Development of 3D-Printed Permeable Reactive Barrier Adsorbents Utilizing Zeolite Composites for Copper (II) Removal in Acid Mine Drainage

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Abstract: Zeolite-based ceramic structures was fabricated using a viscous solution 3D printing (3DP) technique to demonstrate their effectiveness in removing heavy metal ions from acid mine drainage (AMD) runoff. Zeolite, a low-cost hydrated aluminosilicate clay, is widely used in water treatment due to its excellent ion-exchange and adsorption capabilities. In the Philippines, abundant reserves of natural zeolite (Philippine Natural Zeolite, PNZ) have been utilized in various separation and purification applications. However, traditional forms of zeolite—such as loose granules or powders—are difficult to deploy and recover from environmental systems. This study employed a Direct Ink Writing (Eazao Bio) – a commercially available benchtop multi-material 3D printer to create custom, structured zeolite composite devices that are deployable, retrievable, and reusable. These 3D-printed structures offer improved efficiency in extracting heavy metals from AMD. Furthermore, surface modification and functionalization of the 3D-printable ink significantly enhance the adsorption performance of the final product, making it a promising sorbent material for use in permeable reactive barriers (PRBs).

Keywords: Adsorption, 3D printing, Acid Mine Drainage, Heavy Metals

1. Introduction

Acid Mine Drainage (AMD) runoffs from abandoned and existing mining sites in the Philippines are reported to have been affecting water bodies surrounding the sites. Such runoffs are highly acidic and contain non-biodegradable heavy metals that can pose a significant environmental hazard to receiving water bodies. Permeable reactive barrier (PRB) is one of the solutions that is being explored now to manage and treat mining runoffs. The main advantages of the PRB are the stable operation for long treatment time and very low investment and maintenance costs. As some used materials like limestone, concrete cement waste and fly ash in PRB, this study applied additive manufacturing (AM) technology in developing adsorbent materials utilizing zeolites composites. Several papers have presented the use of synthetic and natural zeolites as adsorbent for AMD, but very few had explored the use of AM technologies to the development of adsorbent materials.

In water treatment, the use of zeolites as sorbents have been widely utilized due to its high ion-exchange, molecular sieve effects, high chemical/thermal resistance, and excellent, well-defined porous structure (Khalil et al., 2021). But using zeolites in loose powder form was found to be challenging in terms of deployment, recovery, and reusability. Sorbent powders are structurally unstable and are often packed in treatment columns in which low flowrates are employed just to guarantee effective removal of pollutants and making sure that the materials are held in place. Furthermore, zeolite composites that are conventionally manufactured lack the design flexibility and mechanical robustness, which hinders their recovery and reuse once placed in the pollutant environment (Lyu et al., 2020). It is in this light that through AM/3DP, a robust 3D fabricated zeolite ceramic composites could be used in PRB for the extraction of heavy metal ions. Effective sorption of heavy metals due to its functionalized structure, easy deployment and recovery are its advantages over other existing adsorbent materials.

2. Methods

2.1. *Preparation of Materials and Development of 3D-Printed PRB.*

The procedure used by Bautista-Patacsil et al., (2024) was employed except that copper (II) is the heavy metal used for adsorption experiments. The Philippine natural zeolite (PNZ) with 325 mesh value from LITHOS Manufacturing was used as the adsorbent. As for the ink additives, calcium bentonite was used as the binder, partially hydrolyzed polyvinyl alcohol (PVA) as the plasticizer, hydroxyethyl-cellulose (HEC) as the suspension aid additive, and distilled water (dH_2O) as the solvent.

2.2. Sorption Experiments of Copper and Aluminum using the 3D-Printed PRB

PRBs printed with the optimal formulation conditions underwent column adsorption at varying zeolite:binder ratios (80:20, 85:15, 90:10 w/w) and solution flow rates (1, 2, 3 ml/min) to assess removal efficiency. The initial and final residual heavy metal concentrations were measured using Shimadzu AA-7000 to determine the removal efficiency of the 3D-printed adsorbent.

3. Results

3.1 Design of PRB.

AutoCAD was used in designing the 3D model of the PRB. The PRB is a cylindrical monolith with a square-shaped cross-sectional area composed of layers of cylindrical structures with channel offset orientation of 90°. It has a diameter of 1 inch, cell density of 16 cpsi, and a total height of 2.1 cm. As the layer height of the PRB varied to 0.5 mm, 0.6 mm, and 0.7 mm, the number of layers correspondingly changed to 42, 35, and 30, respectively. The 3D model of the PRB can be seen in Figure 1.

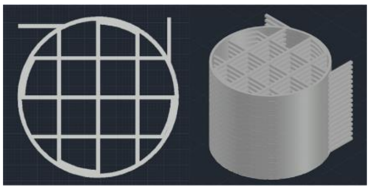

Figure 1. Top view (left) and isometric view (right) of the 3D Model of the PRB

3.2 Development of various prototypes of 3DP adsorbents.

The 3D printed PRBs in this study has an average diameter of 2.16 cm and average height of 1.52 cm. When compared to the designed dimensions (diameter = 2.54 cm; PRB height = 2.1 cm), there was a 14.96% decrease in the diameter while a 27.62% decrease in the height of the PRB (Figure 2). The decrease in size is mainly attributed to the evaporation of water during the air-drying process.

Figure 2. The printed PRB before (left) and after (right) air-drying process.

3.3 Evaluation of the effectiveness of the fabricated 3DP adsorbents for the removal of heavy metals like copper and aluminum.

Preliminary sorption experiments showed only 15.328 % removal of copper when the air-dried PRB was used. Due to the low % removal observed, a calcination post treatment of the PRB at 550 °C was conducted, which increased the % removal of copper to 49.10 %. This suggests that calcination can improve the removal efficiency of copper. The compression tests revealed that uncalcined and calcined PRBs exhibited a maximum compressive strength of 7.90 MPa and 1.24 MPa, respectively. In order to achieve complete removal of copper from AMD, a 2-3 series of PRB sorption experiments should be done.

4. Conclusion

This study successfully develop a 3D-printed zeolite PRB that showed a potential for removing copper from AMD. The calcination process enhanced the adsorptive performance of the zeolite PRB but its compressive strength is reduced significantly. To achieve optimal performance, further refinement in both design of the PRB and post-treatment process is necessary to simultaneously improve copper removal efficiency. Despite the challenges, the results highlight the promising potential of 3D-printed zeolite-based adsorbents for effective AMD remediation.

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