

From the professorship of Soil Physics
of the Faculty of Agricultural and Environmental Sciences

Summary of the cumulative Dissertation

Low-Cost Adsorptive Technologies: Batch Reactor and Fixed-Bed Column Experiments for the Removal of Phosphate from Wastewater

to obtain the academic degree
Doctor of Engineering Sciences (Dr.-Ing.)

at the Faculty of Agriculture and Environmental Sciences
at the University of Rostock

submitted by
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Defence on 31. March 2023

Using low-cost and locally available raw materials to remove phosphate instead of high-cost phosphate removal techniques is one of the viable solutions to prevent aquatic life from excess phosphate discharges. Unfortunately, the widespread use of commercially available activated carbon as an adsorbent for phosphate removal is not economically feasible due to its high operating cost. Therefore, this research aimed to study the possibilities of using low-cost carbon-based (i.e., leftover coal materials) and natural adsorbents (volcanic rocks, i.e., pumice- VPum and scoria-VSco) for the removal of phosphate from synthesized wastewater. The study evaluated the three low-cost and locally available sorbents: coal leftover, VPum, and VSco, using batch and fixed-bed column experiments under various environmental conditions.

Numerous experiments were conducted, and the effects of significant design parameters such as solution pH, initial concentration of phosphate ion, contact time, and adsorbents dose for batch adsorption onto leftover coal, VPum, and VSco were examined. Major parameters (Bed height, influent solution concentration, and solution flow rate) affect fixed-bed column adsorption are also investigated via breakthrough curve analysis. Design of experiment (DoE) software based on the response surface method (RSM) using central composite design (CCD) was used to investigate the effect of two parameters at a time such as initial phosphate concentration, contact time, pH, and adsorbent dose at a time on the adsorption performance of the selected material.

The structure, surface morphology, and chemical compositions of the adsorbents' materials were characterized before and after adsorption. When the crystallinity and amorphousness of the adsorbents were examined using an XRD machine, it was found that the adsorbent used in this study was both crystalline and amorphous. The functional groups found in the adsorbent materials were obtained and identified using the Fourier Transform Infrared (FT-IR) method. The FT-IR spectrum result after adsorption confirmed the interaction with phosphate ions.

The findings from batch adsorptions revealed that the maximum amount of phosphate removed onto leftover coal material was 198mg/kg at a pH of 2.3, while for VPum and VSco were 294 and 169mg/kg at the solution pH of 6.5 and 5.5, respectively. This maximum phosphate removal capacity was obtained at the contact time of 200 min for leftover coal and 300min both for VPum v and VSco. Furthermore, the effects of the adsorbents size on phosphate adsorption from aqueous solution was investigated, and it was obtained that the removal efficiency of phosphate onto leftover coal increased from 66 to 94.5%, from 64 to 91.8%, and from 74 to 92.1% for particle size 0.075 – 0.425mm, less than 0.075mm, and for 0.425 to 2mm respectively. Thus, all

the adsorption experiments, both for batch and fixed-bed column experiments, other than on particle size effect, were performed at a particle size of 0.075 – 0.425mm.

Several adsorption kinetic and isotherm models that describe the adsorption process were also applied. The pseudo-second-order equation best described the experimental data, with a correlation value of $R^2 = 0.99$ for all adsorbents used in this study. However, the phosphate removal process on the adsorbents' surface was found to be complex. Intraparticle diffusion, with the thickness of boundary layer constants of 180 to 209 mg/kg, contributed to the rate determining step. The adsorption equilibrium data for phosphate removal onto adsorbents materials were followed by Langmuir, Freundlich and Dubinin-Radushkevich isotherms at the constant temperature of 20 °C and solution pH examined for this research. The calculated values of the dimensionless separation factor (i.e., 0.03 to 0.87) from the Langmuir constant revealed favorable phosphate adsorption onto the adsorbents' materials.

The effects of competitive anions on the phosphate removal onto the volcanic rock materials, on the other hand, were also studied by applying several anions into the synthesized wastewater using a batch mode experimental setup. The study findings revealed that the presence of competitive anions markedly reduced the removal efficiency of phosphate from the aqueous solution. The adsorptive removal of phosphate was affected by competitive anions in the order: $\text{HCO}_3^- > \text{F}^- > \text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^-$ for VPum, and $\text{HCO}_3^- > \text{F}^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^-$ for VScO.

The adsorption of phosphate onto leftover coal material by continuous-flow fixed-bed column experiments has shown that the breakthrough curve time increased from 190 to 348min with increasing bed height from 5 to 8cm but decreased from 348 to 187min with increasing solution flow rate from 1 to 2 mL/min. The longer the bed height, the longer the time phosphate ions interact with the adsorbent surface. The amount of phosphate removed onto the leftover coal material was also increasing from 190 to 243mg/kg with increasing influent initial phosphate concentration from 10 to 25mg/L which agrees with the previously obtained results from batch experiments. The Adams-Bohart adsorption model with a higher correlation factor (R^2) of 0.98 described the vi continuous flow fixed-bed column phosphate adsorption better than Thomas and Yoon-Nelson model.

In general, the research findings showed that the adsorbents used have an excellent capacity for phosphate recovery because of their high removal efficiency, especially at the optimum phosphate concentration, and medium particle sizes (0.75 mm to 0.425 mm). Overall, the methods look comfortable in preliminary and operating stages as they have relatively low operational and investment costs as the adsorbents are easily

accessible and found at low or no cost. In addition, the results have shown that leftover coal, VPum, and VScO materials have great potential for phosphate removal. However, further research is needed before the generated data can be applied at field scale, and also regenerable adsorbents for further benefits are highly recommended. Furthermore, to increase the removal efficiencies of the adsorbent materials as economically viable adsorbents for phosphate removal, chemical and physical modification of the adsorbents is highly recommended by considering the cost of modification.