An Evaluation of Phosphogypsum (PG) -Derived Nanohydroxyapatite (HAP) Synthesis Methods and Waste Management as a Phosphorus Source in the Agricultural Industry

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As a raw material, phosphorus availability in agriculture has been a critical concern in terms of phosphate rock consumption related to a price-dependent supply-demand chain. Novel approaches have been proposed for alternative phosphorus sources in agricultural applications. Although nano-hydroxyapatite (nHA) is a commonly used bioceramic material, its utilization as an alternative phosphorus fertilizer is an emerging field. Phosphogypsum (PG), a by-product of wet process phosphoric acid production, is a promising raw material for nHA production. With an approximate 300 Mton annual accumulation rate of PG puts pressure on the research for introducing alternative strategies for the resource utilization of legacy PG piles in an environment-friendly and cost-efficient manner. Valorization of PG as the calcium and phosphorus precursor in nHA production would both provide an efficient waste management strategy and low-cost raw material. This study gives a brief review of the various synthesis routes on PG-derived nHA and criticizes nHA utilization as a phosphorus fertilizer.

Keywords: nano-hydroxyapatite, phosphogypsum, phosphorus fertilizer, waste management.

1. INTRODUCTION

Worldwide growth in population triggers some cause-effect chain, including a permanently increasing demand for energy, water, and food, together with some ecological and societal challenges. Agriculture is one of the most affected areas of interest to provide the exponentially rising demand for food, and mineral fertilizers are the most promising and quick problem-solving option [1, 2]. Plant nutrition is the key point to achieve both high yield and maintain soil fertility in agricultural applications [3]. Mineral fertilizers compose of the primary and secondary nutrients together with some trace elements, and they have been applied to the soil to meet the nutrient requirement of plants in case of inadequate nutrient content in the physical structure of soil [4]. However, the use of mineral fertilizers in food production continues to increase day by day due to the insufficient production capacity of organic fertilizers.

Phosphorus (P) is one of the essential nutrients, which helps the conversion of the other nutrients to build blocks for healthy growth. Phosphorus fertilizers are the major P nutrient source for plants, in which P can be uptaken as phosphoric acid (H_3PO_4) derived phosphate salts. Thus, phosphoric acid production is the starting point of commercial phosphorus fertilizer manufacture. Industrial scale phosphoric acid production can be conducted through thermal or wet process methods [5]. Fig. 1 and Fig. 2 shows thermal and wet process methods, respectively. The thermal process allows a high-purity product yield, in which phosphoric acid is generally utilized in food and pharmaceutical applications.

The wet process, on the other hand, is defined as the dissolution of phosphate rock via sulfuric acid (H_2SO_4) at a moderate temperature range (70 – 80 °C), nitric acid (HNO_3) or hydrochloric acid (HCl) can also be utilized on some occasions [7]. Although the thermal process allows a high-purity product yield, it requires high energy cost, and corrosion problems can also be observed in the types equipments. Thus, the thermal method is not economically feasible for industrial-scale phosphoric acid production. The wet process results in a relatively low-grade purity of phosphoric acid, however the economic benefits allow the wet process method feasible for the fertilizer industry; additionally, the ease in the separation of phosphoric acid from the leachate makes wet process the current commercial method for phosphoric acid production [8].

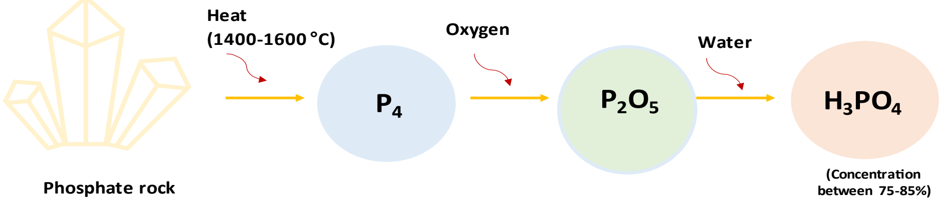

Fig. 1. Thermal process phosphoric acid production method [6]

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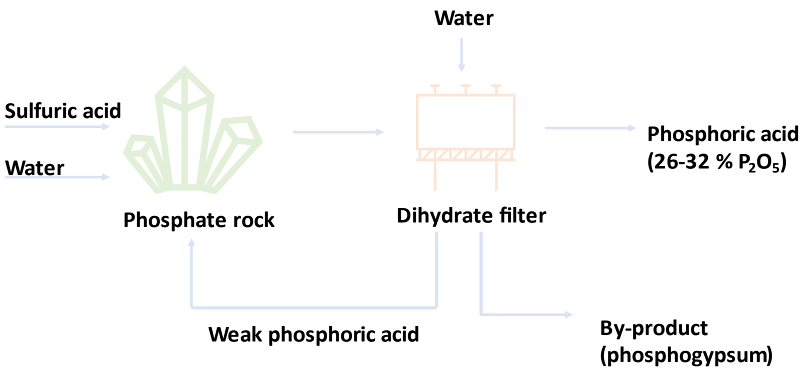

Fig. 2. Wet process phosphoric acid production method [11]

85 % of the phosphoric acid produced via the wet process is utilized in the fertilizer industry [9, 10].

Fertilizer demand forecasts help to account for a long-term plan for achieving a sustainable food chain [12]. Since the green revolution, emerging demand in mineral fertilizers, i.e. phosphate fertilizers has increased the production capacity of phosphoric acid. By the year 2023, annual phosphoric acid production is expected to increase by 50 Mtons, which also accounts for an annual 180 Mtons phosphate-rock mining [13]. Produced phosphoric acid can be used in the production of a series of both liquid or solid phosphate fertilizers, single and/or triple superphosphates (SSP, TSP) and ammonium phosphates (MAP, DAP) are the most generally used products. Fig. 3 shows a schematic illustration of phosphate fertilizers production.

Phosphate fertilizers can be readily adsorbed on the soil surface, resulting in a relatively lower migration rate to the roots of the plants. This results in an inefficient absorption and low bioavailability of the nutrients provided by the phosphorus fertilizer [14]. P uptake efficiency by conventional mineral fertilizers is reported to be in the 5 – 30 % range, resulting an excessive use of phosphate fertilizers. Additionally, the P resource in the phosphate fertilizers is based on phosphoric acid, in which the phosphate rock is the original resource of the P used in agriculture. Limited phosphate rock resources are an increasing concern, since the availability of P in the agriculture has been showing a decreasing trend related to the extensive consumption of phosphate rocks [15].

To sustain an efficient P resource availability, recycling P fertilizers from waste materials have emerged as a promising approach [16, 17]. As an industrial non-metallic waste, phosphogypsum (PG) contains Ca in $CaSO_4{\cdot}2H_2O$ form by > 90 %, and P in P_2O_5 form approximately by 1.8 – 0.9 % by mass, respectively [18, 19]. Although P_2O_5 content in PG is low, annual mass generation enables PG as a promising secondary P resource. Synthetic nano-hydroxyapatite (nHA) contains both calcium and phosphate nutrients, or trace elements such as zinc, copper, and iron can also be impregnated in the structure, resulting an enriched formulation as an alternative fertilizer. Resource utilization of PG is of importance on the economic and environmental issues. This study gives a brief review of synthesis methods of PG-derived nHA, providing a further insight into the utilization of nHA in agriculture as an alternative phosphorus fertilizer.

Phosphogypsum is in the form of $CaSO_4$ in terms of its chemical structure and is used in the production of ammonium sulfate today. However, the release of hydroxyapatite as a by-product in this process has led fertilizer manufacturers to create alternative areas of use [20]. In this sense, the use of hydroxyapatite in the agricultural industry can be considered as a new alternative for the fertilizer industry. This study, by its nature, is a comparison of different methods and aims to give an idea about the researchers' work on new methods. However, industrial-scale studies on the subject are very limited.

In this study, different synthesis methods in the literature were investigated for the use of phosphogypsum in HAP production.

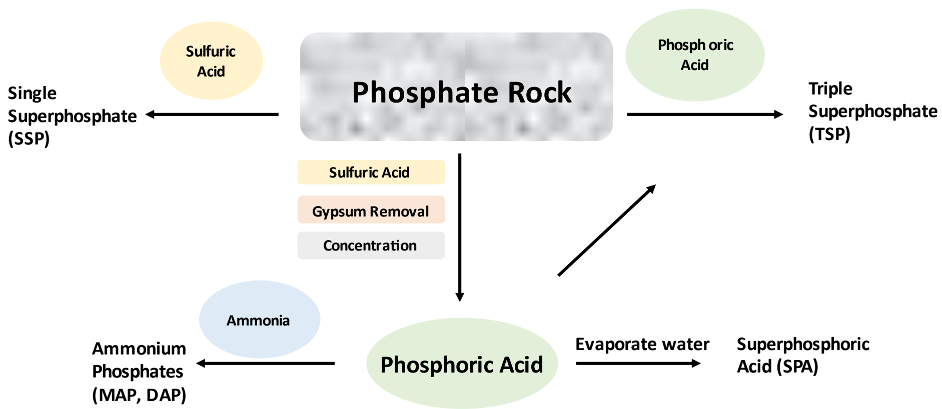

Fig. 3. Schematic illustration of the production routes of phosphate fertilizers

However, it was stated that HAP could be evaluated as an alternative fertilizer and PG used in HAP production could be considered as a secondary raw material source. Due to the compilation nature of the study, it was deemed necessary to explain the different HAP synthesis processes. Because industrial production of hydroxyapatite presents economic challenges. In this study, possible methods were evaluated, and alternative ideas were presented to the researchers.

2. RESOURCE UTILIZATION AND PHOSPHOGYPSUM

Current projections show that the annual phosphate fertilizer consumption would rise approximately by 59.16 Mtons by 2028, accounting for an annual 2.7% growth for the next decade [21]. This permanently increasing demand for phosphate fertilizers result a continuous production rate of phosphoric acid. The current commercial method for phosphoric acid production is the wet process route, resulting in the generation of a solid by-product, phosphogypsum (PG), as 4.5 – 5 folds than the desired product, phosphoric acid, by mass. The annual PG generation rate is approximately 200 – 250 Mtons, following the same growth trend as the phosphoric acid production rate [19, 22].

PG is synthetic gypsum, general structure is based on calcium sulphate dihydrate, together with some impurities such as rare-earth elements (REEs) as well as heavy metals (As, Pb, Cd), phosphate rock-based radionuclides and wet process residues such as phosphates, fluorides and some organic materials [23 – 25]. Resource utilization of the 15 % of the generated PG is generally conducted as building materials, agricultural applications, CO_2 sequestration, REEs extraction, and environmental functional materials. The rest 85 % of PG, like many other industrial by-products, is disposed as open dumps at coastal regions or discarded into the sea, posing its own environmental and ecological concerns in terms of groundwater leakages, soil, and atmosphere pollution [26 – 28].

PG has a complex and changeable structure, so it cannot be defined with a single formulation [29]. However, Ca and P can be available in the structure of PG as in $CaSO_4.2H_2O$ and P_2O_5 form, respectively. Replacement of synthetic reagents with recycled waste or residue-based materials is still an emerging area since this approach provides the utilization of waste resources together with economic and environmental advantages [30].

PG management is a rapidly emerging area of interest in environmental solid waste treatment, in which current research is focused on alternative valorization technologies. Feasible research on resource treatment and valorization technology of PG is of importance to increase the consumption and recycling rate of PG as well as reduce its environmental risks [31].

3. NANO-HYDROXYAPATITE POTENTIAL AS A PHOSPHORUS FERTILIZER

Hydroxyapatite (HA) crystals can be available both naturally and synthetically, and are one of the most popular bioceramic materials in bone tissue engineering applications i.e., bone grafting, dental implants, bioactive ceramic coatings [32, 33]. Natural HA crystals can be available in eggshells, teeth, and bones, whereas synthetic nHA crystals have a high similarity to natural HA on a chemical and crystallographic basis. The chemical and crystallographic accordance of synthetic nHA to those of natural HA makes it a promising biocompatible and bioactive functional material. Besides, synthetic nHA can also be used in various industrial applications such as catalysis, ion exchange, adsorbent and impurity removal [34, 35].

Conventional methods to produce synthetic nHA are proposed to be the precipitation technique, sol-gel method, hydrothermal synthesis, multiple emulsion method, biomimetic deposition, and electrodeposition methods [36]. Novel approaches such as microwave synthesis and atomic-layer deposition methods have been also proposed, providing the production of nHA with desirable structure and properties [37 – 39].

Although application area of synthetic nHA has been widespread, its expensive and complex synthesis methods are still a concern. Studies focusing on simple and cost-effective natural source-derived synthetic nHA synthesis have been proposed for utilization in tissue engineering applications [40]. Although synthetic nHA is a popular bioceramic material, its calcium-phosphate based chemical structure provides readily available nutrients for plants, thus utilization of nHA as a nanofertilizer has been gaining attention. Recent studies published in 2022 regarding the enhancement in the phosphorus uptake efficiency and yield by nHA fertilizer show promising results. Elsayed et al. utilized nHA particles as a phosphorus nano-fertilizer on the Rosmarinus officinalis plants compared to conventional NPK fertilizer. Results showed that the rosemary oil component yield in nHA nano-fertilizer was higher than conventional NPK, showing promising results in improving yield on rosemary plant [41]. Sharma et al. prepared zinc and magnesium doped nHA particles modified with urea to evaluate their performance as fertilizers. They reported that doping nHA particles with Zn and Mg reduced the particle size of nHA, allowing higher accommodation of urea. Nanohybrid fertilizers showed a slow-release performance, increasing dehydrogenase and urease enzyme levels in soil, without any adverse effects. Nutrient uptake efficiency in nHA hybrid fertilizers was enhanced [42].

Utilizing nHA particles as phosphorus fertilizer would trigger research on designing environment-friendly novel synthesis technologies and elaborate the release and uptake efficiency mechanisms by plants. The bioavailability of nHA particles should also be tested by long-term exposure studies [43]. By far, studies propose promising results for nHA as an alternative fertilizer, however, these studies are still in the greenhouse level and need to be supported with long-term field studies [44 – 47].

3.1. Phosphogypsum as a resource for nano hydroxyapatite production

PG, having both Ca and P in its chemical structure, can be utilized to prepare synthetic nHA as the calcium and phosphorus precursor. There have been various studies suggesting a synthesis route for nHA preparation from PG. Zhang et al. utilized the microwave irradiation method to synthesize nHA from PG. They started with 2 g of PG as a basis, added into 50 ml of 10 % hydrochloric acid and the mixture was vigorously stirred for 24 hours. After stirring, the mixture was filtered through a 0.45 µm membrane filter. pH adjustment of the filtrate was conducted with 8 % sodium hydroxide solution until pH was 9, then the solution was filtered again. The filtrate of 2nd filtration was vigorously stirred while 20 ml of 26 % diammonium phosphate solution was added slowly. pH adjustment was conducted with 8% sodium hydroxide solution until pH 11 was reached. Prepared translucent colloid was microwave irradiated at 60 °C for 4 hours in a microwave reactor of 500 W powers equipped with reflux and stirring system. After 4 hours, the solution was cooled to room temperature and filtered with a 0.45 µm membrane filter. The precipitate was washed with deionized water and ethanol, followed by vacuum-drying at 120 °C for 4 hours and then ground into fine powder. The powder was then calcined at 500 °C for 2 hours to obtain nHA particles [48]. A flowchart of the synthesis procedure is given in Fig. 4. Synthesized high-purity nHA particles had a hexagonal structure with a particle size of 20 nm × 60 nm and when reported to have good efficiency in fluoride removal applications from aqueous solutions in accordance with a pseudo-second-order kinetic model defined by the Langmuir-Freundlich equation.

Mousa and Hanna reported a simple and versatile method to synthesize nHA from PG through PG- phosphoric acid in an alkaline medium, diluted ammonium sulfate solution being the by-product of the proposed synthesis route. They firstly mixed PG with tap water and stirred the mixture vigorously at ambient temperature for 30 min to obtain a homogenous PG-water slurry. A stoichiometric amount of phosphoric acid was added, and the pH was adjusted with ammonia solution until the pH was 11. After a 1 h reaction period, the reaction medium was filtered. The cake was dried at 80 °C and calcined at 600 and 900 °C for 2 h to obtain nHA particles [49]. Fig. 5 shows the flowchart of the proposed synthesis route. nHA particles calcined at 600 °C showed poor crystallinity, whereas the crystallinity for those calcined at 900 °C showed a decomposition to the β-TCP phase. nHA particles have a particle size of around 54 – 74 nm and rod-like morphology.

Nasrellah et al. proposed a synthesis route starting with the decomposition of PG with 67 % sulfuric acid. After stirring, the slurry was filtered, and the cake was then treated with H_3PO_4 and pH adjustment was performed with NaOH until pH:11. The mixture was mechanically agitated for 48 h. Finally, the suspension was filtered, and the cake was washed with distilled water, followed by drying at 105 °C and calcined at 600 – 900 °C for 3 h. Fig. 6 shows the flowchart of the proposed synthesis route, which is similar to those which was reported by Mousa and Hanna [50]. Obtained nHA particles were reported to have a Ca:P ratio of 1.667, which is very similar to 1.67, which is found in mammalian bone structure. Synthesized nHA particles showed high crystallinity and purity.

Bensalah et al. performed a hydrothermal synthesis method route to produce nHA from PG. They treated 2 g PG with 0.3 M potassium dihydrogen phosphate solution and stirred for 30 min at ambient temperature. The pH of the solution was adjusted between 5 – 11 by 1 M NaOH solution, further 0.003-0.01 mol Brij 93 surfactant was added to the solution to obtain uniform rod-like nHA particles. Hydrothermal synthesis was performed in a Teflon lined steel autoclave container at 100, 150 and 200 °C for different reaction periods of 1, 2, 6 and 15 h.

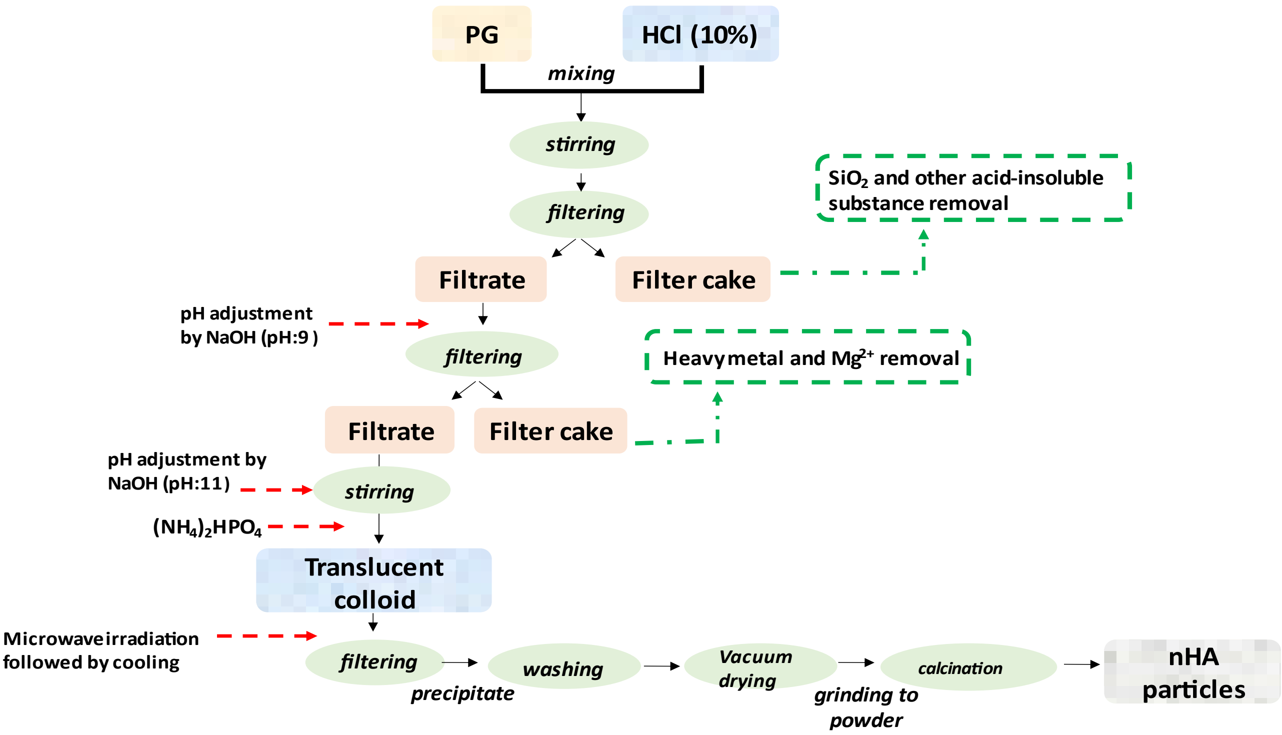

Fig. 4. nHA production process by decomposing PG with HCl based on heavy metal and Mg removal [47]

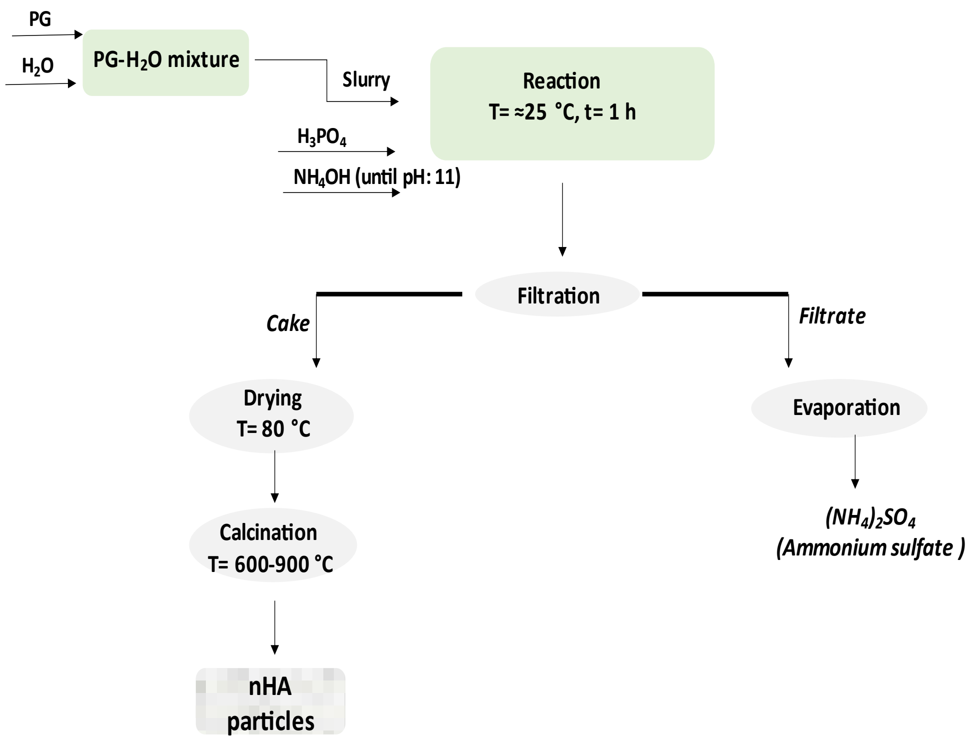

Fig. 5. nHA synthesis using water as solvent from PG by high temperature calcination process (< 900 °C) [48]

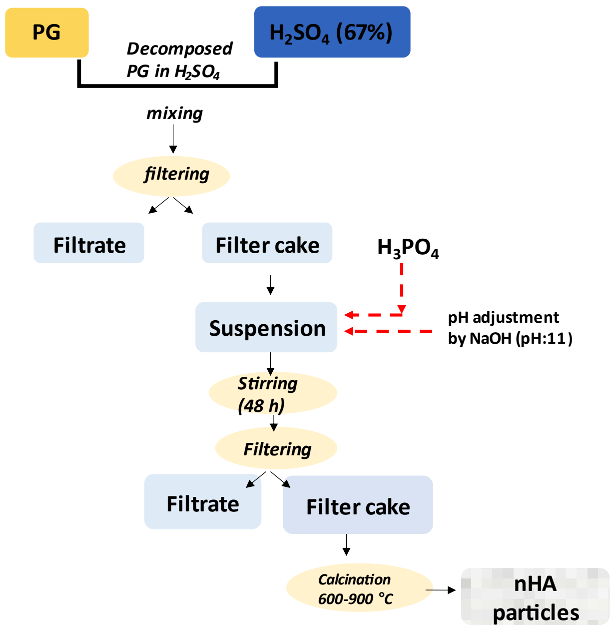

Fig. 6. Production of nHA by decomposition of PG with H_2SO_4 and calcination at high temperature (< 900 °C) [49]

After the reaction was performed, synthesis products were washed with water and ethanol, phase separation was performed by centrifugation. The cake was dried at 70 °C for 24 h [51]. Fig. 7 shows the flowchart of the proposed synthesis route. Characterization studies showed that high purity nHA could be obtained at a strong alkaline medium (pH:11) at relatively high temperatures (200 °C) and long reaction duration (15 h).

According to these synthesis routes proposed in the literature, high purity nHA particles can be successfully synthesized from PG waste. PG is generally recycled for roadbed construction or building materials manufacturing. The utilization of PG as a secondary raw material for nHA synthesis would be a novel approach to an effective waste management strategy. Synthesized nHA particles have high crystallinity, but it should be noted that there might be PG-based impurities in the structure. Pre-treatments and PG purification methods might be required for further utilization of nHA particles. Proposed synthesis routes are simple to operate, however, economic feasibility should be considered in case of scale up studies. Although studies report that obtained nHA particles might potentially be utilized in wastewater treatment applications, having a calcium- phosphate structure makes this material attractive as a phosphorus fertilizer. There are some studies regarding the phosphorus uptake efficiency upon nHA utilization in agriculture. Promising results have been obtained at the greenhouse level; however further field-scale studies are required to support the preliminary studies.

Although industrial fertilizer manufacturers make a significant effort to solve this problem, every step to be taken towards a solution is an important milestone. Because, when every idea that will be put forward is accepted to completely eliminate the problem, the importance of ideas is indisputable.

All the results reported to date on phosphogypsum heavy metal content are efforts to minimize the problem on an industrial scale and show significant differences from one another. Revealing these differences in a single study will present new ideas to researchers on the subject.

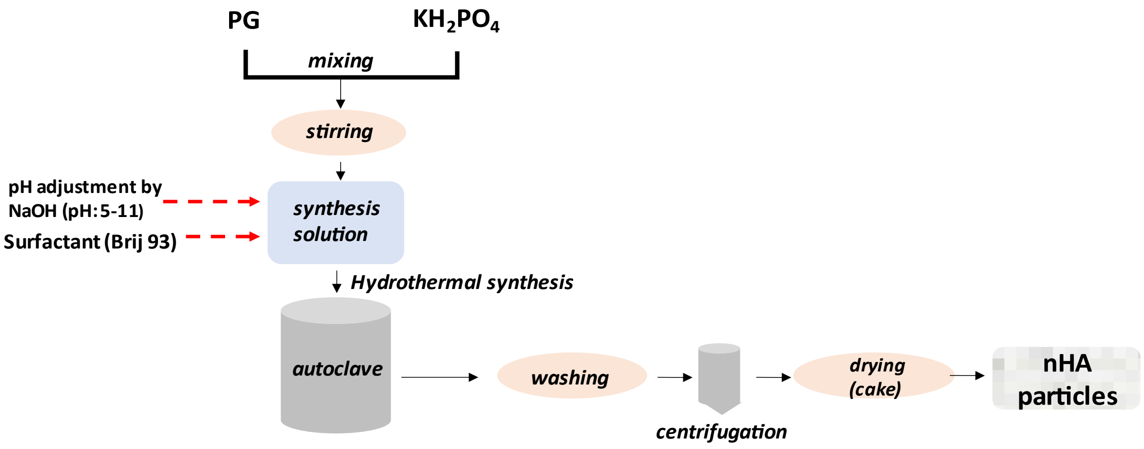

Fig. 7. Production of nHA by degradation of PG with KH_2PO_4 [50]

4. CONCLUSIONS

Phosphorus in agriculture is provided by phosphorus fertilizers, in which phosphate rocks are the primary raw material for conventional phosphorus fertilizers production. Global population increase has directly affected the annual mineral fertilizer production rate, in which phosphorus fertilizers also show an increased production capacity trend. The continued consumption of phosphate rocks has been a concern for phosphorus availability and has resulted in higher prices due to the supply of raw materials. Therefore, studies on the subject have focused on low-cost sources of phosphorus for the production of alternative phosphorus fertilizers and their effectiveness in agricultural applications. PG, which contains both calcium and phosphate in its structure, is a promising candidate for nHA production. It has been attractive to consider a waste material as a raw material. Using this industrial waste material as a secondary source ensures a sustainable waste management strategy and low-cost raw material supply. PG, having both calcium and phosphate in its structure, is a promising candidate for nHA production. Consideration of waste material as a raw material has been attractive. Utilization of this industrial waste material as a secondary resource enables a sustainable waste management strategy and low-cost raw material supply.

There have been various routes to produce nHA from PG, however the suggested application area of PG- derived nHA material is utilizated as an adsorbent in wastewater treatment. Some studies report that PG-derived nHA could be utilized for biomedical applications, however there is a possibility that nHA structure might contain PG-based impurities. Thus, to utilize in biomedical applications, effective purification methods should be employed, followed by proven performance studies. Apart from utilization in wastewater treatment or bioceramic material, nHA could also be used for agricultural applications. Recent studies have focused on strategic and efficient solutions for phosphorus supply-demand balance in agriculture. nHA is a promising alternative phosphorus fertilizer, greenhouse studies in terms of phosphorus uptake efficiency have given promising results. However, these studies should be scaled up to field studies and long-term effects should be observed for more precise evaluation.

While this study reports important studies on heavy metal removal from phosphogypsum on an industrial scale, it aims to provide researchers with alternative methods for the processes they focus on by comparing the application forms. In this respect, it is a known fact that the number of references on heavy metal removal on an industrial scale is quite limited.

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REFERENCES

1. **Roell, M.S., Zurbriggen, M.D.** The Impact of Synthetic Biology for Future Agriculture and Nutrition *Current Opinion in Biotechnology* 61 (1) 2020: pp. 102 – 109. https://doi.org/10.1016/j.copbio.2019.10.004
2. **Tian, X., Engel, B.A., Qian, H., Hua, E., Sun, S., Wang, Y.** Will Reaching the Maximum Achievable Yield Potential Meet Future Global Food Demand? *Journal of Cleaner Production* 294 (1) 2021: pp. 126285 – 12692. https://doi.org/10.1016/j.jclepro.2021.126285
3. **Barbosa, C.F., Correa, D.A., da Silva Carneiro, J.S., Melo, L.C.A.** Biochar Phosphate Fertilizer Loaded with Urea Preserves Available Nitrogen Longer than Conventional Urea *Sustainability* 14 (2) 2022: pp. 686 – 692. https://doi.org/10.3390/su14020686.
4. **Kandpal, G.** Review on Impact of Chemical Fertilizers on Environment *International Journal of Modern Agriculture* 10 (1) 2021: pp. 758 – 763.
5. **Orabi, A.H., Mohamed, B.T., Elyan, S.S.** Simultaneous Separation of Rare Earths and Valluable Actinoid Element from Wet Process Phosphoric Acid Using N-propylpropan-1-amine Extractant *Hydrometallurgy* 205 (1) 2021: pp. 105749 – 105755. https://doi.org/10.1016/j.hydromet.2021.105749
6. **Lv, L., Liao, H., Zhang, T., Tang, S., Liu, W.** Separation of Calcium Chloride from HCl Wet Process Phosphoric Acid Raffinate: Simulated and Experimental Study *SSRN* 2021: pp. 22. http://dx.doi.org/10.2139/ssrn.3971662

7. **Bouchkira, I., Latifi, A.M., Khamar, L., Benjelloun, S.** Modelling and Multi-Objective Optimization of the Digestion Tank of An Industrial Process for Manufacturing Phosphoric Acid by Wet Process *Computers & Chemical Engineering* 156 (1) 2022: pp. 107536 – 107542. https://doi.org/10.1016/j.compchemeng.2021.107536
8. **Li, H., Ge, W., Zhang, J., Kasomo, R.M., Leng, J., Weng, X., Chen, Q., Gao, Q., Song, S., Xiao, L., Tian, C.** Control Foaming Performance of Phosphate Rocks Used for Wet-Process of Phosphoric Acid Production by Phosphoric Acid *Hydrometallurgy* 195 (1) 2020: pp. 105364 – 105372. https://doi.org/10.1016/j.hydromet.2020.105364
9. **Karshiev, B., Seytnazarov, A., Alimov, U., Namazov, S., Reymov, A., Rasulov, A.** Purification of Wet Process Phosphoric Acid by Desulfurization and Ammonization *Vaprosy Khimii I Khimicheskoi Tekhnologii* 1 (1) 2021: pp. 24 – 34. https://doi.org/10.32434/0321-4095-2021-134-1-24-34
10. **Ma, H., Feng, X., Zeng, B.** Self-Anticorrosion for the Combustion Tower of Heat Recovered Thermal Process Phosphoric Acid Production Process *Safety and Environmental Protection* 118 (1) 2018: pp. 330 – 347. https://doi.org/10.1016/j.psep.2018.07.008
11. **Abdelouahed, H.B., Reguigui, N.** Radiotracer Investigation of Phosphoric Acid and Phosphatic Fertilizers Production Process *Journal of Analytical and Nuclear Chemistry* 289 (1) 2011: pp. 103 – 111. https://doi.org/10.1007/s10967-011-1035-9
12. **Tenkorang, F., Lowenberg-DeBoer, J.** Forecasting Long-Term Global Fertilizer Demand *Nutrient Cycling in Agroecosystems* 83 (1) 2009: pp. 233. https://doi.org/10.1007/s10705-008-9214-y
13. **Bounaga, A., Alsanea, A., Lyamlouli, K., Youssef, Z., Boulif, R., Rittmann, B.E.** Microbial Transformations by Sülfür Bacteria Can Recover Value from Phosphogypsum: A Global Problem and a Possible Solution *Biotechnology Advances* 57 (1) 2022: pp. 107949 – 107954. https://doi.org/10.1016/j.biotechadv.2022.107949
14. **An, T., Qin, Y., Cheng, H., Wu, J., Su, W., Meng, G., Wei, H., Sun, C., Liu, Z., Guo, X.** TiO_2-WO_3 Activated Weathered Lignite Coating Phosphate Fertilizer to Improve Longitudinal Migration Efficiency *Journal of Cleaner Production* 351 (1) 2022: pp. 131549 – 131555. https://doi.org/10.1016/j.jclepro.2022.131549
15. **Avşar, C.** A Novel Assessment Strategy for Nanotechnology in Agriculture: Evaluation of Nanohydroxyapatite as an Alternative Phosphorus Fertilizer *Chemistry in Industry* 71 (5 – 6) 2022: pp. 327 – 334. https://doi.org/10.15255/KUI.2021.057
16. **Steckenmesser, D., Vogel, C., Herzel, H., Felix, R.** Thermal Treatment of Sewage Sludge for Phosphorus Fertilizer Production: A Model Experiment *Journal of Plant Nutrition* 45 (8) 2021: pp. 1123 – 1133. https://doi.org/10.1080/01904167.2021.1994595
17. **Azallou, R., Ouerghi, O., Geesi, M.H., Riadi, Y., Ait Taleb, M., Mamouni, R., Lazar, S., Kaiba, A., Kamal, M., Villain, S.** Bovine Bone-Derived Natural Hydroxyapatite-Supported Zncl2 as a Sustainable High Efficiency Heterogenous Biocatalyst for Synthesizing Amidoalkyl Naphthols *Journal of Physics and Chemistry of Solids* 163 (1) 2022: pp. 110533 – 110542. https://doi.org/10.1016/j.jpcs.2021.110533
18. **Wang, J., Dong, F., Wang, Z., Yang, F., Du, M.** A Novel Method for Purification of Phosphogypsum, Physicochemical *Problems of Mineral Processing* 56 (5) 2020: pp. 975 – 983. https://doi.org/10.37190/ppmp/127854,
19. **Calderon-Morales, B.R.S., Garcia-Martinez, A., Pineda, P., Garcia-Tenorio, R.** Valorization of Phosphogypsum in Cement-Based Materials: Limits and Potential in Eco-Efficient Construction *Journal of Building Engineering* 44 (1) 20221: pp. 102506 – 102512. https://doi.org/10.1016/j.jobe.2021.102506
20. **Nakagawa, H., Ohta, J.** Phosphorus Recovery from Sewage Sludge Ash: A Case Study in Gifu, Japan *In Phosphorus Recovery and Recycling* 2019: pp. 149 – 155.
21. **Al Rawashdeh, R.** Estimating Short-Run (Sr) and Long-Run (Lr) Demand Elasticities of Phosphate *Mineral Economics* 664 (1) 2022: pp. 1 – 10. https://doi.org/10.1007/s13563-021-00294-z
22. **Cao, Y., Cui, Y., Yu, X., Li, T., Chang, I., Wu, J.** Bibliometric Analysis of Phosphogypsum Research from 1990 to 2020 Based on Literatures and Patents *Environmental Science and Pollution Research* 28 (1) 2021: pp. 66845 – 66857. https://doi.org/10.1007/s11356-021-15237-y
23. **Chernysh, Y., Yakhnenko, O., Chubur, V., Roubik, H.** Phosphogypsum Recycling: A Review of Environmental Issues, Current Trends, and Prospects *Applied Sciences* 11 (4) 2021: pp. 1575 – 1582. https://doi.org/10.3390/app11041575
24. **Silva, L.F.O., Oliveira, L.S., Crissien, T.J., Santosh, M., Bolivar, J., Shao, L., Dotto, G.L., Gasparotto, J., Schindler, M.** A Revire on The Environmental Impact of Phosphogypsum and Potential Health Impacts Through the Release of Nanoparticles *Chemosphere* 286 (1) 2022: pp. 131513 – 131522. https://doi.org/10.1016/j.chemosphere.2021.131513
25. **Ben Moussa, K., Eturki, S., Van Poucke Bode, S., De Grave, J., Van Ranst, E., Tack, F.M.G., Moussa, M.** Evaluating the Adsorptive Capacity of Three Tunisian Clays Deposits for Several Potentially Toxic Metals in Phosphogypsum Waste *Arabian Journal of Geosciences* 15 (1) 2022: pp. 911 – 923. https://doi.org/10.1007/s12517-022-10073-x
26. **Wu, F., Ren, Y., Qu, G., Liu, S., Chen, B., Liu, X., Zhao, C., Li, J.** Utilization Path of Bulk Industrial Solid Waste: A Review on The Multi-Directional Resource Utilization Path of Phosphogypsum *Journal of Environmental Management* 313 (1) 2022: pp. 114957 – 114962. https://doi.org/10.1016/j.jenvman.2022.114957
27. **El Zrelli, R., Rabaoui, L., Abda, H., Daghbouj, N., Perez-Lopez, R., Castet, S., Aigouy, T., Bejaoui, N., Courjault-Rade, P.** Characterization of the Role of Phosphogypsum Foam in the Transport of Metals and Radionuclides in the Southern Mediterranean Sea *Journal of Hazardous Materials* 363 (1) 2019: pp. 258 – 267. https://doi.org/10.1016/j.jhazmat.2018.09.083
28. **Nizeviciene, D., Vaiciukyniene, D., Vaitkevicius, V., Rudzionis, Z.** Effects of Waste Fluid Catalytic Cracking on the Properties of Semi-Hydrate Phosphogypsum *Journal of Cleaner Production* 137 (1) 2016: pp. 150 – 156. https://doi.org/10.1016/j.jclepro.2016.07.037
29. **Fan, P., Zhang, M., Zhao, M., Peng, J., Gao, K., Huang, J., Yi, W., Zhu, C.** The Influence of Soluble Phosphorus on Hydration Process and Mechanical Properties of Hemihydrate Gypsum under Deep Retarding Condition Materials 15 (7) 2022: pp. 2680 – 2687. https://doi.org/10.3390/ma15072680

30. **Kalbarczyk, M., Szczes, A., Kantor, I., May, Z., Sternik, D.** Synthesis and Characterization of Calcium Phosphate Materials Derived from Eggshells from Different Poultry with and without the Eggshell Membrane *Materials* 15 (3) 2022: pp. 934 – 942. https://doi.org/10.3390/ma15030934

31. **Brückner, L., Elwert, T., Schirmer, T.** Extraction of Rare Earth Elements from Phospho-Gypsum: Concentrate Digestion, Leaching, and Purification *Metals* 10 (1) 2020: pp. 131 – 142. https://doi.org/10.3390/met10010131

32. **Maghsoodi, M.R., Ghodszad, L., Lajayer, B.A.** Dilemma of Hydrpxyapatite Nanoparticles as Phosphorus |Fertilizer: Potentils, Challenges and Effects on Plants *Environmental Technology & Innovation* 19 (1) 2020: pp. 100869 – 100875. https://doi.org/10.1016/j.eti.2020.100869

33. **Halim, N.A.A.., Hussein, M.Z., Kandar, M.K.** Nanomaterials-Upconvertes Hydroxyapatite for Bone Tissue Engineering and a Platform for Drug Delivery International Journal of Nanomedicine 16 (1) 2021: pp. 6477 – 6496. https://doi.org/10.2147/IJN.S298936

34. **Mousa, S.M., Ammar, N.S., Ibrahim, H.A.** Removal of Lead Ions Using Hydroxyapatite Nano-material Prepared from Phosphogypsum Waste *Journal of Saudi Chemical Society* 20 (3) 2016: pp. 357 – 365. https://doi.org/10.1016/j.jscs.2014.12.006

35. **Aslan, N., Özçayan, G.** Adsorptive Removal of Lead-210 Using Hydroxyapatite Nanopowders Prepared from Phosphogypsum Waste *Journal of Radioanalytical and Nuclear Chemistry* 319 (1) 2019: pp. 1023 – 1028. https://doi.org/10.1007/s10967-018-6388-x

36. **Kumar, A.N.** Hydroxyapatite Synthesis Methodologies: An Overview *International Journal of ChemTech Research* 2 (2) 2010: pp. 903 – 907.

37. **Yang, Z., Jiang, Y., Wang, Y., Ma, L., Li, F.** Preparation and Thermal Stability Analysis of Hydroxyapatite Derived from the Precipitation Process and Microwave Irradiation Method *Materials Letters* 58 (27 – 28) 2004: pp. 3586 – 3590. https://doi.org/10.1016/j.matlet.2004.06.046

38. **Kalita, S.J., Verma, S.** Nanocrystalline Hydroxyapatite Bioceramic Using Microwave Radiation: Synthesis and Characterization *Materials Science and Engineering: C* 30 (2) 2010: pp. 295 – 303. https://doi.org/10.1016/j.msec.2009.11.007

39. **DileepKumar, V.G., Sridhar, M.S., Aramwit, P., Krut'ko, V.K., Musskaya, O.N., Glazov, I.E., Reddy, N.** A Review on the Synthesis and Properties of Hydroxyapatite for Biomedical Applications *Journal of biomaterials Science, Polymer Edition* 33 (2) 2021: pp. 229 – 261. https://doi.org/10.1080/09205063.2021.1980985

40. **Arokiasamy, P., Abdullah, M.M.B., Rahim, S.Z.A., Luhar, S., Sandu, A.V., Jamil, N.H., Nabialek, M.** Synthesis Methods of Hydroxyapatite from Natural Sources: A Review *Ceramics International* 48 (11) 2022: pp. 14959 – 14979. https://doi.org/10.1016/j.ceramint.2022.03.064

41. **Elsayed, A.A., El-Gohary, A., Taha, Z.K., Farag, H.M., Hussein, M.S., AbouAitah, K.** Hydroxyapatite Nanoparticles as Novel Nano-Fertilizer for Production of Rosemary Plants *Scientia Horticulturae* 295 (1) 2022: 110851 – 110857. https://doi.org/10.1016/j.scienta.2021.110851

42. **Sharma, B., Shrivastava, M., Afonso, L.O.B., Soni, U., Cahill, D.M.** Zinc- and Magnesium-Doped Hydroxyapatite Nanoparticles Modified with Urea as Smart Nitrogen Fertilizers *Applied Nano Materials* 5 (5) 2022: pp. 7288 – 7299. https://doi.org/10.1021/acsanm.2c01192

43. **Abdelmigid, H.M., Morsi, M.M., Hussein, N.A., Alyamani, A.A., Alhuthal, N.A., Albukhaty, S.** Green Synthesis of Phosphorus-Containing Hydroxyapatite Nanoparticles (Nhap) as a Novel Nano-Fertilizer: Preliminary Assesment on Pomegranate (Punica granatum L.) *Nanomaterials* 12 (1) 2022: pp. 1527 – 1533. https://doi.org/10.3390/nano12091527

44. **Taşkın, M.B., Şahin, Ö., Taşkın, H., Atakol, O., İnal, A., Güneş, A.** Effect of Synthetic Nano-Hydroxyapatite as an Alternative Phosphorus Source on Growth and Phosphorus Nutrition of Lettuce (lactuca sativa l.) Plant *Journal of Plant Nutrition* 41 (9) 2018: pp. 1148 – 1154. https://doi.org/10.1080/01904167.2018.1433836

45. **Tang, S., Fei, X.** Refractory Calcium Phosphate-Derived Phosphorus Fertilizer Based on Hydroxyapatite Nanoparticles for Nutrient Delivery *Applied Nanomaterials* 4 (2) 2021: 1364 – 1376. https://doi.org/10.1021/acsanm.0c02921

46. **Li, C., Rippner, D.A., Manavalan, L.P., Parikh, S.J.** Evaluation of Bacillus Seed Coatings on Soybean Phosphorus Uptake in an Oxisol Fertilized with 32p-Labeled Hydroxyapatite *Plant and Soil* 464 (1) 2021: pp. 273 – 287. https://doi.org/10.1007/s11104-021-04941-w

47. **Gypser, S., Freese, D.** Phosphorus Release from Vivianite and Hydroxyapatite by Organic and Inorganic Compounds *Pedosphere* 30 (2) 2020: pp. 190 – 200. https://doi.org/10.1016/S1002-0160(20)60004-2

48. **Zhang, D., Luo, H., Zheng, L., Wang, K., Li, H., Wang, Y., Feng, H.** Utilization of Waste Phosphogypsum to Prepare Hydroxyapatite Nanoparticles and Its Application Towards Removal of Fluoride from Aqueous Solution *Journal of Hazardous Materials* 241 (1) 2012: pp. 418 – 426. https://doi.org/10.1016/j.jhazmat.2012.09.066

49. **Mousa, S., Hanna, A.** Synthesis of Nano-Crystalline Hydroxyapatite and Ammonium Sulfate from Phosphogypsum Waste *Materials Research Bulletin* 48 (2) 2013: pp. 823 – 828. https://doi.org/10.1016/j.materresbull.2012.11.067

50. **Nasrellah, H., Yassine, I., Hatimi, B., Joudi, M., Chemaa, A., El Gaini, L., Hatim, Z., El Mhammedi, M.A., Bakasse, M.** New Synthesis of Hydroxyapatite from Local Phosphogypsum *Journal of Materials and Environmental Sciences* 8 (9) 2017: pp. 3168 – 3174.

51. **Bensalah, H., Bekheet, M.F., Younssi, S.A., Ouammou, M., Gurlo, A.** Hydrothermal Synthesis of Nanocrystalline Hydroxyapatite from Phosphogypsum Waste *Journal of Environmental Chemical Engineering* 6 (1) 2018: pp. 1347 – 1352. https://doi.org/10.1016/j.jece.2018.01.052