

RECOVERY AND REUSE OF PHOSPHORUS FROM WASTEWATER SOURCES

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Abstract

Phosphorus is a major nutrient for all organisms on earth and has no known substitute. Each year approximately 14×10^6 Mg is applied to arable soils internationally, mostly from mined P. Phosphate rock is a finite resource. It is estimated that phosphate rock reserves will near exhaustion within 70 years at current rates of use. Uncontrolled exploitation of the mineral is likely to lead to a significant increase in the cost of P fertilizers making it out of reach for developing countries. Sustainable resource management including P fertilizer and water is critical for global food security. P recovery by waste water irrigation is cost-effective but not efficient in its application to agricultural land. Approximately 65 % of mined P becomes animal waste; 40% from livestock and 15% to human wastewaters. Recovery from these organic waste streams is the likely source of P recycling for global P sustainability. Although there are increasing numbers of experimental techniques for P recovery from waste waters, such as adsorption to cheap adsorbents and ion exchangers, the most readily applicable techniques involve precipitation of P from wastewaters as Ca or Mg salts. Presently no process competes with P market prices for phosphate rock, although refinements and increasing prices of phosphate rock may result in P extraction from wastewaters becoming economical. Recycling/reuse of P from effluent and innovative means of using this source of P requires considerable research.

Introduction

It has long been recognised that phosphate-based fertilizers are essential and critical nutrients that have helped drive agricultural gains in the past century. All life forms require phosphorus in the form of phosphate, which has an essential role in RNA and DNA and in cellular metabolism. With a growing population, increasing GDP levels and improving lifestyles, there is an ever increasing demand for food production which is only sustainable provided there is adequate supply of all major and minor nutrients. There is no known substitute for phosphorus in agriculture. If soils are deficient in phosphorus, food production is restricted unless this nutrient is added in the form of fertilizer. Hence, to increase the yield of plants grown for food, an adequate supply of phosphorus is essential. With the increased demand for P based fertilizers together with the dwindling sources of phosphate rock, the world may soon run out of P base fertilizers. In a recent workshop in London, the life expectancy of phosphate rock was claimed to be approximately 70 years.

In an excellent article focusing on “The disappearing Nutrient” Gilbert (2009) states that “Every year, China, the United States, Morocco and other countries mine millions of tonnes of phosphate from the ground, the bulk of which is turned into fertilizer for food crops. But such deposits are a finite resource and could disappear within the century.” This is further supported by a recent UNEP report on phosphorus and food production by Syers et al. (2011), in which following a critical analyses of the current state of play on phosphorus these researchers report that “Phosphorus is essential for food production, but its global supply is limited. Better insight is needed into the availability of this non-renewable resource and the environmental consequences associated with its use”.

No matter how limited the supply of primary materials (rock phosphate) is for the production of P based fertilizer, it is highly unlikely that P use for global food production will decline in the new future. This together with the increase in world population that global phosphorus scarcity will be one of the major factors along with water and energy that could threaten global food security. Despite this there have been limited attempts to address global P scarcity. Optimizing agricultural practices while exploring innovative approaches to sustainable use can reduce environmental pressures and enhance the long-term supply of this important nutrient. Clearly, the diminishing supply of phosphate rock is the ticking time bomb that if not managed will severely impact sustainable food production and through this global food security.

In this paper we address major opportunities for enhancing the continued supply of rock phosphate by developing strategies that minimise the use of P based fertilizers. We encourage recovery and reuse of phosphorus from municipal and other waste products and in the efficient use in agriculture of both phosphatic mineral fertilizer and animal manure

Sustainable P

The solution to P shortage in food production systems lie in recapturing and recycling phosphorus, moving it from where there is too much to where there is too little, and developing ways to use it more efficiently. Many strategies are simple and readily available, (Elser and Bennett, 2011). In the past, phosphorus recycling and reuse has involved application of organic waste products after appropriate treatment to soils as an organic amendment. Obvious examples of this include sewage sludge and biosolid application to agricultural and degraded lands (Park et al., 2011). A major problem with this manner of recycling is the association of organic P with inorganic and organic contaminants, and also, the undefined content and availability of encapsulated P. Phosphorus is increasingly being extracted from alternative sources for application as a commercial P fertilizer. Alternative sources of P include municipal waste streams, intensive livestock manure and waste streams such as swine and dairy, animal (abattoir) and vegetable processing plants and industrial by products.

Wastewater treatment plants (WWTP) and animal husbandry facilities are the two most important sources of P for recycling. Despite municipal wastewater representing the greatest source of recycled water compared to farm effluent, P concentrations in wastewater are

typically low. Phosphorus concentrations in municipal wastewater are typically 5-10 mg L⁻¹. Farm effluents, particularly piggery wastewater, contain substantially higher concentrations of P and orthophosphate, reaching in excess of 200 mg L⁻¹ and as high as 2400 mg L⁻¹ P. Piggery effluent in the US produces on average 0.16 kg P/Mg animal weight/day (Çelen et al., 2007). In addition, concentrations of P in animal wastes are substantially higher than what is consumed by humans. Approximately 40% of mined P is contained within animal wastes annually. Only 15% of mined P is estimated to flow through WWTPs (7 % solids, 8% discharged) (Cordell et al., 2009; Rittmann et al., 2011).

The dominant end-use of mined phosphorus resources is the agricultural fertiliser industry. Only around 20% of the phosphorus supplied to agriculture is transferred into agricultural products, of which, only 8% of this is then found in municipal wastewaters. Thus P recycling should address agriculture, food processing and other uses of P as well as domestic wastewaters. Although the P “loss” from wastewater is proportionally low to other areas, P recycling from treatment plants represents an accessible and large source of P. In countries which contain significant areas of arid agricultural land, reuse of wastewater represents a critical irrigation and fertilizer source. In Australia, ~3,300 GL/yr of domestic effluent is discharged and in New Zealand, ~550 GL/yr of domestic effluent is discharged into surface waters. The total mass of P from effluents in Australia per annum is approximately 5 x10⁶ Mg P and in New Zealand 0.4 x10⁶ Mg P. In comparison to P discharge, the total use of fertilizer P in Australia and New Zealand is 0.28 x10⁶ Mg P and NZ = 0.04 x10⁶ Mg P, respectively. Thus the amount P from domestic effluent exceeds agricultural demand by approximately 10-20 fold. Wastewater and biosolids are increasingly used for local agricultural activities, but still large quantities of water and nutrients are lost. The reuse of wastewater for irrigation of agricultural land provides two essential elements of agricultural production: nutrients and water.

Applying wastewater effluent and solid wastes such as biosolids or manure to soil as P fertilizer is a simple and cost effective method of recycling P. Indeed, this has been utilized for many hundreds of years and is likely to continue into the distant future. Organic waste provides numerous additional soil conditioning benefits that inorganic fertilizers do not (Park et al., 2011). However, an important disadvantage is that the bioavailability and solubility of P is not well defined. Phosphorus release from organic species to “available” species will take an often unknown time frame. The presence of P in organic and unknown organic-P species may result in significant losses from agricultural land as runoff or leaching (Phillips, 2002). Increasingly, the extraction of P from wastewaters and solids from waste is aimed at inorganic P fertilizers which can be sold and used commercially.

Phosphorus in waste streams is usually found as organic species, including fragments of plant or animal tissue, nucleic acids, phospholipids etc. Conversion of organic-P from waste materials to commercial fertilizer products with definable solubilities thus demands conversion of organic P to inorganic P forms (Rittmann et al., 2011). Extraction of P from wastewaters can be done from several sources, including liquid phase after separation, effluent (main stream), dewatered or dried sewage sludge and sewage sludge ash or similar

(Levlin et al., 2002). Supercritical water oxidation (SCWO) is increasingly been considered for treatment of wastewater streams and P recovery (Rittmann et al., 2011; Stark et al., 2006).

The low solubility of P mineral phases can be utilized for separation of P from waste water streams:

Calcium (Apatites):



(Stumm and Morgan, 1996)

Struvite:



(Ronteltap et al., 2007)

Struvite precipitation in wastewater occurs spontaneously when sufficient Mg is present in wastewaters. Struvite ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$) in wastewater treatment plants tends to form obstructive scales in pipes and pumps, causing reductions in plant efficiency and elevated maintenance costs. Urine separating toilets have been proposed as a method of recovering P since between 50-80% of P excreted by humans is in urine (Ronteltap et al., 2007). Urine is also has the advantage of being a simpler chemical matrix than raw effluent. Precipitation of P from urine also provides more reliable and pure P salts compared to raw wastewater effluents. The mineral phases which have been recovered with some success includes struvite (an NH_4 and Mg salt), apatites (Ca-P and Ca-P-OH salts) and Ferric phosphate salts ("KREPRO" (Kemwater Recycling PROcess) (Rittmann et al., 2011). Although urine-based precipitation of apatites and struvite has been proposed, separation of struvite, ferric phosphates and apatites can be separated from mixed systems. The precipitation of struvite and utilization as a slow release fertilizer has been commercialized as OSTARA PEARL, which utilizes a fluidized bed reactor to precipitate and separate effluent from struvite crystals. Similarly, Suzuki et al. (2007) demonstrated struvite separation with high purity (95%) from swine wastewater over a 3.5 year period. Struvite solubility is low in water (Eq. 2), however has been shown to dissolve slowly over time in soil environments. Plant growth from struvite application is comparable to conventional P applications from phosphate rock. In contrast, Ca-P salts produced significantly lower plant yield in comparison to rock phosphate and struvite (Rittmann et al., 2011).

Recovery of P from the solids of municipal waste streams is generally very efficient, with most solid recovery processes exceeding 80% of total P (Balmér, 2004). Phosphorus is extracted after sludge has been dried, ashed or otherwise treated using chemical methodologies. Incineration and drying reduce the volume of sludge requiring treatment and increasing P concentrations (sludge: ~10 - 64 g/kg DM) in the sludge. The most common methods involve leaching sludge or ash with dilute acid (hydrochloric acid or sulfuric acid) or

alkaline solutions. Extraction of P is followed by a precipitation reaction using Fe, Ca or Mg, however, Ca and Mg is the preferred salts (Rittmann et al., 2011). For example, the BioCon process incinerates the sludge or dries under heat, leaches the residue with sulfuric acid before separating a range of by-products (Fe, heavy metals) using ion exchange resins (Levlin et al., 2002). Despite the use of Ca and Mg/NH₄ salts for P recovery from wastewaters, no process is presently able to compete with conventional sources of P supply to the market (Balmér, 2004; Rittmann et al., 2011). Other mechanisms of P removal such as ion exchange and adsorption to cheap innovative materials directly from wastewater remain largely at the laboratory stage of development (Rittmann et al., 2011). Recycling/reuse of P from effluent and innovative means of using this source of P requires considerable research to decrease recovery costs.

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