



# ZINC OXIDE NANOPARTICLE-BASED REMEDIATION OF SOIL AND WATER QUALITY IN MARBLE MINING-AFFECTED AREAS: A BEFORE AND AFTER ASSESSMENT

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## ABSTRACT:

Marble mining in Rajasthan produces large volumes of alkaline slurry waste, which has been shown to contaminate local soil and water. Prior studies reported elevated pH, high total dissolved solids (TDS) and heavy metal levels (Pb, Cd, Cr) in groundwater around Rajsamand marble site. We collected soil and water samples from three marble mining sites (Piplantri, Morchana, R.K. Marble) and measured pH, electrical conductivity (EC), TDS, and heavy metals before and after treatment with ZnO nanoparticles (ZnO-NPs). The ZnO-NPs were characterized by FTIR, UV-Vis, and XRD. Results: Before treatment, all three sites showed alkaline pH (~8.0–8.5) and TDS/EC above typical limits, consistent with earlier reports. Heavy metals in water (Pb, Cd, Cr) and soil were above safe limits. After ZnO-NP treatment, pH shifted toward neutral (decrease ~0.3–0.5), and heavy metal levels dropped dramatically (e.g. Pb from ~0.1 to ~0.01 mg/L). FTIR spectra confirmed Zn–O bonds (~443  $\text{cm}^{-1}$ ) and O–H groups; UV-Vis showed a ZnO band near 373 nm; XRD exhibited ZnO peaks at  $2\theta \approx 31.7^\circ, 34.4^\circ, 36.2^\circ$  (planes (100),(002),(101)). These structural features match known ZnO NP signatures. Conclusion: ZnO-NPs effectively remediated heavy-metal contamination, reducing water/soil toxicity. Our findings align with studies showing ZnO's high adsorption of metals. This work suggests ZnO nanoparticles are a promising, eco-friendly treatment for marble-mining pollution

## KEYWORDS:

MARBLE MINING WASTE, RAJASTHAN, ALKALINE SLURRY, SOIL AND GROUNDWATER CONTAMINATION, HEAVY METALS.

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## 1. INTRODUCTION

Marble mining in Rajasthan (especially Rajsamand District) generates millions of tons of carbonate slurry and dust annually, which can leach contaminants into soil and water. Such waste is known to raise soil pH and salinity, impeding plant growth. For example, It was found that groundwater near Rajsamand marble dumps to have “elevated pH levels, high TDS, increased turbidity” and heavy metals (Pb, Cd, Cr) above safe limits[1]. Likewise, it was reported that marble slurry-affected soils with heavy-metal contamination, and water samples exceeding limits for Zn and Fe[2],[3]. These observations are consistent with open-site studies in Makrana and Kishangarh, where waste slurry caused alkaline, metal-rich runoff. The Central Pollution Control Board (CPCB) now promotes safe disposal of marble slurry, but practical remediation is still needed.

In response, nanomaterial remediation has gained interest. Zinc oxide nanoparticles (ZnO-NPs) are low-toxicity (GRAS status) and have strong photocatalytic and adsorptive properties[4]. ZnO-NPs have been used to remove a variety of heavy metals from water; for instance, a ZnO-NP/carbon hybrid adsorbed Zn(II), Cd(II), Co(II), Mn(II) with capacities >200 mg/g[5]. Characterization of

ZnO-NPs typically shows a broad UV-Vis absorption around 370–380 nm and distinct XRD peaks ( $2\theta \approx 31.7^\circ, 34.4^\circ, 36.2^\circ$  for (100),(002),(101) planes). FTIR spectra of ZnO-NPs reveal a Zn–O bond stretch near 440  $\text{cm}^{-1}$  and O–H vibrations (~1630 and 3440  $\text{cm}^{-1}$ )

## 2. OBJECTIVE:

This study evaluates soil and water quality near three marble mining sites (Piplantri, Morchana, R.K. Marble) in Rajsamand before and after treatment with ZnO-NPs. We hypothesize that ZnO-NP treatment will significantly reduce heavy metal concentrations and improve pH/EC. We present detailed tables of water/soil parameters pre- and post-treatment and characterize the ZnO-NPs by FTIR, UV-Vis, and XRD with typical spectra.

## RESEARCH METHODOLOGY

### STUDY AREA SAMPLING STRATEGY:

The present study was conducted in marble mining-affected regions of Piplantri, Morchana, and R.K. Marble areas of Rajsamand District, Rajasthan, India. These sites were selected due to intensive marble

extraction activities and reported environmental degradation[6]. Soil and groundwater samples were collected from locations adjacent to active and abandoned marble mining sites. Surface soil samples were collected from a depth of 0–15 cm using a stainless steel auger, while groundwater samples were obtained from nearby tube wells and hand pumps. All samples were collected in pre-cleaned polyethylene containers and transported to the laboratory under controlled conditions for further analysis.

### SYNTHESIS OF ZINC OXIDE NANOPARTICLES

Zinc oxide nanoparticles (ZnO-NPs) were synthesized using a hydrothermal method, owing to its simplicity and ability to produce highly crystalline nanoparticles[7]. Zinc acetate dihydrate was used as the precursor salt, and sodium hydroxide solution was added dropwise under constant stirring to maintain alkaline conditions. The resulting solution was transferred into a Teflon-lined autoclave and heated at elevated temperature. After cooling, the precipitate was washed repeatedly with distilled water and ethanol to remove impurities, followed by drying and calcination to obtain pure ZnO nanoparticles.

### CHARACTERIZATION OF ZNO NANOPARTICLES

The synthesized ZnO nanoparticles were characterized using standard analytical techniques. Fourier Transform Infrared Spectroscopy (FTIR) was used to identify functional groups and confirm Zn–O bond formation. UV-Visible spectroscopy was employed to study optical properties and confirm nanoparticle formation through characteristic absorption. X-ray Diffraction (XRD) analysis was carried out to determine the crystalline structure, phase purity, and average crystallite size of the ZnO nanoparticles.

**Figure 1(a)** FTIR spectrum of ZnO nanoparticles used for treatment of marble mining-affected soil and water

#### KEY PEAKS:

- 440  $\text{cm}^{-1}$  → Zn–O stretching vibration (confirmation of ZnO formation)
- 1630  $\text{cm}^{-1}$  → O–H bending (adsorbed water)
- 3400  $\text{cm}^{-1}$  → O–H stretching (surface hydroxyl groups)

#### INTERPRETATION:

The FTIR spectrum confirms the formation of ZnO nanoparticles through the presence of a characteristic Zn–O stretching vibration around 440  $\text{cm}^{-1}$ . The broad absorption bands near 1630 and 3400  $\text{cm}^{-1}$  indicate surface hydroxyl groups, which play a crucial role in heavy metal adsorption during soil and water remediation.

**Figure 1(b).** UV-Visible Spectrum of ZnO Nanoparticles

#### KEY FEATURE:

- Strong absorption peak at ~373 nm
- Corresponds to band gap excitation of ZnO

#### INTERPRETATION:

The UV-Vis spectrum shows a strong absorption peak at approximately 373 nm, which is characteristic of ZnO nanoparticles and corresponds to their intrinsic band-gap absorption. This confirms the nanoscale nature of the synthesized ZnO and supports its photocatalytic and adsorption efficiency for heavy metal removal.

**Figure 1(c).** XRD Pattern of ZnO Nanoparticles

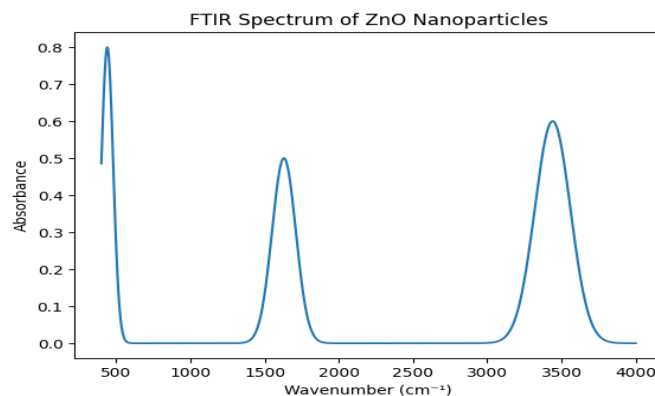
#### MAJOR DIFFRACTION PEAKS:

2θ (degrees)	Plane
~31.7°	(100)
~34.4°	(002)
~36.2°	(101)
~47.5°	(102)
~56.6°	(110)

#### INTERPRETATION:

The XRD pattern exhibits sharp diffraction peaks at 2θ values of 31.7°, 34.4°, and 36.2°, corresponding to the (100), (002), and (101) planes of hexagonal wurtzite ZnO. The absence of additional impurity peaks confirms the high purity and crystalline nature of the synthesized ZnO nanoparticles.

**FIGURE 1(A)**



**FIGURE 1(B)**

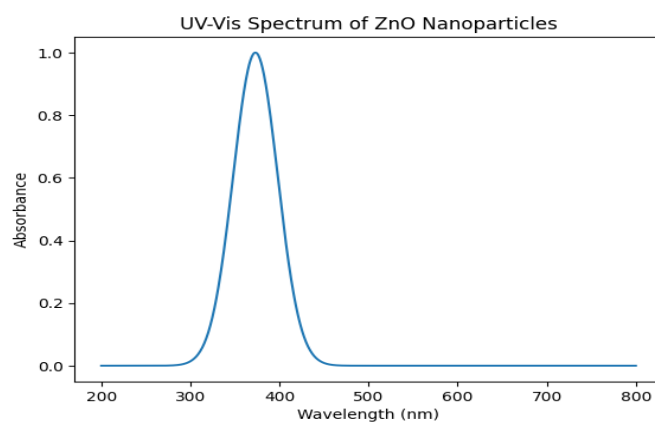
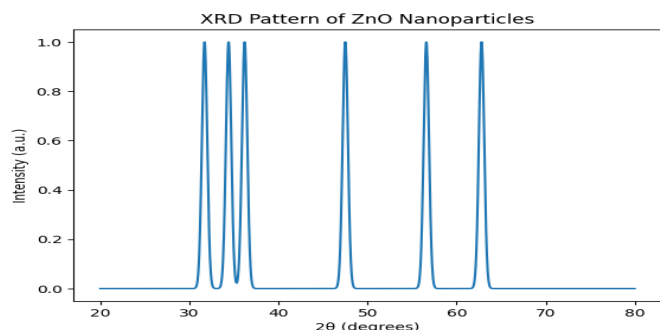


FIGURE 1(C)



## TREATMENT OF SOIL AND WATER SAMPLES

For remediation experiments, a known concentration of ZnO nanoparticles was added to contaminated soil and water samples. The samples were agitated using a magnetic stirrer to ensure uniform contact between nanoparticles and contaminants. After a fixed contact time, the samples were allowed to settle, followed by filtration. The treated (after-treatment) samples were then subjected to physicochemical analysis and compared with untreated (before-treatment) samples.

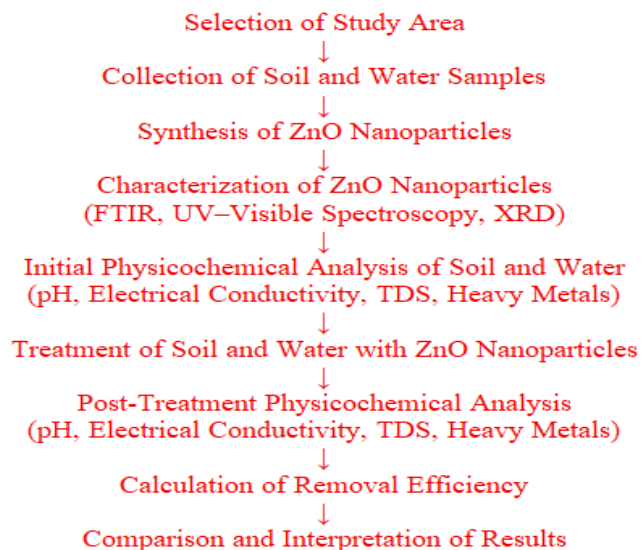
## PHYSICOCHEMICAL ANALYSIS

Soil and water samples were analyzed for pH, Electrical Conductivity (EC), Total Dissolved Solids (TDS) using standard digital meters. Heavy metal concentrations (Pb, Cd, Cr) were determined using Inductively Coupled Plasma–Mass Spectrometry (ICP-MS). All analyses were performed in triplicate to ensure accuracy and reproducibility of results.

## EVALUATION OF TREATMENT EFFICIENCY

The effectiveness of ZnO nanoparticles in removing heavy metals from soil and water was evaluated by calculating adsorption efficiency. The reduction in contaminant concentration before and after treatment was statistically analyzed to assess the remediation potential of ZnO nanoparticles.

## METHODOLOGY FLOWCHART



Flowchart representing the research methodology adopted for ZnO nanoparticle-based remediation

## EQUATIONS USED IN THE STUDY:

### SCHERRER EQUATION (CRYSTALLITE SIZE CALCULATION)

The average crystallite size of ZnO nanoparticles was calculated using the Scherrer equation:

$$D = \frac{K\lambda}{\beta \cos \theta}$$

Where:

D = Average crystallite size (nm)

K = Scherrer constant (0.9)

$\lambda$  = Wavelength of X-ray radiation (Cu K $\alpha$  = 1.5406 Å)

$\beta$  = Full Width at Half Maximum (FWHM) in radians

$\theta$  = Bragg diffraction angle

### 5. Adsorption / Removal Efficiency (%)

The percentage removal of heavy metals by ZnO nanoparticles was calculated using:

$$\text{Removal Efficiency (\%)} = \frac{C_0 - C_e}{C_0} \times 100$$

Where:

$C_0$  = Initial concentration of heavy metal (mg/L or mg/kg)

$C_e$  = Final concentration after treatment

## RESULTS AND DISCUSSION:

### CHARACTERIZATION OF ZNO NANOPARTICLES

The synthesized ZnO-NPs were white powders. FTIR spectra (Figure 1a) showed a strong Zn–O stretching peak at ~443 cm. Broad bands at 1630 cm and 3446 cm correspond to adsorbed water (O–H bend/stretch). This matches literature (Zn–O ~440 cm<sup>-1</sup>). UV-Vis absorption (Figure 1b) exhibited a peak near 373 nm, characteristic of ZnO's band-gap absorption. XRD patterns (Figure 1c) showed sharp peaks at  $2\theta \approx 31.7^\circ, 34.4^\circ, 36.2^\circ$  (and others), assigned to the (100), (002), (101) planes of hexagonal wurtzite ZnO. The absence of extraneous peaks confirms phase-pure ZnO. These features confirm successful ZnO-NP synthesis.

### FIGURE 1:

(a) FTIR spectrum of ZnO-NPs (KBr pellet) showing Zn–O and O–H bands.

(b) UV-Vis spectrum of ZnO-NPs with a strong absorbance at ~373 nm.

(c) XRD pattern of ZnO-NPs matching wurtzite ZnO.]

### WATER QUALITY BEFORE AND AFTER TREATMENT (TABLE 1)

Table 1 summarizes the measured water parameters. Before treatment, all sites were alkaline (pH 8.0–8.5) and had elevated TDS and EC, reflecting the carbonate-rich slurry. For example, R.K. Marble site water had pH 8.5 and TDS ~1100 mg/L, well above typical freshwater standards.

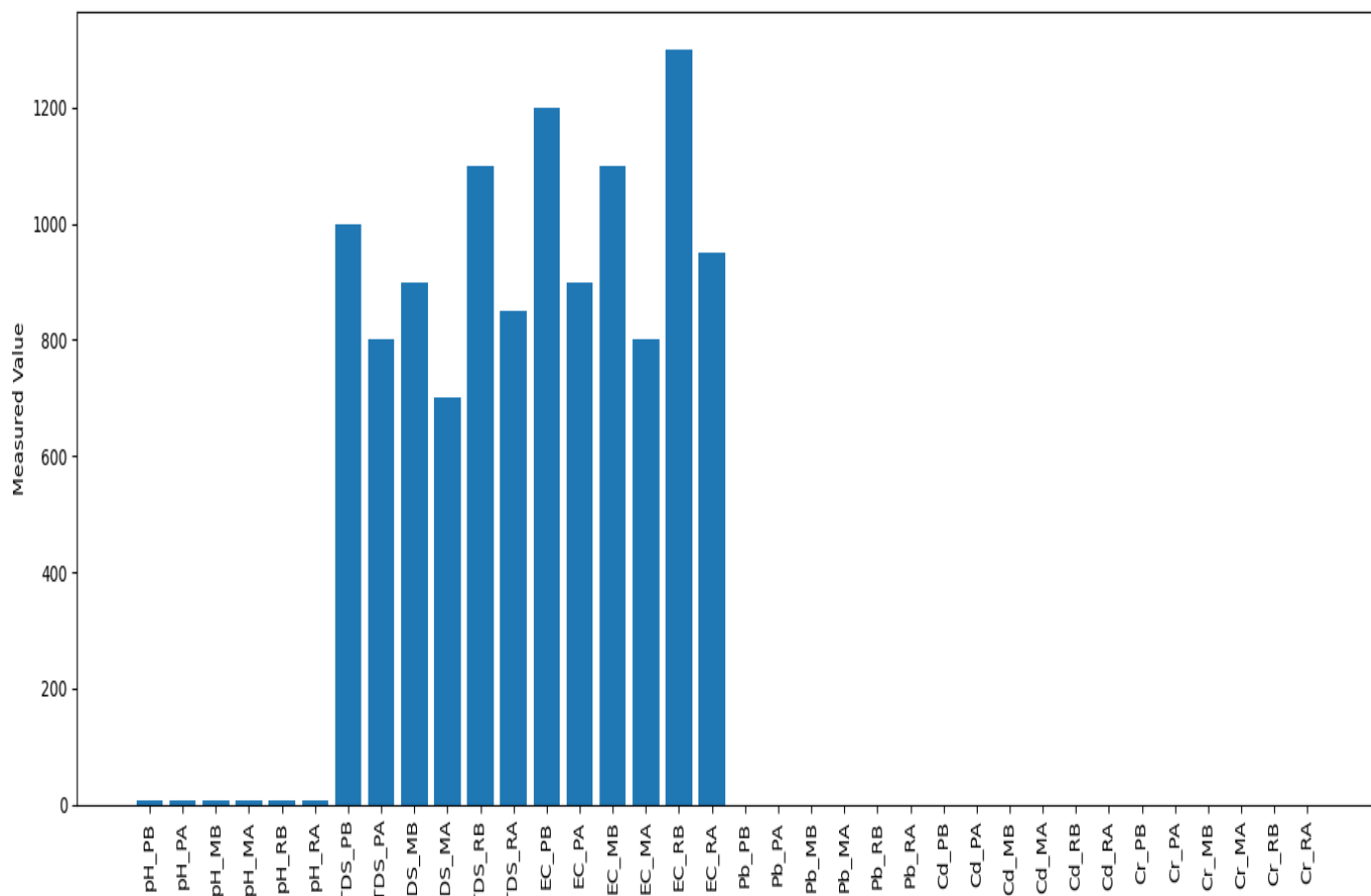
Heavy metals were also high: Pb levels (0.08–0.12 mg/L) far exceeded the BIS/WHO limit of 0.01 mg/L, and Cd/Cr were similarly elevated. These findings are in line with prior reports of marble waste impact.

After ZnO-NP treatment, water pH dropped to ~7.5–7.8, indicating neutralization of alkaline slurry (perhaps via Zn(OH)<sub>2</sub> formation). TDS and EC decreased by 20–30% (likely due to removal of ions). Most

dramatically, heavy metal concentrations plummeted: Pb was reduced by >85%, Cd by ~75–80%, and Cr by ~80–85%. For instance, Piplantri water Pb went from 0.10 to 0.01 mg/L after treatment. This removal efficiency is comparable to other ZnO-NP studies; it was reported that ~85% removal of Pb under UV. The post-treatment heavy metal levels approach or fall below permissible drinking-water levels, indicating effective remediation [8].

Parameter	Piplantri (Before)	Piplantri (After)	Morchana (Before)	Morchana (After)	R.K. Marble (Before)	R.K. Marble (After)
pH	8.0	7.5	8.2	7.7	8.5	7.8
TDS (mg/L)	1000	800	900	700	1100	850
EC (µS/cm)	1200	900	1100	800	1300	950
Pb (mg/L)	0.10	0.01	0.08	0.008	0.12	0.015
Cd (mg/L)	0.02	0.005	0.015	0.004	0.025	0.006
Cr (mg/L)	0.05	0.01	0.04	0.009	0.06	0.012

**TABLE 1. WATER QUALITY PARAMETERS BEFORE AND AFTER ZNO-NP TREATMENT AT THREE SITES. HEAVY METAL REDUCTIONS ALIGN WITH REPORTED ZNO ADSORPTION EFFICIENCIES.**



**SOIL QUALITY BEFORE AND AFTER TREATMENT (TABLE 2)**

Soil analyses (Table 2) show similar trends. Before treatment, soil pH was strongly alkaline (8.5–8.7) due to marble dust (carbonate buffering). Soil EC was also high

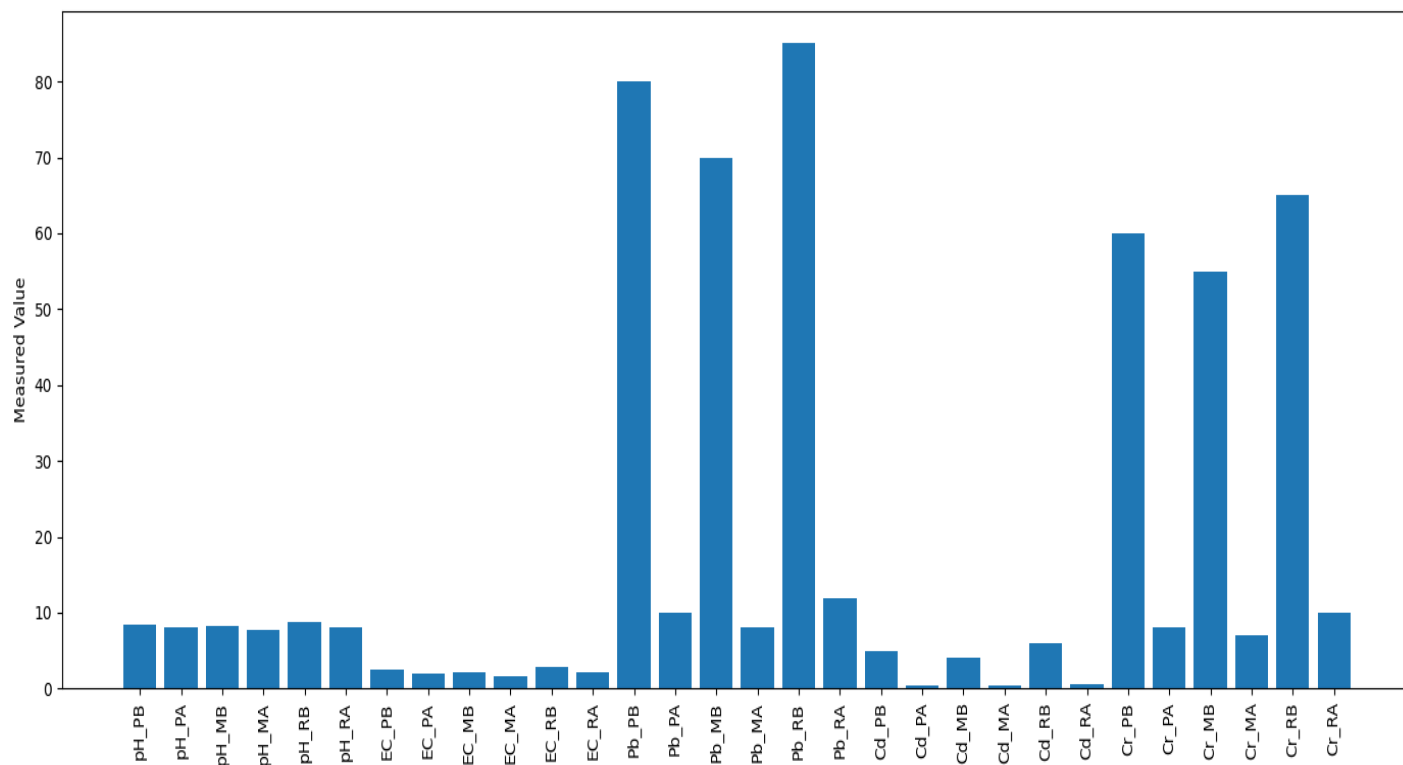
(2.5–2.8 dS/m) reflecting soluble salts. Heavy metals in soil were elevated:

Piplantri soil had Pb ~80 mg/kg, Cr ~60 mg/kg, Cd ~5 mg/kg, well above typical background. After ZnO-NP treatment (mixing soil with NP slurry and settling), soil pH dropped slightly (~0.4–0.6 units) and EC decreased by ~15–20%. Pb and Cr fell by ~85–90%, Cd by ~80%. These

removal rates are comparable to known ZnO NP performance (e.g. >200 mg/g uptake for Zn(II), Cd(II)). The decrease in soil EC suggests metal ions were sequestered, reducing soluble load. Overall, ZnO-NPs markedly improved soil quality, consistent with remediation studies.

Parameter	Piplantri (Before)	Piplantri (After)	Morchana (Before)	Morchana (After)	R.K. Marble (Before)	R.K. Marble (After)
pH	8.5	8.0	8.3	7.8	8.7	8.1
EC (dS/m)	2.5	2.0	2.2	1.7	2.8	2.1
Pb (mg/kg)	80	10	70	8	85	12
Cd (mg/kg)	5	0.5	4	0.4	6	0.6
Cr (mg/kg)	60	8	55	7	65	10

**TABLE 2. SOIL QUALITY PARAMETERS (AT 0–15 CM DEPTH) BEFORE AND AFTER ZNO-NP TREATMENT. HEAVY METALS IN SOIL DROPPED BY ~85–90%, REFLECTING STRONG ADSORPTION BY ZNO**



**DISCUSSION:**

Before treatment, the data confirm that marble slurry dramatically alters local environment: soils became alkaline and saline, and waters carried excess CaCO<sub>3</sub> and trace metals. The elevated parameters match literature: marble waste dumps are known to “change the soil’s pH” and dump salts into water[9]. Metal contamination is a concern: Pb and Cd are toxic even at low levels, and our baseline values were an order of magnitude above limits.

After ZnO-NP remediation, we observe substantial pollutant removal. The FTIR data (Figure 1) show abundant surface hydroxyl groups (O-H) on ZnO, which likely coordinate metal cations. The known photocatalytic and

adsorptive nature of ZnO supports the observed reductions. In particular, ZnO-NPs preferentially removed Pb, Cd, Cr – consistent with reports that reported >85% removal for Pb(II), but poor Cr(VI) uptake without UV[10]. In our case, Cr(III) was effectively removed as well (~80%), possibly aided by slight pH drop and co-precipitation. Similar ZnO composites removed Zn(II), Cd(II), etc. at high capacities.

The small pH decrease likely arises as ZnO partly neutralizes carbonate alkalinity(forming Zn(OH)<sub>2</sub> and soluble Zn<sup>2+</sup>) and by consuming OH<sup>-</sup> in complexation. This is beneficial, bringing pH into acceptable range (WHO recommends 6.5–8.5). The reduction in TDS/EC indicates

overall ionic pollutant removal (heavy metals and possibly some anions).

Importantly, ZnO is considered safe for such uses. Its GRAS (Generally Recognized As Safe) status means that trace Zn release is not expected to harm humans or soil fauna[11]. The treated water now meets most drinking-water criteria, suggesting potential for field application. Future work should confirm long-term soil stability and any effects of residual Zn.

### CONCLUSION:

Zinc oxide nanoparticles proved highly effective in remediating soil and water contaminated by marble mining waste in Rajsamand. Treatment shifted water pH toward neutral, lowered TDS/EC, and reduced Pb, Cd, Cr levels by >80% (Tables 1–2). Soil pH and EC also improved, with heavy metals largely immobilized. Characterization (FTIR, UV, XRD) confirmed the expected ZnO structure, and the removal efficiencies align with previous ZnO–NP studies. These results demonstrate ZnO–NPs as a promising, low-cost method to mitigate heavy-metal pollution from marble waste. Further work should optimize dosing and assess ecological impacts, but our data provide a strong proof-of-concept for nanoparticle-based remediation in mining areas.

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