



Review of Nano-clay Polymer Composites for Controlled Nitrogen Release: Prospects and Limitations

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Abstract

This review paper discusses the potential and limitations of polymer composites for smart nitrogen (N) supply to meet the needs of agricultural crops. Unlike most conventional fertilizers, nano-clay polymer composites (NCPCs) offer a slow-release mechanism that enhances nitrogen use efficiency and reduces its loss to the environment. NCPCs are normally synthesized using solution blending, melt blending and in situ polymerization. Solution blending offers a better clay dispersion in the polymer matrix than melt blending owing to its low viscosity and strong stirring force. NCPCs have been characterized by several techniques, including equilibrium water absorbency, Fourier transform infrared spectroscopy, scanning electron microscopy, X-ray diffraction and nutrient release kinetics. The potential benefits of using these composites are highlighted, including improved nitrogen use efficiency and reduced environmental impacts, as are their prospects for widespread use in agriculture and mitigation of the adverse environmental effects from conventional fertilizers. In addition, the limitations of NCPC technology, such as cost, scalability and potential negative environmental effects, are also investigated. The paper provides a wide perspective on the NCPC technology, including the regulatory environment and policy, industry trends and commercialization potential. NCPCs offer many benefits to increase nitrogen use efficiency and reduce pollution affecting water quality, air quality and climate. The main current barrier to overcome is to reduce production costs, so that farmers may also benefit financially from the higher nitrogen use efficiency and associated reduced amounts of nitrogen wasted to the environment.

Keywords Solution blending · Bentonite clay · X-ray diffraction · Fourier transform infrared spectroscopy · Scanning electron microscope · Equilibrium water absorbency · Nitrogen fertilizer

Introduction

To feed the world's growing population while simultaneously reducing nitrogen (N) pollution, fertilizer must be used in a smarter way than at present [24]. Almost two-thirds of fertilizer nitrogen applied to fields is wasted by loss to the environment, with only one-third effectively utilized by plants. According to the United Nations Conference on Sustainable Development, global N fertilizer use could increase by at least 50% by 2050 (base year 2006) in order to keep up with rising food production for a growing population [96, 112]. On the other hand, excessive

use of N-fertilizers causes ammonia volatilization, nitrous oxide emissions and nitrate leaching, which can adversely affect air and water quality, biodiversity and human health and increase greenhouse gas emissions [12, 23]. Nitrogen fertilizers alone account for approximately 2.4% of world greenhouse gases (GHGs) emissions [34]. Around the world, nitrate entering underground waters through rainfall and irrigation methods is a major concern. Surface and groundwater bodies are being contaminated by nitrate-N ($\text{NO}_3\text{-N}$), partly as a result of using higher fertilizer applications than the dose recommended to meet crop demand [104]. Nitrate concentrations greater than 50 mg L^{-1} in drinking water are deemed unsafe and can lead to adverse health effects such as methemoglobinemia in

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newborn babies [114]. In anaerobic environments, denitrification to unreactive di-nitrogen (N_2) can produce nitrous oxide (N_2O) as a side product [4] which can harm the ozone layer and contribute to global warming [9, 81]. Ammonia volatilization also represents a further waste of fertilizer resources and is a serious concern in neutral and alkaline soils, where it can be especially large, contributing to poor air quality through formation of fine particulate matter ($PM_{2.5}$) [12].

Initiatives are being taken worldwide to control and slow down nitrification triggered by soil bacteria [3]. Apart from the environmental effects of increased N_2O emission, formation of inert N_2 also represents a waste of the substantial energy and money used to produce nitrogen fertilizers, while leading indirectly to more nitrogen pollution (as N_2 emissions mean that more fertilizers need to be produced to achieve food goals, with more concomitant releases) [113].

The nitrogen use efficiency (NUE) or plant absorption of N is typically 30–40% due to surface runoff, leaching, and volatilization [52, 80]. Inefficient use of resources results in significant economic and resource losses, thereby wasting huge amounts of valuable nitrogen compounds that could otherwise contribute to farmer livelihoods [12]. Therefore, increasing NUE with less wasted N provides an opportunity to meet food security goals, allowing more food with the same or smaller fertilizer inputs. This is crucial in terms of lowering environmental and agricultural production costs [126]. Principle 6 of the United Nations Economic Commission for Europe (UNECE) guidance makes it clear that measures to reduce the fraction of N wasted as environmental losses need to be accompanied by increased yield and/or reduced inputs if other forms of N pollution are not to be increased (so-called pollution swapping) [113].

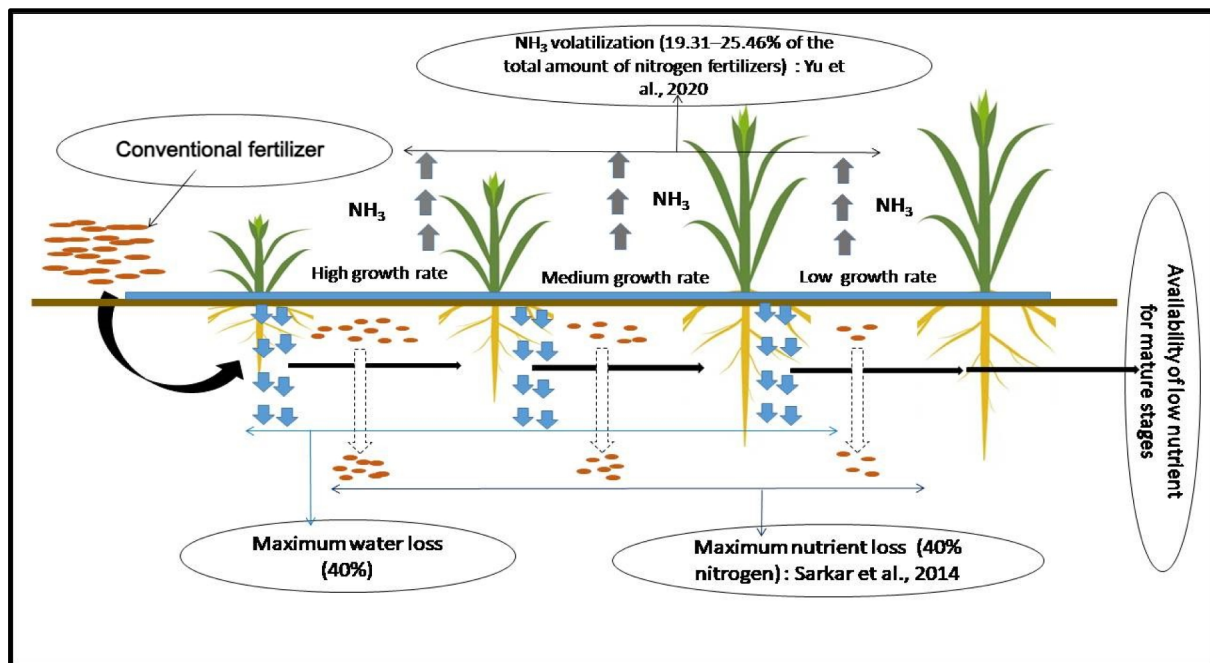
The fertilizer industry is constantly working on enhancing products to minimize the risk to the environment [67] by introducing new types of fertilizers or improving existing ones [6]. For instance, Government of India implemented 100% neem coating to all subsidized agricultural grade urea in the country. Recently, use of nano-clay polymer composites (NCPCs), which incorporate nanoscale clay particles (bentonite, kaolinite, montmorillonite, etc.) into a polymer matrix (mostly polyacrylate for agricultural use) to enhance mechanical and barrier properties, has attracted the attention of researchers and scientists due to their potential for various applications in agriculture and other industries [121]. Nano-clays have been described as ‘thin sheets of silicate materials in the order of 1 nm thick and 70–150 nm wide’ [30]. Most of the nano-clays are manufactured from montmorillonite clays, where their size is reduced and surface modified to be biocompatible with low toxicity and can be intercalated

within the polymer matrix [110]. The use of NCPCs as water management materials for the renewal of arid and desert environments has recently received a lot of attention. Encouraging results have been seen, as they can reduce irrigation water consumption, improve nutrient retention in soil, reduce plant death and increase crop growth [74].

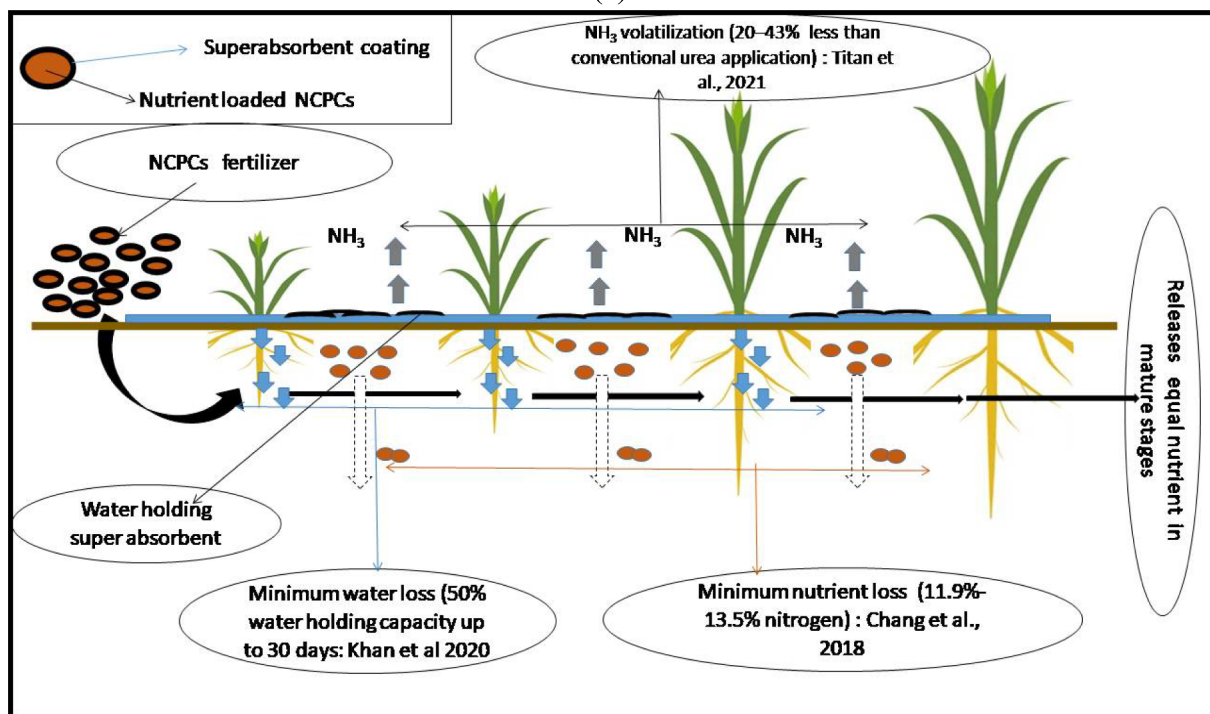
The combination of nano-clays with polymers results in a slow breakdown and they can be ‘loaded’ with nutrients, thereby providing a slow-release form of fertilizer. Such fertilizer may consist of a solid NCPC matrix into which nutrients are impregnated (see Sect. “[Synthesis, Preparation and Characterization of Nano-Clay Polymer Composites](#)”). NCPCs are recognized as a promising new technology for controlling the effective supply of nutrients [123]. The NCPCs have many advantages over conventional fertilizers, including a slower rate of fertilizer removal from the soil by rain or irrigation water, a longer supply of minerals, increased fertilizer efficiency, a lower frequency of application in accordance with normal crop requirements, decreased potential negative effects associated with overdosing and decreased toxicity (Fig. 1) [27]. Besides, NCPCs can be used in a variety of agricultural applications, including as soil conditioners, water-absorbent polymers and as a medium for slow-release pesticides.

The addition of nano-clay to the polymer network increases the cross-link density, which increases the mechanical strength of the polymer composites. This leads to a reduction in pore size, which improves the controlled-release behavior of the composites. The controlled release of nutrients is thereby better synchronized with the growth stages of the plants, increasing biomass yield and nutrient uptake while reducing nutrient loss [126]. In addition to the use of untreated nano-clays, the controlled-release behavior of NCPCs can be further improved by treating the nano-clays with surfactants (e.g., quaternary ammonium salt: cetyltrimethylammonium bromide). For example, surface modification of nano-clays with cetyltrimethylammonium bromide used in NCPCs has been shown to result in better retention of nutrients and an optimal release rate in response to plant needs [123]. Surface-modified nano-clays are inherently hydrophobic, which significantly improves the mechanical and rheological (study of the deformation and flow of matter) properties of NCPCs and thus influences the release and retention of nutrients [94, 136].

The objective of this review paper is to assess the current knowledge of NCPCs as a basis for optimized N delivery for better yield and environmental sustainability. The review seeks to identify the opportunities and challenges associated with these composites on a global scale, shedding light on their potential for improving N-based applications while addressing the associated limitations. Overall, the use of NCPCs for smart delivery of N has the



(a)



(b)

Fig. 1 Schematic presentation of nitrogen and water loss under application of (a) conventional fertilizers versus (b) nano-clay-based fertilizers. [7, 43, 102, 134]

potential to revolutionize agriculture by reducing nitrogen waste, improving yields and minimizing environmental impact [118]. However, further research and development is needed to optimize this technology and bring it to market, as well as to reduce costs.

Why Smart Delivery?

Excessive use of conventional fertilizers leads to economic burden, reduces fertilizer use efficiency and increases nutrient losses. While many nano-fertilizers are still in

development and not widely available, recent research has shown a growing interest in their potential benefits, such as increased nutrient use efficiency and reduced environmental impact compared with most conventional fertilizers (Table 1) [36]. It has been reported that conventional fertilizers (such as urea) are effective for only 10–12 days, while NCPC fertilizers can release nutrients, especially $\text{NO}_3\text{-N}$, for up to 50 days [111]. Here it is important to distinguish between NCPCs and ‘nano-urea’ liquid fertilizer (unspecified proprietary nanoparticles), which has been the subject of significant debate recently [21]. Whereas ‘nano-urea’ may contain nanoparticles in suspension, in NCPCs fertilizers as discussed here, are solid granules (c. 2–4 mm diameter) coated with NCPCs or solid NCPC impregnated with fertilizer, thereby providing both a physical barrier to slow dissolution and a nano-clay complex into which nutrients can be absorbed. To be effective, slow-release N-fertilizers must demonstrate a reduction in N leaching, an increase in N use efficiency and ideally both lower production costs and higher yield compared with conventional fertilizers [25]. Production and sale costs may be higher for coating fertilizers, and this additional cost needs to be more than offset by the financial benefits for farmers.

Polymer-coated fertilizers (i.e., without NCPCs) have until recently represented the most promising sector of controlled-release fertilizers, as these have the ability to provide a slow release and optimal nutrient supply during crop growth. As a result, their use is thought to help both the environment and the economy [53, 66]. Such polymer-coated fertilizers can be further improved by the incorporation of nano-clay, thereby forming the nano-clay polymer complex with increased surface area. A larger surface area can result in even slower release and therefore better uptake of the nutrient by plants [108]. According to Noellsch et al. (2009), applying polymer-coated urea to low-lying fields on clay pan soils may improve crop performance and economic returns compared with applying urea alone, pointing to the potential beneficial interactions of clay, as exploited in NCPCs fertilizers [78]. Polymer-

coated urea may be a viable option for achieving both high yield output and low environmental costs. Soils that had NCPCs applied have been shown to exhibit a lower water desorption rate compared to soils without NCPCs application [74]. As the clay load in NCPCs increases, the water desorption rate decreases [74]. These results show that NCPCs have a high ability of water absorption, water retention and moisture storage. Thus, the superabsorbent NCPC polymer which can absorb and store a lot of water in the soil gradually released the stored water when the soil moisture content decreased [122]. This has been shown to allow in longer irrigation cycles, less frequent watering and increased plant drought resistance [122]. It has been reported that NCPC could save up to 50% of standard fertilizer doses while maintaining yield in crops such as rice and wheat [45].

Synthesis, Preparation and Characterization of Nano-clay Polymer Composites

Methods of Synthesizing Nano-clay Polymer Composites

Three processes that are available for the synthesis of nano-clay polymer composites are solution blending, melt blending and in situ polymerization:

- (a) *Solution Blending* The solution mixing method is commonly used for making polymer nanocomposites with layered silicates (Fig. 2a). The mixing process involves dispersing clay in a polymer solution with vigorous agitation, followed by controlled solvent evaporation and casting of the composite film [91]. A solvent such as water, chloroform, or toluene is introduced to swell the clay’s silicate layers. This swelling increases the interlayer spacing, making it easier for polymer chains to penetrate. However, the swelling behavior varies among clay types, for instance, 2:1 expanding clay minerals like

Table 1 Benefits of smart nutrient delivery through nano-clay polymer composites

| Benefits of smart delivery | Extend of benefits | References |
|--|---|------------|
| Slow release of nutrients | Nutrients released over 40 days longer than conventional fertilizers | [111] |
| High yield output and low environmental cost | 28% higher yield and 250%-300% lower cost benefit over conventional fertilizer | [78] |
| Optimal nutrient supply during crop growth | Decreasing the fertilizer application rate by 20 to 30% over conventional fertilizer | [53, 66] |
| Nutrient use efficiency | Increase of 64% in NUE | [90] |
| High ability of water absorption | Increase of 22% in water absorption after 21 days compared to conventional fertilizer | [122] |

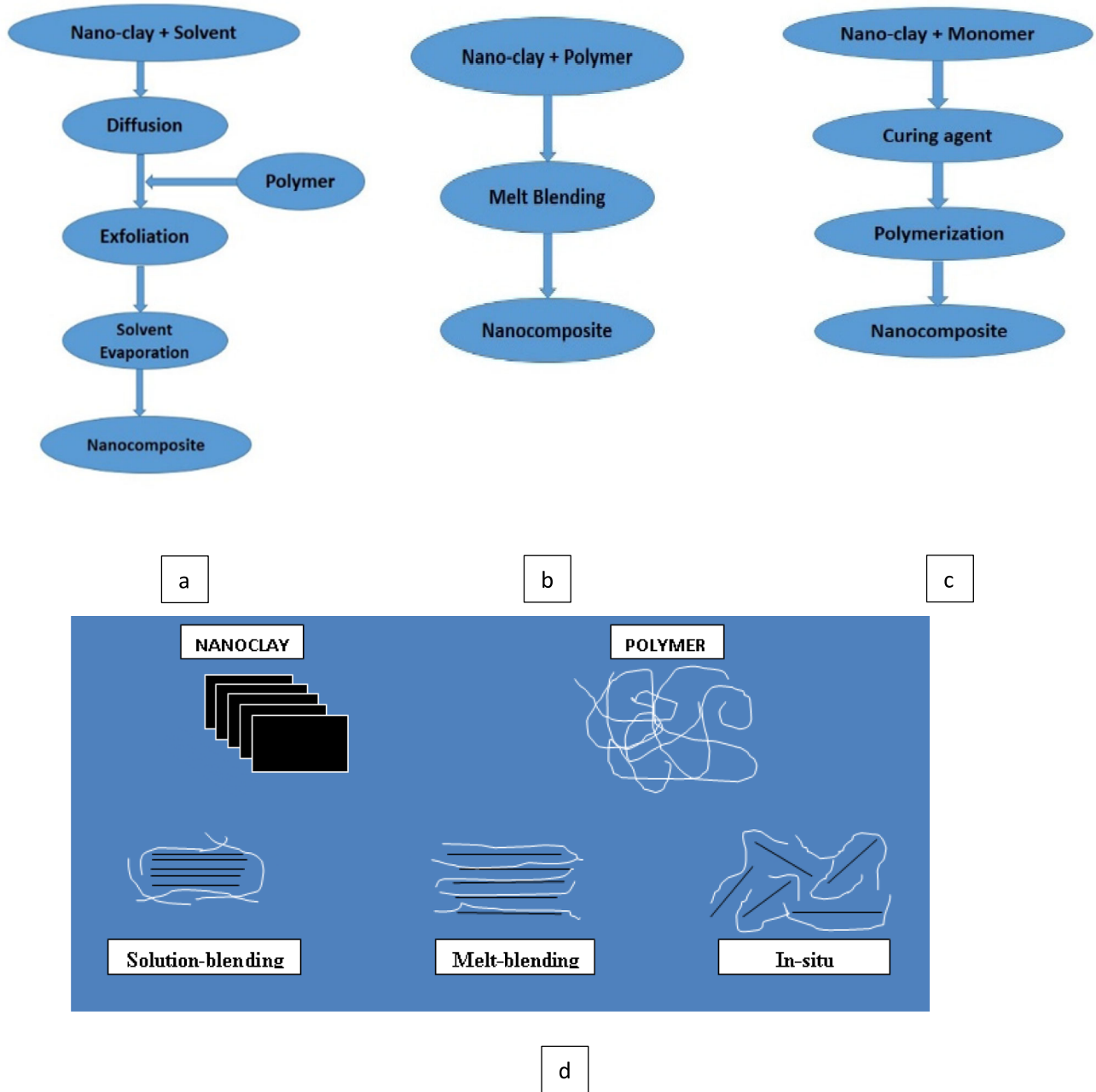


Fig. 2 Synthesis of nano-clay polymer composites by **a** solution blending, **b** melt blending, **c** *in situ* polymerization techniques and **d** the intercalation of nano-clays in polymer matrix that is achieved by each of these three approaches

montmorillonite and bentonite exhibit significant swelling, while minerals like vermiculite have limited swelling. By contrast, 1:1 minerals such as kaolinite and 2:1 non-expanding minerals like illite do not swell. When the polymer is dissolved in the same solvent, the polymer chains can intercalate between the swollen silicate layers of expanding type of minerals [39]. Depending on factors like the polymer, clay type, and processing conditions, the result may be either exfoliation (where the clay

layers are completely separated) or intercalation (where the polymer is partially embedded between the layers but remain stacked). This method enhances properties such as mechanical strength, barrier properties and thermal stability in polymer nanocomposites, as the dispersed clay layers can restrict polymer chain mobility and improve reinforcement.

(b) *Melt Blending* Melt blending is the industrially used process for preparing thermoplastic and elastomeric

polymeric clay/polymer nanocomposites. Using a banbury mixer or an extruder, the polymer is typically heated and mixed with the correct amount of intercalated clay (Fig. 2b). Melt blending takes place in the presence of an inert gas such as argon, N or neon, because these gases create a low-reactivity environment; they prevent unwanted chemical reactions or degradation of the materials involved in this process [50, 92].

- (c) *In situ Polymerization* In situ polymerization methods typically include dispersing nanoparticle fillers in a neat monomer (or multiple monomers) or a monomer solution, followed by polymerization in the presence of the dispersed nanomaterials (Fig. 2c) [85]. Several investigations concerning in situ polymerization methods showed the presence of covalent connections between the matrix and the nano-clay material in the resultant nanocomposites [79].

Solution blending is likely the most widely used approach for producing nano-polymers. In comparison with melt blending, the solution-blending process often results in improved dispersion of clay within the polymer matrix due to its low viscosity and strong stirring forces. However, melt blending is considered more industrially feasible, offering substantial economic potential and environmental benefits, such as lower chemical usage, energy efficiency and reduced solvent utilization [120]. The in situ polymerization method also produces a uniform dispersion and can be easily modified by adjusting polymerization parameters [124]. This can lead to enhanced material properties, but it often requires more complex processing techniques compared to solution blending and melt blending. The in situ polymerization has better intercalation of nano-clay and polymer than the solution-blending and melt blending (Fig. 2d). Among the various techniques, the incorporation of superabsorbents with inorganic nano-sized clays into a pure polymer network can enhance both the strength and swelling capacity of the nano-polymer [102].

Component Materials and Their Sources

Nano-clays, thin silicate sheets measuring approximately 1 nm in thickness and 70–150 nm in width, are derived from montmorillonite clays found in volcanic ash. These clays undergo size reduction and surface modification to yield biocompatible, low-toxicity nano-clays [42]. In the preparation of polymers, such as polyacrylamide, which incorporates nano-clay particles, acrylic acid and acrylamide serve as common monomers [88]. The cross-linking process, facilitated by ammonium persulfate (APS), involves the formation of covalent bonds between polymer

chains, creating a three-dimensional network structure [95]. Additionally, N, N-methylenebisacrylamide, a bifunctional cross-linking agent in polymer chemistry, plays a crucial role in enhancing the mechanical strength and stability of the resulting nano-clay polymer composites [51]. Mostly in two methods NCPCs will be loaded with fertilizer or other components, i.e., encapsulation (absorption of components after drying NCPCs through solution) and impregnation (component was added while NCPCs prepare process is going on).

A Laboratory Preparation Method of Nano-clay Polymer Composites

At the laboratory scale, the solution blending process is commonly used (Fig. 3). For this, acrylic acid (AA) ($C_2H_4O_2$) is dissolved in distilled water and partially neutralized with ammonia (degree of neutralization 60%), which is typically prepared in a three-neck flask equipped with a cooler, a thermometer and a N gas line [57, 105]. The flask is typically placed on a heater-controlled magnetic stirrer. Ammonium persulfate (APS), acrylamide (Am), N, N-methylenebisacrylamide (MBA) and bentonite clays are added to the monomer solution and stirred with a magnetic stirrer. In the presence of N gas, the temperature is gradually increased to 70 °C. The hydroxyl group in the bentonite clay reacts with the initiator (APS), generating a free radical on the bentonite structure. The poly (acrylic acid-acrylamide) branches of the bentonite backbone (or partially poly AA and poly Am) are formed by graft polymerization. The addition of the initiator (APS) leads to rafting and supports the start of homopolymerization. Water is soluble in the homopolymers of poly AA and poly Am (solvent). By using a cross-linker, these homopolymers are cross-linked together (MBA). The amount of initiator, cross-linker and clay determine how much water the nano-clay polymer composites can absorb and the amount of fertilizer that can be released [55, 57, 99]. The final polymerization product is washed several times in distilled water, dried at 100 °C to a uniform weight, ground and stored. Starch can be used instead of acrylamide for the synthesis of NCPCs without changing the slow-release property [98].

Preparation of Nano-clay Polymer Composite Impregnated Fertilizer with Superabsorbent and Moisture Preservation

Dry weighed gels are typically immersed in the aqueous solutions of the two fertilizers (diammonium phosphate (DAP), urea) to establish swelling equilibrium [100]. The swollen gels are then dried, followed by grinding and passing through a sieve to get a desirable particle size for

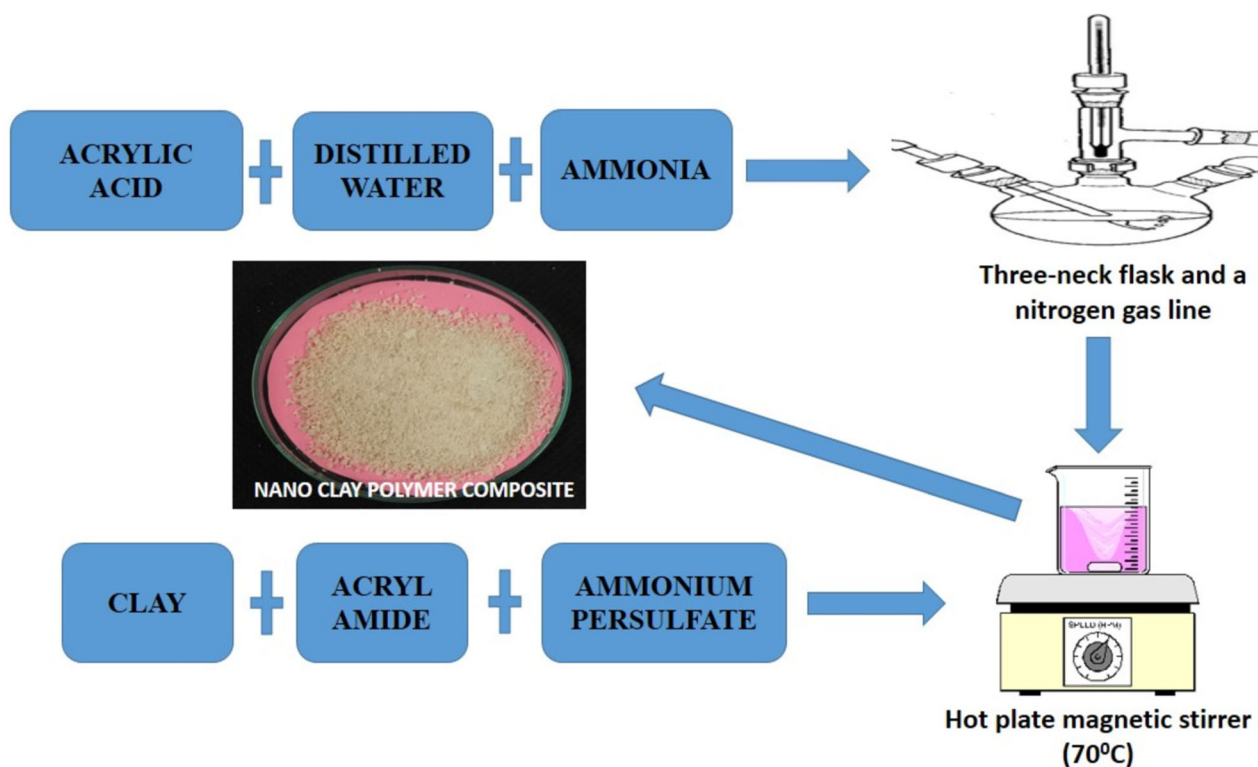


Fig. 3 Complete schematic diagram of a typical laboratory preparation of nano-clay polymer composites

field application (e.g., 2 mm). Graft co-polymerization (one or more types of monomers are polymerized and chemically attached to a pre-existing polymer chain) techniques can be employed for increasing biodegradability of NCPCs. For example, Mandal et al. [63, 64] reported a novel bionanocomposite, i.e., chitosan-grafted nano-clay polymer biocomposite via graft copolymerization techniques. Further, it was also reported that novel starch-grafted nano-clay polymer biocomposite increased biodegradability and water absorbency also increased after starch grafting equilibrium [84].

Characterization of Nano-clay Polymer Composites

Nano-clay polymer composites are characterized using techniques such as equilibrium water absorbency, Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), X-ray diffraction (XRD) and nutrient release kinetics, each with its own advantages and limitations (Table 2). In a comprehensive study by Chatterjee et al. (2023), the structural configuration of nano-clay polymer composites (NCPCs) of polyacrylate and kaolinite nano-clay, which were then impregnated with 1-naphthaleneacetic acid (NAA) and sodium nitrate (NaNO_3), was investigated [8]. The researchers suggested that the

hydroxyl groups ($-\text{OH}$) on the kaolinite surface undergo polymerization with polyacrylate monomer units. This interaction is favored by the formation of hydrogen bonds between kaolinite and polyacrylate, resulted in a strong structural framework for the composite material. This was found to be due to the hydroxyl groups (particularly $\text{Al}-\text{OH}$) on the kaolinite surface reacting with the carboxyl groups of both NAA and NCPC. This reaction is significant as it makes kaolinite an important cross-linking agent within the polymer matrix, improving the overall stability and functionality of the composite [11]. The incorporation of polyacrylate and NAA into the silicate galleries of kaolinite improves the ability of the composite to bind nutrients and allows for controlled release. In addition, the presence of NaNO_3 , a neutral electrolyte, is noteworthy. The study shows that NaNO_3 is absorbed within the polymer network and is present in its undissociated salt form. In contrast to NAA, which forms covalent interactions, the behavior of NaNO_3 is influenced by the cation exchange capacity of kaolinite ($3\text{--}15 \text{ cmol (p}^+) \text{ kg}^{-1}$). As a result, the nitrate anion tends to stay close to the kaolinite mineral and participate in a Donnan membrane equilibrium. This phenomenon occurs rather than penetrating the interstitial spaces within the NCPC, contributing to the unique nutrient release dynamics of the composite.

Table 2 Merits and demerits of different characterization techniques of nano-clay polymer composites

| Characterization Technique | Merits | Demerits |
|--|---|--|
| Equilibrium water absorbency (EWA) | Measures water absorption capacity, essential for applications requiring moisture control Indicates cross-link density and polymer elasticity Useful for assessing nutrient retention and release properties | Sensitive to cross-linker concentration, which may affect reproducibility High clay content may lower EWA due to limited polymer chain flexibility |
| Fourier transform infrared spectroscopy (FTIR) | Identifies functional groups and molecular interactions Detects specific bonding changes, e.g., hydroxyl, carbonyl, and Si–O groups Effective for studying cross-linking and crystallinity variations | Limited to detecting surface interactions Requires proper calibration for complex samples Unable to distinguish between very similar functional groups |
| Scanning electron microscopy (SEM) | Reveals surface morphology and composite structure Allows visualization of clay dispersion (exfoliated, intercalated, or aggregated) Provides insight into microstructure and potential porosity | Limited depth of field in high-magnification images Sample preparation may affect structure (e.g., drying can cause shrinkage) High vacuum requirement can limit observation of hydrated samples |
| X-ray diffraction (XRD) | Determines intercalation or exfoliation states Useful for identifying composite crystallinity Provides insight into polymer–clay interactions at the molecular level | Limited to crystalline or semicrystalline structures May not detect amorphous components effectively Interpretation can be challenging due to overlapping peaks |
| Nutrient release kinetics | Measures nutrient release rates from nano-clay polymer composites Reveals the influence of polymer swelling on release behavior Assesses the diffusion and dissolution properties of nano-clay polymer composites | Can be time-consuming for long-term release studies Requires specific conditions to simulate field application May not account for all environmental factors affecting release |

Equilibrium Water Absorbency

One of the most imperative properties of NCPCs is their water absorption behavior, which can be described by the equilibrium water absorbency (EWA) of the material. The EWA basically depends upon type and quantity of clays intercalated within the polymer matrix. With increase in clay content, the cross-linking density of polymeric matrices increased resulting into increase in EWA [74]. According to Sarkar et al. [102], the introduction of clay particles into the polymer network increased the cross-link density of the polymer, whereupon the elasticity of the polymer chains decreased, so that a high cross-link density means that there is not enough space for water molecules to penetrate the network; this leads to a lower equilibrium water absorbency. But among the variable percentages (8%, 10%, and 12%) of clay with chitosan-grafted zinc-containing nano-clay polymer bio composites, the lower percentage of clay-containing NCPC (8% clay content) had the highest equilibrium water absorption capacity as well as the highest moisture content at a given stress [64]. It is

possible that the presence of a synergistic effect between the –COOH, –COO, –CONH₂, and –OH groups in an NCPC product may influence the water absorption capacity properties [57]. The swelling rate of superabsorbent composites was primarily influenced by swelling capacity, particle size, surface area and superabsorbent density [86]. However, the EWA increased sharply when the amount of cross-linker is decreased in the range of 0.3–0.02% [131]. According to Guo et al. [28], when the amount of cross-linker was less than 0.06%, the water absorption capacity increased up to a value of 75 g g⁻¹ and then gradually decreased. Studies also show that the swelling rate during the first 50 min was higher than that of the later swelling process, i.e., the water absorption capacity was very fast initially before it decreased [122]. Physical filling of kaolin particles in polymers reduces the number of hydrophilic groups, resulting in a reduction in water absorbency [54]. Grafting with biomolecules (chitosan and starch) further increase water absorbency owing to addition of hydrophilic functional groups within NCPC [63].

Fourier Transform Infrared Spectroscopy

The Fourier transform infrared (FTIR) spectroscopy technique is widely used to study the molecular structure and composition of materials (Fig. 4a). The functional groups in the polymer matrix and nano-clay particles can be identified using FTIR spectroscopy (Table 3). Hydroxyl groups ($-\text{OH}$) can be detected in the FTIR spectrum by a large absorption band in the $3200\text{--}3600\text{ cm}^{-1}$ range, which is involved in hydrogen bonding with the nano-clay particles and can impact particle dispersion and orientation in the polymer matrix [68]. Furthermore, the Si–O stretching vibration and Al–O bonding in the clay structure appear in the $1000\text{--}1050\text{ cm}^{-1}$ and $900\text{--}920\text{ cm}^{-1}$ ranges, respectively [44, 75]. Alkyl groups ($-\text{CH}_3$, $-\text{CH}_2$) in the polymer matrix can be detected by absorption bands in the range of $2800\text{--}3000\text{ cm}^{-1}$ [87]. Changes in the degree of cross-linking or crystallinity can be identified using the peak position and intensity of these absorption bands. In the instance of acrylamide and acrylic acid, the carboxylic acid functional group ($-\text{COOH}$) in acrylic acid can be detected in the FTIR spectrum by a large absorption band in the $2500\text{--}3500\text{ cm}^{-1}$ range [71]. An absorption band in the range of $3000\text{--}3500\text{ cm}^{-1}$ with a strong peak around 3200 cm^{-1} identifies the amide functional group ($-\text{CONH}_2$). In the area $1600\text{--}1680\text{ cm}^{-1}$, an absorption band can indicate the presence of the $\text{C}=\text{C}$ double bond in acrylamide [60]. Carbonyl groups ($\text{C}=\text{O}$) and C–H groups in acrylic acid can be identified by an absorption band in the regions $1680\text{--}1725\text{ cm}^{-1}$ and $2800\text{--}3000\text{ cm}^{-1}$, respectively [46, 97]. The ammonium persulfate cross-linker indicates that the ammonium groups in ammonium persulfate can be detected by a prominent absorption band in the $1400\text{--}1500\text{ cm}^{-1}$ region. N-containing functional groups, such as nitrile (CN), can be detected in the FTIR spectrum by absorption bands ranging from 2200 to 2300 cm^{-1} [17]. Absence of OH stretching vibration (3400 cm^{-1}) and weakening of Si–O (1020 cm^{-1}) indicated interaction of clay and monomer during free radical mediated copolymerization reaction [65]. The $-\text{OH}$ stretching vibration characteristics peak (3400 cm^{-1} to 3800 cm^{-1}) recorded in clay and nano-clay disappeared in composites regardless of clay type or clay amount. The absorption band at 1030 cm^{-1} (Si–O stretching) vanished, showing that clays ($-\text{OH}$ groups) and monomers interacted during the copolymerization reaction [63].

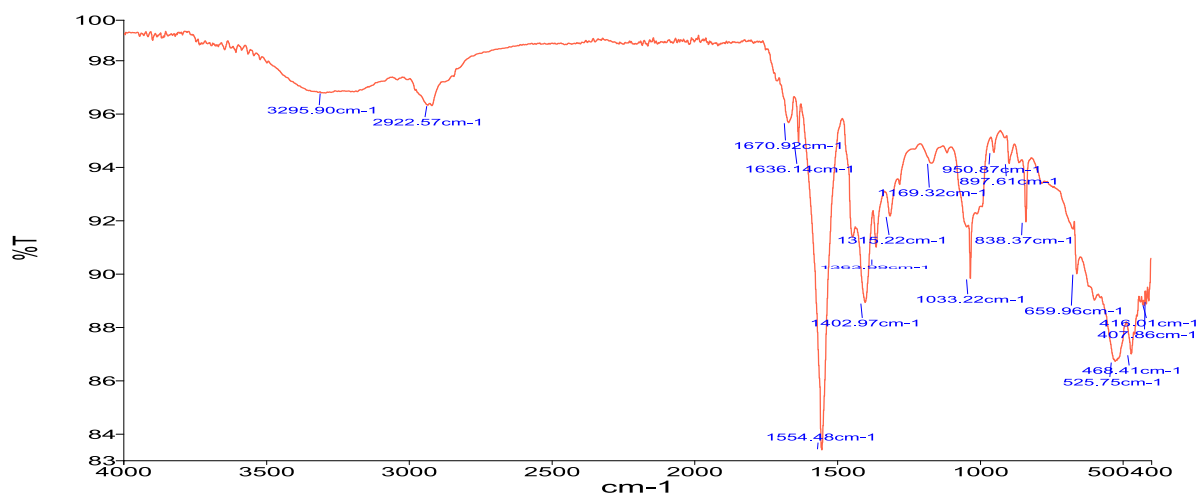
Scanning Electron Microscopy

Various architectures of NCPCs can be observed using scanning electron microscopy (SEM). These structures are determined by the interactions between the polymer matrix

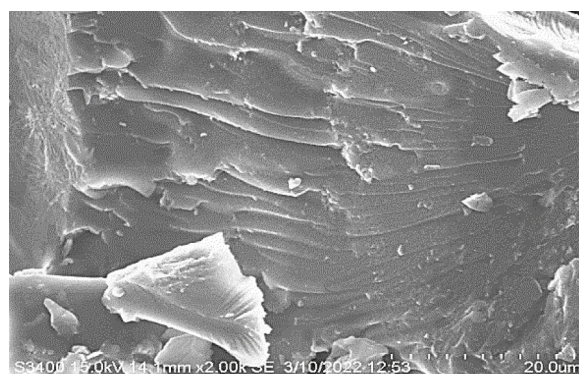
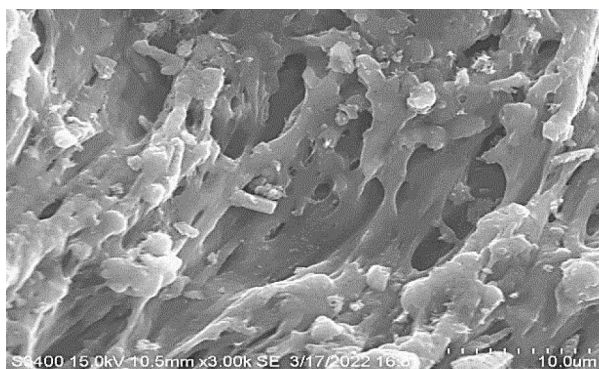
and the clay nanoparticles. They can have a major impact on the composite's overall attributes. Intercalated structures are commonly detected in SEM images of nano-clay polymer composites, where the clay particles are uniformly dispersed in the polymer matrix and stacked in layers between the polymer chains. SEM pictures show a regular pattern of clay layers between the polymer chains (Fig. 4b) [93]. The clay particles are completely dispersed in the polymer matrix in an exfoliated structure. They are separated from each other, which can be seen as a random distribution of individual clay particles in the polymer matrix [45]. When a structure is aggregated, the clay particles in the polymer matrix may group together to form an aggregate that appears as a cluster of clay particles in the polymer matrix. This could have an adverse influence on the composite material's mechanical qualities [38]. The clay particles are irregularly distributed in the polymer matrix of poorly dispersed NCPCs, resulting in zones of high and low clay particle concentration. SEM images show this structure as a rough distribution of clay particles within the polymer matrix [56]. The SEM images indicated that morphologies were fractured with some specific topographies [63]. The surface's texture changed as there was more clay present. As clay content increased, the surface became rougher. Compared to clay at the same clay concentration, nano-clay created a rougher surface topology because of its higher aspect ratio. There was not always homogeneous dispersion from clay aggregates, indicating that clay platelets were dispersed throughout the polymer matrix and created exfoliated nanocomposites. Chitosan-grated superabsorbent hydrogel also contained a highly porous network that lacked mechanical integrity [18].

X-ray Diffraction

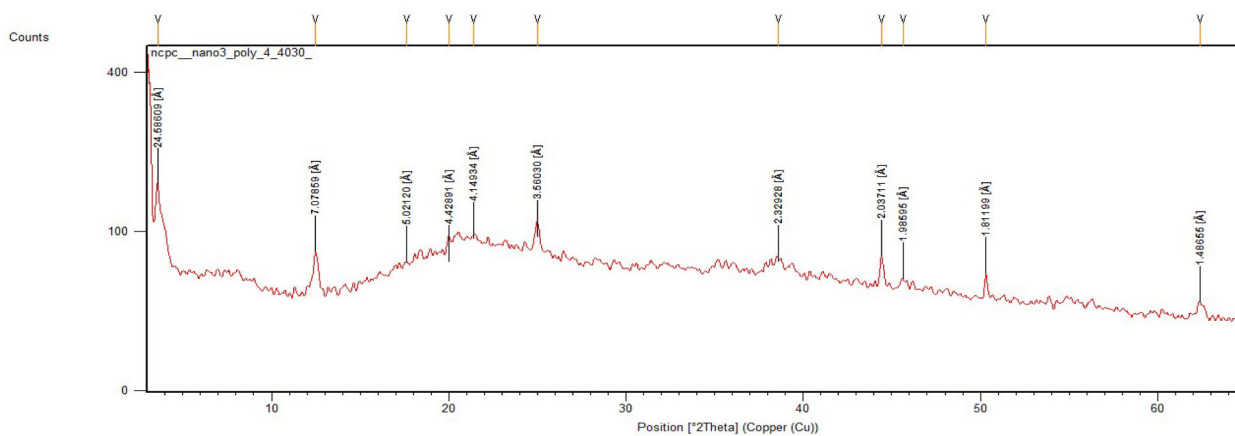
After clay minerals and organic polymers interact, many forms of composite materials are created, including conventional composites and microcomposite materials as well as intercalated and exfoliated composites [117]. Investigations of clay polymer composites using X-ray diffraction (XRD) have revealed the intercalation and exfoliation processes as well as the short-range order of the molecular constituents (Fig. 4c). It is widely acknowledged that during the intercalation process, the polymer separates the platelets as it enters the clay galleries, increasing the gallery spacing (d -spacing) [70]. According to Bragg's law, this would cause the diffraction peak to shift in favor of a smaller angle. When more polymers enter the gallery, the platelets become disorganized and some of them are even pushed away from the clay particle stacks (partial exfoliated). This will cause the XRD peak to have a wider distribution or potentially shift more to the left. While the



(a)



(b)



(c)

Fig. 4 **a** Fourier transform infrared spectroscopy (FTIR), **b** scanning electron microscopy (SEM) and **c** X-ray diffractogram of nano-clay polymer composites [Courtesy: Externally Aided Project 322, funded

by United Kingdom Research and Innovation (UKRI) Global Challenge Research Fund (GCRF) for South Asian N Hub]

Table 3 Fourier transform infrared spectroscopic band range (cm^{-1}) of different functional groups in nano-clay polymer composites

| Functional groups | Band range (cm^{-1}) | References |
|--|---------------------------------|------------|
| Hydroxyl (–OH) groups | 3200–3600 | [68] |
| Si–O stretching vibration | 1000–1050 | [75] |
| Al–O bonding | 900–920 | [44] |
| Alkyl (–CH ₃ , –CH ₂ –) groups | 2800–3000 | [87] |
| Carboxylic acid (–COOH) | 2500–3500 | [71] |
| Amide (–CONH ₂) group | 3000–3500 | [116] |
| C=C double bond | 1600–1680 | [60] |
| Carbonyl (C=O) groups | 1680–1725 | [97] |
| C–H groups | 2800–3000 | [46] |
| Ammonium groups | 1400–1500 | [119] |
| Nitrile (C≡N) groups | 2200–2300 | [17] |

starch/ natural montmorillonite clay hybrids displayed distinct peaks at $2\theta = 4.98^\circ$, the natural montmorillonite clays only showed a single peak at $2\theta = 7.21^\circ$. Additionally, because pure starch is an amorphous substance, it showed a curve in the $1\text{--}10^\circ$ range without any obvious peaks. The formation of a nanocomposite structure with starch intercalation in the gallery of the silicate layers of natural montmorillonite clay was indicated by the appearance of a new peak at 4.98° (d-spacing = 1.77 nm) along with the disappearance of the original nano-clay peak at $2\theta = 7.21^\circ$ (d-spacing = 1.23 nm) and an increase in d-spacing [1]. Although the organically modified nano-clay (I30E) alone produced an intense peak in the region of $2\theta = 3.93\text{--}4.16^\circ$ (d-spacing 2.23 nm) due to the development of traditional composite, starch-I30E hybrids revealed faint peaks immediately below the original peak of the I30E. This implied that little to no intercalation or exfoliation of the starch matrix had occurred [115]. Exfoliation of natural montmorillonite clay with soy protein composites were showed by [49]. They noted from the XRD peak that the multilayer natural montmorillonite clay is delaminated in the aqueous media by the soy protein macromolecules because of the relatively low natural montmorillonite clay content. However, the intercalated structure of natural montmorillonite clay predominates when its level in soy protein matrixes exceeds 16%. This occurrence supports the observation made by Ray and Okamoto [93] that the exfoliated or intercalated nanocomposite structure depends on the natural montmorillonite clay content.

The interactions between the clay and acrylic acid (AA), acrylamide (Am) polymer was also studied by XRD [100]. Physically combining clays obtained from Vertisol with the polymers resulted in sodium-saturated smectite, which had a basal spacing of 12.6 Å. This peak in the polymer/

Vertisol clay composites disappeared after the reaction. This demonstrated both clay exfoliation and polymer intercalation into the clay's stacked silicate galleries. Due to the presence of smectite, Saurabh et al. [104] noticed a peak in the XRD spectra of the commercial nano-bentonite at $2\theta = 6.6$ (d-spacing = 13.66). After the polymerization reaction, a sizable diffraction peak was observed in the physical combination of clay and polymer, and 2θ remained intact, indicating an exfoliated structure in the composite. But earlier, this peak had completely disappeared altogether. In the composite of sodium alginate, polyacrylic acid, polyacrylamide, bentonite, and urea polymer diffractogram, Wen et al. [129] also noted the elimination of the bentonite reflection. The results showed that silicate layers in NCPCs completely exfoliated after nano-clay was incorporated into the polymer matrix. The introduction of lengthy polymer chains into the gallery region of the nano-clay increased the silicate layers' interlayer gap and gave the material an exfoliated appearance.

In X-ray diffractogram analysis, the typical montmorillonite peak ($2\theta = 6^\circ$) became absent in after polymerization [64]. The lack of a typical montmorillonite peak indicated that bentonite clays were completely dispersed into the polymer matrix, implying that these polymers were exfoliated composites. Exfoliation was observed in NCPCs regardless of type or clay content [65].

Release Kinetics of Fertilizer Nutrients from Nano-clay Polymer Composites

The release of nutrients from NCPCs is primarily controlled by diffusion and dissolution mechanisms. Diffusion occurs when water penetrates the polymer network, releasing nutrients through the swollen matrix [1]. The swelling behavior of the polymer can influence the release rate, as superabsorbent polymers (SAP) or biopolymer matrices absorb water, expand and gradually release the embedded nutrients. The dissolution rate of the fertilizer is much faster than for NCPCs. For example, uncoated urea releases more than 85% of its nitrogen within two days due to rapid dissolution in the presence of moisture [32]. In contrast, urea encapsulated in NCPC is released significantly slower, with a controlled release of up to 65% over first 30 days [105]. This shows that NCPCs have the potential to develop controlled-release fertilizers that are tailored to the nutrient requirements of plants, thereby reducing nutrient losses.

Effects of Polymer–Clay Interactions

The interaction between the polymer and the nano-clay is crucial for the release kinetics (Table 4). NCPCs with higher clay content generally have slower release rates due

Table 4 Use of various nano-clays and nutrient sources impregnated within nano-clay polymer composites for controlled nutrient release

| Nano-clay | Nutrient/fertilizer impregnated into the NCPC | Polymer used to establish the NCPC matrix | References |
|-----------------------|--|---|------------|
| Kaolinite | Urea, diammonium phosphate (DAP) | Acrylic acid, Acrylamide | [102] |
| Kaolinite | Monopotassium phosphate (KH ₂ PO ₄) | Acrylic acid, Acrylamide | [122] |
| Bentonite | Microbial fertilizer | Alginate | [31] |
| Bentonite | Zn ²⁺ | Acrylic acid, acrylamide, Chitosan | [63] |
| Bentonite | DAP | Acrylic acid, acrylamide | [123] |
| Bentonite | Urea | Acrylic acid | [104] |
| Smectite | Urea, DAP | Acrylic acid, Acrylamide | [101] |
| Montmorillonite | Potassium phosphate | Polyvinyl alcohol | [29] |
| Montmorillonite | Potassium nitrate | Poly (acrylic acid-co- sodium acrylate) | [22] |
| Halloysite nano-tubes | Urea | Acrylic acid, Acrylamide | [128] |

to a higher cross-linking density within the polymer matrix [64]. This increased cross-linking reduces the diffusion pathways for water and dissolved nutrients, resulting in a more uniform release profile. According to Pirooz et al. (2018) [84], the dispersion of clay platelets in polymer galleries forms a network that restricts the movement of fertilizer molecules and further reduces the release rate of urea.

Role of Coating Materials and Advanced Composites

According to recent research, advanced materials such as superabsorbent carbonaceous microsphere polymers (SPCs) outperform conventional superabsorbent polymers in terms of slow-release properties. Ahmed et al. [1] found that NPK fertilizers coated with SPC remain effective for up to 30 days and significantly delay the nutrient release rate compared to uncoated variants. This improvement is due to the improved water-retaining properties and barrier effect of the composite materials, which enable a longer release time. Further advances in the development of NCPCs focus on optimizing their structure to better control nutrient release. Hydrophobic modifications and the use of layered clays, such as bentonite, improve barrier properties and allow for more targeted nutrient release that corresponds to plant growth stages [135]. These modifications help to reduce the initial erratic release often seen with uncoated fertilizers and provide an even and consistent nutrient supply over time [136].

Role of Modified Nano-clay Polymer Composites in Release and Storage of Nutrients

Nano-clays (montmorillonite, smectite, cloisite, bentonite, kaolinite, vermiculite) can be modified using various surfactants, such as, amines, alkyl cations, ammonium salts,

amino silane to make them more compatible with polymer matrices [5, 26, 123]. Modified nano-clays are referred as ‘organo-clays’ as they exhibit more organophilic characteristics and become compatible with hydrophobic organic polymers [123]. Owing to their large surface area, porosity, adsorption capacity and thermal stability, modified NCPCs can retain nutrients for a longer time, thus exhibiting better barrier properties [123].

Degradation

The degradation of NCPCs in agricultural applications is an important factor to consider in terms of environmental impact and long-term sustainability. Several studies have investigated the degradation of NCPCs in agricultural applications. According to Wang et al. [127], the degradation of poly butylene adipate-co-terephthalate (PBAT) NCPCs containing montmorillonite clay particles in soil takes over 12 months [125]. In that study, the composites were found to degrade faster in soil compared to pure PBAT, and the presence of clay nanoparticles accelerated the degradation process. Organo-montmorillonite clay particles and polyethylene glycol with NCPC were also found to take over 12 weeks to degrade in soil [20]. The composites showed significant degradation and the presence of clay nanoparticles improved the rate of degradation and release of nutrients into the soil [20]. In the case of NCPC’s biodegradation, there was a decrease in cumulative CO₂-C evolution with increasing clay content, which could be explained by the fact that higher cross-linking density made it more difficult for fungal species to break down the polymeric network [64].

Toxicity

While NCPCs have many useful properties, they are to some degree toxic to organisms and toxicity is a concern that must be taken into account as potential disbenefit. The toxicity of NCPCs depends on several factors, including their chemical composition, molecular weight and degree of cross-linking [61, 62]. Low molecular weight polyacrylates NCPC are more toxic than high molecular weight polyacrylates NCPC, likely due to their greater ability to penetrate cell membranes and interact with cellular components [33]. Research indicates that the presence of NCPC elements (such as acrylic acid and acrylamide) can lead to various harmful consequences for organisms, including but not limited to eye, skin and respiratory irritation alongside liver and kidney damage [2, 82]. In addition, these polymers can be persistent in the environment and may accumulate in soil and water, where they can potentially have long-term effects on ecosystems, on which only a few studies have so far been conducted [2, 82]. To minimize the potential toxicity risk of these materials in agriculture, it is important to follow appropriate safety procedures when handling and applying these materials. Additionally, alternatives to polyacrylate-based NCPC, such as natural and biodegradable materials, may be considered when feasible to minimize the environmental impact of agricultural use.

Safety Procedures

Safety precautions are critical for reducing the toxicity risks associated with NCPCs in agriculture and industry. Wearing protective clothing to avoid skin and eye contact, adequate ventilation to reduce the risk of inhalation, and training personnel in safe handling techniques are all effective precautions. In addition, using less toxic alternatives, or biodegradable polymers where possible can help to reduce long-term environmental impacts [83]. Monitoring the application of NCPCs in soil and water is also advised to avoid ecosystem accumulation and toxicity. These practices adhere to recent guidelines from sources like the U.S. Environmental Protection Agency (EPA) and the World Health Organization (WHO) [83].

Agricultural Applications of Nitrogen Impregnated NCPCs

Slow and Sustainable Release of N

Slow-release N-fertilizers with superabsorbents can not only serve as a gradual and sustainable source of N, but

also help meet the Sustainable Development Goals (SDGs) [13]. Unlike untreated N-fertilizers, which release about 90% of the contained nutrients within the first five days, polymers impregnated with fertilizer nutrients are found to have a slow release over longer periods of time, making it plant available for longer [132]. In encapsulated slow-release N-fertilizers, the N dissolved in the soil solution adsorbs on the surfaces of the added polymers and is retained due to the high absorption capacity of the polymers [13]. In this approach, the N taken up into the soil solution and the adsorbed nutrients are gradually released and act as a slow and steady source of N to the plant/crop over a long period of time (for about 30 days). The type of substance used as an adsorbent determines how slowly and continuously the N is released. Some polymer-coated fertilizer may just provide a physical barrier so that the fertilizer leaks out slowly, any superabsorbent character could be additional, but is not essential. The effects of polymers made from different types of clay (kaolinite clay, mica clay, and montmorillonite clay) have been studied experimentally, finding that application of the polymer made from kaolinite clay (1:1 type mineral) resulted in maximum release of nutrients (90%) within 48 h, while application of the polymer made from montmorillonite (2:1 type mineral) resulted in release of only 70% of N and P [100]. Previously, it was found that the nitrogen (N) release of fertilizers such as urea coated with polymers and nano-clays or nano-clay polymer composites (NCPC) was slower than that of uncoated urea, which released 90% of its N by the fifth day [28]. Only 61% of the N in NCPC encapsulated urea was released 30 days after soil application. As a result, it has been claimed that NCPC can serve as a gradual and steady source of N under drought stress and rainfed agriculture [14].

Water Stress Management

One of the most important abiotic stressors threatening food security is water stress, which hampers nearly 50% of global agriculture [48]. The ability of membrane-encapsulated slow-release fertilizer with superabsorbent and moisture conservation is therefore considered important [28]. Numerous strategies have been used to manage water stress, including the use of fertilizers, water stress-tolerant genotypes, and specific compounds that absorb and supply soil moisture during the crop growth period. In this context, nanotechnology has also suggested a number of ways to manage water stress in the environment, such as nano-superabsorbent polymers. These are very small and provide a larger surface area to absorb more water that can be used over a longer period of time, increasing the efficiency of water use by plants and ultimately leading to optimal crop yield [77]. By applying NCPC, the availability of moisture

for longer periods of time would lead to a reduction in the amount of irrigation water needed, especially in dry lands and deserts, as well as an improvement in fertilizer use efficiency with optimal crop production. In addition, these nano-polymers become more affordable compared to conventional supplements currently in use because they have a higher surface area to volume ratio, which increases their absorption capacity and ultimately their efficiency when used for optimal crop production. These absorbents have proven to be effective in horticulture, agriculture, and medical applications [13]. The ability of membrane-encapsulated, slow-release superabsorbent urea fertilizer binds water in soil and thus reduces transpiration loss [28]. The same study demonstrated that the water transpiration of the soil with this superabsorbent polymer after 12 and 21 days was 35.5% and 73%, respectively, while that of the soil without this superabsorbent polymer was 51% and 95%, (15.5% and 22% higher), respectively. Compared with the untreated control, the addition of superabsorbent polymers improved water use efficiency [130]. Crop water use efficiency increased in this study from 125 to 191% at various levels of superabsorbent polymers compared to crops grown in the control treatment.

Better Growth and Yield of Crops

Several published studies have reported better growth and higher yields of crops when using NCPC. To maintain higher N availability in the soil and prevent N losses, N-fertilizer-loaded NCPC could be a beneficial formulation [103]. The use of a superabsorbent polymer and controlled-release urea to increase productivity, water use efficiency and N use efficiency of corn in the North China Plain [19]. Several reports indicate that crop yields have increased with the application of NCPC compared to conventional N-fertilizers (Table 5). The NCPC loaded with sulfur, molybdenum and zinc significantly increased soybean

yield and yield characteristics [89]. According to a study, the use of fertilizer and nitrification inhibitor-loaded NCPCs could be a viable strategy to improve fertilizer use efficiency [104]. By gradually releasing N and controlling the abundance of functional microbes through increased nitrification in the soil and decreased denitrification, a controlled-release N fertilizer successfully increased the yield (16.6%) and N use efficiency (58.79%) of canola compared to the conventional urea treatment [58]. The NCPC can also promote germination of seeds [37]. Effectiveness of these materials in agriculture to improve soil moisture retention capacity (33–57%) and improving plant growth has been assessed in several experiments [109]. In terms of field application, when combined with 100% N through farmyard manure, NCPCs successfully increased lentil grain yield. This application also increased available nutrients and moisture retention capacity in soil, as well as enhanced microbial activity responsible for organic matter decomposition and mineralization [74]. Similarly, Sarkar and Datta [101], while working in pearl millet fields, found that availability of mineral N in soils increased significantly due to addition of fertilizer as NCPC over conventional fertilizer, at the same dose of fertilizer application.

Application of superabsorbent polymers (SAP) has been reported to increase maize yield by 11.2–29.2% at different rates SAP [69]. Compared with the control treatment, studies show that the application of superabsorbent polymers at a rate of 60 kg ha⁻¹ increased cotton production by 12% and water use efficiency by 14% [19]. The application of 90 kg ha⁻¹ superabsorbent polymers and controlled-release urea together resulted in maximum corn yields, water use efficiency, nutrient use efficiency and net income values that were 0.8–32.9%, 0.2–37.4%, 4.1–13.1%, and 2.8–42.1% higher than those of the other treatments, respectively [19]. When highly absorbent polymers were used, agricultural productivity was increased while

Table 5 Comparison of crop yields with nano-clay polymer composites (NCPC) application and conventional N fertilizers

| Crop | Yield increase with NCPC application | Yield with normal N fertilizer | Source |
|--------------|---|---|----------|
| Corn | Higher yield and N use efficiency with superabsorbent polymer and controlled-release urea; 0.8–32.9% yield increase | Lower N use efficiency and yield than NCPC | [19] |
| Soybean | Yield improved with sulfur, molybdenum, and zinc-loaded NCPC; 15.03% production efficiency increase | Standard yield without NCPC additives | [49, 89] |
| Canola | About 16.6% higher yield and 58.79% better N efficiency with controlled-release NCPC | Lower yield and less effective microbial regulation than NCPC | [58] |
| Cotton | About 12% higher yield and 14% water use efficiency with superabsorbent polymer at 60 kg ha ⁻¹ | Lower yield and water efficiency than NCPC | [69] |
| Pearl Millet | Significant increase in mineral N availability and yield with NCPC, particularly in arid conditions | Average yield with conventional fertilizer | [104] |

reducing water needs [41]. The use of NCPCs on soybean as also showed a 15% increase in production efficiency over conventional fertilizer [49].

Reducing Greenhouse Gas Emissions

Only a few studies have investigated the impact of use of NCPCs on greenhouse gas emissions, though early results are promising. The comparative analysis of the effects of N fertilizer on a barley field showed that polymer-coated fertilizer could reduce N₂O emissions from urea application by 35% [107]. Compared with urea, NCPCs were found by the same study to reduce N₂O emissions by 16.1% in rice and 12.4% in wheat. The authors found that the dose of conventional fertilizers could be reduced by up to 50% when using NCPCs without decreasing yields. Although promising in terms of reducing the potential for global warming, the effect of NCPC on increasing N use efficiency or yield in the rice–wheat system has been shown to be even more pronounced [45].

Advantages

Nitrogen-loaded NCPCs enhance nitrogen use efficiency, improve crop yields, and promote better water retention (Table 6). The higher nitrogen use efficiency is attributed to higher N retention in soils by reducing the amount of N lost through leaching or volatilization [15]. Nano-clay particles in the composites can act as a slow-release reservoir of N, gradually releasing N to crops as needed (Fig. 5). This can reduce the risk of over-fertilization and minimize the negative environmental impacts associated with excess N use [16]. In this way, N-loaded NCPCs can enhance soil microbial activity and nutrient cycling, leading to improved soil health and plant growth, which in turn can result in more sustainable agricultural systems [106]. NCPS have the potential to reduce the negative environmental impact of N-fertilizers because the composites can improve N use efficiency and reduce the risk of N leaching into groundwater and surface water [127]. According to Chen et al. [11] N-loaded NCPC increased crop yields in maize, wheat and rice, which they attributed to improved N availability and enhanced soil health.

Considering the overall effectiveness of these NCPCs, they could be recommended based on the demonstration

Table 6 Benefits of different nano-clay polymer composites loaded with nutrient and fertilizer

| Polymer composite loaded with nutrient/fertilizer | Encapsulated or impregnated | Benefit | References |
|---|-----------------------------|--|------------|
| DAP, Urea | Encapsulated | Increased cumulative P and total mineral N recovery (55.2–88.3%, 15.4–27.3%, respectively) | [103] |
| Urea | Encapsulated | Slow release of N (85–90%) | [28] |
| Urea solution | Encapsulated | Slow release of N | [47] |
| Urea | Impregnated | Improved yield (39.91–52.57%) Enhanced water use efficiency (56.21–57.57%) Enhanced N use efficiency (9.34–31.82%) | [19] |
| Urea | Encapsulated | Slow release of nutrient (65%) | [105] |
| Extra pure urea, Nitrification Inhibitor | Encapsulated | Improved water-holding capacity (50%) N use efficiency | [104] |
| Urea + Biochar | Impregnated | Increase yield (16.6%) Enhanced N use efficiency (58.79%) | [58] |
| Urea | Encapsulated | Apparent N uptake efficiency (28.5%) | [135] |
| Urea | Impregnated | N ₂ O emission (35%) | [107] |
| Urea | Encapsulated | Reduced N ₂ O emission (16.1% in rice and 12.4%) Reduced global warming potential Enhanced N use efficiency | [45] |
| Urea | Impregnated | Increased yield (12%) Reduced costs (18–19%) | [133] |
| Urea | Impregnated | Improved N use efficiency (30.65–43.96%) Reduced costs (5.21–11.44%) | [59] |

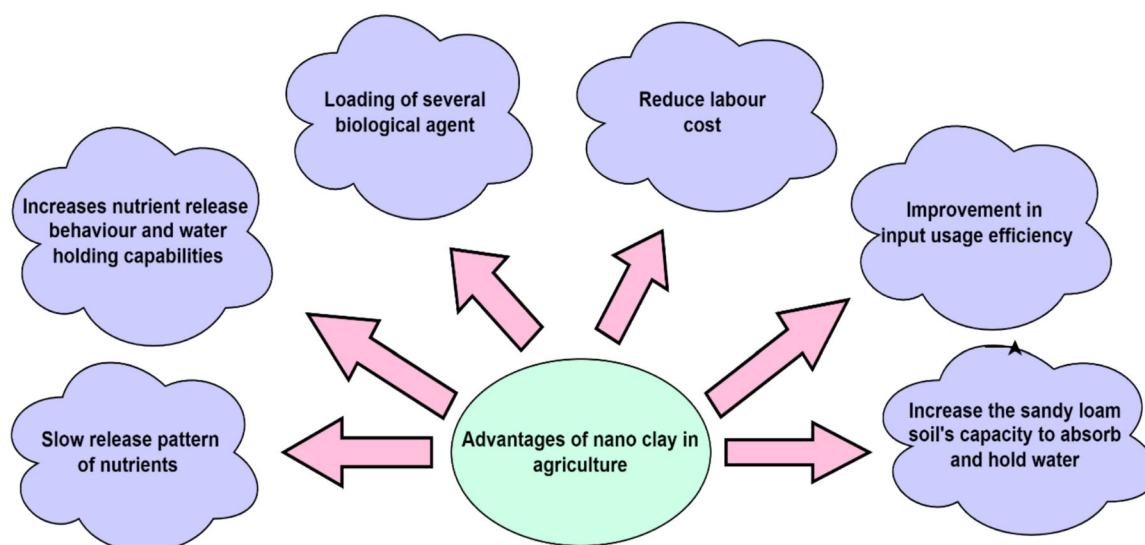


Fig. 5 Key benefits of nano-clay application in agriculture

that they can reduce the amount needed of conventional fertilizers by up to 50% without decreasing rice and wheat yields, which could in turn reduce N_2O emissions [45]. For mustard, an ideal mixture of superabsorbents and slow-release fertilizers could increase fertilizer use efficiency by 50% [58]. Farmers can improve N use efficiency by using slow/controlled-release fertilizer products, particularly in soils with low cation exchange capacity [73].

Disadvantages

Most coated slow-release fertilizers are produced at costs significantly higher than those of conventional fertilizers. Compared with conventional urea, coated or encapsulated smart N was 35% more expensive [10]. When nutrients are not released as expected due to low temperatures, wet or dry soils, or insufficient soil microbial activity, nutrient deficiencies can occur [40]. Some synthetic polymers may not be biocompatible, which would increase the likelihood of toxicity to the environment [72]. In order to be economically attractive for farmers as a basis for large scale adoption, ways need to be found to reduce these costs substantially, so that the benefits accrue to the farmer rather than predominantly the manufacturer.

Future Prospectus of NCPCs

Nano-clay polymer composites have been widely applied, with substantial research conducted to assess for their potential application in different crops for better yield, water use efficiency and nutrient use efficiency, as

indicated by the many studies cited in this review. The intercalation of nano-clay into polymer matrices followed by impregnating with N-fertilizer can lead to the development of materials with both slow-release properties and higher water retention, which can be particularly useful for agricultural applications. There is scope for future research and development of NCPCs in agriculture, for instance:

- (a) *Developing biodegradable NCPCs* such as poly (lactic acid) (PLA) and poly (hydroxyalkanoates) (PHAs). These have received significant attention in recent years [76]. However, their agricultural applications require in-depth research.
- (b) *Cross-linking agents for NCPCs* Future research could explore various other cross-linking agents that can be used to improve the properties of these materials for different applications. There is a potential for developing new types of nano-composite gels, which can be used for agronomic purposes such as controlled-release systems for fertilizers and pesticides. The use of NCPCs in fertilizer application can be explored further to understand the effectiveness of these materials in enhancing crop production and reducing nutrient loss. These materials have the potential to reduce the amount of fertilizer required and increase nutrient uptake by plants, thereby reducing environmental pollution from agricultural activities.
- (c) *Toxicity and environmental impacts* The toxicity of NCPCs to soil fauna and humans needs to be further studied together combined with assessment of environmental impact of these composite materials in agriculture use. It is important to investigate the safety of NCPCs, including their potential to leach

into the soil or water, and their impact on soil microorganisms and beneficial insects. This will ensure that these materials are safe for humans, animals, and the environment.

- (d) *Widening the performance assessment of NCPCs* Nano-clay has been shown to have potential benefits for plant growth and soil stabilization. However, the effects of nano-clay on plant growth and soil properties are not well understood. Future research could investigate the impact of different types and concentrations of nano-clay on plant growth, nutrient uptake, and soil properties such as water retention and permeability.
- (e) *Smart NCPCs* The development of smart NCPCs could enable tuned responds to environmental parameters such as temperature, humidity or pH. For example, this could allow improved release nutrients or pesticides at the right time and in the right place to maximize crop growth and reduce environmental impact.
- (f) *Scalable NCPCs* Currently, the production of NCPCs is often limited to laboratory-scale experiments. Future research should focus on developing scalable and cost-effective processing methods for the production of NCPCs for large-scale agricultural applications.

Policy Requirements

The integration of nanotechnology into agricultural production holds great promise for increasing productivity and sustainability in line with the SDGs. According to the Interagency Task Team (IATT) on Science, Technology and Innovation of United Nations, nanotechnologies such as application of NCPCs can improve nutrient utilization efficiency through controlled-release mechanisms. This is critical for reducing environmental impacts and improving resource management. High efficiency fertilizers such as NCPCs can increase crop yields while reducing nutrient loss, supporting SDG 2 (Zero Hunger). Despite these potential benefits, a balanced approach that takes into account the risks associated with nanotechnology in the agricultural context is required. The long-term environmental impacts of nanomaterials including NCPCs, such as their effects on soil health and biodiversity are still unknown. Regulatory frameworks need to be created that promote both safety and innovation in nanotechnology [35].

Conclusions

Nano-clay polymer composites are a promising area of study for their potential use in fertilizer applications. Applications for NCPCs have become increasingly popular, where these composites show promise for a variety of cutting-edge applications. Nano-clay polymer composites exhibit special qualities when used as superabsorbents, where they provide gradual and uniform water flow, which is of great benefit to agriculture under rainfall and drought stress. By impregnating NCPC with fertilizer, they also serve as slow-release nutrient sources and could provide nutrients such as N to crops over a longer period of time. Nutrient-impregnated NCPC fertilizers are expected to be one of the most effective ways to achieve growth and sustainability and positively impact on agriculture in the near future.

However, further research is needed to determine the long-term effects of these composites on soil health and plant growth. Additionally, it will be important to consider the economic feasibility and scalability of producing NCPCs for fertilizer use on a larger scale. Anticipated additional production costs need to be minimized so that the economic benefits for farmers can be shown to outweigh any additional cost, which would be central to their upscaling and hence achievement of global environmental benefit.

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Declarations

Conflict of interest The authors declare that they have no competing interests or other interests that might be perceived to influence the results and/or discussion reported in this paper. Also, there are no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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