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Valorisation of N and P from waste water by using natural reactive hybrid sorbents: Nutrients (N,P,K) release evaluation in amended soils by dynamic experiments

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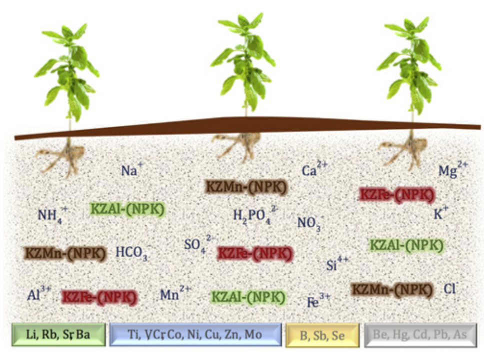
HIGHLIGHTS

- Modified natural zeolites remove ammonium and phosphate from a real wastewater effluent.
- Loaded zeolites were used for soil amendment application.
- Slow nutrient release was revealed by soils amended with loaded zeolites.

GRAPHICAL ABSTRACT



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ABSTRACT

The removal of nutrients (nitrogen (N), phosphorous (P)) from waste water has become a resource recovery option in recent regulations worldwide, as observed in the European Union. Although both of these nutrients could be recovered from the sludge line, >70–75% of the N and P is discharged into the water line. Efforts to improve the nutrient recovery ratios have focused on developing low-cost technologies that use sorption processes. In this study, a natural zeolite (clinoptilolite type) in its potassium (K) form was impregnated with hydrated metal oxides and used to prepare natural hybrid reactive sorbents (HRS) for the simultaneous recovery of ammonium (NH_4^+) and phosphate (PO_4^{3-}) from treated urban waste water. Three unfertile soils (e.g., one acidic and two basic) amended with N-P-K charged HRS were leached with deionized water (e.g. to simulate infiltration in the field) at two- and three-day time intervals over 15 different leaching cycles (equivalent to 15 bed volumes). The N-P-K leaching profiles for the three charged hybrid sorbents exhibited continuous nutrient release, with their values dependent on the composition of minerals in the soils. In the basic soil that is rich in illite and calcite, the release of potassium (K^+) and ammonium (NH_4^+) is favoured by-ion exchange with calcium (Ca^{2+}) and accordingly diminishes the release of phosphate (PO_4^{3-}) due to its limited solubility in saturated calcite solutions (pH 8 to 9). The opposite is true for sandy soils that are rich in albite (both acidic and basic), whereas the release of NH_4^+ and K^+ was limited and the values of both ions measured in the leaching solutions were below 1 mg/L. Their leaching solutions were poor in Ca^{2+}, and the release of PO_4^{3-} was higher (up to 12 mg P-PO_4^{3-}/L). The nutrient releases necessary for plant growth were provided continuously and were controlled primarily by the soil mineral dissolution rates fixing the soil aqueous solution composition (e.g. pH and ionic composition; in particular, the presence of calcite is a

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determinant for nutrient release, especially in alkaline soils). The N-P-K charged HRS sorbents that were used for soil amendment may be an alternative for avoiding nutrient leaching and reaching the goals of soil sustainability in agriculture and reducing the nutrient overloading of surface waters.

1. Introduction

Soil fertility is a crucial feature in the development of agriculture for the worldwide production of food. The essential plant macronutrients are nitrogen, phosphorus and potassium, which are known as the NPK elements (De Castro et al., 2015). Improving the soil hydraulic conductivity and porosity properties has become vital to make these nutrients available for plants (Colombani et al., 2015), and conditioning soil via organic amendments is the preferred option (Laird et al., 2010). However, inorganic amendments with the use of zeolites have been postulated as a better alternative due to their water holding capacity (Xiubin and Zhanbin, 2001), their ability to retain and release NH_4^+ and K^+ due to their high cation exchange capacity (McGilloway et al., 2003) and their ability to control drainage (Bigelow et al., 2004).

The ever increasing population has been accompanied by a complementary increase in the demand for mineral fertilizers and, accordingly, has led to increases in the production of chemicals (e.g., ammonia NH_3) and the use of non-renewable P and K. The excessive use of fertilizers has led to serious problems in the sustainability of agriculture production due to land and water resource degradation instead of simply achieving the purpose, which is to increase the crop yields. Therefore, it is clearly necessary to develop fertilizing systems that provide a complete and controlled nutrient release and simultaneously allow these nutrients to be available for uptake by plants in the short term.

Another problem is the depletion of P, which is predicted to occur in 50–100 years; however, the future availability of P sources has not received an appropriate amount of attention (Rasul and Thapa, 2004). Thus, it is important to take advantage of the opportunities for P recovery and reduce the actual demand (Cordell et al., 2009). Thus, the use of secondary sources of N and P, such as those associated with urban waste waters, has been identified as an alternative for improving soil fertility (Capra et al., 2014). Additionally, K is a macronutrient for plants; but its importance has been underestimated in the agricultural field compared with those of P and N (Simonsson et al., 2007). Sewage sludge (Verstraete et al., 2009), mono-incineration bottom ash (Kalmykova and Karlfeldt Fedje, 2013) and struvite (Su et al., 2014) are the most successful options identified to be rich in nutrients, but such options are not always technically or economically feasible and may have the potential to be banned in future (e.g., limitations on the use of sludge due to presence of emerging contaminants and soil salinization risks). New solutions to recover nutrients from more diluted streams (e.g., treated waste water) have been universally accepted with the use of NH_4^+ and PO_4^{3-} selective sorbents. Such sorbents are known to work either i) on sorption and desorption cycles to produce nutrient rich streams (Guaya et al., 2015; Thornton et al., 2007) or ii) on sorption cycles and then being used in soil amendment for agricultural applications (Gholamhoseini et al., 2013). Natural zeolites have been identified as the best inorganic material for this purpose due to their properties; they are effective sorbents that are safe and easy to work with in ion exchange applications. Zeolites are hydrated crystalline aluminium – silicate materials that include micro- and mesoporosity with alkaline cations and water in their framework structure. Recently, zeolites have received increased attention in the field of agriculture because their physical and chemical properties make them potentially suitable candidates for soil amendments and suitable carriers of plant nutrients (Król et al., 2012; Buondonno et al., 2013). However, when zeolites are applied to recover NH_4^+ from waste waters, the major drawback is their ability to be regenerated. Although several types of regeneration treatments have been studied, most of them are very expensive (Hedström, 2001). Therefore, the direct application of natural zeolites as soil amendments has been reported to be the best option for soils. These zeolites are characterized by diminished nutrient leaching, thereby providing a slow-release fertilizer application (Ming and Allen, 2001), increased crop water and usage efficiency (Gholamhoseini et al., 2013) and a reduced tendency for NH_3 volatilization (Latifah Omar et al., 2010). All traditional fertilizers, including those that are specifically manufactured for the slow release of nutrients, suffer from water leaching during rainfall and/or irrigation activities (Badruzzaman et al., 2012). Chabazite and Clinoptilolite due to their high cation exchange capacity and physical stability (Gualtieru and Passaglia, 2006; Reháková et al., 2004), have been widely used as fertilizers (Coppola et al., 2002; Hong et al., 2012). However, other widely available natural zeolites that have properties similar to those of clinoptilolite could be used as fertilizers but require extensive trials. In the field of irrigated agriculture, zeolites have been used in addition to fertilizers to retain moisture and nutrients such as N, K, Ca, magnesium (Mg) as well as other microelements in the root zone for extended periods (Polat et al., 2004).

Additionally, new management options have been developed for use as nutrient carriers from nutrient-rich waste water streams. For example, the ZeoLIFE project (Faccini et al., 2014) proposed the application of NH_4^+-charged zeolites using an Italian diagenized pyroclastic rock for soil amendment (60 wt% of chabasite mixed with an NH_4^+-rich solution of swine manure) to reduce the need for fertilizers. In a previous study, a natural zeolite in its K form was modified via the impregnation of hydrated metal oxides (HMO) of aluminium (ZKAl), iron (ZKFe) and manganese (ZKMn) for the simultaneous recovery of NH_4^+ and PO_4^{3-} from urban waste waters. However, the difficulty of regenerating these materials makes it necessary to adopt other alternatives for the further utilization of the immobilized nutrients. The novelty of this work is the use of these inorganic nutrient carrier materials, obtained as byproducts from a waste treatment process, as an additive for agricultural amendment applications. The rationale of the study was a hypothesis (Colombani et al., 2015) postulating that inorganic amendments, which improve the physical and hydraulic properties of soils, can minimize the leaching of nutrients. The development of these new products could improve their efficiency as fertilizers, enhance crop yields and provide secondary sources for fertilizers. Therefore, the aims of this work are to (a) evaluate their use as carriers for the nutrients recovered from waste water effluents and (b) assess their further application as soil amendments and slow-release inorganic fertilizers (NPK) for agricultural applications. Finally, the objectives of this study are to i) prepare phosphate and ammonium potassium-charged, metal hydrate impregnated clinoptilolite (ZKFe, ZKAl, ZKMn) from treated waste water effluent, ii) prepare soil-N-P-K mixtures to simulate soil amendment scenarios using three different types of soils (one acidic and two basics), and iii) evaluate the nutrient release rates from amended soils using both batch and column leaching experiments with deionized water.

2. Materials and methods

2.1. Soil sampling

Three different bulk soils samples were collected from the plough layer (top 30 cm) in agricultural field areas of NE Spain, as denoted in Fig. 1, three replicates were obtained from each site, and the sites were Samitier, Huesca (S1) (Longitude −1.4863; Latitude 0.0000), Alella