]. Ex-situ stabilization is the term for a technique that involves using a stabilizing agent rather than a binding material to immobilise pollutants through chemical processes [30]. In the thermal remediation process known as vitrification, polluted soil is heated until it solidifies into glass-like materials. Applying a high-temperature treatment at the contaminated location, results in the development of vitreous material, which can limit the mobility of heavy metals in soil [35]. The soil in the area is subsequently transformed into molten 'lava' and cools to produce glassy substance [31]. The organic pollutants are eliminated while the heavy metals are encapsulated in the glassy matrix. It is comparatively simple to implement compared to other physical remediation techniques [41]. A summary of the implementation of ex-situ remediation techniques has been shown in (Fig. 2(a–d)).

3. Overview of EKR technology for soil remediation

EKR is a developing technique, which has substantial potential for in-situ and ex-situ remediation of fine-grained soil depending on the extent of contamination as well as the nature of the experiment [2]. However, a thorough study on the process is required to implement in-situ operations. An ex-situ treatment process is done with the help of specially designed reactor chambers [48]. The remediation setup includes the following components: a chamber to store the contaminated sample and electrolytes divided by thin and porous compartments (usually filter papers), electrodes, electrolytes, and a power supply. Multimeters and ammeters are used to measure the value of potential and current. The in-situ treatment of contaminated sites, which entails drilling wells in which electrodes are installed and a low DC electric potential is applied [20]. The components of the setup include electrodes placed in a drain created at the contaminated site, fresh and exhausted electrolytes storage vessels, and a power supply. Electrolyte Pumping and conditioning systems at the electrodes are established depending on the field conditions and available facilities [49].

3.1. Past-to-present advancements in EKR

The concept of EKR was introduced by F.F. Reuss in 1808 in which the mobilisation of water as well as other chemical components towards the preferred electrode was executed by introducing an electrical gradient [50]. This was further implemented for the treatment of contaminated soil by Helmholtz in 1879, the efficiency of which was later enhanced by Pellat in 1903 and Smoluchowski in 1921 [51]. Upon further understanding and improvement in the implementation, in the early twentieth century, Ruess applied a DC to a mixture of clay and water, thus leading to the movement of water through capillary action toward the cathode. Upon the removal of electric potential, the flow of water stopped immediately [21], hence demonstrating the common phenomenon of an electrokinetic process. Since then, the same concept has been experimented with, and analysed in different designs and approaches with efficient results [52]. The hybrid EKR technique originated in the late 20th century, during which electrokinetic processes were first proposed as a potentially effective approach to remediate soil and groundwater. Early in the twenty-first century, scientists initiated investigations into the feasibility of integrating electrokinetics with alternative remediation techniques [53]. However, the selection of the remediation method best suitable for a particular condition of soil depends on various factors like sediment and soil characteristics, the concentration of pollutants, nature of contaminated lands, remediation purpose, permissible limit of contaminants in medium, pollutant type, availability of resources and methods, economic conditions, and period of remediation as per requirement [2]. In the last decade, EKR has emerged as a useful technology for the removal of different heavy metals like Cd, Cr, Cu, Pb, Hg, Zn, and U. Apart from heavy metals, it can also be used for the removal of chlorophenols, phenols, trichloroethane, polychlorinated biphenyls, toluene, and acetic acid [13].

3.2. Transport mechanism of EKR technique

The working mechanism of EKR consists of the migration of charged ions upon the application of direct current on soil with the help of electrode buried at a specified distance within the site of remediation. Negatively charged electrodes attract positive ions and

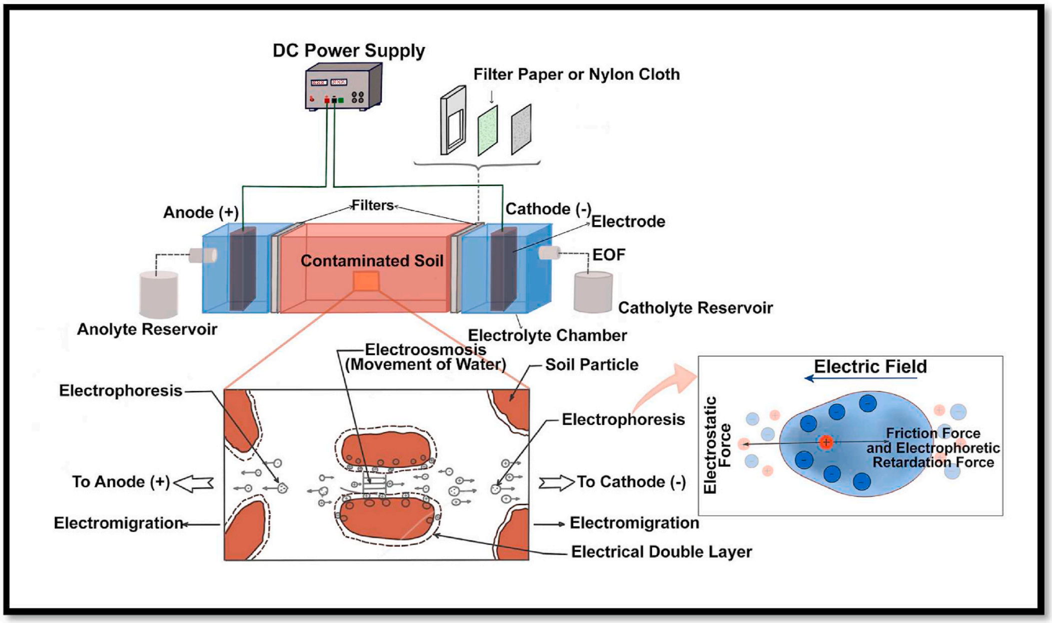

Fig. 3. Soil remediation mechanisms of electrokinetic process [53,55].

positively charged electrodes help in the accumulation of negatively charged contaminants [13]. During this process of accumulation, contaminants may be destroyed, mobilised, or mineralised [20], depending on the electric potential applied. If optimized properly, these contaminants can also be recovered with a good efficiency [50,54]. This process typically works on three mechanisms shown in (Fig. 3).

Electroosmosis: Applied electric field causes a viscous drag within soil with the help of induced charge, causing bulk transport of moisture and electrolytic ions [20]. This phenomenon works on the principle of movement of opposite charges towards each other. When an electric field is applied, electroosmotic flow occurs because cations close to the surface of soil particles (double layer) move towards the cathode [21].

Electromigration: The second transport mechanism generated by the application of an electric field is electromigration, which ionises the metals causing the movement of positively charged (cations) heavy metals towards the cathode [13]. This phenomenon of movement of cations and anions to the oppositely charged electrodes is directly proportional to the concentration of ions in pore water solution and the strength of the applied electric field. The rate of migration of particular ion species under a unit electrical field is called "ionic mobility" [21]. This phenomenon is observed in moist soils where metal ions, chlorides, phosphates, nitrates, and other highly soluble inorganic species are present [13].

During EKR process, electrolysis reactions transpire at the electrodes, generating protons and hydroxyl ions at the anode (Equation (1)) and cathode (Equation (2)), correspondingly.

$$2H_2O \rightarrow O_2\ (\uparrow) + 4H^+ + 4e^-\ \text{(At Anode)} \tag{1}$$

$$4H_2O + 4e^- \rightarrow 2H_2\ (\uparrow) + 4OH^-\ \text{(At Cathode)} \tag{2}$$

These ions undergo electromigration towards the cathode or anode, instigating the establishment of acid and base fronts within the soil, respectively. The resultant alteration in soil pH can exert notable influences on sorption, precipitation, and dissociation reactions, as well as the zeta potential of the soil surface that are the parameters intricately linked to the electroosmotic rate [50].

Electrophoresis: Under the application of an electric field, the migration of colloids or charged particles is called electrophoresis [20]. It is similar to electromigration, as under the application of direct current across a colloidal suspension, colloids and suspended charged particles present in the pore fluid are electrostatically attracted to either the cathode and repelled by the anode or vice versa [21]. Electrophoresis is generally considered for decontamination if the migrating colloids have the contaminants adsorbed on them. This process is considered less important than the other two processes as the EKR phenomenon is influenced by charge densities on the surface of soil particles and their mineralogical composition [56].

The performance of the electrokinetic process implemented for the remediation of soil can be improved by using surfactants [57,58], chelating agents and reagents to control pH. Reagents can be also used to improve the contaminant migration rates to the electrodes. The contaminants can then be removed from electrodes with the help of various processes like ion exchange, precipitation, and electroplating [13].

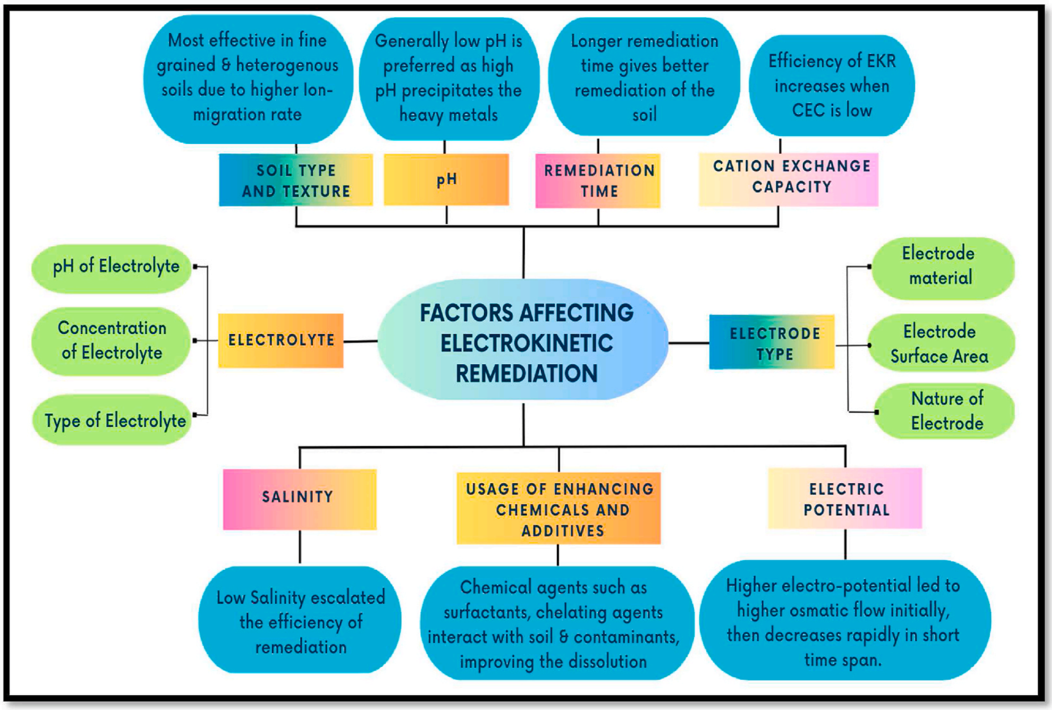

Fig. 4. Factors affecting the performance of the electrokinetic remediation process [63,64].

3.3. Factors affecting performance of EKR

The process of EKR is affected by various factors, which influence the overall process efficiency [59]. They may include soil type, pH of the medium, type of electrolyte used, the time taken for remediation, and electric potential (Fig. 4). The migration of contaminants and their transport mechanism is highly dependent on these factors. EKR is most effective in fine-grained and heterogenous soils as they have a higher ion-migration rate (i.e., higher in sandy soil than in clayey soil) [60]. A lower pH is often recommended for EKR because a higher pH causes the heavy metals to precipitate, preventing the flow of pollutants. When the duration is considered, a longer remediation time gives better decontamination of the soil [19]. The efficiency of EKR increases when the cation exchange capacity (CEC) is high and the salinity of the contaminated soil is low [61]. Also, some of the chemical agents such as surfactants, chelating agents, or salts interact with the soil contaminants, improving the dissolution and transportation of the contaminants. Generally, the osmatic flow increases initially due to higher electro potential; however, it quickly decreases within a short time period [62].

3.4. Economical assessment of EKR technique

The total cost of soil decontamination processes varies depending on a range of variables, such as type and level of pollutants, location of the affected area, technique used to remediate the soil, legal guidelines for soil clean-up, energy tariff rate (if applicable), etc. The estimated values based on literatures referred here are from limited individual studies, rather than average from huge data base. The cost involved for different soil remediations techniques such as soil washing (120–600 $ per tonne), landfill disposal (150–200 $ tonne), solidification/stabilization (50–330 $ per m^3), bioremediation (30–100 $ per m^3), incineration (200–600 $ per tonne), soil flushing (50–80 $ per m^3), chemical oxidation (190–660 $ per m^3) etc. [65] Whereas the cost involved for EKR (150–180 $ per m^3) which is higher when compared to other technologies such as bioremediation, soil flushing etc. But on the other hand, electrokinetic technology has great potential to compete with other available treatment alternatives [66]. The cost of EKR depends on several factors, including size of the site, type of contaminants present, and the level of contamination [57]. It is aesthetically pleasing, easy to use, safe to operate, and its acceptability is higher when compared with other technologies (Fig. 5). show the estimated cost comparison and duration of EKR with its competing technologies. The cost of conventional EKR is directly related to the electricity consumption, unless enhancing agents like ethylenediamine tetra acetic acid (EDTA), sodium hydroxide (NaOH), citric acid ($C_6H_8O_7$) etc. are used for facilitating faster remediation [66]. As per [67]. The electricity consumption for EKR was approx. 1104 kWh/m^3, which according to the commercial price of electricity in Delhi, India would cost around 110 USD at the current time. This cost can increase by up to 5 to 10 times depending upon the type of enhancers used [65]. Its treatment time (up to 36 months) lies towards the higher end just under phytoextraction (up to 40 months) as compared to fixation and landfilling, which would take as high as 9 months to decontaminate the sample [65]. The residue disposal in electrokinetics is one of the very few safety issues that occur to otherwise a

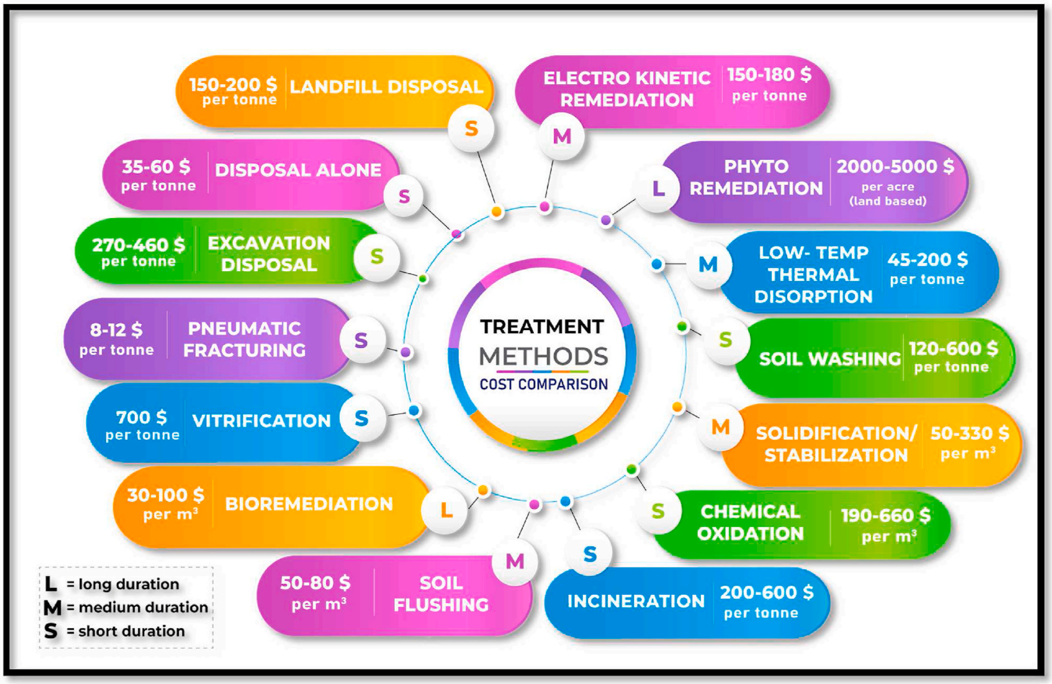

Fig. 5. Cost comparison and duration of different remediation technologies [66,67].

very safe treatment method. The drawbacks such as transport and excavation that occur in fixation do not occur in EKR which also plays a vital role in cost reduction.

3.5. Sustainability indicators of the EKR technique

In the current scenario, remediation methods aim for the pollutant removal from soil while not giving proper attention to components related to sustainability in terms of environmental aspects such as soil quality, energy use, carbon footprint and other socio-economic factors [57]. A remediation activity is deemed sustainable if it aims for a minimal impact goal and is able to sustain with the slightest of long-term effect on the environment alongside considering, the social and economic factors [28]. As defined by the Sustainable Remediation Forum, UK (SuRF-UK) "the practice of demonstrating, in terms of environmental, economic and social indicators, that the benefit of undertaking remediation is greater than its impact" is termed as Sustainable remediation. Sustainability evaluation requires a set of individual norms to be agreed by those carrying out an assessment, which is relevant to the project. These norms are usually understood by combining information about individual indicators in environmental, social and economic aspects [68]. As discussed above, following sustainability indicators shall be considered in the three mentioned aspects. The environmental indicators include– the residual concentration of the pollutant, pH, texture, water carrying capacity and other variables depicting the improved quality of soil, the microbial diversity present in the soil, electrical conductivity and nutrient level in the soil, the positive impact of remediation on biodiversity of soil, the carbon footprint of the process and the energy use pattern of the technique. The socio-economic components include–job opportunities, stakeholder involvement, safety aspect economic costs and benefits and life-span and flexibility of project [69]. All of these indicators should be considered collectively for evaluating the sustainability impact of the clean-up program (Fig. 6).

3.6. Merits and demerits of EKR

EKR is an emergent technology for the removal or extraction of heavy metals from contaminated soil. It is applicable to both ex-situ and in-situ for fine-grained soil [51]. It has many advantages over other conventional methods. EKR is a targetable treatment process, which means it can be applied at a wide variety of soils. Its field application occurs with a very minimal soil disruption unlike soil washing, landfilling etc [6]. It is a safe and easy-to-operate technology whereas solidification, vitrification etc. need higher degree of precautions. EKR has the ability to treat both inorganic and organic contaminants [63]. The post-treatment volume of waste generated is minimum thus reducing the operating cost. However, it has certain limitations such as poor ion transport, higher cost and slow as compared with other techniques [70]. Field application of EKR lacks in targeting mobile contaminants and has a lower radius of influence. This is due to the practical and technical problems in defining a particular contamination source and the intermediate to high threat of contaminating groundwater resources or aqueous contamination zones. Moreover, the whole EKR process is significantly dependent on pH conditions during operation [71]. The acidic conditions favour the discharge of the contaminants into the solution

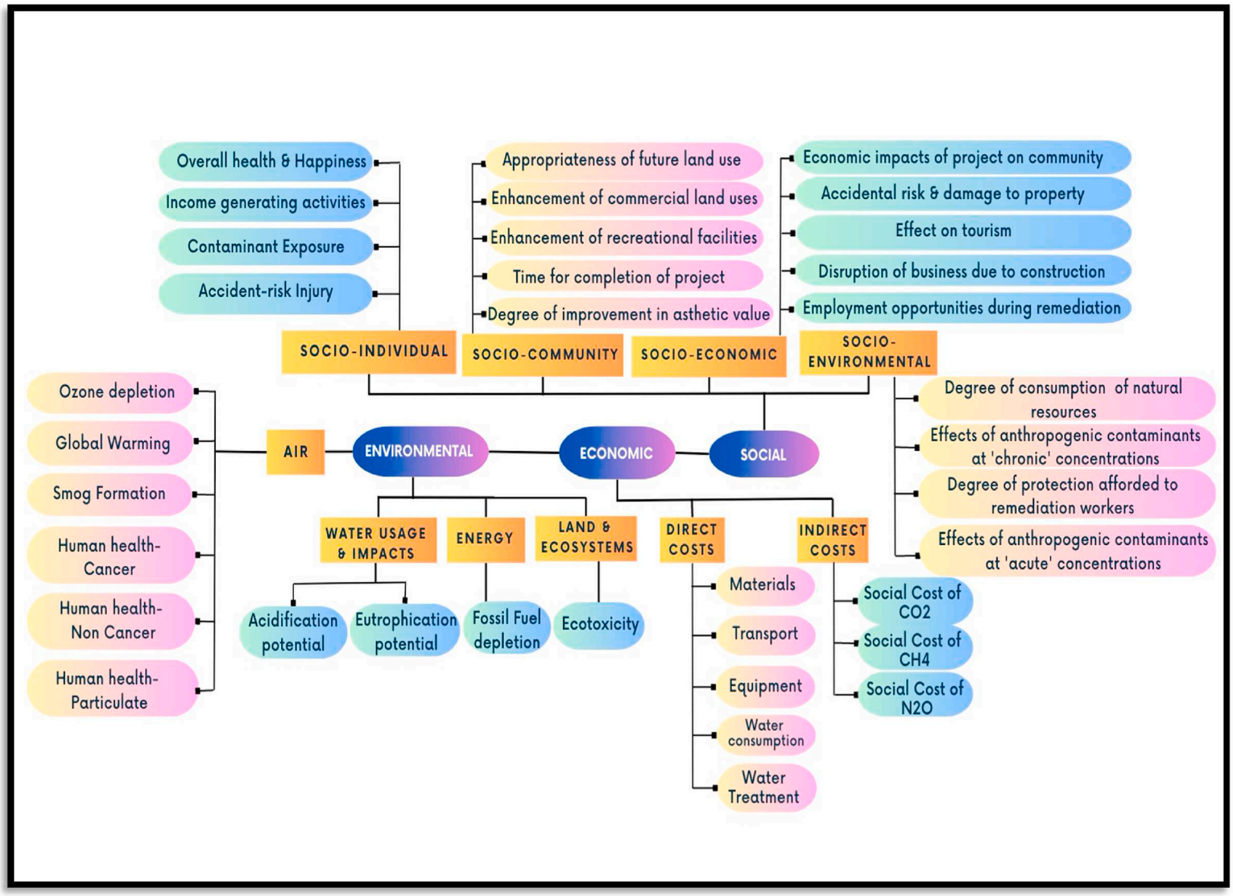

Fig. 6. Sustainability indicators for evaluating the performance of the Electrokinetic soil remediation technique [69].

Table 1
Advantages, disadvantages and limitations of EKR in terms of technology, economy and sustainability [6,16,32,68,69].

Aspect	Advantages and Benefits	Disadvantages and Weaknesses	Limitations
Technology	- Mobilizes pollutants and ions, allowing for efficient remediation of contaminated soils. - Reduces the need for excavation and hauling away contaminated soil.	- Extremely high energy consumption, especially in large-scale applications. - Requires careful monitoring and control to avert unforeseen repercussions.	- Limited effectiveness for some types of contaminants and soil types. - May require long treatment times, especially for deep or highly contaminated soil.
	- Applicable for a wide variety of pollutants, including heavy metals, organics, and inorganic ions.	- Limited to low-permeability soils and may not be suitable for all site conditions.	- The effectiveness depends on soil and contaminant properties and can vary.
Economy	- Reduces costs associated with excavation and disposal of contaminated soil. - Can be a cost-effective solution for highly contaminated sites with deep pollution. - Minimizes the need for transport of contaminated	- High initial investment in equipment and energy consumption. - Maintenance and monitoring costs can be significant. - Technical expertise is required for operation and management.	- May not be cost-effective for small-scale or shallow contamination.
Sustainability	- Reduces environmental impact by avoiding soil excavation and disposal.	- Potential for soil desiccation and pH changes, which can affect soil health.	- May not address the root causes of contamination and may not prevent future contamination.
	- Can help in the remediation of historically contaminated sites.	- Limited long-term effectiveness for some persistent contaminants.	- May require the use of chemicals or reagents, which may have their own environmental concerns.
	- Supports the restoration of soil quality and ecosystem health.	- Requires a source of electricity, which may come from non-renewable sources.	- May not be suitable for highly mobile contaminants.

phase. Other disadvantages include it being a costly and time-consuming treatment process as compared with other techniques. The efficiency of EKR reduces significantly when the target ion concentration is low and the non-target ion concentration is high. It also reduces due to the presence of large rocks and gravels, hematite and carbonates in soil [71]. (Table 1) illustrates the advantages, disadvantages and limitations of EKR in terms of technology, economy and sustainability.

3.7. Development of hybrid EKR

A conventional EKR is one which solely relies on electrokinetic processes such as electroosmosis, electromigration, and electrophoresis without combining with other technologies. The applicability of EKR is limited to the site-specific conditions as well as the availability of the energy to create potential difference within the electrodes. Hence the hybrid EKR evolved, which is a combination of electrokinetics and other remediation techniques better to address diverse types of contaminants and challenging soil conditions [53]. Table 2 presents a comparative evaluation of EKR and Hybrid-EKR based on various governing factors. To overcome the drawbacks of EKR and enhance the removal efficiency, it is coupled with other remediation techniques such as phytoremediation, permeable reactive barrier, bioremediation etc., as represented in (Fig. 7). Hybrid EKR-phytoremediation technique involves the application of an electric field near the growing plant roots, which may increase its remediation capability by mobilising pollutants and nutrients; thus, making it more accessible for plant absorption [72]. With the same technique, 90% of removal efficiency was achieved when maize was used for the biological recovery of soil contaminated with hydrocarbons [73]. Maize was also employed for soil contaminated with atrazine [74]. This combined technique was also employed for the soil contaminated with lead [75]. EKR combined with a permeable reactive barrier was first studied by Ha Ik Chunga and Myung Ho Lee in the year 2007. An atomising slag was used as PRB material for the remediation of artificial clay contaminated with cadmium (Cd) and Trichloroethylene (TCE). Approximately 90% of removal efficiency was achieved for both contaminants [76]. Later on, many studies were conducted for the removal of organic compounds from the soil [77], cadmium from artificially contaminated kaolin by employing Zeolite and Zero Valent Iron (ZVI) as PRB material [78] and Uranium contaminated soil with combined activated carbon and ZVI, as PRB material [79]. Bio-EKR is another hybrid technique in which selective pollutant degrading microbes were used for decontamination. The soil contaminated with tannery effluent mainly chromium was treated using this method. Microbial species such as *Desulfovibrio, Pseudomonas, Bacillus, Clostridium, Halanaerobium* enhanced the remediation process of soil contaminated with heavy metals [17]. Bacterial biosurfactants were used along with EKR for remediating soil contaminated with crude oil hydrocarbons. The maximum removal efficiency of 97% was achieved with the bacterial strain *Bacillus velezensis* AS4 [18].

Cost can vary substantially for a hybrid electrokinetic soil remediation method; variables such as site-specific conditions, the extent and severity of soil contamination, the selection of technology, and local regulations and environmental standards all contribute to this variation [27]. Generally, bio-electrokinetic remediation could involve moderate to high initial expenses depending on the site conditions [57] whereas moderate initial cost may be associated with phyto-electrokinetic remediation, with continuous maintenance costs varying with the duration of the remediation process [81]. Depending on the details of the project, the initial expenses of electrokinetic with permeable reactive barrier remediation could range from moderate to high. In case of electrokinetic with modified electrodes the remediation cost might range from moderate to expensive, depending on the electrode design, scope of the study and complexity of the operation [82].

4. Status of heavy metal soil contamination in India

According to the Central Pollution Control Board (CPCB) report 2021–22, based on the Comprehensive Environmental Pollution Index (CEPI), there are 240 contaminated sites covering 21 states, out of which 127 are confirmed as contaminated sites and the remaining are probable contaminated sites. Among these, 113 sites exist in only four states namely Uttar Pradesh, Odisha, Karnataka and Gujarat [83]. A study conducted by the Indian Council for Agriculture Research (ICAR) and Indian Institute of Soil Science, Bhopal showed that the accumulation of heavy metals in soils occurs mainly due to industrial activities in particular areas and different types of operating industries might lead to varying natures of contamination. The Sukinda Valley in Odisha alone generates about 160 million tons of overburden and releases about 11.73 tons of Cr(VI) every year, making it fourth worst-polluted site in the world [84]. Ranipet and Dindigul districts of Tamil Nadu are surrounded with tannery industry which emits a significant amount of chromium waste into the environment without proper treatment [85]. To evaluate the extent of soil pollution, various studies were conducted around different mining areas across India [86]. In a study at Jharia coalfield, it was found that both Coal Fire-Affected Area (CFA) and

Table 2
A Comparative analysis of EKR and Hybrid-EKR in terms of various aspects [24,27,32,35,51,52].

Aspect	EKR	Hybrid-EKR
Cost	Generally lower initial costs	Potentially higher initial costs due to additional technologies
Environmental Impacts	Minimizes soil disturbance and ecosystem impacts	Impact depends on additional remediation methods integrated
Land Reuse Potential	May have limitations on land reuse	Higher potential for land reuse with integrated techniques
Monitoring	Real-time monitoring capabilities	Monitoring complexity may increase with hybrid approach
Flexibility	Limited flexibility in addressing diverse contaminants	More flexibility in addressing a variety of contaminants
Scale-up Challenges	Relatively easier to scale up	May pose challenges in scaling up due to increased complexity
Public Acceptance	Generally well-accepted due to minimal soil disturbance	Public perception may vary depending on the additional methods
Regulatory Considerations	Compliance with regulations may be straightforward	Compliance may vary depending on the integrated techniques

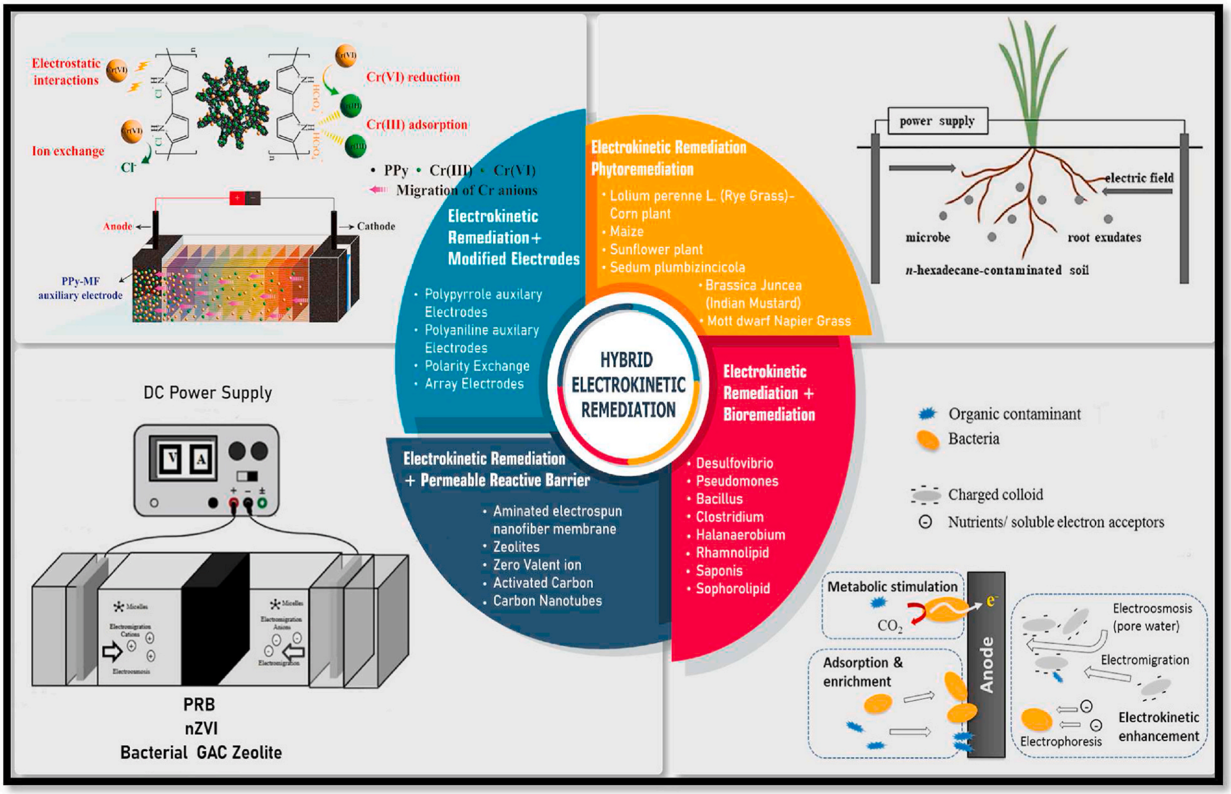

Fig. 7. *Hybrid electrokinetic remediation technique for soil remediation* [66,72,77,80].

Opencast Coal Mine (OCM) area has elevated Cr and Ni concentrations in the nearby soil, while CFA included contamination of soil by V and Zn [38].

Following unsystematic, unscientific dumping methods in the case of municipal waste is a common practice in many Indian cities, which eventually leads to adverse impacts on the environment. Parth et al., 2011 reported the degree of soil contamination due to hazardous waste disposal sites (located in the northwestern part of Hyderabad, India) concerning heavy metal accumulation surrounding the sites. In a study of contaminated soils in three municipal waste dumpsites in Allahabad and Uttar Pradesh, total metal concentrations of Cr, Cu, Fe, Ni, Pb, and Zn (32.46–108.85 mg kg^{-1}) were much more than permissible values [87]. The order of contamination in these dumpsites was Pb > Zn > Fe > Ni > Cu > Cr > Cd (Table 3). summarises the major contaminated sites in different states of India as tabulated; the majority of the contamination is caused by Cr, Cd, Hg, Pb, As, Cu, Ni, and Zn in Madhya Pradesh, Gujarat, Andhra Pradesh, Tamil Nadu, Uttar Pradesh, Jharkhand, Kerala, Karnataka [88]. Certain locations in India are extremely contaminated and require immediate attention.

5. Soil remediation through EKR in India

In 2003 Sanjay et al. carried out EKR study on kaolin contaminated with Cr(VI) to assess the kinetics of electroremediation and identify the rate-controlling mechanism. It was observed that only 31 % of Cr(VI) was remediated after 144 h which was may be due to acid-base neutralization of the soil [21]. Later on, in 2009 Reddy G carried out research on EKR of soil enhanced with reducing agents in laboratory, where. Reducing agents like oxalic acid and ascorbic acid were used to investigate the removal of Cr, Ni, and Co under constant voltage gradient (2.0 V/cm), current changes, pH, redox potential, concentration changes and removal performance of heavy metals. Maximum removal efficiency of 25.38 % was achieved with 0.1 M oxalic acid [77]. In the past decades, many studies have been conducted on EKR with hybrid systems as well in order to enhance the performance of this remediation technique. Researchers have studied the removal efficiency of pollutants with different electrode materials, electrolytes, voltage gradient, combining two or more different techniques etc. [67] implemented EKR for the removal of pollutants such as Cr, Co, Cu, Ni, Zn and Mn. Many other combined (Fe, Cr(VI), Cd(II) and Cu(II))as well as individual pollutants Cr and Cu were also treated with EKR process [95,132,133]. Predominantly, graphite electrodes (cylindrical or plate) were used as they have many advantages over other electrode materials such as lower cost, higher corrosion resistance and easy availability. Other types of electrode such as IrO_2–RuO_2–TiO_2 as anode and Ti as cathode were studied by Annamalai et al. [134]. Various electrolytes for instance distilled water, tap water, EDTA, nitric acid (HNO_3), acetic acid (CH_3COOH), hydrochloric acid (HCl), sulfuric acid (H_2SO_4), ammonium acetate ($NH_4C_2H_3O_2$), citric acid ($C_6H_8O_7$), ammonium citrate ($C_6H_{17}N_3O_7$) etc., were used for different studies [134–136]. In most of the studies the voltage gradient was varied from 0.5 to

Table 3
Sites contaminated with various heavy metals in India

Heavy Metals	Location	Sources	Ref.
Chromium	Sukinda Valley, Odisha	Mining activities	[84]
	Kanpur, Uttar Pradesh	Tannery effluent	[89]
	Gwalior, Madhya Pradesh	Untreated industrial, domestic, and sewage effluents	[90]
	Ranipet, Vellore and Dindigul District, Tamil Nadu	Tannery Industry, Tamil Nadu Chromate and Chemicals Limited (TCCL)	[85]
	Trichy, Tamil Nadu	Tannery effluent	[91]
	South Kaliapani, Odisha	Chromite mining activities	[92]
	West Khasi Hills, Meghalaya	Coal, lime, and uranium mining activities and subsequent roadside deposits	[93]
	Moradabad, Uttar Pradesh	Inappropriate discharge from industries	[5]
Cadmium	Debari, Rajasthan Keshopur, Delhi Madanpur, Delhi IARI, New Delhi Dhapa, Kolkata Sonepat, Haryana RAU, Bihar	Industrial effluents, sewage, polluted river water, and municipal solid waste	[94]
	Okhla, Ghazipur, Bhalswa, Narela-Bawana, Delhi	Municipal solid waste dumping	[95]
	Morigaon, Assam	Paper mill waste discharge	[96]
	Shahjehanpur, Bareilly, Moradabad and Rampur, Uttar Pradesh	Industrial, municipal, and urban runoff	[97]
	Cachar, Assam	Irrigation of soil using wastewater	[98]
	Delhi, India	Ni–Cd battery coatings and plating, stabilizers for plastics, fossil fuel combustion, phosphate fertilizer, and waste incineration	[62]
	Karaidanga, Bantala, West Bengal	Effluents of tannery waste	[37]
	Cochin, Kerala	anthropogenic, industrial, and urbanization activities	[99]
Lead	Patancheru, Andhra Pradesh Surat, Gujarat Manali, Chennai Pali, Rajasthan Thane-Belapur, Mumbai	Waste discharge from industries (Industrial Development Areas)	[100]
	Korba, Chhattisgarh	Coal Mining activities	[86]
	Chandigarh and Ludhiana, Punjab	e-waste recycling process	[101]
	Brahmaputra valley	Usage of agrochemicals	[102]
	Ropar, Punjab	Industrialization and excessive use of various chemical-based pesticides and fertilizers in agricultural fields	[103]
	Kolkata, Bengaluru	Motor vehicle traffic, associated road infrastructure, degraded metal road furniture, industrial processes such as metal production, working and plating manufacture, and working and power generation	[104]
	Barpeta, Assam	Concentrations of chemical constituents influenced by geology and anthropogenic activities	[105]
	BBD Bagh, Ultadanga, Esplanade, Ballygunje Phari, Topsia, Kolkata	Emissions from vehicular traffic, waste incineration, industrial plants, city construction or demolition activities	[87]
	Alluvial Plain	Discharge of untreated industrial effluent	[106]
Mercury	Durgapur, West Bengal	Improper solid waste management	[107]
	Dhanbad, Jharkhand	Mercury mining and its use in gold extraction, coal mining, and its by-products	[108]
	Majnu ka Tila, Kashmiri Gate and Okhla barrage, Sarai Kale Khan and Najafgarh, Delhi	Atmospheric deposition, coal-fired power stations, gold mining, cement production, non-ferrous metal production, and various other industrial sources	[109]
	Southern Sonbhadra, Uttar Pradesh Singrauli District, Madhya Pradesh	Industries like coal mines, thermal power stations, aluminum smelting, cement industries, chlor-alkali industry, and hi-tech carbon industry dump untreated wastes directly into the environment	[110]
	Mithi, Mumbai	Coal combustion, ferrous and non-ferrous metal production, chlor-alkali industry, cement industry, medical industry, and biomass burning	[111, 112]
	Lucknow, Alluvial Plain, North India	Coal combustion in thermal power plants, solid municipal and medical wastes	[113]
	Mahasar, Haryana, Delhi	coal combustion, chlor-alkali industrial units, thermometer factories, steel industries, broken fluorescent lamps, etc.	[114, 115]
Arsenic	Gaighata, West Bengal	Naturally occurring waste discharged from industries	[116, 117]
	North-eastern states of Bihar	Naturally occurring and anthropogenic activities	[118, 119]
	Lakhimpur, Uttar Pradesh	Natural and anthropogenic activities	[120]
	Sarangpura, Daddu Majra, and Burail, Chandigarh	open dumping of garbage, disposal of industrial wastewater, spraying of pesticides and fertilizers in the agricultural fields	[121]
	Barpeta District, Assam	Anthropogenic activities and higher chemical concentration	[105]
Copper	Singhbhum Copper Belt, Jharkhand	Copper mining and industrial activities	[122]

(*continued on next page*)

Table 3 (*continued*)

Heavy Metals	Location	Sources	Ref.
	Malanjkhand Copper Project, Balaghat district, Madhya Pradesh	Acid mine drainage	[97]
	Ramsar, Guwahati	Improper dumping and management of the site	[123]
	Brahmaputra basin, Assam	Anthropogenic activities such as dumping of untreated waste	[124]
	Mettur, Tamil Nadu	Industrialization and extraction of natural resources	[125]
	Coimbatore, Tamil Nadu	Electroplating industries	[126]
Nickel	Ahmedabad, Gujrat	Natural sources such as weathering, erosion of rocks, and volcano eruption, anthropogenic sources such as electroplating, industries effluents, landfills, mining activities, municipal sewage sludge, and paint industry	[127]
	Paradip Port, Odisha	Oil spills, ballast water, domestic waste, ship paint, mining, smelting, household waste, agriculture, aquaculture discharges, and dumping of different hazardous chemicals into the marine ecosystem	[128]
Zinc	Godwa, Udaipur, Rajasthan	Due to activities such as mining, smelting, use of domestic and industrial wastes, burning of fossil fuels, use of leaded gasoline, spraying of arsenic pesticides, and disposal of wastes	[129]
	Okhla, Bhalswa, Noida, Hyderabad and Kadapa	Municipal solid waste dumped for landfilling	[45]
	Deepor Beel, Guwahati	Improper solid waste dumping activities	[96]
	Surat, Gujarat	Industrial activities such as mining, smelter operations, and discharges of coal and bottom fly ash	[130]
	Guwahati, Assam	Unscientific disposal of municipal solid waste	[131]

Table 4
EKR techniques studied in India for decontamination of various Pollutants under different operating parameters

Location	Voltage	Electrodes		Electrolyte	Pollutants	Removal Efficiencies	Ref.
		Material	Size				
Andhra Pradesh, India (L)	2 V/cm	Graphite Cylinder Electrodes	L-15 cm ⌀-1.5 cm	Distilled water, Citric Acid, EDTA	Cr, Co, Cu, Ni, Zn and Mn	Cr-6%, Co-9%, Cu-16 %, Ni-24 %, Zn-11 % and Mn-32 %	[67]
Hyderabad, India (L)	1 V/cm	Graphite plates Electrodes	4 × 6 × 0.5 cm	EDTA, HNO_3, CH_3COOH	Ni, Cu, Zn, Cd and Pb	Cd-78.8 %, Pb-65.3 %, Cu-62.6 %, Zn-60.8 % and Ni-46.4 %	[132]
West Bengal India (L)	0.8 V/cm	Circular porous graphite Electrodes	–	Tap Water	Cr (VI)	80 % @ 120 h	[64]
Telangana, India (L)	1 V/cm	High-density graphite plate Electrodes	4 × 6 × 0.5 cm	EDTA, HNO_3, HCI, H_2SO_4, acetic acid and citric acid	Cd, Pb, Cu, Zn and Ni	Cd-100 %, Pb-52.63 %, Cu-57.62 %, Zn-42.17 %, Ni-47.64 %	[133]
Jharkhand, India (L)	2 V/cm	Plate-type graphite electrodes	3.9 × 3.9 cm^2	Citric acid (1 M)	Cr	77.33 %	[95]
Puducherry, India (P)	2 V/cm	Graphite electrodes	–	Tap Water, 0.1 M Ammonium acetate, Ammonia-acid	Cu	63.95 %	[139]
Uttar Pradesh, India (L)	30 V	Graphite electrodes	–	Deionized water, ammonium citrate	Cd, Cu	Cd- 48.90 %, Cu- 30 %	[136]
Bangalore, India (L)	5, 10, 20, 30, 45, 60 V	Graphite plate electrodes	–	Acetic Acid, EDTA	Fe, Ni, Cd	Fe-1.1 %, Ni-35 %, Cd-16 %	[135]
Karaikudi, India (L)	2 V/cm	IrO_2–RuO_2–TiO_2/Ti and Ti	–	0.1 M $NH_4C_2H_3O_2$	Cl^-, SO_4^{2-}	Cl^--84 %, SO_4^2 -68 %	[134]
Uttar Pradesh, India (L)	35 V	Graphite Electrode	–	Deionized water, Ammonium Citrate	Cd(II) and Cu (II)	Cd(II)-48.8 % and Cu(II)-30 %	[140]
Bhubaneswar, India (L)	25 V	Graphite Electrode	–	Double distilled water	Cr(VI)	31 %	[21]

*(L)- Laboratory scale study, (P)- Pilot scale study.

Table 5
Hybrid EKR techniques studied in India for decontamination of various Pollutants under different operating parameters

Technology	Location	Voltage	Electrodes		Electrolyte	Pollutants	Removal Efficiency	Ref.
			Material	Size				
Bio- EKR (L)	Tamil Nadu, India	2 V/cm	Titanium electrodes	–	2 % NaCl	Diesel hydro-carbons	84 %	[141]
Bio-EKR (L)	Kerala, India	1 V/cm	Graphite electrodes	–	Portable water, 0.2 M EDTA, 0.5 M NaOH	Cr (VI), Fe	Cr(VI)- 71 % Fe- 55 %	[142]
Bio-EKR (L)	Tamil Nadu, India	2 V/cm	IrO_2–RuO_2– TiO_2/Ti and Ti plate electrodes	–	Sterile distilled water	Crude oil	92 %	[143]
Bio-EKR (L)	Tamil Nadu, India	2 V/cm	IrO_2–RuO_2–TiO_2/Ti and Ti plate electrodes	–	Distilled Water, K_2SO_4	Cr, Fe	Cr-78.02 %, Fe-17.24 %	[18]
Phyto-EKR (L)	Tamil Nadu, India	1.5 V/cm	Graphite, iron, aluminium, silicon electrodes	–	Portable Water	Fe, Al, and Si	Fe-.36.47 %, Al-6.87 % and Si-47.07 %	[81]
Phyto-EKR (P)	Andhra Pradesh, India	50 V	Graphite rode electrodes	L-25cm ⌀-1.5 cm	Immersed in Soil	Cr and Cd	Cr- 59.78 % Cd- 63.58 %	[144]
Reducing agent-EKR (L)	Andhra Pradesh, India	2 V/cm	Graphite rode electrodes	L-15 cm ⌀-1.5 cm	Distilled Water, Oxalic Acid, Nitric Acid	Cr, Co, and Ni	Cr-21.55 %, Co-22.07 % and Ni-32.52 %	[145]
Bio-EKR (L)	Tamil Nadu, India	20 V	Titanium electrodes	–	Distilled water	Cr(VI)	90.4 %	[146]

*(L)- Laboratory scale study, (P)- Pilot scale study.

2.5 V/cm [67,133]. The experiments on EKR conducted in India have been summarized in (Table 4) which includes the effectiveness of removing various pollutants as well as the operating conditions in EKR studies. Not only the conventional EKR, but also the Hybrid EKR i.e., combining EKR with other soil remediation techniques such as bioremediation, phytoremediation, permeable reactive barrier etc. was also studied in India. Some of those hybrid EKR studies have been listed in (Table 5).

Government of India has taken several initiatives to improve the quality of agricultural soil as well as cleaning of contaminated sites [84,137]. The contaminated site remediation guideline includes an intricate procedure for the site assessment and remediation including identification, planning, implementation, and post remediation. The EKR is among one of the suggested remediation techniques but is not popular as compared to others such as landfilling, phytoremediation, bioremediation, etc. The requirement of energy and specificity to locality and pollutants are some major limiting factors for this technology in India. However, it can be a favourable option if it is evaluated with the local conditions and renewable energy source is utilized as it would cause little nuisance for its surrounding due to compact nature of equipment used [138].

6. Conclusion

EKR is a rapidly evolving technology, which offers both ex-situ and in-situ soil remediation for various inorganic and organic contaminants. Several field tests have proven the feasibility and efficiency of EKR as compared to other remediation technologies. In India, the first EKR study on soil was conducted using reducing agents. Later, many studies were conducted to remediate soil contaminated with heavy metals as well as toxic and hazardous wastes. Indian researchers reported that EKR combined with other remediation techniques for instance bioremediation, phytoremediation, permeable reactive barrier was successfully employed for the removal of pollutants such as As, Cd, Cr, Hg, Pb, Co, Cu, Ni, Zn, Se, crude oils, diesel etc. from soil. When gauging the efficacy of electrokinetic soil remediation methods, sustainability indicators are crucial instruments. We can ensure that these approaches not only solve environmental concerns but also contribute to a more sustainable and resilient future by thinking about things like energy efficiency, pollutant reduction, cost-effectiveness, and long-term soil health. EKR has the potential to be a truly environmentally benign and socially responsible solution to soil remediation issues, but only if these indications are monitored and optimized. Further research on EKR is required to overcome the limitations such as a higher treatment cost as compared with other techniques, restriction on the radius of influence of the system, time constraint due to time-consuming application, the need of low pH to induce desorption and combination of a variety of remediation techniques, which may be compatible with the EKR process. Since the process significantly depends upon the supply of power to the system, more research is needed on the use of renewable sources of energy for soil remediation. This may help in reducing the cost involved and the carbon footprint, thus making it even more economical and eco-friendly. EKR has the potential to evolve into a highly efficient and effective soil remediation technology in India with significant societal and environmental benefits. However, it should be backed with the right amount of research, infrastructure development, and regulatory guidelines.

Data availability statement

Data will be made available on request.

CRediT authorship contribution statement

J. Akansha: Writing – review & editing, Writing – original draft, Methodology, Formal analysis. **Somil Thakur:** Visualization, Validation. **M Sai Chaithanya:** Visualization, Validation. **Bhaskar Sen Gupta:** Validation, Supervision. **Sovik Das:** Validation, Supervision. **Bhaskar Das:** Visualization, Validation, Supervision, Conceptualization. **N. Rajasekar:** Visualization. **K. Priya:** Visualization.

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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