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PhD Thesis ABSTRACT

Excessive application of phosphorus (P) through conventional fertilizers to maintain crop yield has increased P pollution and created environmental concerns with serious implications to both surface and groundwater resources. To improve the P nutrient uptake and minimize the undesirable impacts of conventional P fertilizers, engineered smart fertilizers such as nanofertilizers are needed. Nano-hydroxyapatite (nHAP) has been studied successfully as a nano-phosphorus fertilizer for various crops. However, to determine the appropriate phosphorus application rate through nHAP application, utilizing transport models like Hydrus 1D to study the nutrient flow and leaching was instrumental in unraveling crucial insights into estimating the dispersivity, distribution co-efficient and diffusion parameters involved with the application of nHAP. The synthesis of nHAP using planetary ball mills (PBM) is a simple, fast, cost-effective green technology, but it involves conducting several laboratory experimental trials to obtain the desired nanoparticle size. Therefore, the first objective of this study was to develop a model for predicting the particle size of nanoparticles synthesized using a planetary ball mill (PBM). The second objective was to apply this model for laboratory synthesis of nano-hydroxyapatite (nHAP). The third objective involved using the synthesized nHAP as a phosphorus (P) source for rice crops to evaluate its impact on various rice growth characteristics. The fourth objective was to model the transport mechanism of phosphorus from nHAP within the soil-plant-water system with the help of Hydrus-1D model.

A conceptual model, *PBM4Nano*, was developed by integrating the kinematics of the PBM process along with the breakage mechanism of a material to determine the particle size at different levels of milling parameters. The model was calibrated for two parameters β (proportionality constant) and C (Material constant) and validated using literature data for different materials (zeolite, fly ash and iron). Similarly, the *PBM4Nano* model was then used for calibrating the particle size of nHAP from literature data then validated with nHAP synthesized in a PBM. The precursor for nHAP synthesized in a PBM were calcinated chicken eggshells treated with phosphoric acid. The synthesized nHAP was applied to rice crops grown in field columns. The nHAP at the recommended dose (nHAP) of 60 kg-P ha^{-1} and half the recommended dose (1/2nHAP) alongside a conventional fertilizer (Single Super Phosphate, SSP) and control (CNT) were considered as treatments (replicated three times) and were studied for three crop seasons (Rabi 2018-19, Kharif 2019-20 and Rabi 2019-20). Then the Hydrus-1D model was used for calibrating the water flow (bottom water flux) and P transport (ortho-P concentrations) using the rabi 2018-19 season data and then validated using the kharif 2019-20 data.

The *PBM4Nano* model was able to calibrate the particle size of zeolite, iron and fly ash material successfully and within acceptable limits of RMSE (25.4-76.17 nm), NRMSE (0.13-2.59 %) R^2 (0.67-0.99) and NSE (0.93-0.99). The milling speed was the most sensitive milling parameter, followed by the vial volume, milling time, and ball-to-powder ratio, whereas material properties were found to be less sensitive. The nanoparticles size nHAP resulted after 10 hours of milling with a milling speed of 500 rpm and they were observed to be mostly oval with an average particle size of 105 nm and P content of 14%. The field column studies indicated an improved plant height, tiller count and yield with nHAP and SSP as compared to CNT resulting in no significant difference between nHAP and SSP. However, a significant difference in ortho-P concentrations was observed for nHAP and SSP for both ponding and leachate waters with higher ortho-P concentrations in SSP. The Hydrus-1D model successfully calibrated and validated the bottom water flux and the ortho-P concentration in the leachate and ponding waters. The value of the distribution coefficient was found to be higher in the case of nHAP as compared to SSP indicating that more adsorption of P to soil particles occurs in nHAP. The longitudinal dispersivity and the diffusion (or precipitation) rate constant were significantly lower in nHAP and 1/2 nHAP than in SSP indicating less local variations in the velocity field of ortho-P in the direction of fluid flow for nHAP treatments. The potential of nHAP for use as P fertilizer can be demonstrated by the ability to sustain the agronomical parameters of rice crops and the reduced P leaching rate and slow-releasing property of the material.

Keywords: *Planetary ball mill, hydroxyapatite, nanofertilizer, rice crop, phosphorus transport, Hydrus- 1D.*