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Graphene oxide-Fe(III) composite containing phosphate – a novel slow release fertilizer for improved agriculture management

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Abstract

Novel materials offer opportunities to develop new types of fertilizers which could potentially increase efficiency of nutrient use in agriculture. Slow-release fertilizers can be more effective than traditional nutrient sources and simultaneously reduce negative impacts of nutrients to the environment. Using low-cost, abundant natural material, graphite rock, a functionalized graphene oxide (GO)/iron (GO-Fe) composite was synthesised and examined as a new carrier of phosphate ions in order to improve nutrient delivery to plants. The morphology of the composite was examined with scanning electron microscopy (SEM) and X-ray diffraction (XRD) was used to determine the presence of crystal phases. The composite was also characterized with thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR). We found that the presence of ferric ions was responsible for attachment of phosphate ions onto the GO-Fe composite, providing a loading capacity of 48 mg P/g. The kinetics of P release were examined using a column perfusion test while P diffusion in three different types of soils was examined using a visualization technique and chemical analysis. Compared with commercial monoammonium phosphate (MAP) fertilizer, application of GO-Fe composite loaded with phosphate (GO-Fe-P) resulted in slower release of P, thus reducing the possibility for leaching or runoff of soluble P to surface and groundwaters.

1. Introduction

The application of the fertilizers, as an essential part of agriculture, is responsible for approximately half of the world's crop production increment each year. However, this is still far away from efficient (Reetz, 2016). Inefficiency in fertilizer usage in agriculture results in introduction of ammonium and nitrogen into soil and water and ammonia to air (Socolow, 1999). Increased input of P is responsible for eutrophication of ground waters, rivers, lakes and coastal marine systems which is recognised as a serious threat to biodiversity and other aquatic ecosystem functions (Huang et al., 2017). When soluble fertilizers are added into soils a series of reactions can occur, such as exchange/adsorption, complexation, precipitation and dissolution, with soil constituents (e.g. Fe-oxides, clay and major ions such as calcium) that influence its fate and bioavailability (e.g. retention, lability and fixation) (Chien et al., 2009; McLaughlin et al., 2011). Numerous studies have shown that only 5 to 30% of the soluble P applied to soils can be recovered from the first crop leaving 70 to 95% as potential residual P that remains non-bio available or that plants may access in subsequent growing seasons (Barrow, 1976; Bolland and Gilkes, 1998). For this reason there has been much interest in the development of slow- or controlled release fertilizers, which can minimise off-site losses and improve agronomic efficiency of fertilizer use (Shaviv, 2001; Shaviv and Mikkelsen, 1993).

The improvement of P fertilizer efficiency in terms of nutrient release and crop uptake is a new global goal and engineering challenge (M. A. Sutton, 2013). One novel approach to this challenge involves the coating of water soluble P with a water insoluble layer, creating a physical barrier that will slow the rate of P release and reduce P leaching or runoff. A number of natural and synthetic polymers have been examined such as starch (Jin et al., 2013; Zhong et al., 2013), cellulose (Tomaszewska et al., 2002; Wu and Liu, 2008a), chitosan (Wu and Liu, 2008b), P(acrylic acid co-acrylamide)/kaolin (Liang et al., 2007), and polydopamine-graft-poly(N-isopropylacrylamide) (M.A. Sutton, 2013). The potential for improvement of fertilizer formulations using nanomaterials (NM) has also been explored. Rather than creating a physical barrier around the fertilizer, the concept to use NMs as carriers for nutrients was taken from the pharmaceutical industry to achieve slow and controlled release (Chen et al., 2004; DeRosa et al., 2010). Although application of NMs or coating of existing commercial fertilizers has shown promising results, in order for these materials to be widely used they need to be cost competitive, appropriate for farm application (e.g. use existing infrastructure and resources) and environmentally safe.

Carbon materials are one of the mostly used materials for agricultural and environmental application (Mauter and Elimelech, 2008). The fact that they are cost effective, environmental friendly and possess desirable physical-chemical properties makes them ideal material for industrial scale application. Biochar, a class of carbonaceous material, typically produced by the pyrolysis of biomass, and its composites were recently investigated for P capture and recovery from waste water (Chen et al., 2017; Marshall et al., 2017). Since discovery in 2004 (Novoselov et al., 2004) a newly emerging carbon material, graphene (GN) has attracted significant attention for a broad range of applications including use as energy-related materials (Kuhn and Gorji, 2016), drug delivery systems (Kiew et al., 2016), sensors (Liu et al., 2012; Xu et al., 2017), and membranes (Jiang et al., 2016). So far, GN and its oxidised form, graphene oxide (GO), having a range of reactive oxygen functional groups and a high specific surface, have been confirmed by many studies as non-toxic and biocompatible materials (Liu et al., 2013; Novoselov et al., 2012). Based on their very high surface area (2600 m²/g) and unique 2-d structure, graphene-based products provide an ideal platform for nutrient loading and investigation of the potential of this new material in slow-release fertilizer manufacture. Following model of biochar, there is an increasing number of studies which are trying to use the advantages that GN/GO composites offer for the sorption of a broad range of elements including heavy metals, organic molecules, drugs and gases (Li et al., 2015; Santhosh et al., 2016). Recently several studies have shown that GN/GO composites have the potential to be used for controlling P pollution (Luo et al., 2016; Tran et al., 2015). These studies were interested in the removal of P from water and did not examine the potential of these materials to release sorbed P to supply an essential macronutrient in agriculture.

The aim of our work was to examine usage of low-cost and abundant graphite rock as a raw material for obtaining slow release fertilizer. By a well-established synthetic procedure graphite rock can be exfoliated into GO, material with high surface area and variety of oxygen functional groups on the surface which can serve as a good base for chemical modification to retain macro- and micronutrients. Initially phosphate (PO₄³⁻) was used as a model anion and the ability of GO to provide a slow-release platform for P was assessed. A schematic diagram of the proposed concept is presented in Figure 1.

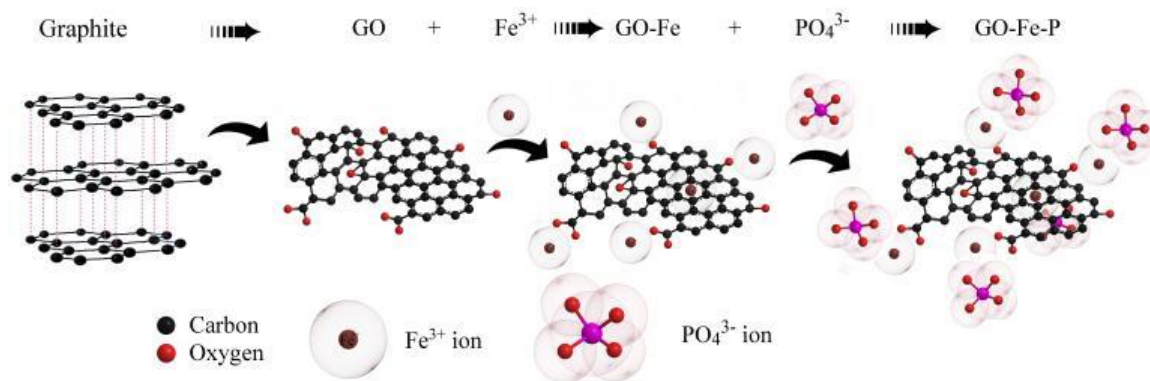


Fig. 1. Schematic diagram of the synthesis procedure of the GO-Fe-P composite.

To improve the loading capacity of P on the surface of GO sheets we selected Fe(III) ions based on their affinity for PO_4^{3-} . Using simple procedures, a GO-Fe composite was synthesised and characterised. After loading of P onto the surface of the GO-Fe composite, the kinetics of P release were examined using column perfusion and soil diffusion methods and compared with MAP as a commercially available P fertilizer.

2. Material and methods

2.1. Graphene oxide (GO) preparation

Natural graphite rock (Eyre Peninsula, South Australia) was sourced from a local mine and milled into a fine powder using a benchtop ring mill (Rocklabs, NZ). The GO sheets were prepared using a modified Hammer method (Kabiri et al., 2015; Marcano et al., 2010). Briefly, a 9 : 1 mixture of concentrated sulphuric acid and phosphoric acid (240:27 mL) was cooled to 4 °C. Under stirring at room temperature the cooled acid mixture was added slowly to the graphite powder (2 g) and potassium permanganate (12 g), then heated to 50 °C for about 12 h, forming a thick paste. The reaction was cooled to room temperature and poured onto ice (300 ml) with hydrogen peroxide (2 ml). The mixture was first washed with distilled water twice, then with hydrochloric acid (32 %) and finally twice with ethanol. For each successive wash, the product was centrifuged at 2950 g for 1 h to remove the product from the supernatant. The light brown GO obtained was vacuum dried overnight at 45 °C.

2.2. GO-Fe(III) composite preparation

Approximately 500 mg of GO was ultrasonicated in 500 mL of deionised water (Milli-Q, Millipore) to obtain a homogenous dispersion. Then, an appropriate mass of FeCl_3 was dissolved in a minimum amount of deionised water and slowly added to the GO, under vigorous mixing, in order to provide a 1:1 (m/m) GO : Fe ratio. The mixture was stirred for 1 h and then centrifuged at 2950g (Thermo Scientific Sorval, H-6000B rotor) for 30 minutes. After centrifugation the supernatant was removed and the GO-Fe composite residue was dried in an oven at 50° C overnight.

2.3. Loading of P onto the GO-Fe(III) composite

For loading of P onto the GO-Fe composite, potassium dihydrogen phosphate (KH_2PO_4) salt was used as a source of soluble P. The GO-Fe composite suspended in deionised water at a concentration of 1 mg/mL was ultrasonicated for 1 h and then KH_2PO_4 salt was added, under vigorous stirring in order to achieve a final concentration of 150 mg P/L. The dispersion was mixed for 24 h and then centrifuged at 2950g for 1 hour. After centrifugation the supernatant was removed and the GO-Fe composite loaded with phosphate (GO-Fe-P) dried in an oven at

50° C overnight. 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).

2.4.Characterisation of GO and GO-Fe(III) composite

The morphology of the GO and GO-Fe(III) composite samples were examined via scanning electron microscopy (Model Quanta 450, FEI, USA). Thermal decomposition of samples was performed under air using a thermogravimetric analyser (Q500, TA Instruments, USA) heating from room temperature to 1000 °C at a rate of 10 °C/min. X-ray diffraction (Model Miniflex 600, Rigaku, Japan) measurements were performed from $2\theta = 5^{\circ}$ – 80° at a scan rate of $5^{\circ}/\text{min}$. Fourier-transform infrared analysis (Nicolet 6700 Thermo Fisher) was used to identify functional groups in materials by scanning in the range of 500 – 4000 cm^{-1} in transmission mode.

2.5.Total P concentration in GO-Fe-P granules

The total concentration of P in the soil and GO-Fe-P granules was determined using an open vessel concentrated acid digestion procedure (3.75: 1.25: 1 mL of concentrated HCl: HNO₃: HClO₄). The soil/granules (~0.2 g) were added into glass tube with 6 ml of mixture of concentrated acids and digested on a heating block at 140 °C for 6 h. After digestion, samples were filtered using 0.45 µm syringe filters (Sartorius) and analysed for total P concentrations using inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Spectro, Kleve, Germany).

2.6.Dissolution kinetics of P from MAP and GO-Fe-P composite fertilizers

Dissolution kinetics for P from GO-Fe-P and MAP, as a reference soluble P source, were conducted using a slightly modified method of Milani et al. (2012). 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. A fraction collector (SuperFrac™, Pharmacia, UK) was used to collect the solutions from the top of the columns every hour for 48 h. The solution pH of all collected fractions was measured using a pH meter (Orion 3 Star, Thermo Scientific, UK). The total P concentrations in each fraction were determined using ICP-OES. All treatments were carried out in duplicate.

2.7.Diffusion of P from fertilizer granules in soils

Table 1. Selected physical and chemical properties for soils.

Soils	pH (H ₂ O)	Organic C (%)	CaCO ₃ (%)	CEC (cmolc/kg)	Clay (%)	Fe _{ox} (mg/kg)	Al _{ox} (mg/kg)	Total P (mg/kg)
Ngarkat	6.8	0.67	< 0.5	3.1	3.2	454	144	2
Black Point	8.5	1.6	< 0.5	16.4	18.1	557	1269	57
Monarto Highland Rd	7.9	1.0	< 0.5	8.2	8.3	351	535	148

The diffusion of P from GO-Fe-P and MAP fertilizer granules was examined in the three type of soils with different physical-chemical characteristics, Ngarkat (N), Black Point (BP) and Monarto Highland Road (MHR). 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 (Rayment, 1992). Soil organic carbon and CaCO₃ content were measured following the procedures described by Rayment and Higginson (1992). The cation exchange capacity (CEC) was determined by the ammonium acetate method at pH 7.0 (Rayment, 1992). The oxalate-extractable Al and Fe concentration was determined according to Rayment and Higginson (1992).

Selected physical and chemical properties of the soils used are given in Table 1. The soils were wetted to field capacity and added into Petri dishes (diameter of 5.5 cm). A GO-Fe-P pellets containing ~6 mg P 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 fertilizer placement. The diameter of the GO-Fe-P composite granules was 4.12 ± 0.01 mm, based on measurement of 10 pellets. MAP fertiliser granules were sieved to obtain granules with a diameter of 2.80 - 3.35 mm. 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 McLaughlin (2014). 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 were divided into an inner section (a circle with a 9 mm radius around the fertiliser granule) and an outer section (soil more than 9 mm away from the fertiliser granule). The soil samples from the inner and outer sections of the circle 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 K/g 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 2950g 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 P in diffusion sections was determined by cold acid extraction with 3M HNO₃ in a liquid: solid ratio of 50 L/kg. The mixture of acid and soil was shaken on an end-over-end shaker for 2 days. The amount of added P recovered in each soil section was calculated using the following equation:

$$M_i = (c_i - c_{bg}) \cdot W_i$$

Where, M_i is the amount of added P(mg) recovered in each soil section; c_i and c_{bg} are the concentration of P (mg/kg) in each soil section for the fertilizer treatments and unamended soils, respectively; and W_i is the weight of dry soil in that soil section (kg).

Standard deviation and analysis of variance (ANOVA) were obtained using SigmaPlot 12.5 v002 software package. The difference between the means were evaluated using Tukey test. The level of significance was $P \leq 0.05$.

3. Results and discussion

3.1. Physical and chemical characterisation of composite

The SEM image of a typical GO structure shows fully exfoliated GO sheets (Fig. 2a,b). Undulations of GO sheets can be seen as a result of the lattice distortion of the original atomic structure of the GN sheets during chemical exfoliation of graphite. With the loading of Fe(III) there appears to be more distinct wrinkling of GO sheets (Fig. 2d, e) which could be attributed to coordination of Fe(III) ions to the various oxygen-containing functional groups of GO (Dong et al., 2013). The SEM-EDX profile of GO showed the expected presence of carbon and sulfur with O as a result of oxidation of graphite

flakes (Fig. 2c). Analysing the surface of GO-Fe, compared to GO an additional peak for Fe appears on the EDX spectra, confirming successful attachment of Fe(III) onto the GO surface (Fig. 2f).

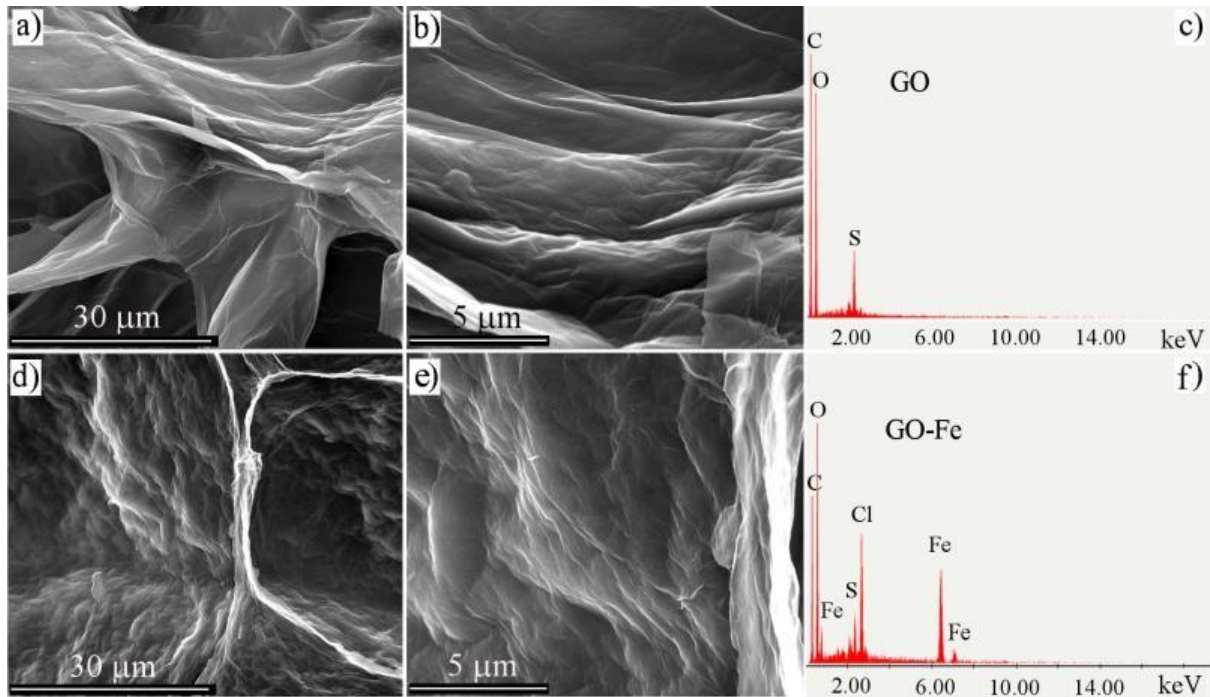


Fig. 2. SEM images of (a, b) GO, (c) SEM-EDX profile of GO, (d, e) SEM images of GO-Fe and (f) SEM-EDX profile of GO-Fe.

The XRD pattern of GO (Fig. 3) is characterised by a diffraction peak at $2\theta = 10.3^\circ$, which is the result of the lateral expansion of the stacked layers of the original GN by the incorporation of the oxygenated functional groups (Dreyer et al., 2010). With loading of Fe(III) ions onto the GO, a complete loss of the diffraction peak was observed. This may have occurred because of the introduced Fe(III) weakened hydrogen bonding amongst the layers which resulted in loss of the layered structure of GO (Dong et al., 2013). The lack of any other peaks in the XRD spectra of GO-Fe suggest either attachment of Fe(III) ions to the surface of GO is occurring without it being oxidised to iron-oxides or there is the formation of iron-oxide clusters in smaller concentrations than the detection limit of the diffractometer.

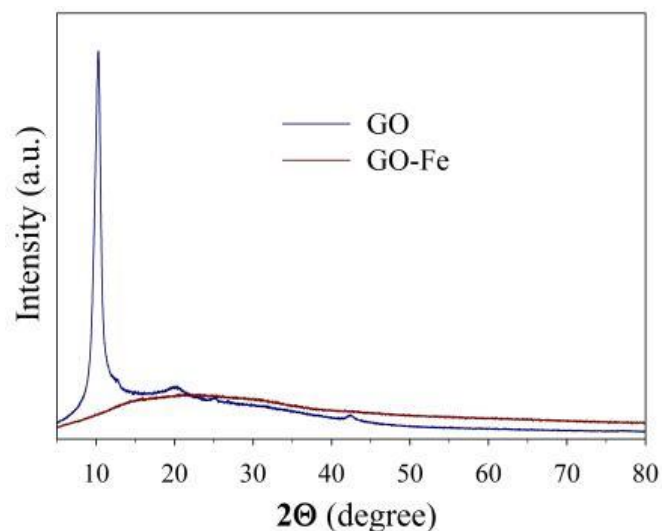


Fig. 3. XRD pattern of GO and GO-Fe.

The FTIR spectra of GO (Fig. 4) showed strong adsorption bands at 1730, 1618, 1220 and 1030 cm^{-1} corresponding to C = O, aromatic C = C, epoxy and alkoxy/alkoxide C - O stretches, respectively (Lambert, 2011). Comparing FTIR spectra of GO with GO-Fe spectra, a decrease of the C = O intensity (1730 cm^{-1}) as well as an increase of the carboxyl O = C - O stretch intensity (1348 cm^{-1}) was observed. The shift of these peaks is likely due to the coordination of Fe(III) ions to the carboxylic group of GO (Park et al., 2008). A noticeable increase of intensity and shift of the C = C peak from 1618 to 1606 cm^{-1} could be attributed to the π electron interaction in the aromatic structure of GO being transformed into cation- π interactions (Wang et al., 2014). In contrast, the peaks for epoxy and alkoxy/alkoxide did not change after loading of Fe(III) ions suggesting that these functional groups were not involved in the sorption of Fe(III) ions onto the GO surface.

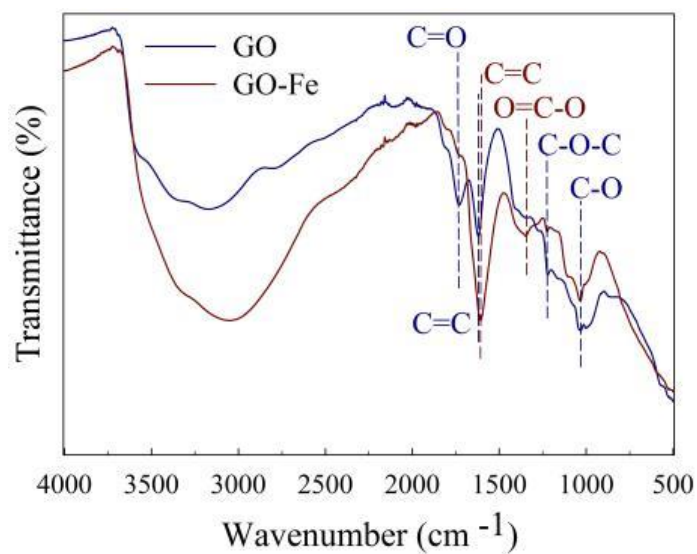


Fig. 4. FTIR spectra of GO and GO-Fe.

In order to quantitatively determine Fe attached to the GO, we performed TGA analysis of the synthesized composite. After heating of the GO-Fe composite from room temperature until 1000° C in air, Fe_2O_3 oxide is obtained as the only product, from which we calculated the percentage of Fe (Dong et al., 2013). The thermal decomposition profiles of GO and GO-Fe are presented in Fig. 5. All weight lost up to 100° C could be attributed to the de-intercalation of water. Further dramatic weight loss from 160 to 450° C was caused by the removal of labile oxygen containing functionalities and pyrolysis of the labile oxygen functional groups (Tran et al., 2015). At 1000° C there was almost complete transition of GO into CO and CO_2 while for the GO-Fe composite, the residual mass represents stable, red coloured Fe_2O_3 . The weight percent of Fe_2O_3 after heating of GO-Fe in air to 1000° C was ~ 21, which corresponds to 14.7 wt % of Fe loaded onto GO.

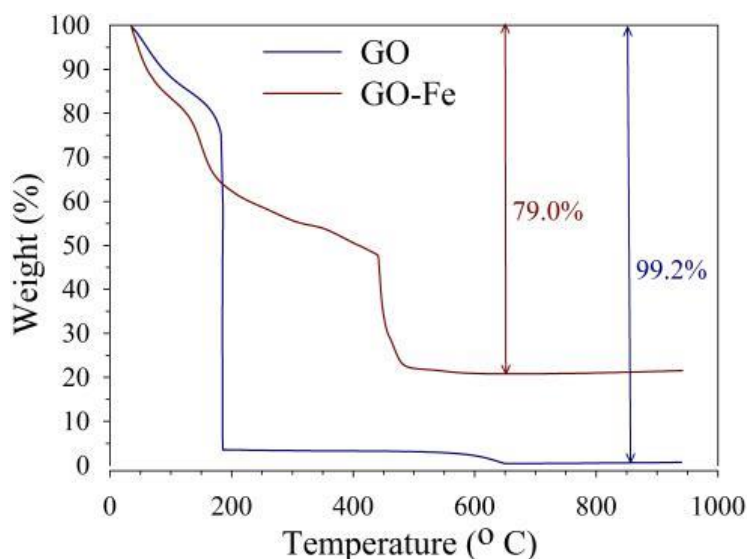


Fig. 5. TGA analysis of GO and GO-Fe.

After successful modification of the GO surface with Fe(III) ions, we examined the loading capacity of P onto the GO-Fe composite. The concentration of loaded P onto GO-Fe, measured after total digestion of our composite with acids, was 48 ± 3 mg P/g. Preliminary experiments found GO without Fe(III) could not adsorb P at all (data not shown), probably due to the negative charge of the GO surface which would repel negatively charged H_2PO_4^- ions (Wang et al., 2015). Modifying the GO surface with Fe(III) ions allowed loading of the GO surface with P in two ways, by decreasing the negative surface charge of GO and by acting as active sorption sites with known high affinity towards H_2PO_4^- ions (Arai and Sparks, 2001).

3.2. Dissolution kinetics of P from MAP and GO-Fe-P composite fertilizers

The dissolution rate of P from GO-Fe-P pellets and commercially available MAP fertilizer granules are presented in Fig. 6a, b. In the case of MAP, fast dissolution of P was found with ~ 85 % of the total P being released in 10 h. After the initial fast release period there was a slower release phase with ~ 4% being released in the following 38 h. By contrast, the release of P from GO-Fe-P was slower, achieving only 9 % release in 48 h.

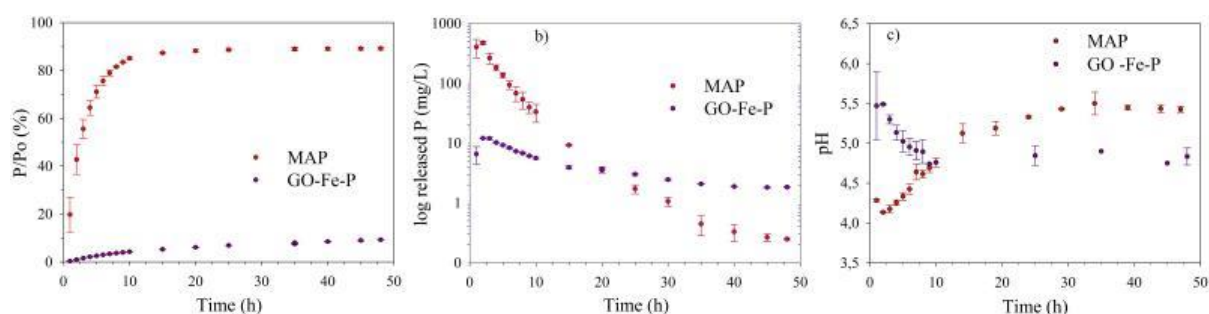


Fig. 6. Kinetics of P release from MAP granules and GO-Fe-P pellets in columns: (a) cumulative release of P (b) solution concentrations of P released over time and (c) changes in the pH of the column eluates from MAP granules and GO-Fe-P pellets. Error bars are standard deviations ($n = 2$).

A notable difference in P release between MAP and GO-Fe-P can be observed in solution P concentrations (Fig. 6b). A rapid release of P from granules and pellets resulted in initial high P concentrations in solutions, especially for MAP granules. High concentrations of P in solutions as a result of fast release from the fertilizer can adversely affect the efficiency of applied P because of the possible precipitation of water soluble P with ions such as Ca and Mg present in soil solutions

(Hedley and McLaughlin, 2005). Lombi et al. (2005) found that using granular MAP in a highly alkaline calcareous soil, over 80% of applied P was located in a zone with radius of 7.5 mm from granule, from which only 15% was isotopically exchangeable and could be considered potentially available to plants. Low availability of P probably reflects the precipitation in the soil of water soluble P from the MAP as mixed Ca/Mg/NH₄⁺ phosphates (Lambert et al., 1979). Using the GO-Fe-P pellet as a fertilizer, slow release and lower concentrations of P in solutions localised close to the application point could prevent the removal of P into non-bioavailable fractions due to precipitation reactions in alkaline calcareous soils. A decrease of pH from the MAP eluates can be related to the fast dissolution of MAP granules (Fig. 6c) (Hettiarachchi et al., 2010; Lehr et al., 1959). After an initial acidification of the eluates (up to 6 h) the eluate pH converged to the initial pH value of the CaCl₂ solution. For the GO-Fe-P composite, a gradual decrease of pH can be seen until 8 h, when the pH of the eluates attained a value 4.9 and remained steady until the end of experiment. The fact that eluate pH did not increase and reach the influent pH indicates the existence of a continuing source of H⁺ ions in the dissolution of the GO-Fe-P composite. It can be assumed that this source of protons is responsible for the dissolution of Fe(III) ions from the GO-Fe-P composite and release of P, which is further supported by the low concentration (~10 µg/L) of Fe measured in the eluted fractions. This continuing release of protons could be particularly beneficial in alkaline soils for minimising P precipitation close to the granule. Furthermore, a small amount of released Fe could be beneficial for the plants grown on soils where frequent application of lime causes Fe deficiency.

Three kinetic models, zero order (Varelas et al., 1995), first order (Mulye and Turco, 1995), and Higuchi (Stauffer and Aharony, 1994) models (Eqs 1, 2 and 3, respectively) were applied with the aim of obtaining further insights into dissolution mechanisms of nutrient from tested fertiliser formulations.

$$\frac{M_t}{M_e} = kt \quad (1)$$

$$\frac{M_t}{M_e} = 1 - \exp(-kt) \quad (2)$$

$$\frac{M_t}{M_e} = kt^{1/2} \quad (3)$$

Where M_t and M_e are amount of nutrient release in time t and at the end of experiment, respectively, and k is rate constant of nutrient release. Dissolution of P from GO-Fe-P was best described using first order model (Fig. S1). Fertiliser formulations that are following first order dissolution profile are typical for porous matrices containing water soluble compound. Release of the nutrient in this way is proportional to the amount of nutrient remaining in the interior (Mulye and Turco, 1995). In contrast to GO-Fe-P, dissolution of MAP is described better with Higuchi model suggesting P release as a diffusion process based on the Fick's law (Costa and Sousa Lobo, 2001).

3.3. Diffusion of P from fertilizers granules in soils

Efficiency and long-term fate of applied fertilizer P depend on the type of soil and physical-chemical properties of the fertilizer. Assessing nutrient release from formulations *in situ* in soil using the visualization method provides a much clearer picture of the likely kinetics of nutrient release in the environment. Visualization of P diffusion was performed in triplicate for each product in each soil and since all replicates showed similar results (overall coefficient of variation was 6.17 %), for the sake of clarity only one replicate per sample per day is presented (Fig. S2). Day 1 after application of MAP we can see fast release and diffusion of P through all three soils. At Day 3 after application of MAP, for the Ngarkat soil, P had diffused throughout the soil in the Petri dish while for the MHR soil it required 49 days for P to diffuse to the edge of the Petri dish. Phosphorus diffusion in soil is controlled mainly by the volume of water-filled pore space in which diffusion may occur and the presence of compounds that can sorb H₂PO₄⁻ or HPO₄²⁻ ions (aluminosilicate minerals, Fe/Al

hydrous/oxide surfaces and Ca/Mg carbonates). From the chemical analysis of the soils (Table 1), we can see that the amount of Fe and Al present in soils follows the trend of the speed of P diffusion through soil, with the fastest diffusion for Ngarkat followed by MHR. For the BP soil at Day 56, P had diffused to reach 34% of the soil area, consistent with this soil having the highest content of Al and Fe (Fig. 7a). Results of the visualisation of P diffusion after GO-Fe-P application showed a gradual release and diffusion of P in all soils. Diffusion of P after 56 days from the application of the GO-Fe-P composite occupied 34, 7 and 16 % of the total soil area for Ngarkat, BP and MHR soils, respectively (Fig. 7a).

Chemical analysis of the soil in the Petri dishes at 56 days confirmed the results from the visualization (Fig. 7b, c), with greater diffusion of P in the Ngarkat and MHR soils and smaller distances of P diffusion in all soils for the GO-Fe-P material compared to MAP.

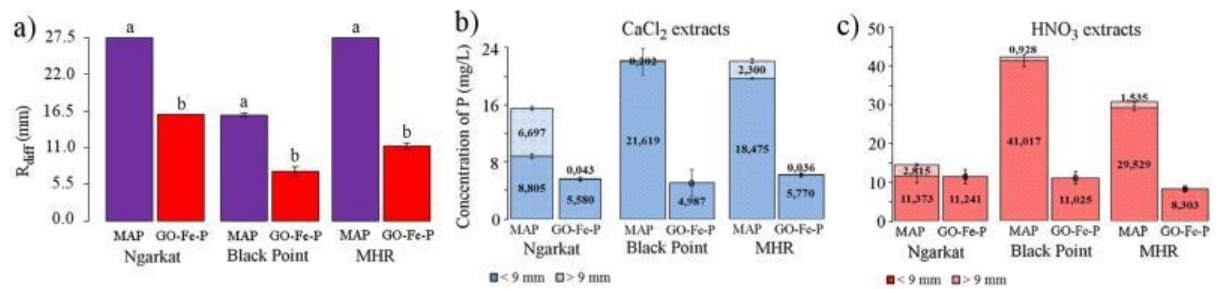


Fig. 7. (a) Radius of visualisation at 56 d after addition of MAP or GO-Fe-P granules to the soils. Concentration of added P recovered at the distance of less or more than 9 mm from the fertilizer application site at 56 d after fertilizer application in the Ngarkat, Black Point and Monarto Highland Road soils from (b) CaCl₂ extracts and from (c) HNO₃ extracts. Phosphorus was applied in the centre of Petri dish at the rate of 8 mg and 6 mg as MAP and GO-Fe-P, respectively. The radius of the P diffusion was determined as $R_{diff} = \sqrt{A/\pi}$ with A as area of diffusion. Error bars are standard deviations (n = 3). Bars with different letters are significantly different at a 5% significance level.

For the GO-Fe-P treatments, 99, 100 and 99% of CaCl₂-extractable P was obtained in the inner circle of N, BP and MHR soils, respectively (Fig. 7b). By contrast P from the MAP granules diffused much further in all three soils, although there were significant differences in diffusion between soils. The differences in chemical-physical properties of the soils had a significantly smaller effect on the release and diffusion of P from the GO-Fe-P composite compared to MAP treatments. The slow release of P from the GO-Fe-P and the constant increase of the radius of diffusion with time implies a constant and slow release of P from the composite, which would avoid precipitation of P close to the granule, especially in calcareous soils (Degryse et al., 2016). Concentrations of Fe measured in CaCl₂ extracts were below the detection limit of the ICP-OES (< 3 ppb) although we measured a small amount of Fe in leachates in the column release study, indicating a strong interaction of released Fe with soil. Efficacy of the GO-Fe-P materials as P fertilizers requires validation by evaluating plant growth and P uptake in a range of soils.

One disadvantage of the GO-Fe-P composite developed here is the relatively low P content (~5%) compared to commercial P fertilizers, which usually contain 10-20% P – this poses constraints for commercial use due to increased transport and application costs. Similar limitations apply to other P-loaded carriers suggested as slow-release fertilizers e.g. layered double hydroxides which generally have P loadings of less than 5% (w/w) (Everaert et al., 2016; Wang et al., 2016). For P-loaded carriers, future work needs to focus on increasing the loading of P (and other macronutrients) so that transport and spreading costs are minimized.

4. Conclusion

Starting from the low-cost and naturally abundant material, graphite, by a simple synthesis route a novel carbonaceous material, GO-Fe, was obtained. GO-Fe composite was found to be effective in retaining up to ~5% P on its surface and releasing P slowly to solution compared to a commercial MAP fertilizer. Visualization and chemical analysis of P diffusion in three soils showed more than 99% of the P released from GO-Fe-P was retained in the composite or in the near vicinity of the application site, confirming the slow release characteristics. This suggests GO-Fe-P composites as promising carriers for P which could enable better usage of added nutrient by plants without negative effects on the environment.

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