Production of environmentally benign Biochar composites for removal of Fluoride and Nitrate from Drinking Water

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by

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CHAPTER 6

Summary

Chapter 1 addresses the critical issue of groundwater pollution, focusing on water contamination by fluoride and nitrate. Elevated levels of fluoride lead to severe health issues like dental and skeletal fluorosis, while nitrate contamination poses risks such as methemoglobinemia, particularly harmful to infants. Among various approaches to pollutant removal, adsorption has emerged as highly effective and efficient. Its simplicity in design, potential for adsorbent recycling, economic feasibility, and minimal generation of harmful residues make it a preferred method. Conventional adsorbents like zeolites, activated carbon, and activated alumina have been utilized but often exhibit limitations in economic viability and adsorption efficiency, particularly for fluoride and nitrate. In recent years, biochar-based adsorbents have gained prominence as sustainable alternatives. Derived from biomass pyrolysis, biochar offers advantages such as high surface area, porous structure, and functional groups conducive to adsorption. These properties enhance its capacity to remove fluoride and nitrate from water effectively. Biochar's economic viability and potential for production from diverse waste biomasses support a circular economy framework.

The background information and the literature review revealed that many conventional adsorbents have been reported for the adsorptive removal of pollutant species but the use of biochar-based adsorbent for the removal of fluoride and nitrate ions has not much explored yet. Compared to traditional adsorbents, biochar-based materials demonstrate superior performance in terms of adsorption capacity and cost-effectiveness. They can be regenerated and reused, minimizing waste and promoting environmental sustainability. Studies indicate that biochar effectively addresses the shortcomings of conventional adsorbents like zeolites and activated carbon, making it a promising solution for water treatment.

Chapter 2 comprehensively outlines the experimental process for batch systems and introduces various characterization techniques used in the study. The synthesis of biochar from sugarcane

bagasse and corn cobs, both obtained from local sources, is described in detail, emphasizing the pyrolysis process under an inert atmosphere to produce the adsorbents. Characterization techniques such as Scanning Electron Microscopy (SEM), Fourier Transform-Infrared (FT-IR) spectroscopy, Zeta potential measurement, X-Ray Photoelectron Spectroscopy (XPS), Energy-Dispersive X-Ray Spectroscopy (EDS), X-ray diffraction (XRD) analysis, and Brunauer-Emmett-Teller (BET) method are thoroughly discussed, providing insights into the physical, chemical, and structural properties of the adsorbents.

The chapter further explores various adsorption isotherm models, notably the Langmuir and Freundlich models, to describe the interaction between the adsorbents and the adsorbates (fluoride and nitrate). Key parameters such as adsorption capacity and affinity constants are examined. Additionally, kinetic models, including the pseudo-first-order and pseudo-second-order models, are applied to the experimental data to understand the adsorption process dynamics.

Chapter 3 of this thesis focuses on the removal of fluoride from drinking water using a composite material of cerium oxide and biochar (CeO_2/BC). While fluoride is an essential micronutrient, excessive concentrations can lead to severe health issues, including skeletal abnormalities, dental fluorosis, and Alzheimer's disease. Various methods exist for fluoride removal, but adsorption stands out for its cost-effectiveness and efficiency. Cerium, despite its expense, is highly effective due to its insolubility and affinity for fluoride over a wide pH range. By combining cerium with biochar—a cost-effective and environmentally friendly material—a potent hybrid adsorbent is created. The biochar was produced by pyrolyzing sugarcane bagasse and then treated with a cerium nitrate solution. This mixture was stirred and treated with ammonia to precipitate cerium oxide onto the biochar surface. The resultant CeO_2/BC

composite, which had a surface area of 260.05 m^2/g, was formed using a straightforward chemical precipitation technique and subsequently dried and ground for use.

Characterization of the CeO_2/BC composite revealed significant findings. SEM images showed an increase in pore size and smoother surfaces post-cerium incorporation, while EDAX confirmed the presence of cerium, carbon, and oxygen. XRD patterns indicated the crystalline nature of the cerium-modified biochar, and BET analysis showed a decrease in surface area but an increase in pore volume and diameter upon cerium modification. FTIR spectra confirmed the presence of different functional groups and CeO_2 nanoparticles in the biochar. The point of zero charge for CeO_2/BC was around pH 7. The modified biochar demonstrated higher fluoride removal efficiency compared to both unmodified biochar and cerium oxide alone, with a 10% loading of cerium oxide being optimal. Fluoride removal efficiency increased with adsorbent dose up to 3 g/L. CeO_2/BC was effective across a pH range of 4-10, with maximum removal efficiency at pH 4, and efficiency decreased at higher pH levels. The presence of bicarbonate, sulfate, chloride, and nitrate ions reduced fluoride removal efficiency to varying degrees. The Langmuir adsorption isotherm and a pseudo-second-order kinetic model best described the adsorption process, with a maximum Langmuir adsorption capacity of 16.14 mg/g for fluoride concentrations ranging from 5 to 40 mg/L. The adsorption process was determined to be non-spontaneous. XPS and pH_{PZC} analyses suggested that fluoride removal occurred primarily through ion exchange and electrostatic attraction, with the adsorbent remaining effective for up to four cycles after regeneration with NaOH.

Chapter 4 is the extended study of adsorbent used in chapter 3 (CeO_2/BC) for nitrate removal. Here we found that as synthesized adsorbent CeO_2/BC was not very effective in nitrate removal so we first pre treated the biochar's surface with different activating agent (H_2O_2, KOH, and HCl) before cerium impregnation using precipitation method. Characterization results

indicated successful modification of the biochar. XRD analysis confirmed the amorphous nature of the raw biochar and the successful integration of crystalline cerium oxide into its structure. BET analysis revealed a mesoporous structure beneficial for adsorption, though the surface area slightly decreased after modification. FTIR analysis identified functional groups crucial for adsorption and confirmed the interaction between cerium and the biochar. SEM images showed changes in biochar morphology, including pore formation and cerium particle deposition. Zeta potential measurements revealed pH-dependent surface charge characteristics, influenced by the presence of cerium.

We found that H_2O_2-treated biochar (HCB) was found to be most effective for nitrate removal after testing all the pretreated biochar's. Further experiments were conducted to assess HCB's ability to remove nitrate from water under various conditions. The results showed that HCB successfully removed a significant amount of nitrate from the water, with a maximum removal efficiency of 78%. To understand the mechanism behind nitrate removal, the researchers analyzed the adsorption process using kinetic and isotherm models. The findings suggest that the process primarily involves chemical bonding (chemisorption) between nitrate and the biochar surface. The Langmuir isotherm model best described the adsorption behavior, indicating that the available adsorption sites on the biochar were homogeneous. The Langmuir isotherm calculates theoretical BC's maximum adsorption capacity to be 15.2 mg/g for HCB and 7.5 mg/g for HB.

Chapter 5 explored the potential of waste-derived calcium oxide (CaO) from electric geyser scaling waste (EGWS) to modify corn cob biochar (CBC), creating an efficient adsorbent for fluoride (F^-) and nitrate (NO_3^-) removal from water. This approach aligns with the circular economy framework by developing a cost-effective and environmentally sustainable adsorbent. Calcium oxide was synthesized from EGWS and used to modify corn cob biochar

through a ball-milling process, resulting in CaO@CBC. Thermogravimetric analysis (TGA) of EGWS revealed two stages of weight loss, indicating successful conversion to CaO. XRD analysis confirmed the presence of CaO and its incorporation into the biochar matrix. BET analysis demonstrated an increase in surface area and porosity, enhancing adsorption capabilities. FTIR analysis identified functional groups and changes post-adsorption, indicating effective interaction with F^- and NO_3^-. SEM analysis showed a heterogeneous structure with well-defined particles, confirming successful CaO impregnation. pHpzc analysis indicated high adsorption capacities for both contaminants across a broad pH range (2-11). Adsorption kinetics followed a pseudo-second-order model, suggesting chemisorption mechanisms, and the Langmuir isotherm model fit well, showing high maximum adsorption capacities of 18.36 mg/g for F- and 19.27 mg/g for NO_3^-, surpassing other reported materials. Thermodynamic studies indicated spontaneous and exothermic uptake reactions for both contaminants. Mechanistic insights from pH studies, XPS analysis, and FTIR suggested that electrostatic attraction, inner-sphere complexation, and ion exchange were involved in the adsorption process.

The effective utilization of EGWS for producing CaO contributes to waste management and resource utilization, aligning with circular economy principles. The use of waste materials and the simple ball-milling method make this approach environmentally sustainable and economically viable. These findings suggest that CaO@CBC can be a practical solution for water treatment, addressing global challenges of water pollution, and contributing to the achievement of SDG 6 (Clean Water and Sanitation) and SDG 12 (Responsible Consumption and Production).

CHAPTER 7

Suggestions for future work

Based on extensive experimentation and research, the following suggestions are recommended for future work in the application of adsorption technology, particularly for the removal of anionic pollutants:

1. Focus on Multisolute Systems: Since drinking water often contains multiple solutes, future research should address the various competitive effects that occur during adsorption in multisolute systems.

2. Pilot Plant Studies: Conduct pilot plant studies using raw water samples. Perform cost analysis to determine the most suitable adsorbent for removing specific pollutants.

3. Real Water Samples: Carry out adsorptive remediation studies using real water samples collected from various pollution sources. This approach will provide a better understanding of the practical utility of the adsorbent.

4. Continuous-Flow Systems: Evaluate the applicability of the developed composites in continuous-flow water treatment systems to facilitate real-world implementation.

5. Sustainable Regeneration Methods: Explore efficient and sustainable methods for desorbing fluoride and nitrate from spent biochar composites to enable their regeneration and reuse.