Carbothermally Synthesized, Lignin-Based, Embedded And Surface Deposited Nano Zero-Valent Iron for Water Purification: Characteristics and Applications

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***Abstract*— Synthesizing tailor-made materials for remediating wastewater polluted with contaminants of emerging concerns, has become a major concern of the scientific community. Nanoscale zero valent iron (nZVI) together with a biochar (BC) support provide advantageous materials for wastewater purification via adsorption, reduction, complexation and advanced oxidation mechanisms. Two approaches to nZVI-composite engineering have been reported: embedding in support matrix and surface depositing, where the latter being more common. Nonetheless, the behavior of embedded material towards contaminant remediation has not yet been sufficiently studied. Furthermore, the remediation capability of these two materials has not been comparatively evaluated. The present study focuses on preparing and extensively characterizing two materials; nZVI embedded in (Lig-e-nZVI) and surface deposited (Lig-s-nZVI) on lignin BC with subsequent comparative analysis of remedial action of the two materials. SEM, SEM/EDX, XRD, FTIR, proximate and ultimate analysis, point of zero charge, iron leaching and regeneration studies were carried out using pristine lignin BC as the control material. Porous and non-porous structures of the carbothermally prepared materials where crystalline iron was embedded or surface coated were compared along with their surface and bulk elemental compositions. It was evident that although the surface iron content is high in Lig-s-nZVI, the total iron content in both the materials were same. Loaded iron was confirmed to be in the zero valent state as per the observed XRD peak patterns. Surface functional groups and overall surface charge of the materials and iron leaching and depletion of remediation capacity were also analyzed. Pharmaceutical precursors p-nitroaniline (pNA) and p-nitrophenol (pNP) were used as sample molecules in this study due to their toxicity and health effects owing to persistence and bioaccumulation. Synergistic adsorptive and degradative behavior of the materials towards pNA and pNP showed an optimum pH of 3.0 and an optimum contact time of 60 minutes. Higher initial adsorption capacity was observed for Lig-s-nZVI and high sustainability and stability was portrayed by Lig-e-nZVI over the regeneration cycles. Both materials showed comparatively increased adsorption capacities in a simulated wastewater matrix. Therefore, it is conclusive that Lig-s-nZVI is of improved remedial capacity towards organic contaminants whereas, Lig-e-nZVI is a better candidate in action over time. Providing a thorough comparison of the properties and remediation performance of nZVI-BC composites synthesized using two commonly employed methods is expected to offer fresh insights to the scientific community.**

Keywords*— *Biochar, Nanoscale zero-valent iron, Lignin, p-nitroaniline, p-nitrophenol

I. INTRODUCTION

Remediating contaminants of emerging concerns (CECs) has recently drawn excessive attention of the scientific community. Owing to its appreciable reactivity due to the low standard reduction potential of -0.41 V, ability to participate in active oxidation processes, and less toxicity, nanoscale zero-valent iron (nZVI) is considered as a strong candidate for wastewater purification [1]. However, nZVI particles alone are prone to rapid passivation and agglomeration where the necessity of a supporting material and a capping agent arises to alleviate the drawbacks [2].

Biochar (BC) is renowned as an excellent solid support for nZVI as a result of its porous carbon structure, surface functionality, abundance, ease of production, eco-friendliness and low cost [3].

Two approaches to nZVI composite engineering have been reported: embedding in support matrix and surface depositing, where the latter being more common [4, 5]. Nonetheless, the behavior of embedded material towards contaminant remediation has not yet been sufficiently studied. Furthermore, the remediation capability of these two materials has not been comparatively evaluated.

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Two materials, nZVI embedded in and surface deposited on lignin biochar (Lig-BC) were carbothermally synthesized and comprehensively characterized. Materials synthesized via carbothermal reduction are substantially stable and the production process is easy, relatively cheap and doesn't require excessive use of toxic chemicals. Our project aims at enhancing the current knowledge by filling the gap of comparative evaluation of physicochemical characteristics and remedial action of the materials. In this regard, adsorption behavior of sample molecules, p-nitroaniline (pNA) and p-nitrophenol (pNP) on Lig-BC supported surface coated nZVI (Lig s-nZVI) and Lig-BC supported embedded nZVI (Lig e-nZVI) were studied using pristine Lig-BC as the control material.

II. MATERIALS AND METHODS

A. Materials

All the reagents utilized in this study were of analytical grade. p-Nitrophenol was obtained from Sisco Research Laboratory PVT Ltd. (Mumbai India) and ethanol which was used to dissolve PNP was purchased from Sigma Aldrich (St. Louis, MO). Hydrochloric acid and sodium hydroxide pellets used for pH adjustments were from Sisco Research Laboratories Pvt. Ltd. DI water was provided by Biobase Biodustry (Shangdong) Co.Ltd. A sieve of mesh size 0.5 mm and 1 mm were used to obtain the required particle size of BC. Biologix (Shangdong, China) 50 mL polypropylene centrifuge tubes were used in all batch adsorption studies. A shaking water bath was used for all batch studies and was operated at 125 rpm for all the experiments carried out. Spectroscopic measurements were carried out using UV-Visible Spectrometer. A Muffle furnace was used for the preparation of biochar. pH measurements were obtained by Multi-Parameter Meter.

B. Methodology

Synthesis of Lig-s-nZVI - BC was prepared by pyrolyzing lignin at 300 °C and mixing with iron, with subsequent pyrolysis at 1000 °C for an hour.

S*ynthesis of Lig-e-nZVI* – Iron solution was added to Kraft lignin powder and subjected to pyrolysis at 300 °C, which was followed by pyrolysis at 1000 °C.[4].

Synthesis of Lig-BC control - Lignin powder was subjected to gradual pyrolysis at 300 °C and then at 1000 °C for another hour. processes. Materials were sieved to a particle size of < 0.25 mm and stored under inert conditions.

Surface morphology, elemental composition of the surface and surface functional groups of the three prepared materials were analyzed by the use of SEM, SEM/EDX and FTIR respectively. Presence of ZVI was confirmed via XRD characterization. Point of zero charge (pH_{PZC}) for the materials was determined by the pH drift method. Proximate and ultimate analysis were also carried out.

Optimum pH and contact time for pNA and pNP removal were evaluated through batch sorption experiments. Adsorption capacities (Qs) were derived from modeled isotherms. Regeneration studies were carried out for four cycles and the effect of iron leaching towards and stability of each material were evaluated. Behavior of the synthesized materials in wastewater was analyzed using a simulated water matrix with humic and fulvic acids.

III. RESULTS AND DATA ANALYSIS

Less-porous surface morphology of Lig-BC, highly porous structure with embedded iron particles in Lig-e-nZVI and less porous structure with surface deposited iron clusters in Lig-s-nZVI were observed by SEM images.

XRD peak pattern of Lig-s-nZVI showed a sharp distinct peak at 43.60° while Lig-e-nZVI showed a peak combination at 43.60° and 44.60° in 2ɵ.

Optimum pH for pNA and pNP remediation was found to be 3.0 and optimum contact time was concluded as 60 minutes.

A significant enhancement in the percentage removal of pNA has been observed in simulated wastewater matrix than the reverse osmosis (RO) water for both surface-deposited and embedded materials. Regeneration studies denoted a steady decrease of Q of pNA for the engineered materials.

IV. DISCUSSION

Lig-BC is a good support in the material synthesis as it is soluble in organic solvents and is capable of forming a stable lignin-ferric complex [4]. As shown in SEM images, due to utilization of Kraft lignin, the porosity of the BC is minimal. [4]. SEM/EDX results show that Lig-s-nZVI has a high surface iron loading than Lig-e-nZVI, whereas, according to the proximate analysis the approximately similar ash content suggest that both the materials have similar iron loadings.

The XRD peak patterns of Lig-e-ZVI and Lig-s-ZVI confirmed the predominant existence of crystalline nZVI in the materials. [4]. The optimum pH for the remediation of pNA and pNP was found to be 3.0. Optimum contact time was concluded as 60 minutes for both molecules. There is a direct correlation between the amount of iron on/in the material and the remedial action of materials.

Proposed interactions of the contaminant molecules with BC are charge-assisted H-bonding, H-bonding and electron donor-acceptor interactions [3]. Depending on the pH of the solution and the pH_{PZC} of the materials, the adsorption mechanisms will be changed. At the utilized optimum conditions, the material exhibited a net positive charge. However, the existing electron donating moieties could still act as binding sites for the contaminant molecules. As far as remedial mechanisms are concerned, apart from degradation via reduction and advanced oxidation processes, nZVI itself possesses adsorption sites for contaminant molecules. [6].

Both Lig-s-nZVI and Lig-e-nZVI materials portray enhanced removal of pNA in the simulated wastewater matrix. Proposed biochar-based interactions: (A) charge-assisted H-bonding, (B) H-bonding, (C) electron donor-acceptor interactions.

V. CONCLUSION

Both Lig-s-nZVI and Lig-e-nZVI show higher removal efficiencies for organic molecules than Lig-BC. Out of the two, Lig-s-nZVI shows a much-improved remedial action owing to the readily available Fe^0 on the surface. It suggests that the Fe^0 in the material surface has a direct involvement in contaminant remediation. However, the stability of Lig-e-nZVI is substantially higher due to less iron leaching. While the findings contribute to the existing knowledge on the remedial action of embedded and surface deposited nZVI, further investigation is needed through future research on the effects of feedstock, production conditions, and different target compounds to gain a better understanding.

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