

ACCEPTED VERSION

Ivan B. Andelkovic, Shervin Kabiri, Rodrigo C. da Silva, Ehsan Tavakkoli, Jason K. Kirby, Dusan Losic and Michael J. McLaughlin

Optimisation of phosphate loading on graphene oxide-Fe(iii) composites-possibilities for engineering slow release fertilisers

New Journal of Chemistry, 2019; 43(22):8580-8589

This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2019

Published at: <http://dx.doi.org/10.1039/c9nj01641d>

PERMISSIONS

<http://www.rsc.org/journals-books-databases/journal-authors-reviewers/licences-copyright-permissions/#deposition-sharing>

Deposition and sharing rights

When the author accepts the licence to publish for a journal article, he/she retains certain rights concerning the deposition of the whole article. This table summarises how you may distribute the accepted manuscript and version of record of your article.

Sharing rights	Accepted manuscript	Version of record
Share with individuals on request, for personal use	✓	✓
Use for teaching or training materials	✓	✓
Use in submissions of grant applications, or academic requirements such as theses or dissertations	✓	✓
Share with a closed group of research collaborators, for example via an intranet or privately via a scholarly communication network	✓	✓
Share publicly via a scholarly communication network that has signed up to STM sharing principles	⌚	×
Share publicly via a personal website, institutional repository or other not-for-profit repository	⌚	×
Share publicly via a scholarly communication network that has not signed up to STM sharing principles	×	×

⌚ Accepted manuscripts may be distributed via repositories after an embargo period of 12 months

8 December 2020

<http://hdl.handle.net/2440/120180>

ARTICLE

Optimisation of phosphate loading on graphene oxide-Fe(III) composites – possibilities for engineering slow release fertilisers

Ivan B. Andelkovic^{a, b, *}, Shervin Kabiri^b, Rodrigo C. da Silva^a, Ehsan Tavakkoli^{a, c, d}, Jason K. Kirby^e, Dusan Losic^b and Michael J. McLaughlin^a

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Current commercially available phosphorus (P) fertilisers, which are highly soluble salts, are susceptible to surface runoff to waterways, and leaching to groundwaters where soils are light/medium textured. Here, we report the synthesis of a graphene oxide (GO)/iron (GO-Fe) composite, a promising carrier for loading P. The GO-Fe carriers loaded with P acted as slow release fertilisers with tunable loading/release properties. The amount of P loaded onto GO-Fe composite was 15%, similar to commercial products. Investigation of morphology, spectroscopic and chemical analysis revealed a complex loading mechanism of Fe onto GO. Iron, as an active center for P sorption, could interact with the oxygen functional groups at the edge of GO sheets as well as the π -electron system of the aromatic part of GO. Column perfusion studies, visualisation of P diffusion in soils and chemical analysis of soils after diffusion showed the composites to have slow-release properties. Pot experiments using wheat and our composites resulted in the same yield as using highly soluble commercial fertiliser.

Introduction

The need to produce food for more than 7 billion people has resulted in an increase of global land-based cycling of phosphorus (P). Excessive usage of P in some parts of the world and insufficient use in others has interfered with the natural P cycle. Consequences of the out of balance P cycle can be seen in major environmental issues that we are experiencing today.¹ Besides current problems with the usage of P fertilisers and with a finite amount of P being rapidly depleted, addressing P supply is an urgent priority for humanity.² Therefore, the development of new P fertiliser formulations which will increase the efficiency of nutrient usage and result in more sustainable agriculture management is a priority. Current use of P fertilisers, due to specific interactions of P with soil physical and chemical constituents, is not always efficient. For example, in soils of low P status up to 80% of applied P can become fixed into non-plant available forms in soils.³ Two of the main factors related to the specific interactions of applied P fertilisers with soils are their chemical form and solubility.^{4, 5} Research efforts for improving fertiliser efficacy have been oriented towards examination of various chemical compounds having different solubility and P release rates.⁶⁻⁸ Highly water-soluble P fertilisers have the drawback of often being fixed into non-available fractions in the soil due to the rapid

reaction/interaction of P with soil constituents (e.g. precipitation as calcium-phosphates, interaction with Fe and/or Al-oxides/hydroxides, etc.).⁹ Substantial research effort has been invested into development of slow-release fertilisers that can more closely match the plant need for nutrients during growth.¹⁰⁻¹³ Slow-release P fertilisers can be developed by coating of highly soluble P fertiliser with different organic and inorganic materials.¹³⁻¹⁶ In order to be suitable as a coating, the material needs to be inexpensive and environmentally safe, while the synthesis procedure should be simple. Ultimately, fertiliser with a desired release rate of nutrient should be obtained.

In our previous study, a graphene oxide (GO) modified with Fe(III) ions (GO-Fe) was synthesised to form a composite and examined as a carrier for P.¹⁷ Using low cost, naturally abundant materials, graphite and iron, with a simple synthesis and modification procedure, we obtained a composite material that has the potential to be tailored to meet the specific plant requirements as a slow-release P fertiliser. Identified as an active sorption site for P, Fe(III) ions, which can be bonded to different functional groups of GO, offer attachment and release of Fe and subsequently P depending on the strength of the GO-Fe bond. An initial study showed potential for use of the composite as a slow-release P fertiliser. However, as a major drawback, low P content (~5 %) was identified, similar to layered double hydroxides.^{7, 18}

The aims of this study were to further optimize loading of Fe and subsequently P onto GO as a composite granular fertiliser, determine the mechanisms involved, examine the behaviour of GO-Fe loaded with P (GO-Fe-P) as a slow-release P fertiliser in soil and compare its efficiency to a commercially available granular product.

Materials and methods

^a School of Agriculture, Food and Wine, The University of Adelaide, PMB 1, Waite Campus, Glen Osmond, SA 5064, Australia

^b School of Chemical Engineering, The University of Adelaide, SA 5005, Australia

^c NSW Department of Primary Industries, Wagga Wagga Agricultural Institute, Wagga Wagga, NSW 2650, Australia

^d Graham Centre for Agricultural Innovation, Charles Sturt University, Wagga Wagga, NSW 2650, Australia

^e CSIRO Land and Water, Environmental Contaminant Mitigation and Biotechnology Program, PMB 2, Glen Osmond, SA 5064, Australia

Graphite powder (250 μm diameter) (Eyre Peninsula, South Australia) was supplied from a local mining site. Analytical grade chemicals were used directly without further purification. High-purity water (18.2 M Ω .cm at 25 $^{\circ}\text{C}$, pH of 5.6) was used throughout the study, unless otherwise stated.

Synthesis of XGO-Fe(III) composites

Graphene oxide was prepared by oxidation of natural graphite powder (250 μm) according to the improved Hummer's method (supplementary material).^{19, 20} XGO-Fe(III) composite (where X represents initial GO concentration in mg L^{-1}) was obtained through a simple one-step reaction. Briefly, 0.50 g of GO was suspended in 5.0, 2.5, 1.0, 0.50, 0.25, 0.125, 0.050 and 0.025 L of deionised water in order to obtain 0.1, 0.2, 0.5, 1.0, 2.0, 4.0, 10.0 and 20.0 g GO L^{-1} , respectively, while the pH of the suspension was adjusted to < 2 using 1 M hydrochloric acid (HCl). FeCl_3 (1.45 g), was added to the GO suspension (GO : Fe = 1 : 1 (w/w)) as a source of Fe(III) ions, under vigorous stirring. The mixture was stirred for 1 h and then centrifuged at 2950 g (Thermo Scientific Sorval, USA) for 1 h. After centrifugation the supernatant was removed and the XGO-Fe(III) composite residue was freeze dried. No washing step was included to remove loosely bound Fe, in order to maximise the Fe content of the composite. The synthesis method was found to be repeatable across batches.

Loading of P onto XGO-Fe(III) composites

For loading of P onto the XGO-Fe(III) composite, potassium dihydrogen phosphate (KH_2PO_4) salt was used as a source of soluble P. Namely, 0.10 g XGO-Fe(III) composite was suspended in 5.0, 2.5, 1.0, 0.50, 0.25, 0.125, 0.050 and 0.025 L of deionised water in order to obtain 0.1, 0.2, 0.5, 1.0, 2.0, 4.0, 10.0 and 20.0 $\text{g XGO-Fe(III) L}^{-1}$, respectively. KH_2PO_4 salt was used as a source of P. 0.22 g of KH_2PO_4 salt was added to the suspension of GO, keeping the GO:P ratio constant (1:0.5, w/w) in the suspensions, under vigorous stirring and the pH was adjusted to 6 with sodium hydroxide (NaOH) solution. The dispersion was mixed for 1 h and then centrifuged at 2950 g for 1 h. After centrifugation, the supernatant was removed and the XGO-Fe(III) composite loaded with P (XGO-Fe-P) was freeze dried. The dried composite was homogenized using a mortar and pestle and pressed into 40 mg pellets using a desktop pill presser (TDP 5, LFA Machines Oxford Ltd, UK).

Characterisation

The morphology of the composite samples was examined using scanning electron microscopy (SEM) (Model Quanta 450, FEI, USA). Fourier-transform infrared spectroscopy (FTIR) (Nicolet 6700 Thermo Fisher, USA) was used to identify functional groups in materials by scanning in the range of 500–4000 cm^{-1} in transmission mode. Ultrasonication of 0.1, 1.0 and 10 GO g L^{-1} suspensions for SEM analysis was performed using a Branson Sonifier 450 (Emerson, USA). The duty cycle was set on 60 and

output control was 9. The suspension was placed in an ice bath and sonicated for 10 min.

Total Fe and P concentration in GO-Fe-P composites

The total concentration of Fe and P in the XGO-Fe(III) and XGO-Fe-P samples were determined using an open vessel concentrated acid digestion procedure (3.75: 1.25: 1 mL of concentrated HCl: HNO_3 : HClO_4).^{21, 22} The samples (~ 0.1 g) were added into a glass reflux tube with 6 mL of concentrated acids mixture and digested on a heating block at 140 $^{\circ}\text{C}$ for 6 h. After digestion, samples were filtered using 0.45 μm syringe filters (Sartorius) and analysed for total Fe and P concentrations using inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Spectro, Kleve, Germany). The amount of Fe, or Fe and P, loaded onto XGO-Fe(III) and XGO-Fe(III)-P composites (U), was calculated using equation (1):

$$U = \frac{CV}{m} \quad (1)$$

Where C is concentration of Fe/P measured in solution obtained after acid digestion of composite (mg L^{-1}), V is volume of solution (L), U is amount of Fe/P loaded onto XGO-Fe/XGO-Fe-P composites (mg g^{-1}) and m is mass of the composite (g). Loading experiments were performed in duplicate.

Optimization of P loading into GO-Fe(III) composite

A kinetic study was performed for the loading of P onto 10GO-Fe(III) by adding 1.06 g of KH_2PO_4 to 100 ml of suspension of GO-Fe (1.00 g) under vigorous stirring while pH was adjusted to 6 using NaOH. A fixed volume of suspension was removed from the beaker at predetermined time intervals and filtered using 0.45 μm filters to measure amount of adsorbed P.

The effect of pH was examined by suspending 0.10 g of GO-Fe composite into 10.0 mL of water followed by addition of 0.11 g of KH_2PO_4 under vigorous stirring and adjustment of initial pH in a range from 3 to 10 using NaOH solution. After 1h of mixing suspensions were filtered using 0.45 μm filters.

For the equilibrium isotherm study 0.10 g of GO-Fe composite was suspended into 10.0 mL of water, KH_2PO_4 was added in a range from 0.015 to 0.150 g of P and pH was adjusted to 6 using NaOH solution. Suspension was stirred for 1 h and then filtered using 0.45 μm filters. Concentration of P in samples was determined using ICP-OES. The P removal capacity (Q) was calculated using equation (2):

$$Q = \frac{(C_0 - C_t)V}{m} \quad (2)$$

Where C_0 is the initial P concentration (mg L^{-1}), C_t is concentration at time t (mg L^{-1}), Q is amount of P loaded onto 10GO-Fe(III) composite (mg g^{-1}), V is the suspension volume (L) and m is the mass of composite (g). Experiments were performed in triplicate.

Dissolution kinetics of P from MAP and GO-Fe-P composite fertilisers

The dissolution kinetics for P from GO-Fe-P and monoammonium phosphate (MAP), as a reference soluble P source, were conducted using a slightly modified method of Milani et al.²³ Fertiliser granules with a total mass of 20 mg of P for GO-Fe-P and MAP were placed into polypropylene columns (150 mm×15 mm) between acid-washed glass wool. A 10 mM CaCl₂ solution (pH 6) was introduced from the bottom of the columns using a peristaltic pump with a constant flow rate of 10 mL h⁻¹. A fraction collector (SuperFracTM, Pharmacia, UK) was used to collect the solutions from the top of the columns every hour for 48 h. The total P concentrations in each fraction were determined using ICP-OES. All treatments were carried out in duplicate.

The diffusion of P from GO-Fe-P and MAP fertilizer granules was examined in three soils with different physical-chemical characteristics, Port Wakefield (PW), Black Point (BP) and Monarto (M). The soils were collected from the top 10 cm of the soil profile from agricultural regions in South Australia, air dried, and sieved to <2 mm before use. Soil pH was measured in 1 : 5 soil/water extract. Soil organic carbon was measured using procedure by Matejovic.²⁴ The CaCO₃ content was determined following the procedure described by Martin and Reeve.²⁵ The cation exchange capacity (CEC) was determined by the ammonium acetate method at pH 7.0.²⁶ The oxalate-extractable Al and Fe concentration was determined according to Rayment and Higginson.²⁷

Selected physical and chemical properties of the soils used are given in Table S1. The soils were wetted to field capacity and added into Petri dishes (diameter of 5.5 cm). A GO-Fe-P pellet or a MAP granule containing ~8 mg P, was added into the centre of each Petri dish, in a 5-mm deep hole that was carefully closed after the fertiliser placement. Each treatment was performed in triplicate. The Petri dishes were incubated at 25° C, and P diffusion was visualized at 1, 3 and 7 days and every 7 days thereafter until 56 days from the application of fertilizer according to the method of Degryse and McLaughlin²⁸. Briefly, Fe-oxide impregnated paper was exposed to the soil surface for 5 to 30 min. The P onto the paper was coloured using a modified malachite-green method, and the dried papers were scanned and analysed with image processing software (GNU Image Manipulation Program, v. 2.8, Free Software Foundation, Boston, MA) to quantify the size of the P diffusion zone in soils. At day 56, the soils in Petri dishes were divided into an inner section (a circle with a 9 mm radius around the fertiliser granule) and an outer section (the soil more than 9 mm away from the fertiliser granule). The soil samples from the inner and outer sections were oven dried and homogenised using a mortar and pestle. A 1 mM CaCl₂ solution was added to the soil so that a liquid: solid ratio of 10 L Kg⁻¹ was obtained. The resulting suspensions were equilibrated on an end-over-end shaker for 3 days and 5 mL of solution was sampled after centrifuging at 2950 g for 30 min. The solution was filtered over a 0.45 µm filters. The filtered solutions were analysed by ICP-OES to determine the concentration of P.

The total concentration of fertiliser P in diffusion sections was determined by cold acid extraction with 3M HNO₃ in a liquid: solid ratio of 50 L kg⁻¹. The mixture of acid and soil was shaken

on an end-over-end shaker for 2 days and 5 mL of solution was sampled after centrifuging at 2950 g for 30 min. The solution was filtered over a 0.45 µm filters. The filtered solutions were analysed by ICP-OES to determine the concentration of P.

Pot experiment

Pot experiments were performed with wheat (*Triticum aestivum*) grown for six weeks on the three soils, PW, BP and M. Phosphorus was applied at a rate of 15 mg P kg⁻¹, either as MAP or 10GO-Fe-15P composites in pellet form. Control treatments, soils without added P, were also included. Each treatment was replicated four times. Pots (12 cm in diameter), lined with a plastic bag, were filled with 1 kg of air dried, sieved soils. Soils were moistened with basal fertiliser solution to field capacity. The basal fertiliser solution was made up using urea, KCl, MgSO₄·7H₂O, H₃BO₄, CuSO₄·5H₂O, MnCl₂·4H₂O and ZnCl₂ and supplied (in mg kg⁻¹): 50 N, 40 K, 40 Mg, 53 S, 2 B, 3 Cu, 2 Mn and 3 Zn for BP and M soils and 30 N, 20 K, 10 Mg, 13 S, 1 Cu, 1 Mn and 1 Zn for PW soil. The fertiliser granules were applied at equidistant points 3 cm below the soil surface, 2 cm from the edge of the pot. After 2 days 5 pre-germinated wheat seedlings were planted at 1 cm depth and thinned to two after 10 days. Plants were grown in a temperature controlled glasshouse at 27/10° C day/night temperature, watered daily to field capacity with pots arranged in a completely randomised design. Pot positions were randomised every 7 days. Four weeks after planting a top-up application of N (30 mg N kg⁻¹ as urea) for all three soils and Mg (10 mg Mg kg⁻¹ as MgSO₄·7H₂O) for PW and M, was done to prevent N and Mg nutrient deficiency. After six weeks of growth, shoots were harvested by cutting plants 1 cm above the soil surface, oven dried at 60° C for 48 h, and dry weight recorded. The dried material was ground, digested in a hot HNO₃ and analysed by ICP-OES.

Standard deviation, as a measure of quantitative dispersion of data sets, as well as analysis of variance (ANOVA) were obtained using SigmaPlot 12.5 software package. The difference between the means were evaluated using Tukey test. The level of significance was P ≤ 0.05.

Results and discussion

Physical and chemical characterisation

Loading of Fe(III) onto GO sheets and subsequently P (Fig. 1) increased with increase of initial GO concentration. A noticeable decrease can be seen in the concentration of Fe(III) present in XGO-Fe-P composites for X values ≤ 4 after loading of P (Fig. 1b), compared to the initial amount of Fe in XGO-Fe(III) composites (Fig. 1a). In order to gain an insight into the mechanism of Fe and P loading and explain the increase of Fe(III) sorption with increased initial GO concentration, plus explain the leaching of Fe(III) during P sorption, we first examined the morphology of 0.1, 1.0 and 10.0 g GO L⁻¹ materials as a representative of low, medium and high initial GO concentration, respectively, using SEM.

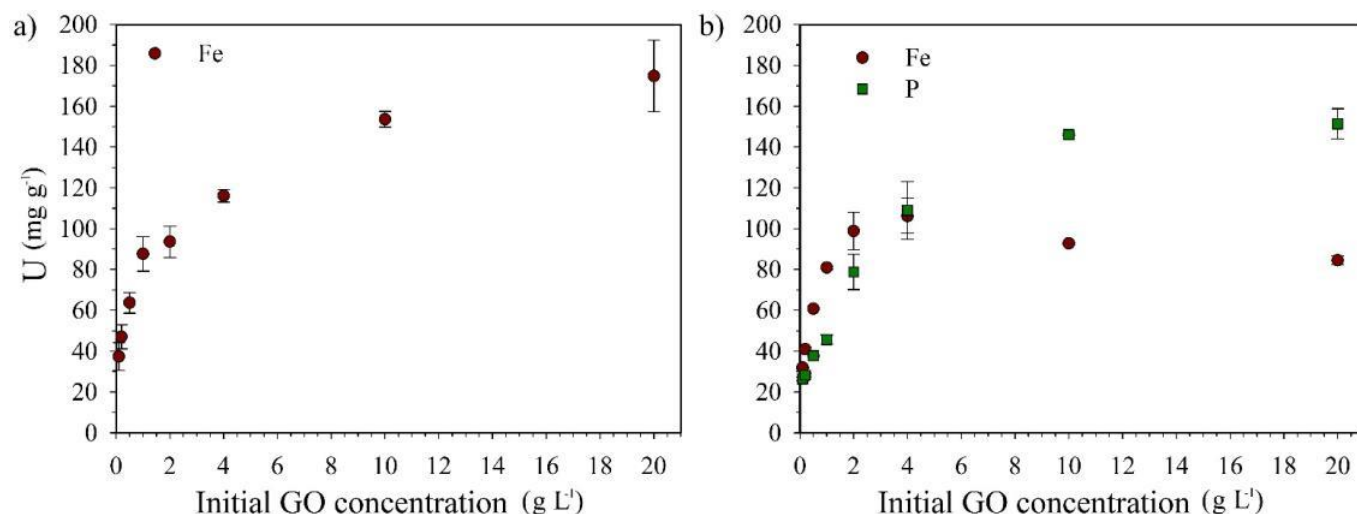


Fig. 1. Effect of initial GO concentration on the amount of loaded a) iron, b) iron and phosphorus. Error bars present standard deviations ($n = 2$).

Different morphologies of 0.1, 1.0 and 10g GO L⁻¹ samples could be the result of induced stacking of GO sheets with increasing GO concentration. Wire-like nanoscrolls forming a macroporous network can be seen for the 0.1GO sample (Fig. 2a). The mechanism of macroporous network formation can be explained by the presence of well dispersed single GO sheets which undergo conformational change into more stable forms by twisting and rolling.²⁹

Conformational changes are a result of an increased surface stress of GO sheets during growth of ice crystals in the freeze-drying process. With an increase of the initial GO concentration, aggregation of GO sheets into stacked layers and the subsequent freeze-casting process result in the formation of a mesoporous GO structure, as seen for 1GO and 10GO samples (Fig. 2b, c).²⁹ Ultrasonication of the 1 g/L GO sample resulted in disaggregation and exfoliation of GO sheets leading to the

formation of nanoscrolls and a macroporous structure, typical of the presence of well-dispersed single sheets of GO (Fig. 2d). With the addition of Fe(III) ions to the GO suspension, Fe(III)-carboxyl and Fe(III)- π -electron interactions with the carboxyl groups at the edges of the GO sheets and with the aromatic component of the GO structure, respectively, are responsible for the Fe(III) sorption.¹⁷ The strength of these interactions were examined by measuring the amount of Fe(III) after acid digestion of GO-Fe materials washed 3 times for 15 min (45 min in total) with DI water at a 1:100 solid:solution ratio (Fig. 3). Washing of GO-Fe material obtained from the reaction of Fe(III) with 0.1 g GO L⁻¹ suspension did not remove attached Fe. Low amounts of Fe(III) ions attached to the GO and their resistance to washing indicates that there is a strong interaction between Fe(III) ions and the GO surface through the small number of carboxyl groups present at the edge of individual GO sheets.³⁰ An increase of the initial GO concentration could enable intercalation of Fe(III) ions between stacked layers of GO sheets and interactions of Fe(III) ions with alkoxide and hydroxyl

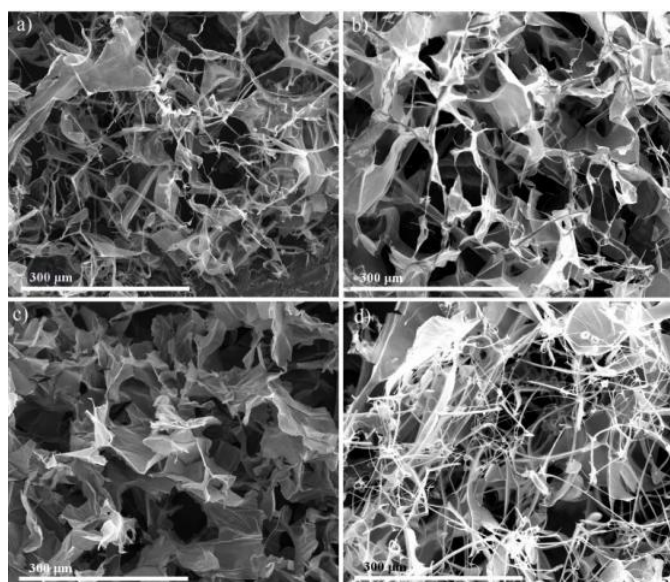


Fig. 2. SEM images of GO obtained after freeze drying of suspensions a) 0.1 g GO L⁻¹, b) 1 g GO L⁻¹, c) 10 g GO L⁻¹ and d) 1 g GO L⁻¹ (ultrasonicated).

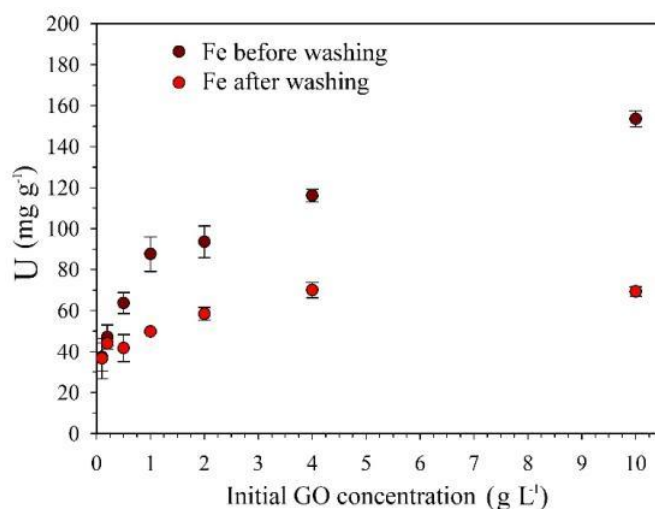


Fig. 3. Amount of loaded iron at increasing initial GO concentrations before and after washing. Error bars represent standard deviations ($n = 2$).

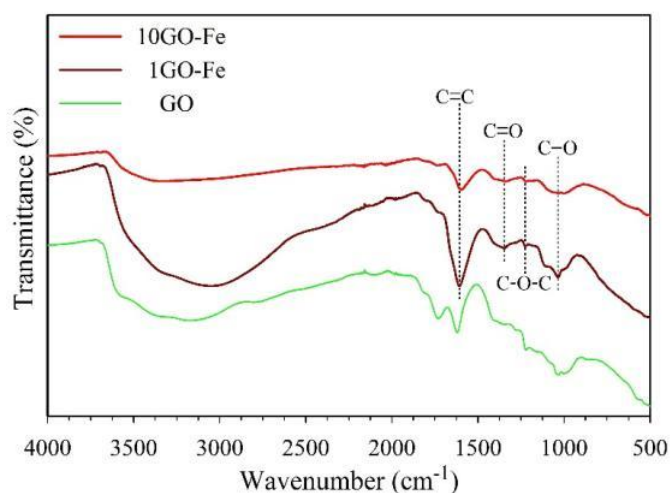


Fig. 4. FTIR spectra of GO, 1GO-Fe and 10GO-Fe.

functional groups present in the basal plane of GO.³⁰⁻³² These interactions are weaker than Fe(III)-carboxyl interaction and likely could not retain Fe(III) ions during washing.

SEM analysis and Fe analysis of XGO-Fe(III) composites after washing suggest that in suspensions of GO where GO sheets are present as well-dispersed single sheets, Fe(III) ions are firmly attached to the carboxyl groups at the edges of GO sheets. With an increase of initial GO concentration, aggregation of GO sheets into stack layers is more pronounced and Fe(III) ions, beside interaction with carboxyl groups at the edges of GO sheets, can intercalate between layers of GO where they are weakly bounded to the alkoxy/alkoxide and hydroxyl groups of the GO basal plane and easily washed out with water. Comparison of FTIR spectra of 1GO-Fe and 10GO-Fe (Fig. 4) further supports this conclusion. Strong adsorption bands present for the 1GO-Fe composite at 1608, 1347, 1220 and 1033 cm^{-1} which can be attributed to the aromatic C=C, carboxy C=O, epoxy C-O and alkoxy C-O vibrations³³, respectively, were much weaker in the 10GO-Fe composite. This is commonly interpreted as evidence of coordination of metal ions to the functional groups at the GO surface.³⁰ Using 10g GO L^{-1} as the initial GO concentration for loading of Fe(III) ions, FTIR results suggest intercalation of Fe(III) ions between layers of GO sheets and more pronounced interaction with functional groups at the basal plane of GO, which further enhances cross-linkage of individual GO sheets.^{30, 34}

Based on the above results, the 10GO-Fe(III) composite, with a high amount of loaded Fe, was chosen as the best candidate for further optimisation of P loading.

Kinetics of P loading onto the 10GO-Fe composite

There was very fast adsorption of P onto the 10GO-Fe composite, reaching equilibrium within 40 minutes (Fig. 5a). Generally, three different mechanisms are believed to be involved in phosphate sorption at lamellar structures: 1) diffusion of P across the so-called liquid film surrounding the sorbent; 2) intraparticle transport within the particle; and 3) chemisorption (sorption/desorption of P molecules on/from the sorbent surface).³⁵ To examine adsorption mechanisms of P sorption onto the 10GO-Fe composite, two mathematical models were applied, a pseudo-second order³⁶ (Eq. 3) and an intraparticle diffusion model³⁷ (Eq. 4):

$$\frac{t}{Q_t} = \frac{1}{kQ_e^2} + \frac{t}{Q_e} \quad (3)$$

$$Q_t = k_i t^{1/2} \quad (4)$$

Where Q_e and Q_t (mg g^{-1}) are the amount of P sorbed at equilibrium and time t (h). k ($\text{g mg}^{-1} \text{h}^{-1}$) and k_i ($\text{g mg}^{-1} \text{h}^{-1/2}$) are the pseudo-second model and intraparticle diffusion rate constants, respectively.

It can be seen that the pseudo-second order model provides a good correlation for the sorption of P onto the 10GO-Fe composite (Fig. 5b). Beside the fact that the correlation coefficient is close to 1, the calculated Q_e value from the pseudo second order model is in good agreement with the experimentally obtained Q_e value, which further confirms the ability of this model to describe sorption of P to this material. A good fit of experimental data to the pseudo second order model is usually associated with systems where overall sorption is controlled by a chemisorption process.³⁸ The intraparticle diffusion model is often used to investigate if diffusion is the rate limiting step in the sorption process.³⁸ From Fig. 5c we can see that the intraparticle plot is not linear over the entire time range and that the intercept of the fitting curve of the first segment was not zero, implying that intraparticle diffusion is involved but not the only rate controlling step in the P sorption process. Because the pseudo second order model is able to

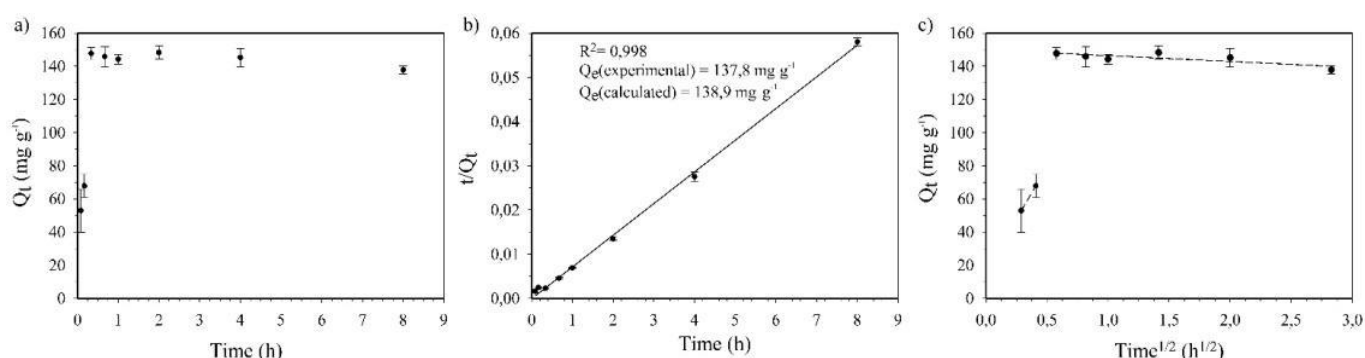


Fig. 5. a) Effect of contact time on the loading amount of P, b) pseudo-second order model and c) intra-particle diffusion model for kinetic of P loading onto the 10GO-Fe composite. Initial P concentration 2.5 g L^{-1} , sorbent dosage 10 g L^{-1} , initial pH 6.0. Error bars represent standard deviations ($n = 3$).

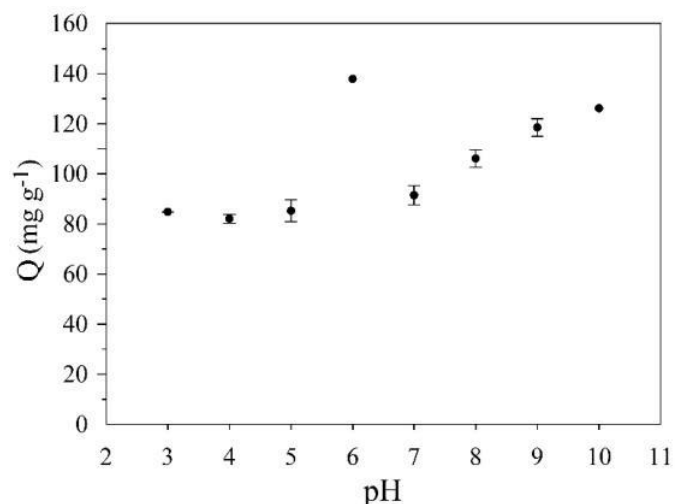


Fig. 6. Effect of pH values on the loading amount of P. Initial P concentration 2.5 g L^{-1} , sorbent dosage 10 g L^{-1} . Error bars represent standard deviations ($n = 3$).

represent systems for which other mechanisms beside surface reactions governs the overall process rate, we can suggest that chemisorption and intraparticle diffusion are controlling steps in P sorption onto this 10GO-Fe composite.³⁸ Similar results have been found for P sorption on Mg/Al layer double hydroxide³⁹ and Fe-Zr binary oxide⁴⁰.

Effect of pH

In the system where Fe(III) ions are attached to the carboxylic groups at the edges of the GO sheets and oxygen groups in the basal plane of GO sheets, with an increase in pH we could expect an increase in the amount of PO_4^{3-} ions loaded onto this GO-Fe system, as a result of formation of an electrostatically favourable ternary surface complex, GO-Fe-P, with Fe as a bridging ion.⁴¹ From Fig. 6 we can see that there was no effect of pH on the loading of P below pH values of 5, while the highest loading was achieved at pH 6. With a further increase of pH, an excess of OH^- ions, their competitive sorption to the GO-Fe as well as possible coprecipitation of P ions with favourable formation of $\text{Fe}(\text{OH})_3$ at higher pH values could be responsible for the decrease in the amount of P loaded at pH values > 6 . Similar results, showing that an increase of pH from 2 to 6 had no effect on P(V) removal using a GO-Cd(II) system while the highest removal was achieved at pH 7.5 due to formation of a ternary GO-Cd-P surface complex, were reported by Ren et al.⁴¹ We should also bear in mind that a change in the phosphate speciation and possible conformational changes of GO sheets that happens with the change of pH could affect the chemical reactivity of the GO-Fe composite and could be partly responsible for these results.^{42, 43}

Adsorption isotherms

The Freundlich isotherm model was applied to describe P sorption onto the 10GO-Fe(III) composite (Fig. S1). Freundlich⁴⁴ (Eq. 5) model can be expressed with the following equations:

Table 1 Freundlich isotherm parameters for P loading at 10GO-Fe composite

Isotherm type	Isotherm parameters sorption of P
Freundlich	$R^2 = 0,988$
	$K_f = 54 \pm 5$
	$n = 2.08 \pm 0.17$

$$Q_e = K_f C^{1/n} \quad (5)$$

Where C is the equilibrium concentration of P in supernatant (mg L^{-1}), Q_e is the equilibrium amount of P adsorbed per weight of 10GO-Fe(III) composite (mg g^{-1}), K_f is the Freundlich equilibrium constant related to the adsorption capacity, $1/n$ is an empirical parameter related to the intensity of adsorption. Isotherm parameters obtained by fitting of the experimental data to the Freundlich isotherm model are presented in Table 1. It can be seen that the Freundlich model gives a good description of a P sorption process, suggesting that sorption happens at the energetically heterogeneous sites of 10GO-Fe(III) composite.⁴⁵ Obtained maximum adsorption capacity for P was $193 \pm 27 \text{ mg g}^{-1}$ (Fig. S1.) demonstrates high loading potential of P onto 10GO-Fe(III) composite and achievement of the % of P in the composite similar to % in commercial fertilizers. The Freundlich constant n is found to be > 1 ($n=2.08 \pm 0.17$) which is an indicator of favourable sorption of P to the 10GO-Fe(III) composite.

Column release

Based on the results presented above we speculate that the GO composites could be engineered in order to have a desired release rate of P. Strong attachment of Fe ions to the carboxylic groups at the edges of the GO sheets could be achieved during loading of Fe by using a low initial GO concentration. For example, choosing 1 g GO L^{-1} as the initial concentration for loading of Fe ions, 1GO-Fe composite was obtained. The release rate of P loaded onto 1GO-Fe with 5 % P (1GO-Fe-5P) was examined using a column perfusion method and found to have a slow release of P, achieving 9 % release in 48 h. Using a higher initial GO concentration, stacking of GO sheets occurs, providing a new mechanism for Fe loading onto GO - intercalation of Fe ions between stacked GO sheets. This new mechanism enables loading of additional amounts of Fe and P onto GO through interactions of Fe with alkoxy/alkoxide and hydroxyl groups at the basal planes of GO. Compared to carboxyl-Fe interactions these interactions are weaker which result in a faster release of P from the GO-Fe composite. Accordingly, for the 10GO-Fe composite loaded with 15 % P (10GO-Fe-15P), a faster release of P was observed, resulting in 42 % of total P released in 48 h (Fig. 7a). It is important to note that, with the usage of XGO-Fe-P composites, the majority of P remained in the pellet even after 48h. In the case of MAP we can see a substantially faster release rate, with 90% of applied P released in the first 10h. Dimiev et al. recently reported that prolonged exposure to water

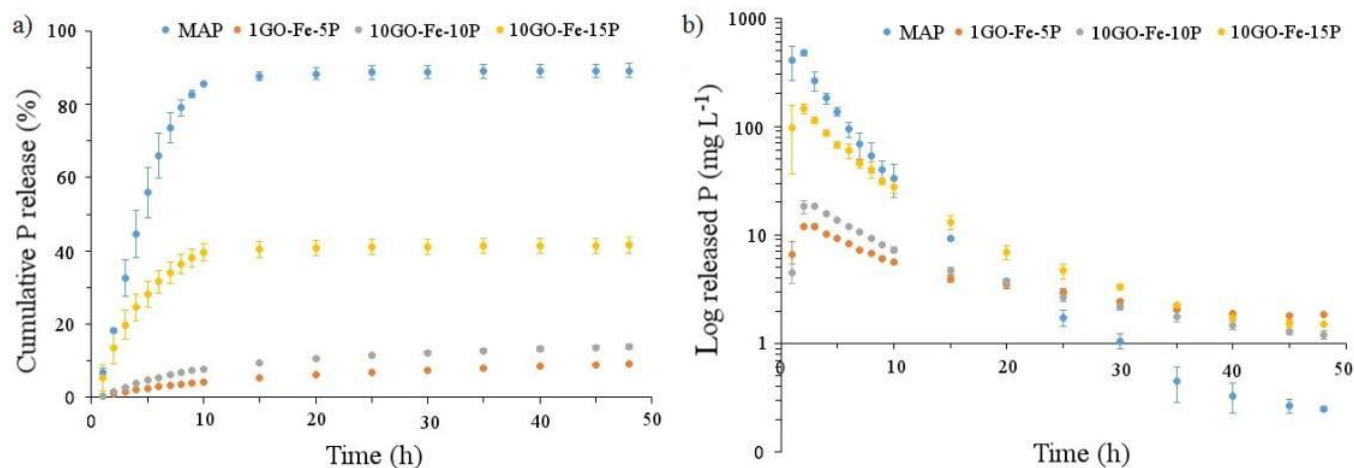


Fig. 7. Kinetics of P release from MAP granules, 1GO-Fe-5P, 10GO-Fe-10P and 10GO-Fe-15P pellets in column a) cumulative release of P and b) solution concentrations of P released over time. Error bars represent standard deviations ($n = 2$).

gradually degrades GO to humic acid-like structures. Based on this, we can assume that after placement of the XGO-Fe-P pellet in the soil, gradual degradation of the XGO-Fe-P composite by water should provide steady, slow release of residual P present in the pellet.⁴⁶

Besides the initial concentration of GO as a factor that influences loading capacity and release rate of P from XGO-Fe-P composites, another factor can be the ratio of XGO-Fe : P used during loading of P. Similar to intercalation of different chemical species into layered structures^{47, 48}, a lower XGO-Fe : P ratio during loading of P onto the 10GO-Fe composite results in an increase on the amount of intercalated P (Fig. 7a). In general, by applying a specific XGO-Fe : P ratio during P loading onto the XGO-Fe composite, we can obtain fertiliser with a specific % P content and a specific release rate of P. For example, using a 1 : 0.5 = 10GO-Fe : P ratio (w/w) during loading of P onto 10GO-Fe resulted in 10 % of P loaded onto the 10GO-Fe composite (10GO-Fe-10P). This 10GO-Fe-10P composite showed a slower release rate of P compared to the 10GO-Fe-15P composite, obtained using a 1 : 1 = 10GO-Fe : P (w/w) loading ratio, releasing 14 % of P within 48 h (Fig. 7a). All XGO-Fe-P composites, 1GO-Fe-5P, 10GO-Fe-10P and 10GO-Fe-15P, show the property of a slow-release fertiliser compared to MAP. Furthermore, an increase of the P concentration in the initial fractions with the increase of P amount loaded at GO-Fe

composite can be seen (Fig. 7b). Compared to MAP, where a burst of P release and high P concentrations are evident in the first 10 fractions followed by fast decrease of P concentrations in the following fractions, using XGO-Fe-P composites the change in the concentration of P with time was not so drastic. This gradual and tailorable release of for the XGO-Fe-P composites could assist synchrony with plant demand for P and reduce potential losses to runoff immediately after fertilizer application.

Diffusion of P through the soil

As we pointed out in the Introduction, key factors that influence the behaviour and fate of applied fertiliser are the type of soil and physical-chemical properties of the fertiliser. In order to assess the behaviour of the 10GO-Fe-15P composite as a P carrier, visualisation of P diffusion in three different soils was performed and results were compared with MAP. Fig. 8a showed that within 56 days, P from MAP reached the outer section of the Petri dish for the Monarto soil while for PW and BP soils P diffused 21 and 16 mm from the point of MAP application, respectively. Slower diffusion of P through the BP soil can be explained by the presence of high amounts of Fe/Al, compared to PW and Monarto soils, and their well-known interaction with P.⁴ Using the 10GO-Fe-15P composite, the

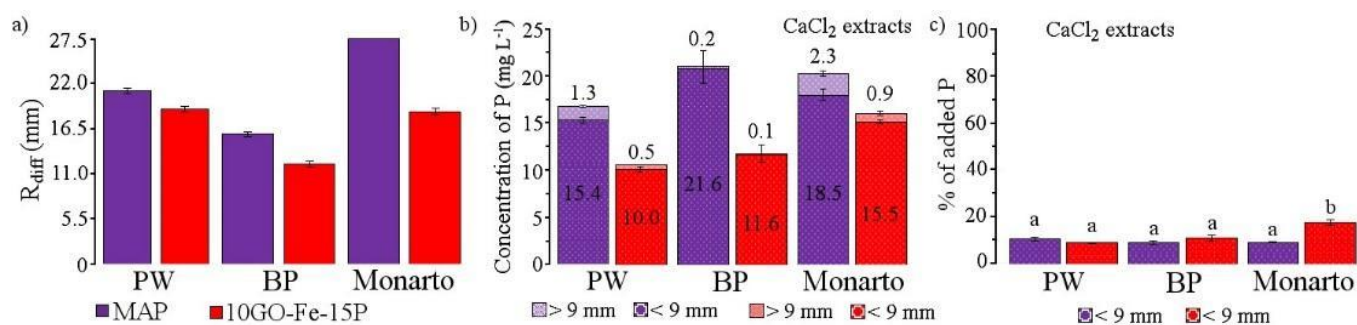


Fig. 8. a) Radius of diffusion of P at 56 d after addition of MAP granules or 10GO-Fe-15P pellets to the soils, b) concentrations of added P extracted by CaCl₂ recovered at a distance of less than, or more than, 9 mm from the fertiliser application site at 56 d after fertiliser application and c) percentage of added P extractable by CaCl₂ recovered at a distance less than, or more than, 9 mm from the fertiliser application site. Error bars present standard deviations ($n = 3$). Different letters signify significant differences ($P \leq 0.05$).

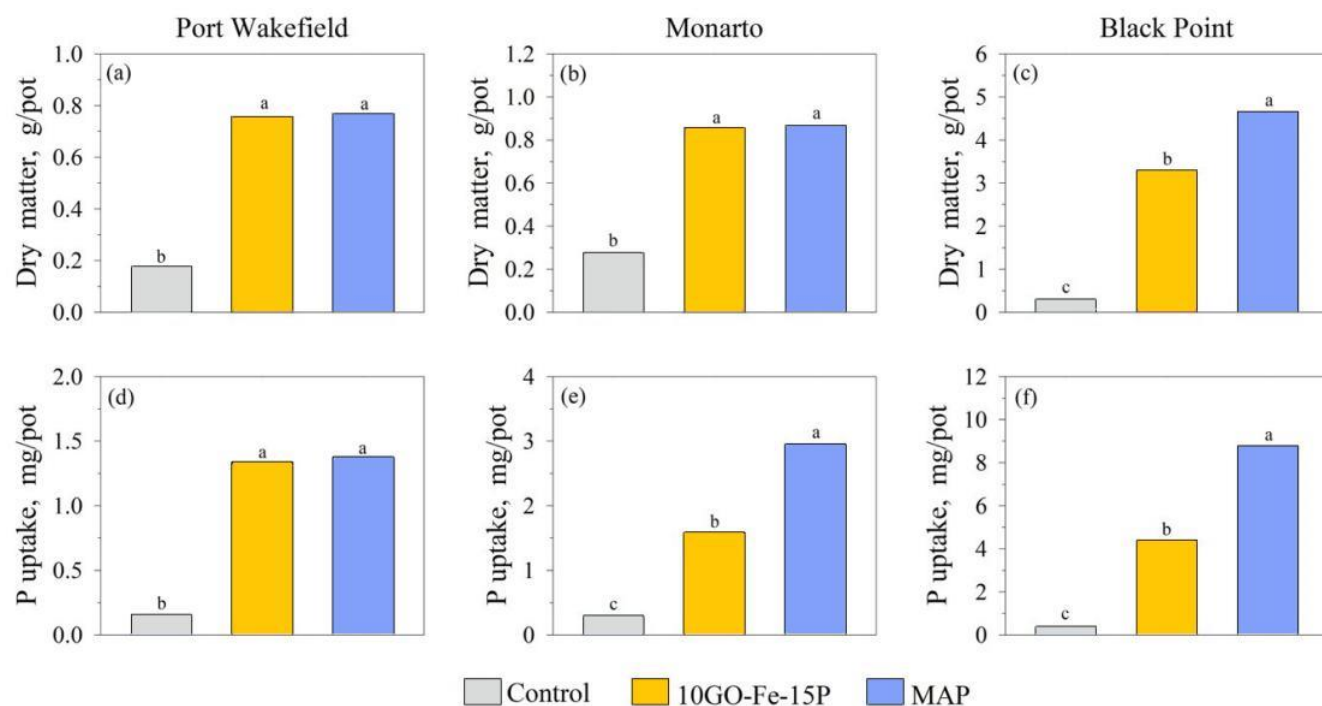


Fig. 9. Dry matter yield (top) and P taken up by wheat (bottom) in Port Wakefield (a, d), Monarto (b, e) and Black Point (c, f) soils without added P (Control) and with P added at 15 mg kg^{-1} as 10GO-Fe-15P or MAP in granular form. Different letters signify significant differences ($P < 0.05$)

extent of P diffusion through soils was lower, resulting in a smaller radius of diffusion than those obtained in the MAP treatments. The smaller radius of diffusion for all three soils for the 10GO-Fe-15P composite compared to MAP supports our previous result obtained in the column release experiment, confirming the slow release property of the 10GO-Fe-15P composite.

Concentrations of P in CaCl_2 extracts of soils sampled $> 9 \text{ mm}$ from application site were higher for MAP treatment in all three soils, compared to the 10GO-Fe-15P composite, which is in agreement with the obtained radii of diffusion from visualisation experiments (Fig. 8b). The highest concentration of P in the $> 9 \text{ mm}$ fraction of the soil was for Monarto soil with the fastest rate of P diffusion followed by PW and BP. Analysis of soil from inner soil sections ($< 9 \text{ mm}$) showed that the percentage of P recovered as easily-extractable P was significantly higher for Monarto soil with the 10GO-Fe-15P treatment compared to the MAP treatment, while there was no significant difference amongst the treatments for the other two soils (Fig. 8c).

Plant study

Growth of wheat was very limited in all three soils without addition of P fertiliser (Fig. 9). With the addition of fertiliser treatments dry yields were significantly increased, confirming that used soils are highly responsive to P application. There was no significant difference in yield between MAP and 10GO-Fe-15P composite treatment in PW and Monarto soils (Fig. 9a and 9b) while application of MAP resulted in significantly higher yield in BP soil compared to 10GO-Fe-15P application (Fig. 9c).

The amount of P taken up by wheat was also affected by the P sources. Both 10GO-Fe-15P and MAP resulted in similar P uptake in PW soil (Fig. 9d), whereas in Monarto and BP soils MAP outperformed the GO-based P composite (Fig. 9e and 9f). Lower dry yield with the usage of slow-release P compared to fully soluble fertilisers was reported previously in soils with high P fixing capacity, which is the case with our BP soil. The slower P release from the fertiliser may impose a yield penalty in soils highly deficient in P, as observed in our study for BP soil, suggesting that slow release sources may not be suitable to meet crop demands under such situations. On the other hand, for PW and Monarto soils, the supply of P to the plant through the slow-release 10GO-Fe-15P composite was enough to produce the same dry yield as the MAP treatment.

Although the agronomic performance of the 10GO-Fe-15P composite was at best similar to highly soluble commercial fertiliser under the current experimental design, we hypothesised our new fertiliser formulation may present a successful performance in areas prone to leaching or runoff losses. This would be due to its slower P release pattern, which acts as a protection against P losses to water bodies compared to fully soluble unprotected conventional P fertiliser formulations. This would potentially bring both an environmental benefit by mitigating P losses to freshwaters and also an agronomic gain since P would be kept in the rootzone, becoming available to the crops all season long. Future works may confirm this hypothesis.

Conclusions

The results of our study show the potential of using GO-Fe-P composites as slow release P fertilisers. A simple change in experimental conditions of GO-Fe-P synthesis enables engineering the amount and release rate of P, to match specific plant needs and soil type. Although our loading procedure results in percentage of loaded P similar to those in commercially used, highly soluble fertilisers, column release studies and visualisation of P diffusion in soils confirmed that GO-Fe-P formulations still keep their slow release property. A plant study using wheat and 10GO-Fe-15P composite in PW and Monarto soils resulted in the same wheat yield as using highly soluble commercial fertiliser. Further experiments are required to assess potential benefits of GO-Fe-P slow release fertiliser formulations in reducing the risks from P runoff/leaching and in agronomic efficacy in multiple cropping years.

Conflicts of interest

“There are no conflicts to declare”.

Acknowledgements

The authors thank the support of the Australian Research Council (ARC) funding ARC DP 150101760 and ARC IH 150100003 (Graphene Enabled Industry Transformation) for financial support to this work. The support from The University of Adelaide, the School of Agriculture, Food and Wine, and the School of Chemical Engineering is acknowledged. The authors also thank Dr. Fien Degryse, Bogumila Tomczak, Ashleigh Broadbent and Colin Rivers for their advice and technical support.

References

1. F. K. Bomans E., Gobin A., Mertens J., Michiels P., Vandendriessche H., Vogels N., *Addressing phosphorus related problems in farm practice*, Report P/OO/027, European Commission by the Soil Service of Belgium, Heverlee, Belgium, 2005.
2. , !!! INVALID CITATION !!! 2-4.
3. K. G. Raghothama, *Annual Review of Plant Physiology and Plant Molecular Biology*, 1999, 50, 665-693.
4. M. Hedley and M. McLaughlin, in *Phosphorus: Agriculture and the Environment*, eds. J. T. Sims and A. N. Sharpley, American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America, Madison, WI, 2005, DOI: 10.2134/agronmonogr46.c7, pp. 181-252.
5. A. E. Johnston and I. R. Richards, *Soil Use and Management*, 2003, 19, 45-49.
6. F. Degryse, R. Baird, R. C. da Silva and M. J. McLaughlin, *Plant and Soil*, 2016, DOI: 10.1007/s11104-016-2990-2, 1-14.
7. M. Everaert, F. Degryse, M. J. McLaughlin, D. De Vos and E. Smolders, *Journal of Agricultural and Food Chemistry*, 2017, 65, 6736-6744.
8. A. G. Sinclair, P. D. Johnstone, L. C. Smith, M. B. O'Connor and L. Nguyen, *Fertilizer research*, 1993, 36, 229-238.
9. M. J. McLaughlin, T. M. McBeath, R. Smernik, S. P. Stacey, B. Ajiboye and C. Guppy, *Plant and Soil*, 2011, 349, 69-87.
10. M. Anstoetz, T. J. Rose, M. W. Clark, L. H. Yee, C. A. Raymond and T. Vancov, *PLOS ONE*, 2015, 10, e0144169.
11. A. Shaviv and R. L. Mikkelsen, *Fertilizer research*, 1993, 35, 1-12.
12. A. Olad, H. Zebhi, D. Salari, A. Mirmohseni and A. Reyhani Tabar, *New J Chem*, 2018, 42, 2758-2766.
13. H. Gharekhani, A. Olad and F. Hosseinzadeh, *New J Chem*, 2018, 42, 13899-13914.
14. L. Wu, M. Liu and L. Rui, *Bioresource Technology*, 2008, 99, 547-554.
15. J. Treinyte, V. Grazuleviciene, R. Paleckiene, J. Ostrauskaite and L. Cesoniene, *Journal of Polymers and the Environment*, 2017, DOI: 10.1007/s10924-017-0973-x.
16. T. Li, S. Lü, Y. Ji, T. Qi and M. Liu, *New J Chem*, 2018, 42, 19129-19136.
17. I. B. Andelkovic, S. Kabiri, E. Tavakkoli, J. K. Kirby, M. J. McLaughlin and D. Losic, *Journal of Cleaner Production*, 2018, 185, 97-104.
18. M. P. Bernardo, F. K. V. Moreira and C. Ribeiro, *Applied Clay Science*, 2017, 137, 143-150.
19. S. Kabiri, D. N. H. Tran, S. Azari and D. Losic, *ACS Applied Materials & Interfaces*, 2015, 7, 11815-11823.
20. D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu and J. M. Tour, *ACS Nano*, 2010, 4, 4806-4814.
21. B. A. Zarcinas, M. J. McLaughlin and M. K. Smart, *Commun Soil Sci Plan*, 1996, 27, 1331-1354.
22. R. D. Armstrong, K. Dunsford, M. J. McLaughlin, T. McBeath, S. Mason and V. M. Dunbabin, *Plant and Soil*, 2015, 396, 297-309.
23. N. Milani, M. J. McLaughlin, S. P. Stacey, J. K. Kirby, G. M. Hettiarachchi, D. G. Beak and G. Cornelis, *Journal of Agricultural and Food Chemistry*, 2012, 60, 3991-3998.
24. I. Matejovic, *Commun Soil Sci Plan*, 1997, 28, 1499-1511.
25. A. E. MARTIN and R. REEVE, *Soil Science*, 1955, 79, 187-198.
26. G. P. Gillman and E. A. Sumpter, *Modification to the compulsive exchange method for measuring exchange characteristics of soils*, 1986.
27. G. E. H. Rayment, F. R., *Australian Laboratory Handbook of Soil and Water Chemical Methods*, Port Melbourne Inkata Press, Melbourne, 1992.
28. F. Degryse and M. J. McLaughlin, *Soil Science Society of America Journal*, 2014, 78, 832-842.
29. Y.-E. Shin, Y. J. Sa, S. Park, J. Lee, K.-H. Shin, S. H. Joo and H. Ko, *Nanoscale*, 2014, 6, 9734-9741.
30. S. Park, K.-S. Lee, G. Bozoklu, W. Cai, S. T. Nguyen and R. S. Ruoff, *ACS Nano*, 2008, 2, 572-578.
31. L. Wu, L. Liu, B. Gao, R. Muñoz-Carpena, M. Zhang, H. Chen, Z. Zhou and H. Wang, *Langmuir*, 2013, 29, 15174-15181.
32. G. Zhao, X. Ren, X. Gao, X. Tan, J. Li, C. Chen, Y. Huang and X. Wang, *Dalton Transactions*, 2011, 40, 10945-10952.
33. V. Chandra, J. Park, Y. Chun, J. W. Lee, I.-C. Hwang and K. S. Kim, *ACS Nano*, 2010, 4, 3979-3986.
34. R. R. Amirov, J. Shayimova, Z. Nasirova and A. M. Dimiev, *Carbon*, 2017, 116, 356-365.
35. K.-H. Goh, T.-T. Lim and Z. Dong, *Water Research*, 2008, 42, 1343-1368.
36. Y. S. Ho and G. McKay, *Process Biochemistry*, 1999, 34, 451-465.

37. S. Sen Gupta and K. G. Bhattacharyya, *Advances in Colloid and Interface Science*, 2011, 162, 39-58.
38. W. Plazinski, W. Rudzinski and A. Plazinska, *Advances in Colloid and Interface Science*, 2009, 152, 2-13.
39. C. Novillo, D. Guaya, A. Allen-Perkins Avendaño, C. Armijos, J. L. Cortina and I. Cota, *Fuel*, 2014, 138, 72-79.
40. F. Long, J.-L. Gong, G.-M. Zeng, L. Chen, X.-Y. Wang, J.-H. Deng, Q.-Y. Niu, H.-Y. Zhang and X.-R. Zhang, *Chemical Engineering Journal*, 2011, 171, 448-455.
41. X. Ren, Q. Wu, H. Xu, D. Shao, X. Tan, W. Shi, C. Chen, J. Li, Z. Chai, T. Hayat and X. Wang, *Environmental Science & Technology*, 2016, 50, 9361-9369.
42. R. L. D. Whitby, A. Korobeinyk, V. M. Gun'ko, R. Busquets, A. B. Cundy, K. Laszlo, J. Skubiszewska-Zieba, R. Lebeda, E. Tombacz, I. Y. Toth, K. Kovacs and S. V. Mikhalovsky, *Chemical Communications*, 2011, 47, 9645-9647.
43. H. Shen, Z. Wang, A. Zhou, J. Chen, M. Hu, X. Dong and Q. Xia, *RSC Advances*, 2015, 5, 22080-22090.
44. H. Freundlich, *Colloid & capillary chemistry*, Methuen, London, 1926.
45. C.-h. Yang, *Journal of Colloid and Interface Science*, 1998, 208, 379-387.
46. A. M. Dimiev, L. B. Alemany and J. M. Tour, *ACS Nano*, 2013, 7, 576-588.
47. Y. Matsuo, K. Tahara and Y. Sugie, *Carbon*, 1996, 34, 672-674.
48. Y. Matsuo, K. Hatase and Y. Sugie, *Chem Mater*, 1998, 10, 2266-2269.