Follow-Up Application of *Spondias Mombin* Modified Nano-Sorbent for Trace Metals Remediation

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**Abstract:** Environmental pollution, specifically soil contamination by trace metals, is a significant problem that has caused widespread concern around the globe due to its grave negative effects on the fragile ecosystem. Zero-valent iron nano-compound modified with *Spondias mombin* leaves extract was employed in the removal of Zinc (Zn), Chromium (Cr), Lead (Pb), and Nickel (Ni) from contaminated soil. The metal compositions in both plant and soil were evaluated using Atomic Absorption Spectrophotometer (AAS). The result showed that the pH conditions for optimum removal efficiency (%) of Zn (70.53%), Pb (98.89%), and Ni (99.99%) were in the range of 7 < pH ≤ 12 while Cr (98.67%) was in the range of 3 < pH ≤ 7. The result revealed that the adsorbent dosage for optimum removal efficiency (%) was 0.2 g for Cr (99.99%) and Pb (98.89%) while 0.8 g for Zn (57.51%), and Ni (99.99%). The optimum contact time was 15 min for Cr (99.99%) and Pb (86.38%) while 120 min for Zn (52.43%) and Ni (99.99%). The modified nano-compound showed higher removal efficiency (%) for Ni (99.99%) under the same condition. This study has revealed that the modified adsorbent can serve as an effective and efficient eco-benign matrix for soil remediation.

**Keywords:** Nano-Compound, Soil Remediation, *Spondias Mombin*, Adsorption, Atomic Absorption Spectrophotometer

1. Introduction

The alteration of soil mechanism by the presence of pesticides, petroleum and related products, polycyclic aromatic hydrocarbons (PAHs), heavy metals, and chlorophenols has necessitated actions by scientists [1-3]. Soil contamination has immensely affected food chain and by extension affected animals and humans that directly depend on the products of soil practice. According to research reported by FAO and ITPS [4], soil contamination is the third most dangerous threat to the functionality of soil in Europe and Eurasia, fourth in North Africa, fifth in Asia, seventh in the Northwest Pacific, eighth in North America, ninth in Latin America and Sub-Saharan Africa. In addition, according to the status of the World's Soil Resources Report, some contaminants can cause soil acidification, and nutrient imbalances which are the two key issues in several areas of the world [4]. The contamination of the soil due to point sources emanate from emissions, solid discharge and effluents from vehicle exhaustion, factories, and metals from mining and smelting while non-point sources spread from pesticide use, soluble salts (synthetic and natural), municipal and industrial waste disposal in agriculture, and improper use of chemical fertilizers [5-7].

However, soil pollution arising from household wastes, agricultural wastes, oil spills, gas flaring, used lubricating oil, etc. are the major components of pollution in Nigeria. Vastly, the uncontrolled establishment of mechanic workshops in Nigeria has made oils, lubricants, metallic parts, acids, etc. from different kinds of automobiles and generator engines discharge into open soil, water drains and farmland [8]. Contaminated soils have discrete organic and inorganic substances that can annul their natural balance and metals are the most represented [9]. Generally, metals are defined based on the physicochemical characteristics such as ductility, conductivity, ligand specificity, and atomic number [10, 11]. These elements are naturally present in small amounts in the soil, but their existence in the soil has risen geometrically since the advent of industrialization [12, 13].
Trace metals are complex kinds of pollutants and most difficult to remediate in nature and hence, degrade soil quality, food crops, and water bodies, and threaten the health of animals and human beings. Metals like cadmium (Cd), lead (Pb), chromium (Cr), arsenic (As), mercury (Hg) are relatively toxic to humans while zinc (Zn), nickel (Ni), copper (Cu) are more relatively toxic to plants [14].

There are several conventional physical and chemical approaches for contaminated soil remediation and the majority of which have been found to be less cost-effective [15]. Hence, some of these processes lead to the generation of secondary by-products that are not environmentally benign and require additional effort to treat. However, thermal desorption, dig and dump, photo-catalyst, vitrification, and soil washing/flushing, are some of the traditional methods for handling contaminated soil. These techniques, on the other hand, run the risk of being relatively costly, time-consuming, and causing secondary pollution [9].

In the light of the above issues, using a cheap and eco-friendly biosorbents would eliminate the use of chemicals that can be toxic to the soil by affecting its normal properties and provide treatments that are economic, effective, sustainable, and competitive. Most remediation techniques only transform soil pollutants into their fewer toxic forms rather than complete removal of toxic substances.

The synergy between phyto-remediation and nano-technology have proven to be the panacea for the complete stabilization of the soil from further oxidation or recombination of these toxic metals in the soil during and after remediation [16-19].

The plant extract used in this combination strategy is obtained from *Spondias mombin* leaves. *Spondias mombin* belongs to the cashew family called Anacardiaceae. It is a tropical angiospermous tree, which grows up to 22 m high; the leaves are about 20-30 cm long and under hairy. This produces an abundant harvest of pierisrapae fragrant panicle flowers that begin green then becomes a lightweight golden yellow when ripe. It is readily common in Brazil, Nigeria, and many other tropical forests of the planet [20].

The *Spondias mombin* extracts has been successfully utilized in the remediation of polycyclic aromatic hydrocarbons (PAHs), total petroleum hydrocarbons (TPHs), and total hydrocarbon content (THC) from polluted soil [21].

This study therefore is a follow-up application of *Spondias mombin* with Zero Valent Iron Nanoparticle (Sm-nZVI) was calculated using the expression in equation 1.

\[
R_{\text{eff}} = \frac{C_0 - C_{\text{eq}}}{C_0} \times 100
\]

Where,

- \(R_{\text{eff}}\) = removal efficiency,
- \(C_0\) = initial concentration of the trace metals in mg/kg,
- \(C_{\text{eq}}\) = equilibrium concentration of the trace metals in mg/kg.

2.2. Trace Metal Content of Crude Soil and Plant Sample Evaluation Using AAS

The soil sample and the pulverized plant sample were acid-digested using ASTM [22] method. Soil portion (0.5 g) and plant portion (0.5 g) were weighed and placed in a 125 ml beaker each. A 100 ml of distilled water and 0.5 ml of HNO₃ were added respectively to each beaker and afterward, 5 ml of HCl was added. The mixtures were heated for 2 hrs and 45 min in the oven, until the volume was reduced to 20 ml. The samples were taken out, filtered to eliminate any solids, and then transferred to a 100 ml volumetric flask for volume adjustment. The trace metals such as Zn, Cr, Pb, and Ni were analyzed using AAS (model no: GBC AA).

2.3. Biosynthesis and Characterization of *Spondias Mombin* with Zero Valent Iron Nanoparticle (Sm-nZVI)

The synthesis, biosynthesis, characterization procedures adopted by Ayomide *et al*. [21] was applied.

2.4. Remediation Parameters

The batch adsorption procedure was carried out in triplicate and the average result adopted as a working value. The removal efficiency for the trace metals using of *Spondias mombin* with Zero Valent Iron Nanoparticle (Sm-nZVI) was calculated using the expression in equation 1.

2.4.1. Effect of Adsorbent Dosage

A mixture of contaminated soil was prepared using 5 g of contaminated soil and 50 ml of distilled water and different dosages of Sm-nZVI (0.2, 0.4, 0.6, 0.8 g) were added respectively. The mixture was agitated for 30 min and held at 27°C, with a pH 7.0 ± 0.2 and a stirring speed of 200 revolutions per minute (rpm). Afterwards, the mixture was filtered through Whatman No. 1 filter paper and the metals analyzed using Atomic Absorption Spectrophotometer (AAS) (model no: GBC AA).

2.4.2. Effect of Contact Time

A solution of contaminated soil was prepared using 5 g of contaminated soil and 50 ml of distilled water and 0.2 g of Sm-nZVI was added at different contact times of 15, 45, 60, and 120 min. The mixture was agitated at 27°C, pH 7.0 ± 0.2 and the stirring of the solution was fixed at 200 rpm. The mixture was then filtered through Whatman filter paper No 1.
and metals analyzed using AAS.

2.4.3. Effect of pH

A mixture of contaminated soil was prepared using 5 g of contaminated soil and 50 ml of distilled water and 0.2 g of Sm-nZVI was added at different pH of 3, 7, 9 and 12. The mixture was agitated for 30 min at 27°C with the stirring speed set to 200 rpm. The mixture was then filtered through Whatman No 1 filter paper. The filtered mixture was analyzed for metals using AAS.

3. Results and Discussion

3.1. Initial Concentrations of Metals in the Crude Soil and Plant Samples

The results in Table 1 displayed that the soil was vastly contaminated of Zinc (Zn), Chromium (Cr), Lead (Pb), and Nickel (Ni) with concentration of 176.80 mg/kg, 487.90 mg/kg, 291.80 mg/kg, and 124.90 mg/kg. The high values of Zn, Cr, Pb, and Ni may be as a result of varied contributions from both agricultural and industrial applications, human activities, burnt automobiles, brakes and wears from automobile tires, indiscriminate dumping of electronics and lead acid car batteries and wear of brake linings through mechanical abrasion [23].

<table>
<thead>
<tr>
<th>S/N</th>
<th>Metals</th>
<th>Soil sample (mg/kg)</th>
<th>*Target value of soil (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Zinc (Zn)</td>
<td>176.80</td>
<td>40.00</td>
</tr>
<tr>
<td>2</td>
<td>Chromium (Cr)</td>
<td>487.90</td>
<td>100.00</td>
</tr>
<tr>
<td>3</td>
<td>Lead (Pb)</td>
<td>291.80</td>
<td>238.00</td>
</tr>
<tr>
<td>4</td>
<td>Nickel (Ni)</td>
<td>124.90</td>
<td>35.00</td>
</tr>
</tbody>
</table>

*Target values represent the desirable maximum levels of metals in unpolluted soil [24].

In addition, the results in Table 2 revealed that Zn, Cr, and Pb with values 10.79 mg/kg, 8.35 mg/kg and 35.11 mg/kg were high in the plant indicating pollution by the soil. However, Ni was insignificant and within the permissible limit.

<table>
<thead>
<tr>
<th>S/N</th>
<th>Metals</th>
<th>Plant sample (mg/kg)</th>
<th>*Target value of soil (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Zinc (Zn)</td>
<td>10.79</td>
<td>0.60</td>
</tr>
<tr>
<td>2</td>
<td>Chromium (Cr)</td>
<td>8.35</td>
<td>1.30</td>
</tr>
<tr>
<td>3</td>
<td>Lead (Pb)</td>
<td>35.11</td>
<td>2.00</td>
</tr>
<tr>
<td>4</td>
<td>Nickel (Ni)</td>
<td>0.30</td>
<td>10.00</td>
</tr>
</tbody>
</table>

*Permissible value of plant [24]

3.2. Effect of Adsorbent Dosage

The removal efficiency (%) of the metals changed according to bio-sorbent dosage in Figure 1. The result revealed that the initial concentration of Zn reduced from 176.8 mg/kg to 107.7, 87.09, 81.02 and 75.13 mg/kg for 0.2, 0.4, 0.6, and 0.8 g with removal efficiencies of 39.08, 50.74, 54.17 and 57.51% respectively. The initial concentration of Ni after being treated with Sm-nZVI reduced from 124.9 mg/kg to 108.4, 99.45, 18.48 and 0.001 mg/kg with removal efficiencies of 13.21, 20.38, 85.20 and 99.99% respectively. For Cr, the removal efficiencies decreased from 99.99 to 85.53, 83.16 and 81.46% as the Sm-nZVI dosage was increased from 0.2, to 0.4, 0.6 and 0.8 g respectively and also same trend for Pb [25]. The removal efficiencies decreased from 99.99 to 96.29, 81.33, and 76.90% as the Sm-nZVI dosage was increased from 0.2 to 0.4, 0.6 and 0.8 g respectively. However, the removal efficiencies for Zn and Ni increased as the Sm-nZVI dosage was increased. This may be explained by the fact that higher Sm-nZVI dosage produced more active sites or active molecules on the surface, and a large number of these metals adhered to the Sm-nZVI surface, resulting in a faster reaction rate [26-28].

The results further showed that as the Sm-nZVI dosage was increased, the removal efficiencies for Cr and Pb decreased. The optimal dosage of 99.99% removal efficiencies was recorded for Cr and Pb at 0.2 g [29]. As a result, there was no further increase in removal efficiencies above 0.2 g. Furthermore, the decrease in Cr and Pb removal efficiencies may be due to their concentrations in the Spondias mombin plant used to synthesize the nano-compound.

It is worthy of note that the removal pattern of the biosynthesized nano-sorbent may be due to the surface morphology as demonstrated by the SEM and XRD results [21]. Hence, the required Sm-nZVI dosage serves as a factor that must be considered in practical/field application for optimal removal efficiencies of these metals.

3.3. Effect of Contact Time

The time variations in Figure 2 revealed that as the agitation time was increased from 15 to 45, 60, and 120 min, the removal efficiency of Zn increased from 42.36 to 52.44%. Nickel (Ni) removal efficiency (%) increased from 19.94 to 99.99%. This simply implies that at equilibrium, the amount of reduced Ni and Zn at the Sm-nZVI surface increased with time. However, since Zn has a lower reduction potential than Ni, adsorption mechanism was predominant, while the removal mechanism for Ni was both reduction and surface complex formation [30, 31]. However, Cr and Pb had their removal efficiencies decreased from 99.99 to 69.07% and 86.38 to 3.98% as the contact time with Sm-nZVI was...
increased from 15 to 120 min. Cr and Pb have the maximum removal efficiencies of 99.99% and 86.38% at a contact time of 15 min while Ni and Zn have maximum removal efficiencies of 99.99% and 78.85% at 60 min. This could be due to the fact that under the same conditions, Cr and Pb have better immobilization effect than Ni and Zn [32]. This study revealed that the optimum time for Ni and Zn removal was 60 min while that of Cr and Pb was 15 min.

3.4. Effect of pH

The pH variations in Figure 3 revealed that as the pH was increased from 3 to 12, the removal efficiency of Zn increased from 34.22 to 70.53%. The result also showed that the removal efficiency (%) of Cr increased from pH 3 to 9 but decreased at pH 9 to 12. In addition, from pH 3 to 12, the removal efficiency (%) of Pb increased from 56.34 to 98.83% respectively. More so, from pH 3 to 12, the removal efficiency (%) of Ni increased from 5.44 to 99.99%. The removal efficiency (%) of the trace metals was found to be highly pH dependent [33]. This result was expected because of the presence of the bioactive ingredients and functional groups present in both the plant and biosynthesized samples as reported by the phytochemical screening and FTIR results [21].

The result clearly revealed that the Cr removal efficiency rate (%) was much higher in the acidic condition i.e., 3 < pH ≤ 7 than in the alkaline condition i.e., 7 < pH ≤ 12 [26]. The release of Fe$^{2+}$ and the deposition of Fe oxide on the biosorbent (Sm-nZVI) surface caused the higher Cr removal at 3 < pH ≤ 7. At this pH range, there was an inhibition which resulted in competition, leading to more active sites for electron transfer between Sm-nZVI and Cr. The lower Cr removal rate under 7 < pH ≤ 12 may be due to the rapid precipitation of Fe$^{3+}$ and Cr$^{3+}$ oxyhydroxides which formed passivation layer on the surface of the bio-sorbent (Sm-nZVI) [21] and inhibited electron transfer between Sm-nZVI and Cr (VI), hence, lowering the reduction rate. At pH 9 and 12, Zn, Pb, and Ni had high removal efficiencies. The implication was that the removal of Zn, Pb, and Ni was faster and even rapid for Ni under alkaline conditions. The precipitation of these metal ions as insoluble Zn(OH)$_2$, Pb(OH)$_2$, and Ni(OH)$_2$ on the surface of Sm-nZVI could explain the drastic increase in Zn, Pb, and Ni at pH 9 and 12.

Furthermore, by regulating the surface charge of Sm-nZVI, solution pH may influence contaminants removal using Sm-nZVI [34]. This study concludes that at pH 3 and 7, surface adsorption was primarily responsible for the removal of Cr, Zn, Pb, and Ni, while at pH 9 and 12, both adsorption and surface complex formation (precipitation) were responsible for the removal of Zn, Pb, and Ni.

4. Conclusion

The results of the batch study successfully suggested that the modified nano-compound has unique characteristics for Zn, Cr, Pb, and Ni removal from contaminated soil medium. The performance of biosynthesized material (Sm-nZVI) varied significantly with respect to adsorbent dosage, contact period or agitation time, and pH. The result revealed that the parameters investigated were critical for optimum removal performance. The results also revealed that the mechanism of removal of these metals were adsorption, oxidation, reduction, and precipitation. The output of this study exposes the potency and effectiveness of Sm-nZVI of its cost effectiveness, availability, sustainability, simplicity, and environmental benignancy.

Competing Interests

The authors declare that they have no competing interests.

References


