

Remediation of Heavy Metals From Presco Campus Dumpsite Using Nano-Zero Valent Iron Supported *Justicia Carnea* Leaves Extract

Otu Mercy Oluchi¹, Nworie Felix Sunday^{1*}, Otu Christian Glory²

¹Department of Industrial Chemistry, Ebonyi State University, Abakaliki, Nigeria

²Science Laboratory Technology Department, Akanu Ibiam Federal Polytechnic, Unwana, Nigeria

*Corresponding author, e-mail: nworie.sunday@ebsu.edu.ng

Abstract— This study investigated the green synthesis of nano zero-valent iron (nZVI) supported *Justicia carnea* leaves extract and its application in remediating heavy metal-contaminated dumpsite soil at PRESCO Campus, Ebonyi State University. The UV–V is spectroscopy revealed a strong absorption peak at 276 nm, confirming Fe⁰ formation while FTIR analysis identified phytochemical functional groups responsible for reduction and stabilization. The untreated soils contained elevated levels of heavy metals, including Cr, Mn, Fe, Co, Ni, Cu, Zn, and Pb. The synthesized nZVI showed remediation potential, with metal removal efficiencies varying across species and experimental conditions. Fe exhibited the highest uptake, reaching up to 92%, while Mn, Co, Cu, Zn, and Pb showed moderate to high removal. Adsorption was influenced by pH, temperature, contact time, and adsorbent concentration, with optimum removal observed at pH 7 and 39.85 °C. Isotherm analysis was described by both the Langmuir and the Freundlich models, indicating heterogeneous surface interactions. Kinetic evaluation revealed metal-specific behavior: Mn (and partially Pb) followed pseudo-second-order kinetics, suggesting chemisorption, whereas Cr, Fe, Co, Cu, and Zn followed pseudo-first-order trends, reflecting a combination of physisorption and chemisorption mechanisms. Overall, the findings highlight *Justicia carnea*-mediated nZVI as a sustainable material for remediation of heavy metals in contaminated soils.

Keywords: Nano zero-valent iron, *Justicia carnea* extract, Green synthesis, Heavy metal adsorption, Soil remediation, Dumpsite contamination, Adsorption kinetics, Adsorption isotherms, Environmental nanotechnology, Sustainable remediation.

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1. Introduction

Heavy metal contamination is a global phenomenon that disrupts the ecosystem and poses serious risks to human health. Major contributing factors include rapid urbanization, land-use transition, and industrial development, particularly in highly populated and emerging countries [1], [2]. Heavy metals are both anthropogenic and natural in origin, and some, such as chromium (Cr), vanadium, and nickel (Ni), are essential to human health in minor quantities. Indeed, these metals play an important role in cellular activity. However, some heavy metals have harmful effects on the environment as well as on living organisms [3]. Human exposure to heavy metals occurs primarily through inhalation, ingestion, and dermal contact, and toxicity is largely dependent on concentration and duration of exposure [4]. Cobalt (Co), copper (Cu), nickel, iron (Fe), manganese (Mn), zinc (Zn), molybdenum (Mo), and selenium (Se) are essential micronutrients but may cause severe health complications when consumed beyond safe limits [5], [6], [7], [8], [9], [10]. Other metals such as arsenic (As), cadmium (Cd), chromium, and lead (Pb) are not essential for human health and can cause serious health complications even at low concentrations [11], [12], [13], [14], [15], [16], [17].

In Abakaliki, southeastern Nigeria, municipal waste management practices have contributed significantly to soil contamination. A 2024 spatial analysis reported that approximately 77.5% of 373 waste collection points in the city are unofficial and concentrated within residential areas, resulting in heterogeneous waste streams comprising domestic refuse, electronic waste, and healthcare-related materials [18]. Such unmanaged dumpsites serve as continuous sources of heavy metals, which gradually migrate into surrounding soils and groundwater systems [19]. The persistence and bioaccumulation potential of these metals raise serious environmental and public health concerns, highlighting the need for effective remediation approaches suitable for complex soil matrices [20], [21].

Conventional soil remediation techniques, including excavation, vitrification, and chemical stabilization, are often constrained by high operational costs, limited effectiveness in highly contaminated soils, and the generation of secondary waste [22], [23]. Consequently, adsorption-based remediation has gained attention due to its simplicity, cost-effectiveness, and adaptability to field-scale applications [24], [25]. Among various adsorbents, iron-based nanomaterials particularly nano zero-valent iron (nZVI) have demonstrated strong potential owing to their high surface area, redox activity, and ability to immobilize or transform a wide range of contaminants [26], [27], [28]. Despite these advantages, the practical application of nZVI is often limited by particle agglomeration, reduced mobility, and instability under environmental conditions [29], [30].

To address these limitations, green synthesis approaches using plant extracts have been developed to enhance nZVI stability while minimizing environmental toxicity. *Justicia carnea* leaves are rich in flavonoids and phenolic compounds that function as natural reducing and capping agents, facilitating the eco-friendly synthesis of stabilized nZVI particles [31]. While green-synthesized nZVI has been reported for contaminant removal in aqueous systems, its application to heterogeneous municipal dumpsite soils remains limited, particularly in developing regions. Moreover, comprehensive evaluations of adsorption behavior under varying pH, temperature, contact time, and adsorbent dosage using *Justicia carnea* supported nZVI are still scarce in the literature.

Therefore, this study focuses to synthesize nano zero-valent iron using *Justicia carnea* leaves extract and evaluate its effectiveness for the immobilization and removal of heavy metals from dumpsite soil in Abakaliki, Nigeria. The study aims to provide insight into the remediation performance of green-synthesized nZVI under different operational conditions, contributing to sustainable and locally adaptable soil remediation strategies.

2. Method

2.1 Preparation of Buffer Solutions

Buffer solutions were prepared to maintain stable pH conditions during the soil remediation experiments. All solutions were prepared using analytical-grade reagents and distilled water, and pH values were verified using a calibrated digital pH meter. Acidic buffer solution (pH 3–6) was prepared by mixing 0.1 M acetic acid and 0.1 M sodium acetate in appropriate ratios to obtain pH values 3, 4, 5, or 6.

Neutral buffer solution (pH 7) was prepared by mixing 0.1 M sodium dihydrogen phosphate (NaH_2PO_4) and 0.1 M disodium hydrogen phosphate (Na_2HPO_4) and adjusting the pH to 7. Alkaline buffer solution (pH 8–10) was prepared using a carbonate-bicarbonate system by combining 0.1 M sodium carbonate (Na_2CO_3) and 0.1 M sodium bicarbonate (NaHCO_3) in suitable proportions to obtain pH 8, 9, and 10.

2.2 Soil Sample Collection

Soil samples were collected from the PRESCO Campus dumpsite, Ebonyi State University. The surface layer was cleared of debris, and soil was sampled at 0–15 cm depth using a soil auger. A total

of 300 g of soil was stored in clean, dry plastic containers, sealed, labeled with location and date, and kept in a cool, dry place.

2.3 Justicia carnea Collection

Fresh *Justicia carnea* leaves were collected from Amaike Aba village, Abakaliki LGA, identified by a botanist, washed, shade-dried, and ground into fine powder using an agate mortar.

2.4 Preparation of Justicia carnea Leaf Extract

Ten grams of the powdered leaves were boiled in 100 mL distilled water for 10 minutes, cooled, and filtered. The filtrate served as the reducing and stabilizing agent for nZVI synthesis.

2.5 Synthesis of Nano Zero-Valent Iron (nZVI)

Nano zero-valent iron was synthesized using a green reduction method. A 0.1 M $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution was prepared by dissolving 2.78 g of the salt in distilled water. The solution was transferred into amber bottles to minimize oxidation, and stirred at 500 rpm at room temperature (25°C). Fifty milliliters of *Justicia carnea* extract was added dropwise under continuous stirring for one hour. The formation of a black precipitate indicated the successful reduction of Fe^{2+} ions to zero-valent iron nanoparticles. The precipitate was separated by centrifugation, washed repeatedly with distilled water followed by ethanol to remove residual impurities, and oven-dried at 60 °C for 3 hours. The dried nZVI was stored in airtight containers for subsequent remediation experiments.

2.6 Soil Digestion

For elemental analysis, soil samples were subjected to acid digestion using freshly prepared aqua regia ($\text{HCl}:\text{HNO}_3$, 3:1 v/v). Approximately 2.0 g of air-dried and sieved soil was weighed into a digestion vessel, and 16 mL of the acid mixture was added. The mixture was allowed to react at room temperature until effervescence subsided, indicating the dissolution of metal-bearing phases.

The digested samples were filtered using Whatman No. 42 filter paper and diluted to a final volume of 50 mL with distilled water. The resulting solutions were analyzed for heavy metal content using X-ray fluorescence (XRF).

2.7 Analytical Technique (XRF Analysis)

The heavy metal content of soil samples before and after treatment was determined using X-ray fluorescence (XRF) spectroscopy. XRF was chosen because it allows rapid, multi-element, non-destructive analysis of total metal concentrations in heterogeneous soil samples. While XRF cannot distinguish between adsorbed, reduced, or precipitated forms of metals and has limited sensitivity for trace concentrations, it is appropriate for evaluating overall removal efficiency in batch remediation studies.

2.8 Remediation Study

2.8.1 Contact Time

Soil (10 g) and nZVI (0.05 g) were mixed with 20 mL distilled water and stirred for 6, 20, and 24 hours. Samples were centrifuged and analyzed by XRF.

$$\text{Removal Efficiency (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

2.8.2 pH Variation

The effect of pH was assessed at pH 3, 7, and 9 using the buffers prepared in Section 2.1. Soil (10 g) was treated with 0.05 g nZVI and 20 mL buffer, shaken for 1 hour, separated, and analyzed with XRF. Removal Efficiency determined as seen in equation (1)

2.8.3 Concentration Variation

Different nZVI masses (0.05 g, 0.07 g, 0.09 g) were converted to molarities (0.0448 M, 0.0627 M, 0.0806 M) using Fe⁰ molar mass (55.845 g/mol) and 20 mL solution volume:

$$M = \frac{\text{mass (g)}}{\text{molar mass} \times v} \quad (2)$$

Each concentration was tested at constant conditions (1 hour, pH 7, 39.85°C). Samples were filtered and analyzed by XRF. Removal Efficiency determined as seen in equation (1)

2.8.4 Temperature Variation

The soil–nZVI mixture (10 g and 0.05 g) was treated at 34°C, 39.85°C, and 44.85°C using a beaker-in-beaker water bath. Time (60 min), pH (7), and nZVI mass (0.05 g) were kept constant. Samples were filtered and analyzed. Removal Efficiency determined as seen in equation (1)

2.9 Adsorption Isotherm Studies

Equilibrium adsorption of heavy metals onto *Justicia carnea*-supported nZVI was evaluated using Langmuir and Freundlich models. The Langmuir model assessed maximum adsorption capacity and monolayer interactions, while the Freundlich model described heterogeneous surface adsorption. Fitting the data to these models provided insight into removal capacity and adsorption mechanisms under varying pH, temperature, contact time, and nZVI dosage

2.10 Kinetic Studies

Heavy metal removal by nZVI was analyzed using pseudo-first-order (PFO) and pseudo-second-order (PSO) models. The PFO model indicates physisorption-controlled rates, while PSO considers chemisorption and electron transfer. Equilibrium was determined by monitoring removal over time, and model fit was evaluated using R² and RMSE. This approach acknowledges that removal involves combined adsorption, reduction, and precipitation mechanisms.

3. Result and Discussion

3.1 Characterization of *Justicia carnea* extract

3.1.1 UV-Visible Analysis

The UV–V is spectrum of the synthesized nano zero-valent iron (nZVI) supported *Justicia carnea* extract as seen in Figure 1 exhibited a distinct absorption peak at 276 nm with a maximum absorbance of 1.671 a.u. This peak corresponds to π – π^* transitions of aromatic and conjugated biomolecules such as phenols, flavonoids, and tannins, which act as reducing and stabilizing agents during nanoparticle formation [32], [33], [34]. Similar absorption patterns have been reported in previous studies, with bands observed at 260–320 nm for plant-mediated nZVI [35] and maxima in the 270–300 nm range confirming Fe⁰ formation [36], [37]. Comparable result has also been reported for green-synthesized Nzvi [38]. Therefore, the observed peak at 276 nm peak in this study confirms the successful synthesis of Fe⁰ nanoparticle using *Justicia carnea* leaf extract.

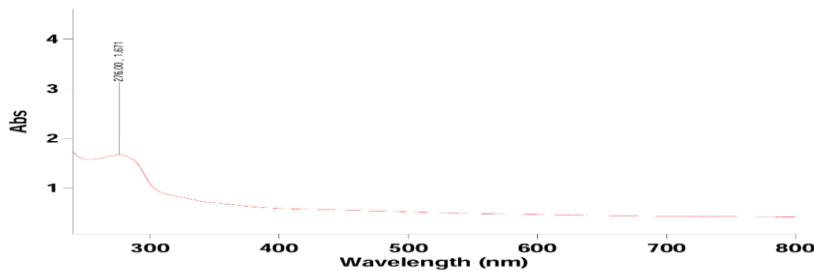


Figure 1. UV–Visible Spectroscopic Analysis of Synthesized nZVI Supported *Justicia carnea* Extract

3.1.2 FTIR Analysis

The FTIR spectrum of the synthesized nZVI supported by *Justicia carnea* extract (Figure 2) revealed several distinct bands corresponding to functional groups involved in nanoparticle formation. A broad peak at 3283–3296 cm^{-1} is attributed to O–H stretching vibrations from phenolics, alcohols, or moisture, confirming the presence of phytochemicals that act as reducing and stabilizing agents [39]. Similar broad O–H absorption has been reported previously, highlighting the role of hydroxyl groups in nanoparticle stabilization [36]. A sharp peak at 2148–2186 cm^{-1} , corresponding to $\text{C}\equiv\text{C}$ or $\text{C}\equiv\text{N}$ stretching, indicates structural changes or the formation of new functional groups during $\text{Fe}^{2+}/\text{Fe}^{3+}$ reduction. The strong absorption at 1615.8 cm^{-1} corresponds to $\text{C}=\text{O}$ stretching, consistent with earlier reports at 1630 cm^{-1} [36], suggesting the involvement of carbonyl and aromatic groups in iron binding and reduction. Notably, peaks at 754 cm^{-1} and 691 cm^{-1} correspond to Fe–O stretching vibrations, confirming successful formation of iron nanoparticles. These observations are consistent with previous green synthesis studies, validating the formation of iron–oxygen bonds [40], [41], [42].

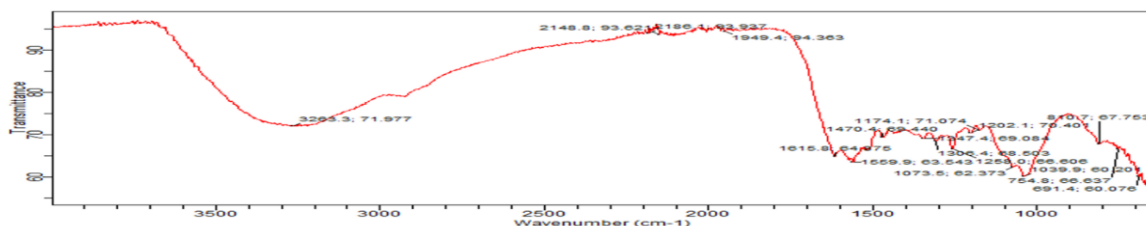


Figure 2. FTIR Vibrational Bands of Synthesized nZVI Supported *Justicia carnea* Extract

3.2 Heavy metal composition before treatment

Table 1 shows the concentrations of heavy metals in soil samples collected from the PRESCO dumpsite before treatment. All measured metals exceeded the WHO permissible limits for soils [43], [44], indicating significant contamination. Iron (Fe) exhibited an exceptionally high concentration of 71,650 mg/kg, likely originating from discarded batteries, cables, and other electronic waste. Elevated copper (Cu) levels (8,590 mg/kg) suggest contributions from metal scraps and corrosion-prone materials. Other metals such as chromium (Cr), manganese (Mn), cobalt (Co), nickel (Ni), zinc (Zn), and lead (Pb) also exceeded recommended limits, reflecting mixed anthropogenic inputs typical of municipal dumpsites. Similar contamination patterns have been reported in dumpsite soils across Nigeria and other developing regions [45], [46], emphasizing the need for effective remediation strategies.

Table 1. Heavy Metal composition of PRESCO Dumpsite Soil (mg/kg)

Metals	PRESCO (mg/kg)	WHO Limit(mg/kg)
Cr	880	100
Mn	1,490	500
Fe	71,650	-
Co	110	20-50
Ni	400	35
Cu	8,590	36
Zn	1,110	50
Pb	2,870	85

3.3 Effect of Contact Time on Metal Adsorption

PRESCO dumpsite soil: Figure 3 showed that Fe adsorption was 90.91% at 6 h, slightly increasing to 92.24% at 20 h before decreasing to 86.05% at 24 h. Manganese adsorption rose from 18.79% to 32.21% at 20 h and 67.78% at 24 h. Copper showed moderate adsorption (25.37% at 6 h to 31.78% at 20 h) before declining, while lead exhibited high uptake (65.5% at 6 h) but fell sharply to 20.2% by 24 h. Chromium showed negligible adsorption, and nickel was measurable only at 20 h (45%). These trends align with [47] who reported rapid early-stage uptake of Ni(II), Pb(II), and Cu(II) onto orange peel due to abundant active sites, slowing as surfaces approached saturation. The decline in Fe and Pb at 24 h here likely reflect equilibrium saturation or partial desorption, consistent with kinetic limitations.

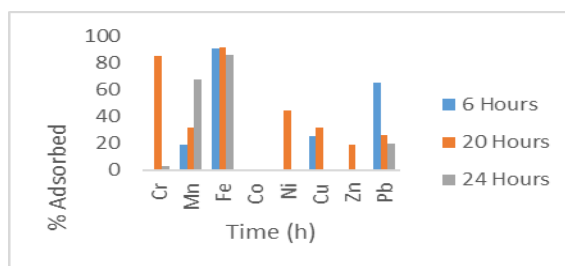


Figure 3. Dumpsite soil-nZVI contact time variation.

3.4 Effect of pH on Heavy Metal Adsorption

In figure 4, it is clear that Fe exhibited high adsorption across all pH levels, peaking at pH 7 (85.3%) and slightly decreasing at pH 9 (14.8%). This trend indicates that iron adsorption was favored at neutral pH, likely due to reduced competition from H^+ ions and increased surface deprotonation of the adsorbent, which enhanced electrostatic attraction of Fe^{2+} ions. Similar behavior was observed for Mn and Zn, which increased with pH, attaining 50.3% and 52.3% respectively at pH 9. In contrast, Ni and Co adsorption declined sharply at higher pH, suggesting possible precipitation or the formation of insoluble hydroxides at basic conditions.

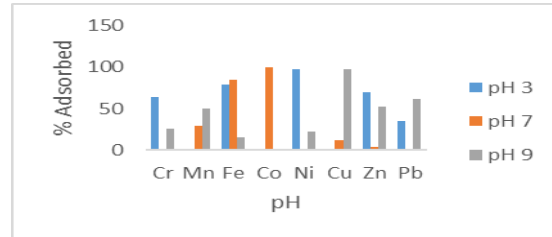


Figure 4. Dumpsite soil-nZVI pH Variation

3.5 Effect of Concentration on Heavy Metal Adsorption

Figure 5 showed that adsorption generally increased with concentration for most metals, with Mn (65.1%), Fe (88.8%), and Co (90.9%) reaching the highest uptake at 0.0806 M. This trend suggests that higher metal ion concentrations enhance the mass transfer driving force, improving surface interaction and ion exchange with the adsorbent. However, Ni decreased steadily from 42.3% at 0.0448 M to 15% at 0.0806 M, while Pb peaked at 84.3% at 0.0627 M before dropping to 0% at the highest concentration, likely due to active site saturation or competitive inhibition. A similar concentration-dependent trend was reported by [48] where Fe(II) and Ni(II) removal by activated coconut shell and corn cob increased initially but decreased at higher concentrations. The higher Fe uptake compared to Ni was attributed to stronger affinity between Fe^{2+} ions and active binding sites, consistent with these results.

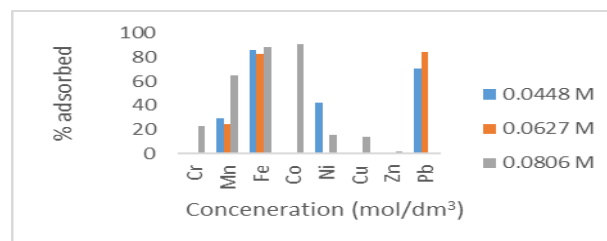


Figure 5. Dumpsite soil-nZVI Concentration Variation

3.6 Effects of temperature on heavy metal Adsorption

In Figure 6, iron consistently exhibited high adsorption (>80%) across all temperatures, indicating strong and stable soil affinity. Chromium adsorption increased with temperature, from none at 34 °C to 44.31% at 44.85 °C, suggesting endothermic behavior. Manganese adsorption declined with temperature, indicating exothermic interaction. Cobalt and nickel peaked at 39.85 °C before decreasing at 44.85 °C, showing that moderate temperatures favor adsorption, while higher temperatures promote desorption. Lead uptake was highest at 44.85 °C, reflecting endothermic adsorption, whereas zinc steadily declined, indicating weaker bonding [49]. Overall, iron dominated adsorption, while other metals displayed mixed temperature responses, suggesting multiple simultaneous mechanisms.

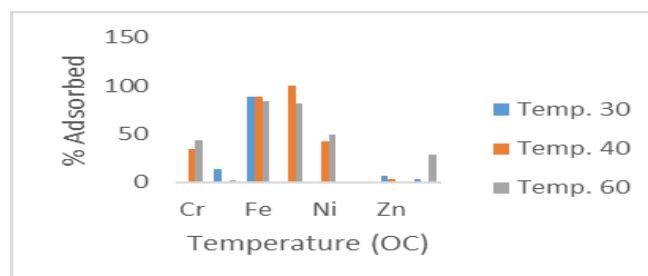


Figure 6. Dumpsite soil-nZVI Temperature

3.7 Adsorption Isotherms Models

3.7.1 Langmuir Model

The Langmuir isotherm results for the Presco soil show that the R^2 values for Fe (0.9994), Ni (1.000), Pb (1.000), and Mn (0.9796) indicate a strong correlation with the Langmuir model [50] implying that the adsorption data fit well mathematically, as seen in figure 7, even though the adsorption process itself was not favorable, R_L values for Mn (1.08), Ni (1.043), and Pb (1.802) are greater than 1, indicating unfavorable adsorption [51] while the extremely high value for Fe (89.0) suggests a very weak or negligible interaction with the nZVI surface. Although the data fit the Langmuir model mathematically, actual removal involves adsorption, reduction, and precipitation, highlighting the limited affinity of nZVI for some metals under the tested conditions.

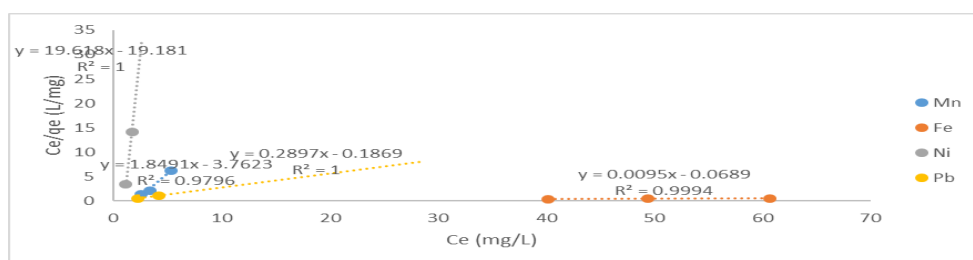


Figure 7. PRESCO dumpsite soil Langmuir Model

3.7.2 Freundlich Model

It is evident in figure 8, that Fe and Pb again exhibited strong adsorption ($K_F=230.07$ and 9.02) with excellent fits ($R^2 = 0.996$ and 0.982). Mn also showed moderate capacity with good correlation, suggesting the Freundlich model adequately describes adsorption in this soil [52]. The values of the Freundlich constant (n) related to adsorption intensity for Mn, Fe, and Pb adsorption were found to be -1.057 , -6.238 , and -1.545 , respectively. These values are all less than 1, indicating that the adsorption followed chemisorption [53], [54], [55].

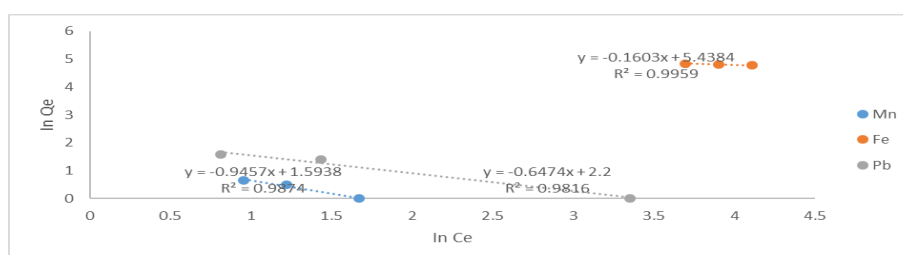


Figure 8. PRESCO dumpsite Soil Freundlich Model

Across the soils, Fe consistently exhibited the highest K_F , followed by Pb and Cu, confirming nZVI's strong potential for immobilizing these metals. The generally negative Freundlich exponents (n) suggest non-ideal adsorption, likely due to soil heterogeneity and metal competition. High R^2 values show that the Freundlich model adequately describes adsorption for most metals, particularly Fe, Pb, and Cu. Similar trends have been reported for Cd^{2+} on nZVI, confirming chemisorption as the dominant mechanism [56].

3.8 Adsorption Kinetics of Heavy Metals

The adsorption kinetics of heavy metals on nZVI were evaluated using pseudo-first-order (PFO) and pseudo-second-order (PSO) models. PFO reflects physisorption controlled by available sites, while PSO captures chemisorption via electron sharing or exchange. Results varied by metal as seen in table 2, PSO fitted Fe best ($R^2 = 0.99$), indicating chemisorption dominance, while Cr followed PFO ($R^2 = 0.99$) as seen in figure 9 suggesting primarily physical adsorption. Pb showed good fits to both models, slightly favoring PSO ($R^2 = 0.97$), implying a mix of physical and chemical mechanisms. Mn also aligned with PSO as seen in figure 10 supporting surface-controlled adsorption. These trends confirm that adsorption mechanisms differ by metal depending on interaction strength with nZVI, consistent with literature [57].

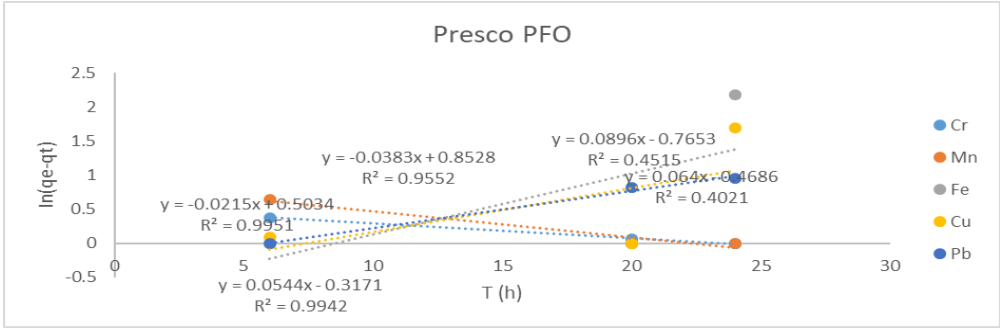


Figure 9. Pseudo-First-Order

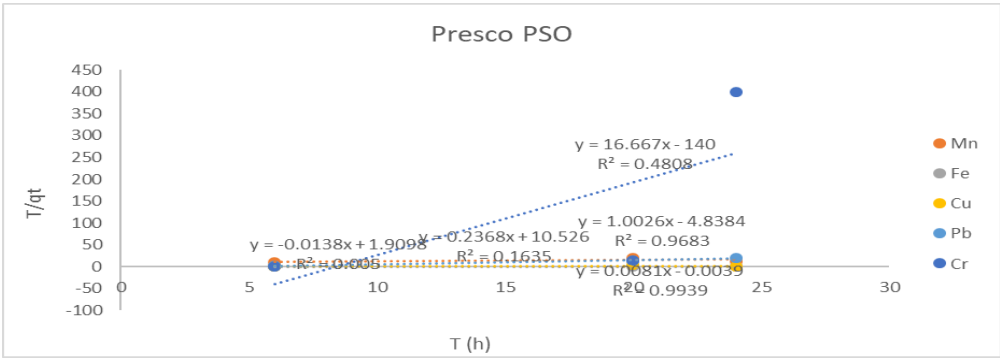


Figure 10. Pseudo-First-Order

Table 2. Model Constants

Metal	Langmuir model constants			Freundlich model constants			PFO model constants			PSO model Constants		
	Q _{max}	R _L	R ²	n	K _F	R ²	K ₁	Q _e	R ²	K ₂	Q _e	R ²
Cr	-	-	-	-	-	-	0.02	1.65	0.99	-2.04	0.06	0.48
Mn	0.541	1.08	0.98	-1.06	4.92	0.99	0.04	2.34	0.96	0.01	4.22	0.16
Fe	105.3	89.0	0.99	-6.23	230.1	0.99	0.09	0.47	0.45	-0.02	123	0.99
Co	-	-	-	-	-	-	-	-	-	-	-	-
Ni	0.051	1.04	1	-	-	-	-	-	-	-	-	-
Cu	-	-	-	-	-	-	0.06	0.63	0.40	0.01	-	0.01
											72.4	
Zn	-	-	-	-	-	-	-	-	-	-	-	-
Pb	3.452	1.80	1	-1.55	9.03	0.98	0.05	0.73	0.99	-0.21	0.99	0.97

4. Conclusion

Nano zero-valent iron (nZVI) supported *Justicia carnea* extract was successfully synthesized through a green reduction method and characterized using UV–Vis and FTIR, confirming the formation of stable Fe⁰ nanoparticles. The nZVI showed appreciable removal of heavy metals, reaching up to 92% for Fe and moderate to high removal for Mn, Co, Cu, Zn, and Pb. Adsorption followed both Langmuir and Freundlich isotherms, reflecting heterogeneous surface interactions. Kinetic analysis indicated that chemisorption (PSO) dominated for Mn and partially Pb, while other metals followed physisorption (PFO). These results demonstrate that *Justicia carnea*-supported nZVI is a sustainable, cost-effective, and environmentally friendly material for remediating heavy metal-contaminated soils, highlighting its practical potential for polluted dumpsites.

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