Chapter 14 Nanotechnology in the Arena of Changing Climate



Nintu Mandal, Rajiv Rakshit, Samar Chandra Datta, and Ajoy Kumar Singh

Abstract Technological interventions in the changing climatic conditions seem to be imperative in formulating adaptation and mitigation strategies. Nanoscience, the study of matter at atomic or nano $(1 \text{ nm} = 10^{-9} \text{ m})$ scale can be one of the viable options/ interventions in increasing input use efficiency, effective pest control and drought management in agriculture to address the ill issues of climate change in agriculture. The chapter discussed about the Nanotechnology to play important role in development of intelligent delivery of agrochemicals, development of novel superabsorbent polymers, real time monitoring of agrochemicals via nanobiosensors, increased resilience and resilience of microbes under heat stress which are very relevant in changing climate scenario.

Keywords Nanotechnology · Climate change · Impact · Mitigation

14.1 Introduction

Climatic aberrations are increasing day by day causing adverse impact on essential ecosystem functions. Spatial and temporal shifting of amount and frequency of rainfall is affecting agricultural operations in a massive way. Climatic extremities (Heat wave, cold wave *etc*) are affecting agricultural production system in a bigger way.

Surface temperature is projected to rise over the twenty-first century under all assessed emission Scenarios (IPCC 2014). It is very likely that heat waves will occur more often and last longer, and that extreme precipitation events will become

N. Mandal (🖂) · R. Rakshit

S. C. Datta

Impact and Adaptation, https://doi.org/10.1007/978-3-319-90086-5_14

Department of Soil Science and Agricultural Chemistry, Bihar Agricultural University, Sabour, Bhagalpur, Bihar, India

Division of Soil Science and Agricultural Chemistry, Indian Agricultural Research Institute, New Delhi, India

A. K. Singh Bihar Agricultural University, Sabour, Bhagalpur, Bihar, India

[©] Springer International Publishing AG, part of Springer Nature 2019

S. Sheraz Mahdi (ed.), *Climate Change and Agriculture in India:*

more intense and frequent in many regions. The ocean will continue to warm and acidify, and global mean sea level to rise (IPCC 2014). There are multiple mitigation pathways that are likely to limit warming to below 2 °C relative to pre-industrial levels (IPCC 2014). These pathways would require substantial emissions reductions over the next few decades and near zero emissions of CO_2 and other long-lived greenhouse gases by the end of the century. Implementing such reductions poses substantial technological, economic, social and institutional challenges, which increase with delays in additional mitigation and if key technologies are not available. Limiting warming to lower or higher levels involves similar challenges but on different timescales (IPCC 2014).

Technolological interventions in the changing climatic conditions seem to be imperative in formulating adaptation and mitigation strategies. Nanoscience is the study of matter at atomic or nano $(1 \text{ nm} = 10^{-9} \text{ m})$ scale. Nanotechnology deals with fabrication of materials at nanoscale. Nanomaterials are materials having at least one dimension in 1–100 nm scale as per USEPA (United State Environment Protection Agency). Nanotechnological interventions in increasing input use efficiency, effective pest control and draught management in agriculture are of utmost importance in present day agriculture and in future also.

14.2 Intelligent Delivery of Agrochemicals

14.2.1 Rhizosphere Controlled Release Nutrient Formulations

14.2.1.1 Major Nutrient Formulation

Montmorlonitic nanoclay separated from Vertisol was employed for controlled release N, P formulation by Sarkar et al. 2014. They prepared series of nanoclay polymer composites (NCPCs) by using various clay minerals *viz*. Kaolinite (Alfisol), Smectite (Vertisol) and Mica (Inseptisol) and concluded that smectitic type of clays were most suitable for NCPC preparation owing to its higher specific surface area and high aspect ratio. The types of composites were exfoliated types were confirmed by disappearance of typical bentonitic peak within polymer matrixes (Fig. 14.1).

In case of the NCPC incorporated with clay I (the kaolinite dominated clay) and clay II (the mica-dominated clay), the reaction occurred on the surface of the clays. However, the polymer layer penetrated into silicate layers, and the clay was exfoliated when clay III (the smectite-dominated clay) was introduced. The equilibrium water absorbency and nutrient release rate decreased (Fig. 14.2) with the incorporation of clay into the polymer matrix because of the increase in crosslinking points and the decrease in the mesh size of the NCPCs as compared to those in the pure polymer.



Fig. 14.1 Randomly oriented powder XRD patterns of the clay, polymer/ clay composite, polymer, and polymer1clay physical mixture for (A) clay III(A) and (B) clay III(B)

14.2.1.2 Micronutrient Formulations

Zincated nanoclay polymer composites (ZNCPCs):

NCPC based micronutrient formulation was reported by Mandal and his coworkers (Mandal et al. 2015; Mandal et al. 2018). Bentonitic nanoclay were separated through ultracentrifugation and used as a diffusion barrier in the acrylic acid (AA) and acrylamide (Am) copolymer masteries using ammonium persulphate(APS) as initiator and N, N, Methylene Bis acryalmaide (NNMBA) as crosslinker. Zn was loaded as Zn-citrate. Laboratory release study revealed that nanoclay were more effective as compared to clay in slow release behaviour (Fig. 14.3). Olsen-P content in soil also increased in ZNCPC treatments owing to citrate Solubilization of native soil P (Fig. 14.4).



Fig. 14.2 Release of N and P from the DAP-loaded NCPCs incorporated with different kinds of clay (10 wt %) in distilled water. I, II and III represents clay separated from Alfisol, Inseptisol and Vertisol respectively. A and B indicates with and without aluminosilicates respectively



Fig. 14.3 Release of DTPA extractable Zn in soils during incubation experiment *T1*: 8% clay; *T2*: 10% Clay; *T3*: 12% Clay; *T4*: 8% Nanoclay; *T5*: 10% Nanoclay; *T6*: 12% Nanoclay and *T7*: ZnSO₄. 7 H₂O

14.3 Superabsorbent Nanocomposites for Soil Moisture Conditioner Novel Superabsorbent Nanocomposites: Improvement in Moisture Retention and Available Moisture Content in Soil

Novel superabsorbent nanocomposites are recently being reported as promising materials in improving moisture retention characteristics in soil. Singh et al. 2011 prepared a novel nanosuperabsorbent composite (NSAPC) by in situ grafting polymerization and cross-linking on to a novel biopolymer of plant origin (complex heteropoly saccharide in nature) in the presence of a clay mineral using a green chemistry technique. The inorganic clay mineral acted as additional network point, resulting in increase in crosslinking with increase in clay content, manifested in decreased water absorbency.



Fig. 14.4 Release of Olsen- P in soils during incubation experiment T1: 8% clay; T2: 10% Clay; T3: 12% Clay; T4: 8% Nanoclay; T5: 10% Nanoclay; T6: 12% Nanoclay and T7: ZnSO₄. 7 H₂O

Addition of test hydrogels to soil and soil-less media significantly increased the availability of water to plant compared with control (Fig. 14.5). In case of soil-less medium, the lower rate of application (0.5%) was as effective as higher rate (0.75%) for both the gels. This observation was substantiated by the values of onset wilting point in amended and unamended plant growth media (Fig. 14.6). As is clear, because of more availability of water in gel amended treatments, the permanent wilting point approached in the amended soil in 4.7–6.3 days compared with 2.4 days in control. Delay by 1.4–3.6 days was observed in soil-less media.

Effect of NSAPC on water absorption and retention characteristics (Fig. 14.6) of sandy loam soil and soil-less medium was also studied as a function of temperature and tensions. Addition of NSAPC significantly improved the moisture characteristics of plant growth media (both soil and soil-less), showing that it has tremendous potential for diverse applications in moisture stress agriculture



Fig. 14.5 Effect of gel addition on available water from soil (a) and soil-less media (b)

14.4 Interaction of Microbes with Nanomaterials Under Changing Temperatures

Resistance and resilience are considered as the ecological concepts of high policy relevance. Almost any study could be considered in terms of resilience, in that the common experimental format – the effect of X on Y – will have information about the effect of a disturbance on the system if X is a disturbance. To get an understanding of resilience, there needs to be a measurement soon after the disturbance to gauge resistance and then several subsequent measurements to assess the pattern of resilience. The time period can be a matter of days in a laboratory incubation, or even minutes for some physical measurements (Zhang et al. 2005), through to years for field-based observations and is generally related to the nature of the disturbance. Studies have investigated the resilience of microbial communities to disturbance due to human activities such as land use and agricultural practices. But, impact assessment of



Fig. 14.6 Moisture release curves of soil (a) and soil-less media (b) amended with P-gel and NSAPC

nanomaterial addition (Zn and Fe nanomaterial) as extraneous substances added to soil system on soils resistance and resilience were still unidentified under heat stress and thus the hypothesis of the current experiment was that the addition of nanomaterials could have considerable implications on the resistance and resilience of soil organisms against abiotic stress, such as high temperature.

Kumar et al. (2016) showed that Fluorescien Diacetate Hydrolysing (FDA) activity was significantly reduced when the concentration of nano Fe was increased from 10 ppm (22.37 µg fluorescein released g^{-1} dry soil h^{-1}) to 40 ppm (18.08 µg fluorescein released g^{-1} dry soil h^{-1}) at P < 0.05. Data showed no significant differences between nano Zn @ 10 ppm (25.00 µg fluorescein released g^{-1} dry soil h^{-1}) and nano Zn @ 40 ppm (24.74 µg fluorescein released g^{-1} dry soil h^{-1} reflecting no changes in FDA activity at different doses of nano Zn. With respect to resistance and resilience indices of FDA activity against heat stress, it was observed that the nano Zn @ 10 ppm and nano Fe @ 10 ppm treatment had the greatest stress resistance,



Fig. 14.8 Resilience index of FDA activity in soil after heat stress (48 °C for 24 h) under various doses of nanomaterial

with an index rating of 0.48 and 0.43 respectively (Fig. 14.7). Resistance index values of control was 0.37, there was no significant difference between treatments supplied with higher doses of nanomaterial (Zn or Fe @ 40 ppm) (P < 0.05).

Resilience indices of all the treatments varies from -0.01 to 0.16 after 90 days of incubation. It was observed that all the treatments supplied with nanomaterials showed a statistically similar resiliency against the heat stress after 90 days (Fig. 14.8). Although the control treatment showed a higher resilience index upto 56 days, but there was sharp decline in the resilience indices after 70 (-0.20) and 90 days (-0.01).

With respect to resistance indices of microbial biomass carbon against heat stress, it was observed that the nano Fe @ 40 ppm treatment had the greatest stress



Fig. 14.10 Resilience index of MBC activity in soil after heat stress (48 $^{\circ}$ C for 24 h) under various doses of nanomaterial

resistance, with an index rating of 0.69, which was statistically comparable to nano Zn@ 40 ppm with an index rating of 0.68 and nano Fe@ 10 ppm with an index rating of 0.67 (Fig. 14.9). Recovery rate of microbial biomass carbon showed a similar pattern as in the enzymatic activity. Although the resilience indices were lower during the first 56 days, but the recovery indices were maximum after 90 days of incubation. Nano Zn @ 40 ppm and nano Fe @ 40 ppm had the greatest stress resilience with an index rating of 0.28 and 0.29 respectively after 90 days of incubation. The lower dose (10 ppm of nano Zn and nano Fe) of nanomaterials used in this experiment also showed a positive resilience index (index rating of 0.14 and 0.24 for nano Zn and nano Fe respectively) (Fig. 14.10).

14.5 Thermal and Hydrolytic Stability of Soil Enzymes: Immobilization of Soil Enzymes on Double Layer

Acid phosphatase was immobilized on layered double hydroxides of uncalcinedand calcined-Mg/Al-CO₃ (Unc-LDH-CO₃, C-LDH-CO₃) by the means of direct adsorption by Zhu et al. 2010. Optimal pH and temperature for the activity of free and immobilized enzyme were exhibited at pH 5.5 and 37 °C. The Michaelis constant (Km) for free enzyme was 1.09 mmol mL⁻¹ while that for immobilized enzyme on Unc-LDH-CO₃ and C-LDHCO₃was increased to 1.22 and 1.19 m molmL⁻¹, respectively, indicating the decreased affinity of substrate for immobilized enzymes. The residual activity of immobilized enzyme on Unc-LDH-CO₃ and C-LDH-CO₃at optimal pH and temperature was 80% and 88%, respectively, suggesting that only little activity was lost during immobilization.

The deactivation energy (Ed) for free and immobilized enzyme on Unc-LDH- CO_3 and C-LDH- CO_3 was 65.44, 35.24 and 40.66 kJ mol⁻¹, respectively, indicating the improving of thermal stability of acid phosphatase after the immobilization on LDH- CO_3 especially the uncalcined form. Both chemical assays and isothermal titration calorimetry (ITC) observations implied that hydrolytic stability of acid phosphatase was promoted significantly after the immobilization on LDH- CO_3 especially the calcined form (Fig. 14.11).

Reusability investigation showed that more than 60% (Fig. 14.12a, b) of the initial activity was remained after six reuses of immobilized enzyme on Unc-LDH-CO₃ and C-LDH-CO₃. A half-life (t1/2) of 10 days was calculated for free enzyme, 55 and 79 days for the immobilized enzyme on Unc-LDH-CO₃ and C-LDH-CO₃when stored at 4 $^{\circ}$ C.

Layered double hydroxides of uncalcined- and calcined-Mg/Al- CO₃ were used successfully as supports for the immobilization of acid phosphatase by the means of



Fig. 14.11 Hydrolytic stability of free (F-E) and immobilized acid phosphatase on LDHs (I-E on Unc-LDH-CO₃ and I-E on C-LDH-CO₃)



Fig. 14.12 (a) Reusability of immobilized acid phosphatase on LDHs (I-E on Unc-LDH-CO₃ and I-E on C-LDH-CO₃). (b) Storage stability of free (F-E) and immobilized acid phosphatase on LDHs (I-E on Unc-LDH-CO₃ and I-E on C-LDH-CO₃)

direct adsorption. Little activity loss, excellent thermal stability, hydrolytic stability, reusability and storage stability of the immobilized acid phosphatases revealed their promising potentials for practical application in the fields such as agricultural production and environmental remediation.

14.6 Nanobiosensors for in Changing Climate

Now-a-days, nanotechnology and nanomaterials are intertwined in the construction of almost every bioelectronics or biosensor devices due to their exceptional physicochemical, electrical, optical and mechanical properties. Nanomaterials have overcome the obstacles of low sensitivity, selectivity and analytical interference of old methods by controlling the size, shape and composite (Marx et al. 2004).

14.6.1 Real Time Urease Activity Monitoring

Nanobiocomposite Sensors:

Biosensors are reported for different enzymatic activity detection. Presence of urea can be detected based on the detection of Urease (Ur) and Glutamate dehydrogenase (GLDH). Ur catalyzes decomposition of urea into hydrogen bicarbonate and ammonium ions (NH₄⁺). NH₄⁺ ions are known to be unstable and easily disperse in the environment. GLDH immediately catalyzes the reaction between NH₄⁺, α -ketoglutarate (α -KG) and nicotinamide adenine di nucleotide (NADH) to produce NAD⁺ and α -glutamate. Immobilization of Ur onto a suitable matrix is crucial for the development of an electrochemical urea sensor. In this context, metal oxide nanoparticles-chitosan (CH) based hybrid composites have attracted much interest for the development of a desired biosensor.

Metal oxide nanoparticles such as iron oxide (Fe₃O₄), zinc oxide (ZnO), cerium oxide (CeO₂) etc. have been suggested as promising matrices for the immobilization of desired biomolecules. These nanomaterials exhibit large surface to volume ratio, high surface reaction activity, high catalytic efficiency and strong adsorption ability that can be helpful to obtain improved stability and sensitivity of a biosensor. Moreover, nanoparticles have a unique ability to promote fast electron transfer between electrode and the active site of an enzyme. Among various metal oxide nanoparticles, Fe₃O₄ nanoparticles due to biocompatibility, strong superparamagnetic behaviour and low toxicity have been considered as interesting for immobilization of desired biomolecules.

The proposed mechanism relating to the preparation of CH-Fe₃O₄ nanobiocomposite film and immobilization of Ur-GLDH onto CH-Fe₃O₄ nanobiocomposite film is shown in Fig. 14.13. It can be seen that surface charged Fe3O4 nanoparticles interact with cationic biopolymer matrix of CH via electrostatic interactions and hydrogen bonding with NH₂/OH group to form hybrid nanobiocomposite. The Ur-GLDH molecules exist in anionic form at pH 7 because pH of solution is above isoelectric point (5.5) of Ur-GLDH molecules that facilitate interactions with positively charged CH of nanobiocomposite via electrostatic interactions (Fig. 14.13). In the nanobiocomposite, presence of Fe₃O₄ nanoparticles results in increased electroactive surface area of CH for loading of the enzymes due to affinity of the Fe₃O₄ nanoparticles towards oxygen atoms of enzymes. This suggests that Ur-GLDH mol-



Fig. 14.13 Proposed mechanism for preparation of CH-Fe₃O₄ nanobiocomposite and immobilization of Ur-GLDH onto CH-Fe₃O₄ nanobiocomposite film



Fig. 14.14 Biochemical reaction during electrctrochemical detection of urea using Ur-GLDH/ CH-Fe₃O₄ nanobiocomposite

ecules easily bind with charged CH-Fe₃O₄ hybrid nanobiocomposite matrix via electrostatic interactions.

The proposed biochemical reaction during the urea detection is shown in Fig. 14.14. Ur catalyzes hydrolysis of urea to carbamine acid that gets hydrolyzed to ammonia (NH₃) and carbon dioxide (CO₂). GLDH catalyzes the reversible reaction between α -KG and NH₃ to NAD⁺ and linked oxidative deamination of

L-glutamate in two steps. The first step involves a Schiff base intermediate being formed between NH3 and α -KG. The second step involves the Schiff base intermediate being protonated due to the transfer of the hydride ion from NADH resulting in L-glutamate. NAD⁺ is utilized in the forward reaction of α -KG and free NH₃ that are converted to L-glutamate via hydride transfer from NADH to glutamate. NAD⁺ is utilized in the reverse reaction, involving L-glutamate being converted to α -KG and free NH₃ via oxidative deamination reaction. The electrons generated from the biochemical reactions are transferred to the CH -Fe₃O₄/ITO electrode through the Fe(III)/Fe(IV) couples that help in amplifying the electrochemical signal resulting in increased sensitivity of the sensor (Kaushik et al. 2009).

14.6.2 Pesticide Detection

Along with the existing practices, nanomaterials including carbon nanotubes (CNTs) (multi-wall CNTs and single-wall CNTs), metal nanoparticles (MNPs) [gold (Au) and silver (Ag)], graphene and graphene-based nanocomposites, nanocrystal coordination polymers, quantum dots (QDs) and magnetic NPs have had the opportunity to be used in various OPs bio-detection systems (Laschi et al. 2008).

14.7 Conclusion

Nanotechnology seems to play important role in development of intelligent delivery of agrochemicals, development of noel superabsorbent polymers, real time monitoring of agrochemicals *via* nanobiosensors, increased resilience and resilience of microbes under heat stress which are very relevant in changing climate scenario.

14.8 Future Prospects

Nanotechnological developments in agricultural sciences are still in infancy. Long term evaluation of nanoproducts (fertilizers, pesticides, nanogels, biosensors and heat stable enzymes) under various agroclimatic conditions, diverse soil types and crop ecologies would give specific solutions for tacking ever changing agricultural production constraints.

References

- IPCC. (2014). Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Core Writing Team, R.K. Pachauri and L.A. Meyer (eds.)]. IPCC, Geneva, Switzerland, p 151.
- Kaushik, A., Solanki, P. R., Ansari, A. A., Sumana, G., & Ahmad, S. (2009). Iron oxide-chitosan nanobiocomposite for urea sensor. *Sensors and Actuators B Chemical*, 138, 572–580.
- Kumar, A. (2016). Microbial resistance and resilience of balanced fertililized and nanomaterials added soils under heat stress. M.Sc thesis submitted to Department of Soil Science and Agricultural Chemistry, Bihar Agricultural University, Sabour, Bhagalpur, Bihar, India.
- Laschi, S., Bulukin, E., Palchetti, I., Cristea, C., & Mascini, M. (2008). Disposable electrodes modified with multi-wall carbon nanotubes for biosensor applications. *Irbm*, 29, 202–207.
- Mandal, N., Datta, S. C., & Manjaiah, K. M. (2015). Synthesis, characterization and controlled release study of Zn from Zincated nanoclay polymer composites (ZNCPCs) in relation to equilibrium water absorbency under Zn deficient Typic Haplustept. *Annals of Plant and Soil Research*, 17, 187–195.
- Mandal, N., Datta, S. C., Manjaiah, K. M., Dwivedi, B. S., Kumar, R., & Aggarwal, P. (2018). Zincated Nanoclay polymer composites (ZNCPCs): Synthesis, characterization, biodegradation and controlled release behaviour in soil. *Polymer-Plastics Technology and Engineering*, 1. https://doi.org/10.1080/03602559.2017.1422268.
- Marx, S., Zaltsman, A., Turyan, I., & Mandler, D. (2004). Parathion sensor based on molecularly imprinted sol-gel films. *Annals of Chemistry*, 76, 120–126.
- Sarkar, S., Datta, S. C., & Biswas, D. R. (2014). Synthesis and characterization of Nanoclay– polymer composites from soil clay with respect to their water-holding capacities and nutrientrelease behavior. *Journal of Applied Polymer Science*, 131. https://doi.org/10.1002/app.39951.
- Singh, A., Sarkar, D. J., Singh, A. K., Parsad, R., Kumar, A., Parmar, B. S., & Singh, B. S. (2011). Studies on novel nanosuperabsorbent composites: Swelling behavior in different environments and effect on water absorption and retention properties of sandy loam soil and soil-less medium. *Journal of Applied Polymer Science*, 120, 1448–1458.
- Zhang, B., Horn, R., & Hallett, P. D. (2005). Mechanical resilience of degraded soil amended with organic matter. Soil Science Society of America Journal, 69, 864–871.
- Zhu, J., Huang, Q., Pigna, M., & Violante, A. (2010). Immobilization of acid phosphatase on uncalcined and calcined mg/Al-CO₃ layered double hydroxides. *Colloids and Surfaces B: Biointerfaces*, 77, 166–173.