

Lignin Based Embedded and Surface Deposited Nanoscale Zero Valent Iron for Cd(II) Remediation

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Abstract— Vast industrialization occurring throughout the world has led to a drastic increase in water pollution by heavy metals. Cd is a heavy metal that has garnered significant concern due to its toxicity and adverse health effects on humans and other living organisms. Recent studies have focused on the application of Biochar (BC) supported carbothermally produced Nanoscale Zero Valent Iron (nZVI) for the remediation of a variety of contaminants. However, only limited research has been carried out to assess and compare the mechanisms of Cd removal and remediation efficiency by different types of carbothermally prepared nZVI. To address this issue, the present study investigated the application of two nanocomposites, Lig-eG@nZVI and Lig-sG@nZVI, produced through two carbothermal reduction routes at 1000 °C. In Lig-eG@nZVI, nZVI was embedded in the Lignin Biochar (Lig-BC) matrix while in Lig-sG@nZVI, nZVI was deposited on the Lig-BC surface. In this study, enhanced uptake of Cd(II) was observed with increasing pH with maximum uptake at pH 6. Cd sorption at 30 °C was evaluated using the Langmuir, Freundlich, Temkin, Redlich-Peterson, Sips, Toth and Jossens adsorption isotherm models. The experimental data was best fitted to Sips isotherm model, with a maximum Sips capacity of 9.688, 8.102 and 6.665 mg g⁻¹ at 30 °C and pH 6 for Lig-eG@nZVI, Lig-sG@nZVI and Lig-BC, respectively. The two composites showed enhanced remediation due to the synergistic effect of remedial mechanisms of both nZVI and Lig-BC components. Possible adsorption mechanisms for BC include cation- π interactions, electrostatic attractions and surface complexation precipitation with minerals. Owing to the nearly identical standard redox potential of Cd with zero valent iron, the feasibility of Cd(II) remediation through reduction is very low and the only viable removal mechanism is sorption or surface complex formation. Fast remediation kinetics were observed for the three materials. According to thermodynamic studies conducted, the overall adsorption processes of all three materials were confirmed to be physisorptive, endothermic and spontaneous in nature. This study bridges the existing knowledge gap by conducting a comprehensive evaluation on the application of Lig-eG@nZVI, Lig-sG@nZVI and Lig-BC for the remediation of Cd(II) in aqueous media.

Keywords—Nanoscale zero valent iron, Biochar, Lignin, Cadmium remediation

I. INTRODUCTION

Cadmium is a highly toxic heavy metal that is currently attracting the attention of environmentalists. Therefore, the remediation of Cd in contaminated wastewater is essential. Owing to their substantial surface area and fairly strong reducing power due to its low standard reduction potential, Nanoscale Zero Valent Iron (nZVI) particles have amassed a lot of interest for their activity as remediation agents for treating polluted water [1]. However, they require supporting materials such as Biochar (BC) to alleviate the issue of agglomeration and passivation [2].

The present study investigated the application of two nanocomposites, Lig-eG@nZVI and Lig-sG@nZVI, produced through two carbothermal reduction routes at 1000 °C to remediate cadmium. In Lig-eG@nZVI, nZVI was embedded in the Lignin Biochar (Lig BC) matrix while in Lig-sG@nZVI, nZVI was deposited on the surface of Lig-BC [3, 4]. Heavy metals can be remediated using nZVI via sorption or reduction depending on their reduction potentials.

To date, only limited research has been carried out to assess and compare the mechanisms of Cd removal and remediation efficiency by different types of carbothermally prepared nZVI supported on BC. This research endeavors to address and bridge the existing knowledge gap by undertaking a comprehensive evaluation and comparison of Lig-eG@nZVI and Lig-sG@nZVI for the remediation of Cd(II). The study holds significant importance as it contributes to enhancing the scientific community's understanding of the remediation characteristics of the two composites, with Lig-BC serving as the control material, in the effective removal of Cd(II) from aqueous media.

II. MATERIALS AND METHODOLOGY

A. Materials

All reagents used were of analytical grade and were used directly without further purification. Cadmium nitrate tetrahydrate, nitric acid, sodium hydroxide pellets and ferric nitrate nonahydrate were purchased from Sisco research laboratories (Mumbai, India). Powdered kraft lignin was purchased from Domtar Corp. USA. A test sieve of mesh size 0.25 mm was used to obtain the required particle size of

materials. Required amounts of chemicals were weighed using a Radwag electronics analytical balance. Deionized (DI) water was obtained from a Biobase Biodustry water purifier. A Portable Multi-Parameter Meter was used for pH measurements. A shaking water bath was used for all batch studies and was operated at 120 rpm for all experiments conducted. A flame atomic absorption spectrophotometer was used for elemental analysis.

B. Methodology

Nanocomposites of nZVI supported on BC was produced via two routes of carbothermal synthesis. Lig-eG@nZVI was produced by dissolving lignin in ethanol and mixing with iron precursor prior to a two-step pyrolysis process. This allowed the nZVI to be embedded in the carbon structure of Lig-BC upon pyrolysis [4]. Lig-sG@nZVI was prepared by mixing Lig-BC with the iron precursor and pyrolyzing which results in the deposition of nZVI particles on the Lig-BC surface [5]. Thereafter, a comprehensive analysis of the effect of pH, effect of contact time, isotherm studies, thermodynamic studies and regeneration studies were carried out for the two nanocomposites along with Lig-BC as the control. All batch adsorption experiments were conducted using 25 mg of each material in 50 mL centrifuge tubes using 25 mL of Cd solution and were shaken at 120 rpm. The amount of Cd(II) remaining after adsorption in filtrates were quantified using the AAS in flame mode with an air-acetylene flame.

III. DATA ANALYSIS AND RESULTS

Higher pH values favored enhanced remediation in all three materials with the maximum uptake recorded at pH 6. Results obtained suggest fast adsorption kinetics of remediation for all three materials.

The experimental data best fitted the Sips isotherm model, with a maximum Sips capacity of 9.688 mg g⁻¹, 8.102 mg g⁻¹ and 6.665 mg g⁻¹ at 30 °C for Lig-eG@nZVI, Lig-sG@nZVI and Lig-BC, respectively. The thermodynamic parameters obtained suggest that the adsorption processes are spontaneous and feasible for all three materials. According to the results of the regeneration study, the removal of Cd by Lig-eG@nZVI and Lig-sG@nZVI decreased from 54.9% to 7.2% and 40.1% to 2.3% respectively, by the second regeneration cycle.

IV. DISCUSSION

It was observed that the Cd(II) removal efficiency improved when the initial pH of the solution increased, suggesting that the adsorption mechanism is affected by the surface charge. This can be attributed to the negatively charged BC surface which allows greater sorption of divalent cations due to greater affinity (According to parallel studies the pHPZC of Lig-eG@nZVI, Lig-sG@nZVI and Lig-BC was recorded to be 4.60, 5.24 and 4.45, respectively). Lower adsorption capacities and removals recorded at lower pH values can be due to competition by H⁺ ions in the medium for the same adsorption sites. From the results obtained, it is evident that the equilibrium pH has not considerably changed during the adsorption process. This can be due to surface complexation being the mechanism of removal rather than ion exchange during the sorption process.

Possible adsorption mechanisms for BC include cation- π interactions, electrostatic attractions and surface complexation. In addition, the cyclic aromatic π -system of BC can function as a π -donor [2]. Owing to the nearly identical standard redox potential of Cd with zero valent iron, the feasibility of Cd(II) remediation through reduction is very low, and the only viable removal mechanism is sorption or complex formation [6].

Results obtained for the effect of contact time suggest fast adsorption kinetics for the remediation of Cd by Lig-eG@nZVI, Lig-sG@nZVI and Lig-BC with no visible trend of increase in adsorption with time. The best-fitting Sips model suggests that multilayer, non-ideal sorption occurs via a heterogenous surface in all three materials [6].

The positive ΔH° values for all three materials confirmed an endothermic adsorption process. In this study, the enthalpy values obtained for the three materials are less than 20 kJ mol⁻¹ indicating that the adsorption of Cd(II) on the three materials is a physisorptive process [6]. The significant decrease in Cd(II) regeneration by the materials may be due to structural damage caused to the Fe(0) component in both composites by the nitric acid solution.

It was confirmed that both composites have similar amounts of iron after digesting and quantifying iron content using Flame Atomic Absorption Spectrophotometry. According to SEM-EDX data obtained, Lig-eG@nZVI has a % atomic iron composition of 13.0% while Lig-sG@nZVI has a composition of 22.7%. As Lig-eG@nZVI showed a lesser surface iron percentage than Lig-sG@nZVI, it is evident that that the core of Lig-eG@nZVI possesses iron.

V. CONCLUSIONS AND RECOMMENDATIONS

The present investigation reports the successful application of Lig-eG@nZVI, Lig-sG@nZVI and Lig-BC for the remediation of Cd(II) in aqueous medium, thus helping bridge the existing knowledge gap. However, the assessment of a better alternative for material regeneration and shelf life analysis is imperative in future studies. From the results of this research, it can be concluded that both Lig-eG@nZVI and Lig-sG@nZVI can be used as efficient remediation agents for the removal of Cd(II) in aqueous systems.

ACKNOWLEDGMENTS

The authors acknowledge the support from the Institute of Chemistry Ceylon [Grant No. 21-02].

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