



## Review

# Phosphorus sorption and recovery using mineral-based materials: Sorption mechanisms and potential phytoavailability



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## ABSTRACT

Recovery and re-use of P within hitherto unexploited waste streams may serve to reduce pressure on limited phosphate rock reserves. Since the mid-20th century there has been a dramatic increase in the use of mined phosphate rock for food production. Although economically exploitable quantities of phosphate rock are found in several countries, food security in those areas without domestic phosphate rock reserves is potentially vulnerable. Development and utilisation of efficient, cost-effective techniques for P recovery from solid and liquid waste materials may also reduce energy and/or material requirements for P acquisition. Phosphorus may be removed from solution via selective sorption to a solid phase and direct use of the material as a fertilizer or soil conditioner, or the sorbed P may subsequently be stripped from the solid sorbent and chemically precipitated as a high-purity fertilizer. Ideal sorbents for P recovery from solution possess high phosphate sorption capacity and selectivity, are capable of kinetically rapid P sorption from solution, and are stable materials resistant to degradation during both P sorption and desorption. This review provides a critical assessment of P sorption to a range of mineral-based materials and the potential application of these materials to P recovery schemes.

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## 1. Introduction

Phosphorus is essential for all living organisms and is used extensively in a variety of key cellular functions. Phosphorus is relatively rare in the lithosphere, constituting 1180 ppm on average and 0.1% of the total elemental composition (Fairbridge, 1972; Taylor, 1964), only a fraction of which is available for plant uptake. Annual application of 40–120 kg mineral P<sub>2</sub>O<sub>5</sub> fertilizer per ha (approximately 18–52 kg P/ha) are required to maintain agricultural productivity (Ott and Rechberger, 2012).

About 90% of global P demand is for food production (Smit et al., 2009). Historically, human and animal excreta, bone meal, guano and phosphate rock have been sources of P for agricultural crops; however, since the mid-20th century population growth concomitant with increased food demand and urbanisation have resulted in a dramatic increase in the use of mined phosphate rock as compared to other P sources. According to the Food and Agriculture Organization of the United Nations (UNFAO, 2006), 70–80% of the necessary future increases in crop production must come from agricultural intensification. The use of fertilizers plays a critical role in increasing yields but some estimates indicate that existing phosphate rock reserves may be depleted within 50–120 years (Cordell et al., 2009; Fixen, 2009; Smit et al., 2009). Potential responses to P scarcity may include increased cost, more efficient P use, and P recovery and re-use.

There is no substitute for P; access to a reliable, on-going P supply is essential to ensure long-term, sustainable food security. Whilst economically exploitable quantities of phosphate rock are found in several countries (IFA, 2009), food security in those areas without domestic phosphate rock reserves is potentially vulnerable in the case of global P shortfalls. Supply-side approaches to the issue of declining rock P resources include exploration and more intensive exploitation of existing phosphate rock reserves. In addition, demand for phosphate rock can be reduced via a combination of low-tech and high-tech solutions, including mitigation of soil erosion, development of more-targeted methods of fertilizer application, and the creation of new, P-efficient crops.

Along with efficient use of P fertilizers in agriculture, recovery and recycling of P from wastewater and waste materials provides a key opportunity to increase the life expectancy of global P reserves. Recovery and re-use of P within hitherto unexploited solid and aqueous waste streams may further serve to reduce pressure on limited phosphate rock reserves and may also reduce energy and/or material requirements for P acquisition. Phosphorus can potentially be removed from solution via selective sorption to a solid phase and direct use of the material as a fertilizer or soil conditioner. Alternately, the sorbed P may subsequently be stripped from the solid sorbent and chemically precipitated with Mg or Ca salts as a high-purity fertilizer. Herein, we provide a critical assessment of P sorption to a range of mineral-based materials and the potential application of these materials to P recovery schemes.

### 1.1. Phosphorus sources

#### 1.1.1. Geologic materials

Phosphate rock deposits include: sedimentary marine phosphorite deposits (phosphorites); carbonatites and alkaline igneous rocks; and guano deposits. The principal industrial mineral in all deposit types is apatite in the form of fluorapatite (Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F) or carbonate fluorapatite (Ca<sub>5</sub>(PO<sub>4</sub>CO<sub>3</sub>)<sub>3</sub>F). About 85% of the phosphate rock mined is derived from phosphorites whilst the remaining 15% comes from igneous phosphate rock resources. Secondary aluminophosphate minerals formed by apatite weathering, such as crandallite (CaAl<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>(OH)<sub>5</sub>H<sub>2</sub>O), are not suitable for phosphate extraction. Guano deposits, which are comprised of amorphous

and crystalline phosphates originally deposited in bird excrement, are primarily located on tropical coral islands and have largely been depleted.

Phosphate rock is a finite, non-renewable resource, but there is on-going debate regarding the extent of global phosphate rock reserves. The International Fertilizer Development Center (IFDC) recently estimated worldwide phosphate rock reserves of 60,000 Mt, approximately 85% of which is located in Morocco (Van Kauwenbergh, 2010). Based on current production rates of 160–170 Mt/year these reserves could last between 300 and 400 years; however, demand for increased food production concomitant with increasing global population is likely to increase the demand for synthetic P fertilizer and decrease the expected lifespan of current economic phosphate rock reserves. As the cost of phosphate rock increases in response to demand and/or as lower-cost phosphate rock deposits are depleted, suppliers can be expected to employ increasingly expensive technology and require use of additional raw materials and processing media to generate phosphate rock ore concentrates. Marginal deposits and alternative technologies may become economically viable when the phosphate concentrate price increases.

#### 1.1.2. Mining residues

The efficiency of phosphate rock mining and processing varies between locations; however, processing of phosphate rock generates a substantial quantity of residues which can be categorised as waste rock, phosphatic tailings, phosphogypsum, and process water. A recent study in China, one of the world's largest producers and consumers of P fertilizers, showed 39% P resource use efficiency in 2003 (Zhang et al., 2008). For each tonne of phosphate rock mined 0.39 t P was used to produce fertilizer, 0.56 t was discarded at the mine site and 0.05 t was manufacturing waste.

For each tonne of phosphate processed from phosphate rock, 3–6 tonnes of phosphogypsum are generated, and global phosphogypsum stockpiles are increasing by >110 Mt per annum (Lottermoser, 2010; Wissa, 2003). Phosphogypsum is commonly stored in large piles near the processing facilities. Process waters from phosphate rock processing are typically disposed along with phosphogypsum; thus, phosphogypsum stockpiles contain very low pH waters potentially enriched in fluoride, sulphate, phosphate, ammonia, radionuclides, metals and/or metalloids (Lottermoser, 2010). There are currently few approved uses for phosphogypsum due to impurities contained within the material.

### 1.2. Wastewater

Introduction of excessive P to water bodies from non-point and point sources including the release of untreated or inadequately treated domestic, municipal or industrial wastewater can significantly alter the ideal stoichiometric Si:N:P nutrient ratio of 16:16:1 in aquatic systems (Redfield, 1958), resulting in eutrophication. Various techniques such as chemical precipitation, adsorption, reverse osmosis, biological removal, and constructed wetlands have been employed to remove P from water. Research in the area of P recovery by chemical precipitation has largely focused on the recovery of struvite (NH<sub>4</sub>MgPO<sub>4</sub>·6H<sub>2</sub>O), particularly in the case of domestic wastewater treatment.

The main commercial process for P removal from wastewater effluent is chemical precipitation with Fe, Al or Ca, which involves the addition of cationic salts to water containing phosphate, precipitation of insoluble phosphate complexes, and separation of precipitates from the aqueous phase. Although some P-containing precipitates may be recycled through land application of sludge commercial chemical precipitation of P from wastewater does not generate a valuable product as P is removed along with various other compounds and materials, some of which are toxic.

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