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Double-boiled linseed and mustard oil-based formulations to prepare oil-coated controlled release fertilizers

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ABSTRACT

Controlled nutrient release is one of the best fertilizer management options to enhance nutrient recovery efficiency and minimize environmental pollution. The research was conducted at Division of Soil Science and Agricultural Chemistry, ICAR-Indian Agricultural Research Institute, New Delhi during 2019–20 with the aims to formulate four oil-based formulations from different combinations of double-boiled linseed (*Linum usitatissimum*) and mustard (*Brassica juncea*) oils for coating diammonium phosphate (DAP) and to assess nitrogen (N) and phosphorus (P) release from them against uncoated DAP. Results revealed that oil-based formulation with 100 wt% linseed oil (Oil-4 formulation) showed maximum variation in weight over the 30 days of curing; whereas, oil-based formulation containing 25 wt% linseed oil + 75 wt% mustard oil (Oil-1 formulation) had lowest variation in weight during curing. The N and P release pattern from oil-based formulations of coated DAP over 30 days in water medium with reference to uncoated DAP revealed that Oil-1 coated DAP formulation released lesser quantities of N and P than Oil-2 coated DAP; while 8% levels of coating material released lesser N and P than the 4% levels of coating. Compared to First-order kinetics model, the N and P release data were better fitted to Korsmeyer-Peppas model, which revealed that nutrient release from uncoated DAP followed Quasi-Fickian diffusion. Except 8%-Oil-2-DAP, all the oil-based formulations of coated DAP followed anomalous (Non-Fickian) diffusion. Thus, it may be concluded that double-boiled linseed and mustard oil-based formulations (Oil-1 formulation) of coated DAP could be an alternative option to produce cost effective controlled release fertilizers.

Keywords: Controlled release fertilizers, Diammonium phosphate, Korsmeyer-Peppas model, Linseed oil, Mustard oil

World population will surpass 9.2 billion by 2050 (UN 2013). Thus, intensive agriculture is the utmost necessary action should be conducted in order to feed the ever increasing population. Fertilizer is the inevitable part of intensive agriculture. However, recovery efficiencies (NREs) of the N- and P- fertilizers are hardly 35-40% and 15–20%, respectively. Therefore, increasing recovery efficiency of N and P-fertilizers in cost-effective manner is necessary to increase farm income and to reduce environmental pollutions from nutrient losses. Best possible way to enhance NREs is the use of controlled release fertilizers (CRFs). The CRFs are the fertilizers with slow and controlled nutrient release capacity that possibly synchronize with plant nutrient demand (Trenkel 2010). Several researchers formulated CRFs by nutrient loading in hydrogel polymer matrix (Sarkar *et al.* 2015), surface coating of commercial fertilizers (Sarkar *et al.* 2018, 2020, 2021) and nano-fractions of unconventional resources (Roy *et al.* 2015, 2018a, 2018b). Among which surface coating is most popular and economically feasible.

Oil-based formulations could be one of the most suitable to coat the fertilizers because of its hydrophobic nature and easy accessibility. However, drying of oil-coating is practically a problem. In contrary, drying oils like linseed oil (*Linum usitatissimum*) may reduce drying time without any mechanical intervention. Ease of availability, low-cost, lower quantity of mono-unsaturated fatty acids (MUFAs, single double-bond in carbon-chain) and higher quantity of poly-unsaturated fatty acids (PUFAs, two or more double-bond in carbon chain) resulted linseed oil a good material for surface coating (Svane 2006). Thus, mixing of linseed oil with other oils having lower quantity of PUFAs could

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be a better option for its widespread utilization (Scrimgeour 2005). Mustard (*Brassica juncea*) oil contains higher MUFAs and lower PUFAs and its ease of availability in every Indian kitchen made it suitable to synthesize oil-based formulations along with drying oil for coating of fertilizers. However, very scarce information is available on oil-based formulations to prepare CRFs. Therefore, this article aims to formulate and identify the best oil-based formulations for fertilizer coating, and to assess nutrient release kinetics from coated fertilizers.

MATERIALS AND METHODS

The present laboratory experiment was conducted at the Division of Soil Science and Agricultural Chemistry, ICAR-Indian Agricultural Research Institute, New Delhi, India during 2019–20. For this experiment, commercially available linseed oil and mustard oil were obtained from local market. Linseed oil was dark amber coloured having saponification equivalence (SE, amount of oil saponified per unit mol of KOH) 292 g oil/mol of KOH; while mustard oil was brownish yellow coloured with SE 299 g oil/mol of KOH. Mustard oil was used as is purchased, while the linseed oil was boiled on a magnetic stirrer-cum-heater under constant stirring at 300 rpm for 2 h in open air condition with the assumption that the heating and oxidation will increase ionization of carboxyl groups (-COOH) and breaking of C=C double bonds and initiation of free-radical polymerization. Resulted boiled linseed oil became denser and darker in colour called double boiled linseed and used subsequently for oil-based formulations.

Initially four oil-based formulations namely, (i) Oil-1 formulation (25% linseed oil + 75% mustard oil); (ii) Oil-2 formulation (50% linseed oil + 50% mustard oil); (iii) Oil-3 formulation (75% linseed oil + 25% mustard oil); and (iv) Oil-4 formulation (100% linseed oil) were prepared using linseed and mustard oil by heating the mustard oil for 30 min at 70 ºC followed by mixing of boiled linseed oil at pre-defined ratios under constant stirring at 200 rpm. Finally, one set of each oil-based formulations were poured in petri-dish for periodical assessment of per cent change in weight (W%) and another set was stored in air-tight container for further fertilizer coating. The W% was assessed over the period of 30 days and calculated using the Eq 1.

$$W(\%) = \frac{(wi - wt)}{wi} \times 100 \qquad (1)$$

where, *Wi* and *Wt* correspondingly represents the initial weight of oil-based formulations and weight at time *t*. Based on minimum change in weight and drying ability two oil-based formulations were finally chosen for further coating of fertilizer. In this experiment, commercial grade di-ammonium phosphate (DAP) contained 18% N and 46% P_2O_5 was used as nutrient (fertilizer) core and it was coated @ 4 and 8 wt% on a rotating coater at room temperature. Coated fertilizers were then dried under hot-air and stored in container for nutrient (N and P) release experiment.

An incubation experiment was conducted with four oil-based formulations of coated DAP (4%-Oil-1-DAP, 8%-Oil-1-DAP, 4%-Oil-2-DAP and 8%-Oil-2-DAP) and uncoated DAP as reference to see the nutrient release pattern in distilled water for 30 days at 30ºC under laboratory condition. The release of N and P was determined individually by measuring their concentration in distilled water at 1, 3, 5, 10, 20 and 30 days. The N content was determined by Kjeldahl method using a steam distillation unit; while P content was determined spectrophotometrically after developing vanadomolybdo-phosphate yellow colour method at 420 nm wavelength using UV-VIS spectrophotometer (Jackson 1973). To identify the nutrient release rate, release and transport mechanism the nutrient release data from oil-based formulations coated-DAP and uncoated DAP were fitted to First-order kinetics model (Eq 2) and Korsmeyer-Peppas Model (Eq 3).

$$\ln M_t = \ln M_0 - K_1 \qquad (2)$$

$$M_t/M_0 = K_m.t^n \qquad (3)$$

where, M_0 and M_t correspond the initial concentration and concentration of nutrients (N and P) in solution at time *t*; the K_1 and K_m are the first-order rate constant and Korsmeyer-Peppas constant, respectively; whereas, *n* is Korsmeyer-Peppas exponent indicate release mechanism. Best fitted model was chosen based on coefficient of determination (R^2) adjusted coefficient of determination (Adj R^2) and standard error of estimate (SEE). Higher values of R^2 and Adj R^2 and lesser value of SEE predict a model fits better.

RESULTS AND DISCUSSION

Oil-based formulations and properties: To assess the initial characterization of oils used, a robust review of literature was done. The reviewed literature suggested that linseed oil contained ~23% MUFAs and 74% PUFAs; whereas, mustard oil contained ~60% MUFAs and 36% PUFAs. Among PUFAs, α-linolenic acid (18:3 9c12c15c) is the major component that is responsible for polymerization upon heating in air (Scrimgeour 2005). On the other hand, W% of different oil-based formulations revealed that all the formulations gained weight during first 5 to 10 days of curing (drying).

It is depicted that the magnitude of weight gain (Fig 1) was highest for 100% linseed oil (Oil-4 formulation, 7.3%) followed by Oil-3 formulation (4.7%), Oil-2 formulation (2%) and Oil-1 formulation (0.7%). The increased weight could be due to oxidation of polymeric chain, absorption of oxygen and formation of hyperoxides. The PUFAs are prone to form *penta-dienyl* radicals, which starts polymerization and form elastic linseed oil-based polymers. Auto-oxidation polymerization of PUFAs in linseed oil formulation involved free-radical initiation, propagation and termination (Juita *et al.* 2012). Svane (2006) reported that weight of linseed oil increased up to 10% during first 10 days of curing. However, lesser increase in weight was associated in Oil-1 formulation which could be due to formation of less stable intermediates like *allylic* radicals from MUFAs in mustard oils that hinders proper polymerization during curing,

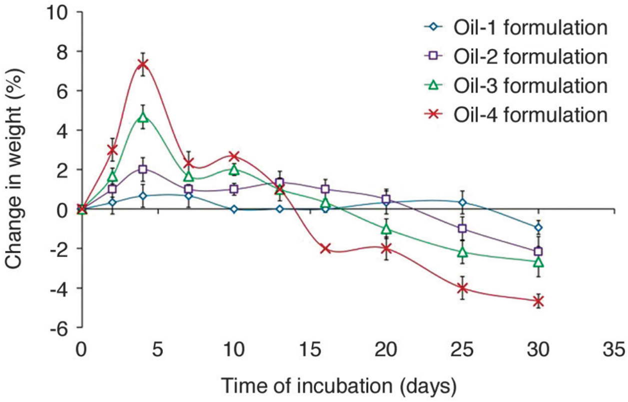

Fig 1 Per cent change in weight of different oil-based formulations during curing for 30 days in aerobic condition.

thereby lesser chance of surface cracking due to shrinkage of oil-based coated formulations.

With the advance of periods of curing, the surface of oil-based formulations became wrinkled because of the weight loss which was measured at different days of curing. Results indicated that here also the highest weight loss was measured in Oil-4 formulation (4.7%) followed by Oil-3 formulation (2.7%), Oil-2 formulation (2.2%) and least was in Oil-1 formulation (1.0%) (Fig 1). The weight loss could be the result of hydrolysis of ester-linkages in the oil-based formulations and simultaneous losses of volatile and degraded compounds. Literatures also reported that on drying, volume of linseed oil film may reduce the volume by ~8% (Svane 2006). Based on this findings, Oil-1 formulation and Oil-2 formulations were considered for the coating of DAP at 4 and 8 wt%.

Fertilizer coating and nutrient release kinetics from coated fertilizers: Nutrient release pattern from oil-based formulations coated DAP and uncoated DAP is presented in Fig 2. During incubation, uncoated DAP released ~90% N and 77.5% P at 5 days after incubation (DAI); whereas, coated DAPs like 4%-Oil-1-DAP, 8%-Oil-1-DAP, 4%-Oil-2-DAP and 8%-Oil-2-DAP released ~15.6, 7.8, 18.2 and 8.0% N, and ~14.7, 6.8, 10.2 and 8.4% P, respectively at 5 DAI.

Overall, Oil-1 formulation and Oil-2 formulations coated DAP released ~55.5 and 64.7% N; whereas, P release was ~51.3 and 59.4%, respectively. Higher linseed oil content in Oil-2 formulations may cause surface cracking of coatings of the Oil-2 coated DAP, which resulted in greater nutrient release. The release pattern of N and P from the 4% and 8% coating of both Oil-1 and Oil-2 shows similar release pattern till day 3rd after which a drastic increase in release pattern of N and P observed. This could be due to hydrophobic nature of the oil-formulations. But with time, surface cracking of the coating materials may be the reason behind it. Further, higher content of linseed oil causes more surface contractions, which could be the reason for more release in Oil-2 formulation coated-DAP. Indeed, level of coatings (@ 4 and 8 wt%) had vast impact on slow release properties of oil-based formulations coated DAP. Increased coating level (@ 8 wt%) reduced N (50.9% in comparison with 69.2% for 4% coating level) and P release (51.8% in comparison with 58.9% for 4% coating level) from oil-based formulations coated DAP. Suri and Datta (1995) reported that linseed oil-coated urea significantly reduced the N release as compared to uncoated urea and increased the dry matter yield (direct application as well as residual) of maize. Sarkar *et al.* (2017; 2020) reported that increased coating percentage of poly(vinyl alcohol) and liquid paraffin coated DAP reduced the N and P release.

Based on coefficient of determination (R^2), adjusted coefficient of determination (Adj R^2) and standard error of estimate (SEE) it was confirmed that the nutrient release

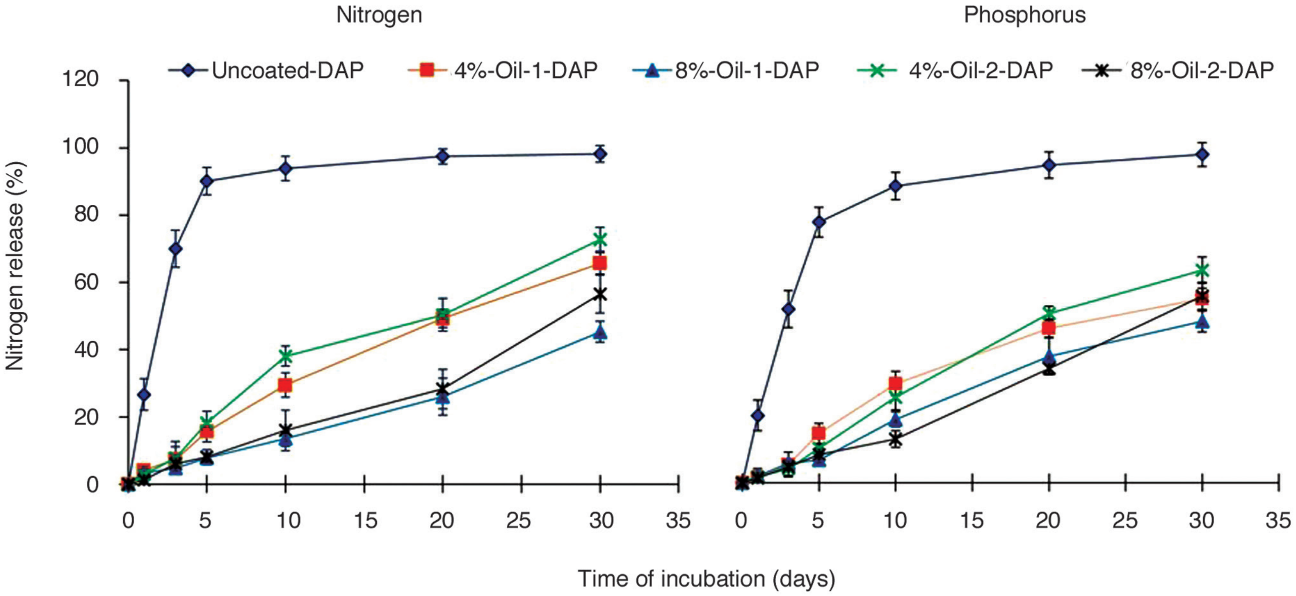

Fig 2 Nitrogen and phosphorus release pattern from 4%-Oil-1-DAP, 8%-Oil-1-DAP, 4%-Oil-2-DAP and 8%-Oil-2-DAP in comparison with Uncoated-DAP.

Table 1 Comparison of N and P release kinetics from oil-based formulations of coated DAP and uncoated DAP using First-Order Kinetic Model and Korsmeyer-Peppas Model

Nutrient release	Products evaluated	First-Order Kinetic Model			Korsmeyer-Peppas Model		
		R^2	Adj. R^2	SEE	R^2	Adj. R^2	SEE
N release	Uncoated-DAP	0.431	0.396	20.46	0.964	0.954	5.164
	4%-Oil-1-DAP	0.765	0.751	0.542	0.918	0.913	0.320
	8%-Oil-1-DAP	0.860	0.851	0.393	0.902	0.895	0.329
	4%-Oil-2-DAP	0.648	0.626	0.805	0.887	0.880	0.455
	8%-Oil-2-DAP	0.795	0.785	0.586	0.955	0.953	0.273
P release	Uncoated-DAP	0.587	0.561	18.96	0.936	0.920	5.066
	4%-Oil-1-DAP	0.673	0.653	0.786	0.929	0.924	0.367
	8%-Oil-1-DAP	0.833	0.823	0.484	0.972	0.971	0.197
	4%-Oil-2-DAP	0.784	0.771	0.651	0.962	0.958	0.278
	8%-Oil-2-DAP	0.845	0.835	0.512	0.978	0.976	0.194

kinetics fitted better to Korsmeyer-Peppas Model than the First-order rate kinetics (Table 1). To obtain exact nutrient release exponent (n) of Korsmeyer-Peppas Model, the first 60% fractional nutrient release (M_t/M_0) data was used as per the recommendation of Korsmeyer and Peppas (1984).

The exponent (n) was used to characterize nutrient release mechanism and nutrient transport mechanism; where $n<0.5$ represents Quasi-Fickian diffusion and non-swelleble matrix diffusion; while $n=0.5$ represents Fickian diffusion and non-swelleble matrix diffusion; and $0.5<n<1.0$ represents Anomalous (Non-Fickian diffusion) and nutrient released through both diffusion and relaxation (Korsmeyer and Peppas 1984). Further, $n=1.0$ represents case II transport and zero order release; while $n>1.0$ represents super case II transport and relaxation or erosion. The kinetics data revealed that N and P release from uncoated DAP followed non-swellable matrix diffusion and Quasi-Fickian diffusion (Table 2). Whereas, N release from oil-film coated DAP was due to both diffusion and relaxation and followed anomalous (Non-Fickian transport). Similarly, P release from 4%-Oil-1-DAP, 8%-Oil-1-DAP and 4%-Oil-2-DAP followed anomalous (Non-Fickian transport) due to both diffusion and relaxation. However, 8%-Oil-2-DAP followed super case-II transport due to either relaxation or erosion.

Bortoletto-Santos *et al.* (2016) suggested that the value of $n>1$, indicated that nutrient release was highly restricted by the polymeric or oil coating, which also indicated that lag period of nutrient release may tends to infinite. Coating of urea with 2 wt% of castor and soybean oil reduced the N release by 14 days; whereas, 5 and 7 wt% coatings extends the N release by 42 days (Bortoletto-Santos *et al.* 2020). Overall, this study demonstrated that Oil-1 formulation showed minimal variation in weight during curing. From Korsmeyer-Peppas release exponent (n), it was confirmed

Table 2 Parameters (n, K_m) of Korsmeyer-Peppas model, release and transport mechanisms of N and P release

Nutrient release	Products evaluated	n	K_m	Release mechanism	Transport mechanism
N release	Uncoated-DAP	0.23	24.2	Non-swellable matrix diffusion	Quasi-Fickian diffusion
	4%-Oil-1-DAP	0.70	0.64	Both diffusion and relaxation	Anomalous (Non-Fickian transport)
	8%-Oil-1-DAP	0.73	0.34	Both diffusion and relaxation	Anomalous (Non-Fickian transport)
	4%-Oil-2-DAP	0.77	0.46	Both diffusion and relaxation	Anomalous (Non-Fickian transport)
	8%-Oil-2-DAP	0.87	0.16	Both diffusion and relaxation	Anomalous (Non-Fickian transport)
P release	Uncoated-DAP	0.30	14.8	Non-swellable matrix diffusion	Quasi-Fickian diffusion
	4%-Oil-1-DAP	0.75	0.42	Both diffusion and relaxation	Anomalous (Non-Fickian transport)
	8%-Oil-1-DAP	0.73	0.34	Both diffusion and relaxation	Anomalous (Non-Fickian transport)
	4%-Oil-2-DAP	0.93	0.15	Both diffusion and relaxation	Anomalous (Non-Fickian transport)
	8%-Oil-2-DAP	1.19	0.02	Either relaxation or erosion	Super case-II transport

that uncoated DAP followed Quasi-Fickian nutrient diffusion and oil-based formulations coated DAP followed anomalous (Non-Fickian) diffusion during nutrient release. The nutrient release from oil-based formulations coated DAP reduced significantly in comparison with uncoated DAP. Higher coating percentage of DAP caused greater reduction in N and P release. Therefore, oil-based formulations of coated DAP will extend the period of nutrient release which in turn, will supply nutrients for longer period, thereby increase nutrient use efficiency. Therefore, the oil-based formulations (particularly Oil-1 formulation) could be used as an alternative to produce cost effective controlled release fertilizers.

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