Optimization of the production of a complete fertilizer formulation by batch impregnation using clinoptilolite zeolite as carrier

N B J Catli, V P Migo, C G Alfafara, M C Maguyon-Detras and C C P Brutas

Department of Chemical Engineering, College of Engineering and Agro-Industrial Technology, University of the Philippines Los Baños, College, Los Baños, Laguna, 4031, Philippines

Email: njcatli1@up.edu.ph

Abstract. Fertilizer inefficiencies caused by uncontrolled and rapid nutrient release pose serious environmental threats and economic losses. Adsorption of nutrients in carriers such as clinoptilolite zeolite (CZ) has been proven to be effective in minimizing environmental pollution and improving the duration of nutrient availability in soil. In this study, a complete fertilizer was formulated via the batch impregnation of the combination of nutrient sources, such as urea, calcium hydroxyapatite (CaHAp), and muriate of potash (MoP), in CZ carrier in a 1:1 ratio. Carrier pre-treatment was done by washing CZ with deionized water and ethanol, followed by calcination at 600 °C for 4 hours. The process has 86.92% recovery and increased the cation exchange capacity (CEC) of the carrier from 41.30 cmol(+) /kg soil to 47.7630 cmol(+) /kg soil. The effect of mixture factors (% Urea : % CaHAp : % MoP ratio) and process factors (mixing time and sonication time) on the total nitrogen (N), phosphorus (P), and potassium (K) content was investigated using an Optimal (Combined Mixture) Experimental Design. Statistical analysis showed the direct effect of the mixture factors and the insignificant effect of the process factors on the said responses. The optimum conditions obtained via numerical optimization is as follows: (1) 50 : 23.99 : 14.61 : 11.39 (% PCZ : % Urea : % CaHAp : % MoP) ratio, (2) mixing time of 158.57 minutes, and (3) sonication time of 30 minutes. This resulted to a fertilizer with a total N, P, and K content of 4.65 %, 2.76 %, and 5.42 %, respectively. Moreover, it has about 1.96 % bound N, 0.28 % bound P, and 2.93 % bound K due to a successful adsorption process. The adsorption process has a high fertilizer yield of 96.49 %. DLS analysis revealed that the optimized product has an average particle size of 4105.8 nm; thus, it cannot be characterized as a nanofertilizer. Cost analysis showed that the formulated complete fertilizer is priced at Php 465.82 per kilogram, which is more expensive than the 14-14-14 conventional fertilizer due to higher cost of production. However, the possible slow/controlled release property of the NPK-PCZ fertilizer could offset the high price due to longer availability of nutrients in soil. As such, this could mean lower rate of fertilizer application thus allowing to save up in resources and manpower.

Keywords: Complete fertilizer; Plant nutrients; Adsorption; Optimization; Clinoptilolite Zeolite

1. Introduction

The increase in population has been leading to increasing food demands which must be met in a sustainable way. This paved the way for the development of fertilizers whose nutrients are bound in carriers to facilitate their release. This controlled release characteristic solves the environmental and economic problems that conventional fertilizers pose. The main goal of this study is to optimize the
process conditions which will give a complete fertilizer with maximum nitrogen, phosphorus, and potassium content. These three nutrients are primary nutrients which contribute the most to the growth and developments of plants, thus, are needed in large amounts [1]. Nitrogen is responsible for leaf growth and chlorophyll synthesis, potassium is vital in stem and root growth as well as protein synthesis while phosphorus is useful in the development of various plant parts such as fruits, flowers, roots, etc. [2].

2. Materials and Methods

2.1 Materials
The clinoptilolite zeolite purchased from Saile Industries was pretreated by first washing it with deionized water, pure ethanol, and with deionized water again in a 1:1 (v/w) ratio [3]. Afterwards, it was calcined at 600 °C for 4 hours [4] using a Thermo Scientific Thermolyne D1 Large Tabletop Muffle furnace (Model: F30438).

Urea purchased from Yara Fertilizers Philippines Inc. was used as the nitrogen (N) source, calcium hydroxyapatite (CaHAp) from Carl Roth GmbH + Co. KG was used as the phosphorus (P) source, and the potassium (K) ions came from Muriate of Potash (MoP) fertilizer.

The vanadomolybdophosphoric acid reagent was prepared by first dissolving 25 grams of ammonium molybdate in 300 mL water and 1.25 grams of ammonium vanadate in 5 N nitric acid (HNO₃). The two solutions were completely mixed until a clear yellow solution was obtained and then diluted to 1 liter using distilled water.

2.2. Experimental Design
Design Expert® Software Version 11 was utilized to generate an Optimal (Combined) Mixture Design in order to optimize the formulation of the complete fertilizer. This design is a special type of Response Surface Methodology (RSM) and was chosen since both mixture (% Urea : % CaHAp : % MoP) and process factors namely mixing time and sonication time was considered for the study. The factor levels used are summarized in table 1.

Table 1. Summary of the factors and levels used in the study.

| FACTOR       | FACTOR TYPE   | LOW LEVEL | HIGH LEVEL |
|--------------|---------------|-----------|------------|
| %Urea        | Mixture Component | 5 %       | 40 %       |
| %CaHAp       | Mixture Component | 5 %       | 40 %       |
| %MoP         | Mixture Component | 5 %       | 40 %       |
| Mixing time  | Process Factor | 60 minutes | 180 minutes |
| Sonication time | Process Factor | 30 minutes | 90 minutes |

2.3. Fertilizer Formulation
Preparation of the complete fertilizers is a four-step method composed of: weighing the needed amount of raw materials, mixing, sonication, and drying. The NPK-PCZ complete fertilizer is composed of 10 grams of the clinoptilolite zeolite fertilizer and 10 grams total of the various nutrient sources. The amount of each nutrient source in the mixture was obtained from the generated experimental design. One hundred mL of distilled water was added to the solid raw materials prior to mixing.

The resulting slurry was mixed for a specified time using a shaker with a fixed speed of 180 rpm. Afterwards, it was immediately subjected to ultrasonication using an Emmi®-H30 ultrasonicator with an ultrasonic power of 180 W. The length of time of mixing and sonication depended on the generated experimental design. Moreover, both mixing and sonication were done at room temperature. The fertilizer blend was quantitatively transferred to a petri dish then oven-dried at (80 ± 5) °C to obtain the solid complete fertilizer.

2.4. Nutrient Content Analyses
Standard methods were employed to get nitrogen (N), phosphorus (P), and potassium (K) content of the formulated fertilizers. A semi-automatic Kjeldahl set-up was used to get the total N content. Prior
to P and K content determination, the fertilizers were digested via the wet ashing method using concentrated nitric acid (HNO₃) and hydrochloric acid (HCl) in a 1:10:30 (w:v:v) ratio. P content was determined using the vanadomolybdophosphoric acid colorimetric method while flame photometry was done to know the K content. A UV-VIS Spectrophotometer (Model: UV-1280) was used for the colorimetric method while a Sherwood Model 410 Flame photometer for the flame photometry method.

2.5. Optimization of the Conditions for Fertilizer Synthesis
The significant effect of the experimental factors to the responses (N, P, and K content of the fertilizer) were investigated through Analysis of Variance (ANOVA) at $\alpha=0.05$. In total, three response surface models, one for each nutrient response, were generated. These models were used altogether to identify the process conditions which maximizes the nutrient loading of the complete fertilizer. The optimum conditions were experimentally verified, and the optimally synthesized fertilizer was characterized.

2.6. Characterization of the Optimally Synthesized Fertilizer Product
The total and bound nutrient contents of the optimized fertilizer were determined using the previously discussed standard methods of analysis. For the bound nutrient content determination, the optimized fertilizer was briefly washed with an appropriate solvent for the removal of any unbound nutrients, and then oven-dried at $(80 \pm 5)$ °C. Distilled water was used to dissolve excess N and K while 10 mL of 1 N HCl was used to wash 1 gram of the fertilizer for the removal of excess P [5]. Use of strong acids and large amounts of acid is not recommended since the solubility of PCZ increases with decreasing solvent pH [6]. Additionally, the amount of distilled water used is based on the solubility of urea and potassium chloride at room temperature to prevent the dissolution of successfully adsorbed nutrients.

A Dynamic Light Scattering (DLS) particle size analyzer was used to measure the particle size of the fertilizer, which was then checked for compliance to the criteria set by USDA stating that for an agricultural product to be classified as nano, it must have 1 nm - 1 000 nm particle size. A suspension was made from 0.01 grams of the optimized product and 100 mL of water. It was sonicated for 10 minutes then transferred to a cuvette, with minimal agitation, and read using a DLS particle size analyzer (Model: SZ-100).

Energy Dispersive X-Ray Spectroscopy (EDS) gives information regarding the elemental composition of a sample. Small amounts of untreated and pretreated was sent to Shimadzu Philippines Corporation, Bonifacio Global City, Taguig, Philippines for the EDX Spectroscopy. The results were analyzed and compared and served as a tool for the effectivity of the pretreatment of the clinoptilolite zeolite carrier.

3. Results and Discussion

3.1. Pre-treatment of the Clinoptilolite Zeolite Carrier
The purpose of pre-treatment is to remove impurities, such as water and other chemical species, trapped in the cages and channels of the zeolite structure, and has been reported to increase the carrier’s pore volume and cation exchange capacity (CEC) [7]. Pre-treatment caused the carrier to change color from an original off-white to reddish-brown due to exposure to high temperatures, and to have finer particles with less tendency to clump together. The process employed has a recovery of 86.92%.

The enhanced effectivity of CZ as a carrier was proven by comparing the EDS result before and after treatment, which showed the reduction in the amount of the compounds of the exchangeable cations after carrier pre-treatment. This translates to a decrease in the number of cations found in the channels of CZ, freeing up active sites for nutrient impregnation. This was corroborated by the target carrier’s slightly increased cation exchange capacity (CEC) from 41.30 cmol(+)/kg to 47.76 molc/kgsoil.

3.2. Response Surface Models
The %N content of the fertilizers ranged from 0.21% to 13.57%. The resulting response surface model, in its coded form, is presented in equation (1).

$$(\%N_{\text{total}})^{1/2} = 2.96A + 1.02B + 1.18C + 0.1115AB -1.5AC - 0.8096BC + 10.39ABC \quad (1)$$
The significant model terms, based on their p-values, are the linear mixture terms, A, B, and C, the two-way interaction term AC, and the three-way interaction ABC. Due to the principle of hierarchy, terms AB and BC were added despite having insignificant effect on the response.

The amount of P in the fertilizer blends ranged from 0.28% to 7.70%. The coded experimental model relating %P and the factors is shown in equation (2). In this case, only the linear mixture terms A, B, and C significantly affected the said response.

\[ \%P_{\text{total}} = 0.9639A + 7.21B + 0.8821C \]  

On the other hand, equation (3) defines the coded response surface model for the last response which is the K content of the fertilizer. It was found that the K content of the fertilizer has a wide range of 0.25% to 22.34%. Like the N response, the experimental model which best describes the data is a square root model.

\[ (\%K_{\text{total}})^{1/2} = 1.47A + 1.26B + 4.26C + 1.18AC + 2.73BC – 0.2837CE \]  

Factor coding for the three response surface models is as follows: A - % Urea; B - %CaHAp; C - %MoP; D – Mixing Time; and E – Sonication Time

3.3. Effect of the Mixture Factors

It was observed that the N, P, and K content of the NPK-PCZ fertilizer mainly depended on the amount of their respective nutrient sources. The factors affecting the incorporation of ions in zeolite are as follows: pH, temperature, ionic concentration of the solution it is immersed in, mass and particle size of the zeolite [6]. Hence, it follows that increasing the amount of the nutrient sources increases the number of ions in the solution thereby also increasing the extent of the adsorption of the corresponding nutrient onto the PCZ carrier.

Urea, when dissolved in water, dissociates into ammonium ions (NH\(_4^+\)) as in equations (4) and (5).

\[ (\text{NH}_2\text{CO}) \rightarrow \text{H}_2\text{O} \rightarrow 2\text{NH}_3 + \text{CO}_2 \]  

\[ \text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^- \]  

Increasing the amount of urea results to an increase in the ionic concentration of NH\(_4^+\) in the solution. On the other hand, as the amount of MoP is increased, more K\(^+\) ions became available in the solution. Faster and more efficient equilibrium will ensue since the driving force, which in this case is the concentration gradient, is improved. The incorporation of NH\(_4^+\) and K\(^+\) in the PCZ carrier is via simultaneous adsorption and ion-exchange reactions [6].

On the other hand, the anionic nature of the PO\(_4^{3-}\) from CaHAp makes its adsorption onto the negatively charged PCZ carrier limited and is only adsorbed by forming stable complexes with the cations initially present on the carrier’s surface [6]. CaHAp dissociates to Ca\(^{2+}\) and PO\(_4^{3-}\) when exposed to acidic environment [8]; however, this was hindered by the addition of urea which makes the mixture basic. Hydroxyapatite is adsorbed onto CZ through the formation of weak electrostatic bonds between the calcium residue and the carrier [9].

The negative effects of the other mixture components on the response values are due to several reasons: decreased ionic concentration of the desired ions (for the particular response), increased ionic concentration of the undesired ions (for the particular response), ion selectivity of the PCZ carrier, and competition for the active sites.

Additionally, the selectivity of zeolite for the concerned ions played an important role in the effect of the mixture components to the several responses. The selectivity of the carrier for the different ions are as follows: K\(^+\) > NH\(_4^+\) > Ca\(^{2+}\) > PO\(_4^{3-}\) [10]. Increasing the amount of the ions which has more affinity
with the carrier results to a decreased adsorption rate for the ions in which zeolite has less affinity, which is mainly because of competition for the active sites.

Ion-exchange between by Ca$^{2+}$ and NH$_4^+$ and K$^+$ happens since CZ has higher selectivity towards those ions [9] which leads to the release of the hydroxyapatite resulting to a decrease in the amount of adsorbed P. It should be noted though that addition of NH$_4^+$ and K$^+$ ions could have been advantageous for P adsorption if phosphorus is in its PO$_4^{3-}$ form since these cations are additional sites for the indirect adsorption of the anion to the PCZ carrier.

3.4. Effect of the Process Factors

Mixing is mainly for attaining homogeneity and ensuring that the different compounds come in contact with each other [11]. It is possible that homogeneity was already attained even before the low value of mixing time was achieved; thus, the effect of this process factor is not observable anymore.

On the other hand, sonication is useful in increasing the surface area and pore radius of zeolite [12]. Theoretically, this should have improved the number of adsorption sites and made ion-exchange easier but instead had no effect on the total N and P content of the NPK-PCZ fertilizer. It is probable that the exposed sites were already saturated even before the low level of sonication time was achieved. However, it was found that there is an indirect effect between the amount of adsorbed K$^+$ ions and sonication time, which contradicts the theoretical effect of sonication to adsorption. However, the sonication step was done after mixing, meaning that ions have already adsorbed onto the CZ. Therefore, since sonication works by chipping away at the surface of the particle to produce the desired characteristics, ions originally adsorbed onto the surface chipped away may have been likewise removed.

The use of short mixing and sonication time is enough to produce the NPK-PCZ fertilizer with the maximum nutrient content. This is also advantageous since energy consumption and product price has a direct relationship.

3.5. Optimum Conditions for the Fertilizer Formulation

The 3D surface model graphs showing the conditions which produces the fertilizer with the maximum nutrient content are shown in figure 1.

![3D surface model graphs for the optimization of the (a) total nitrogen (N), (b) total phosphorus (P), and (c) total potassium content of the NPK-PCZ fertilizer.](image)

**Figure 1.** 3D surface model graph for the optimization of the (a) total nitrogen (N), (b) total phosphorus (P), and (c) total potassium content of the NPK-PCZ fertilizer.

The conditions which will give the maximum nutrient content are found in the regions with warmer colors. Design Expert® Software Version 11 employed numerical optimization using the response models generated for each response and considering the factor ranges which gave the maximum for each response. The optimum conditions are summarized in table 2.

**Table 2.** Conditions which maximized the nutrient content of the complete fertilizer.

| FACTOR | FACTOR TYPE | OPTIMUM VALUE |
|--------|-------------|---------------|
| A      | C: Muriate of Potash (%) | 40 |
| B      | B: Calcium Hydroxyapatite (%) | 40 |
| C      | E: Sonication Time (minutes) | 5 |
| E      | E: Sonication Time (minutes) | 30 |
| D      | D: Carboxymethyl cellulose (%) | 4 |

(b)
3.6. Total and Bound Nutrient Content of the Optimally Synthesized Complete Fertilizer
A complete fertilizer was synthesized using the obtained optimum conditions and was analyzed for its total and bound nutrient content. The bound nutrients were those which were successfully adsorbed onto the channels and cages of the pretreated clinoptilolite zeolite (PCZ) carrier. These are the nutrients which may be released in a later time therefore possibly giving the fertilizer its slow-release characteristics. The nutrient contents of the optimally synthesized complete fertilizer are tabulated in table 3.

Table 3. Total and bound nutrient content of the optimized complete fertilizer.

| PARAMETER  | VALUE | PARAMETER  | VALUE |
|-----------|-------|------------|-------|
| Total N (%) | 4.66  | Bound N (%) | 2.50  |
| Total P (%) | 2.76  | Bound P (%) | 0.28  |
| Total K (%) | 5.42  | Bound K (%) | 2.93  |

The ratio of the nutrients in the NPK-PCZ fertilizer is found to be: 1.68:1:1.96 (N:P:K). It was desired to have a ratio where the amount of N is greater than the other two since it is the nutrient most needed by plants in high amounts. Due to the nature of the design and the difficulty of incorporating N because to its volatile nature, the response values recorded for N is generally less than those read for K. However, the difference with the amounts are not large that therefore this ratio is still acceptable.

From table 3, 53.56% of the nitrogen, 10.18 % of the phosphorus, and 54.06 % of the potassium was reported to be bound in the zeolite. The rest are assumed to be on the surface of the zeolite and are expected to be released immediately upon application. The bound nutrients are those expected to be released over time.

3.7. Particle Size Analysis
The particle size of the optimized NPK-PCZ fertilizer was determined using the DLS particle size analyzer. Findings showed that the optimized product is composed of particles whose sizes range from \((4105.8 \pm 1588.6)\) nm. This was much higher than 1000 nm limit that the USDA has set for nanoparticles used in agriculture; hence, the optimized NPK-PCZ fertilizer cannot be classified as a nanofertilizer. However, the relatively low value of the polydispersity index (0.86 ± 0.42) serves as an indication of the homogeneity of the particle size distribution of the fertilizer.

3.8. Fertilizer Yield and Cost Analysis
The process used in the production of the NPK-PCZ fertilizer has a 96.89% yield. Cost analysis based on only the raw materials showed that the formulated complete fertilizer is priced at Php 465.82 per kilogram. As of May 2019, a complete (14-14-14) fertilizer is priced at Php 1, 119.87/50 kg or approximately Php 22.34/kg [13]. The commercial complete fertilizer has 14 % of nitrogen, 6.11 % of phosphorus, and 11.62 % of potassium while the synthesized fertilizer has 4.66 % of nitrogen, 2.76 % phosphorus, and 5.42 % of potassium. Considering the nutrient content of each, the synthesized NPK-fertilizer is essentially more expensive that those already found in the market.

Generally, compound fertilizers are relatively more expensive than combined fertilizers due to the additional production cost needed to produce a fertilizer whose individual granules contain each nutrient [14]. However, compound fertilizers are more desirable since there is little risk of unequal nutrient distribution during application. Additionally, the possible slow/controlled release property of the NPK-PCZ fertilizer could prove to be economic in the long run since longer nutrient availability in the soil could mean lower rate of fertilizer application, saving up in manpower and material.

4. Conclusion
A complete fertilizer synthesized by impregnating nitrogen, phosphorus, and potassium in a pretreated clinoptilolite zeolite carrier was optimized to maximize its nitrogen (N), phosphorus (P), and potassium (K) content. The mixture factors significantly affect the responses such that increasing the amount of nutrient sources increases the corresponding nutrient content of the NPK-PCZ fertilizer. Mixing time does not have a significant effect while a low sonication time was favorable.

Numerical optimization using the models generated for each response showed that an optimal NPK-PCZ fertilizer containing 4.66 % N, 6.32 % \( \text{P}_2\text{O}_5 \), and 6.54 % \( \text{K}_2\text{O} \) may be synthesized from a mixture that is 50 % PCZ, 23.99 % urea, 14.61 % CaHAp, and 11.39 % MoP that is mixed and sonicated for 158.57 minutes and 30 minutes, respectively. It was found out that 53.56 % of the N, 10.18 % of the P, and 54.06 % of the K were successfully adsorbed and may be available over time.

The optimized NPK-PCZ fertilizer has a particle size range of 4105.8 nm ± 1588.6 nm thus it may not classified as a nanofertilizer. The fertilizer has homogenous particle size since it has a polydispersity index of 0.86 ± 0.42.

The process used in the synthesis of the NPK-PCZ fertilizer has a 96.89 % yield. The product is priced at Php 465.82 per kilogram, which is more expensive compared to the conventional fertilizers currently available in the market. However, this may be offset by the possible slow/controlled release property of the NPK-PCZ fertilizer.
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