

Nanoclay biopolymer composites: Synthesis, characterization and nitrogen release under controlled conditions

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ABSTRACT

As the production sector of N fertilizer challenged by energy crisis of the world and consumption sector is challenged by the environmental impacts, there is an urgent need to improve the nitrogen use efficiency for the sustainable growth of agriculture sector. The controlled release/ slow-release N fertilizers are smart choices to serve this purpose. So, this manuscript aims to synthesise nano clay bio-polymer composites (NCBPC) and using it for controlled N release. Nano clay bio-polymer composites were prepared by aqueous copolymerization of acrylic acid with acrylamide in presence of bentonite nano clay and starch as a partial replacement for synthetic polymers. Maize and wheat flour (maida) were used as starch source at 20 and 30% replacement level to synthesise different NCBPC products. The resulting products were characterized using FTIR and SEM which revealed the participation of bentonite and starch in the polymerization reaction at the nano level. The incubation study in soil disclosed the slow-release of nitrogen by these materials. Therefore, bentonite clay with cereal grain flours may be used for the synthesis of nano clay bio-polymer composites for slow-release of nitrogen.

Keywords: Nano clay bio-polymer composites, urea, slow release/controlled release N fertilizer, bentonite, maize flour

INTRODUCTION

Only 15% of nitrogen (N) used for overall food production serves the true purpose, rest 85% of N lost during the process of production and consumption. This injection of N, increasing the reactive nitrogen content in the atmosphere which crossed 240 Tg in 2020, results in N cascade in the atmosphere, soil and water systems (Galloway *et al.*, 2021). Higher N fertilizer consumption with poor N use efficiency is a matter of concern regarding climate change as nitrous oxide, a potential greenhouse gas produced during denitrification process contributes to global warming (Fagodiya *et al.*, 2017). Improvement in use efficiency of fertilizers helps to reduce the unit cost of production and enhances the agricultural productivity (Mala, 2013). Apart from slow-release property, controlled release N fertilizer products supply nutrients as per plant metabolic need (Azeem *et al.*, 2014). In this regard, the nano clay polymer and bio-polymer composites emerging as promising technology as controlled release N fertilizers. Composites are the products derived from two or more constituent

materials having significantly different properties from that of original materials which remains separate and distinct within their structures. If at least one of the phases having dimension in nano metre range, then they are characterized as nanocomposites. If nanocomposites constitute of natural bio-polymer materials and inorganic solids, they would be classified under nano bio-polymer composites. They have different preparation methods and properties like degradability. A standard protocol for preparation of nano clay polymer composites (NCPCs) was developed by Liang and Liu (2007) where aqueous solution of partially neutralized acrylic acid and acrylamide were copolymerized in presence of kaolin nanoclay. Introduction of inorganic clay materials in super absorbents improves the properties like strength, expansion properties and decreases the production costs (Liang and Liu, 2007). Also, these inorganic clays found to reduce the permeability and increase the stability of NCPCs. Super absorbent materials can hold water up to more than thousand times of their own weight, which was even retained under pressure. Synthetic polymeric compounds like acrylic acid and

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acrylamide are widely used for preparing polymer composites (Kirti *et al.*, 2020). But these materials have problems with their degradability and high production cost (Kiatkamjornwong *et al.*, 2002). Use of bio-polymers as partial replacement might address these issues. Because of this advantage, natural polymers such as starch (Li *et al.*, 2007, Lu *et al.*, 2009), gelatin (Marandi and Hosseinzadeh, 2007), pectin (Yoshimura *et al.*, 2005), protein (Zhang *et al.*, 2011), cellulose (Xie *et al.*, 2011) and chitosan (Wu *et al.*, 2008) were extensively used for preparing NCPCs. Therefore, the present study is aimed to synthesize and characterize nano clay bio-polymer composites and study the release pattern of nitrogen from nitrogen loaded nano clay bio-polymer composites under controlled conditions.

MATERIALS AND METHODS

The nanoclay polymer composites (NCPCs) material was prepared by radical polymerisation technique between acrylic acid and acrylamide using standard procedure given by Liang and Liu, 2007. Commercially available bentonite used as a nano clay. Acrylic acid was partially neutralized with ammonia solution in a three necked vessel and distilled water was added to it. Later acrylamide, bentonite, N,N'-methylene-bis-acrylamide (NNMBA) and ammonium persulphate was added to the vessel in sequence. The NNMBA acted as cross-linking agent and ammonium persulphate as a free radical initiator. Throughout the process, the vessel was kept on magnetic stirrer cum heater and temperature was kept at 105°C, 390 rotations per minute and whole system was maintained under N₂ gas environment. In the end, NCPC was prepared by vigorous exothermic process. Later the NCPC was fractured by hand and dried in oven at 60°C. Later urea solution was used to load N in this material. The NCPC acted as base material for preparation of nanoclay bio-polymer composites (NCBPCs). In case of NCBPC, 20 and 30% of this acrylic acid-acrylamide synthetic polymer was replaced by bio-polymer derived from starch. Starch was mainly obtained by maize and maida flour to get Mz-20, Mz-30, Md-20 and Md-30 NCBPC products, respectively and other procedures remained same for synthesis of NCBPC materials.

For characterization of NCPC and NCBPCs, the characteristic functional groups of starch, clay and polymer were determined by employing Fourier Transform Infrared Spectrometry (FTIR) in the region 600–4000 cm⁻¹ using KBr pellets. Surface morphology of the polymer materials were also characterized by using scanning electron microscope (SEM) using the Tescan Vega-3 LMU SEM operated at 10 kV HV and working distance (WD) 14.39 mm. Nitrogen release study was conducted with 20 g of soil in 100 ml beaker and brought up to field capacity. Polymer composites containing 0.05 g N were taken in muslin cloth and incubated in the beaker containing soil at room temperature. Mineral N content was analysed after 2, 4, 7, 14 and 28 days after incubation. The NO₃⁻ content was determined by the modified Greiss-Ilosvay method and NH₄⁺ content was determined by Indophenol-blue method (Keeney and Nelson, 1983).

RESULTS AND DISCUSSION

The FTIR spectra of bentonite, starch sources (flour), NCPC and NCBPCs were shown in Figure 1. The peak at 1032 cm⁻¹ of bentonite was attributed to the stretching of hydroxyl groups whereas the peaks at 698 and 3698 cm⁻¹ was due to the stretching of Si–O–Mg, and Al–OH group, respectively (Sarkar *et al.*, 2021). The flour materials showed characteristic peak at 1650 cm⁻¹ due to the –CH₂–OH stretching vibration (Wu *et al.*, 2006). The weakening of peak around 1030 cm⁻¹ was due to the grafted polymerization between OH group of clay and the monomer during the polymerization reaction indicating the dispersion of clay in the polymer matrix (Liang and Liu, 2007, Saurabh *et al.*, 2019). Poly-acrylic acid in its FTIR spectra showed peaks at 1569-1409 cm⁻¹ related to the C=O stretching of acrylate whereas the protein grafted poly-acrylic acid this peak was shifted to 1564-1408 cm⁻¹ (Zhang *et al.*, 2011).

In case of both NCPC and NCBPCs characteristic peak was observed around 1730 cm⁻¹ due to C=O bond in acrylate unit and peak around 1620 cm⁻¹ was due to the carbonyl moiety of acrylamide unit in polymer. The peak around 1170 cm⁻¹ of NCPC and NCBPCs was due to CO–O stretching of acrylate unit. The peak around 1670 cm⁻¹ was due to conjugated free acetyl carbonyl group and band at around

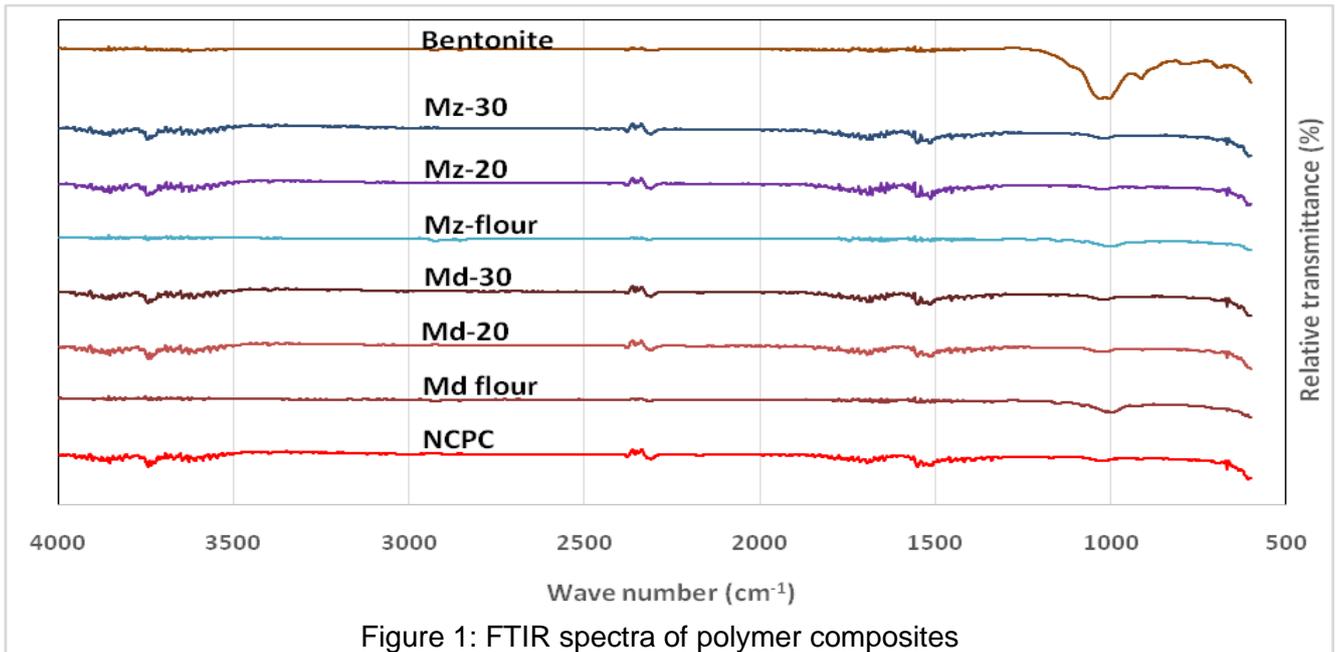


Figure 1: FTIR spectra of polymer composites

1620 cm^{-1} was due to C=N of imine group both present in NCPC and NCBPC products. The characteristic band around 1450 cm^{-1} was due to C=H compound of NCPC and NCBPCs. The strong bands around 3400 and 3800 cm^{-1} was due to the stretching vibration of Mg-OH, Al-OH

or Fe-OH structural hydroxyl groups' characteristic of montmorillonite group (Sarkar *et al.*, 2014). The band around 500-700 cm^{-1} was attributed to the angular deformation of Si-O-Al bond.

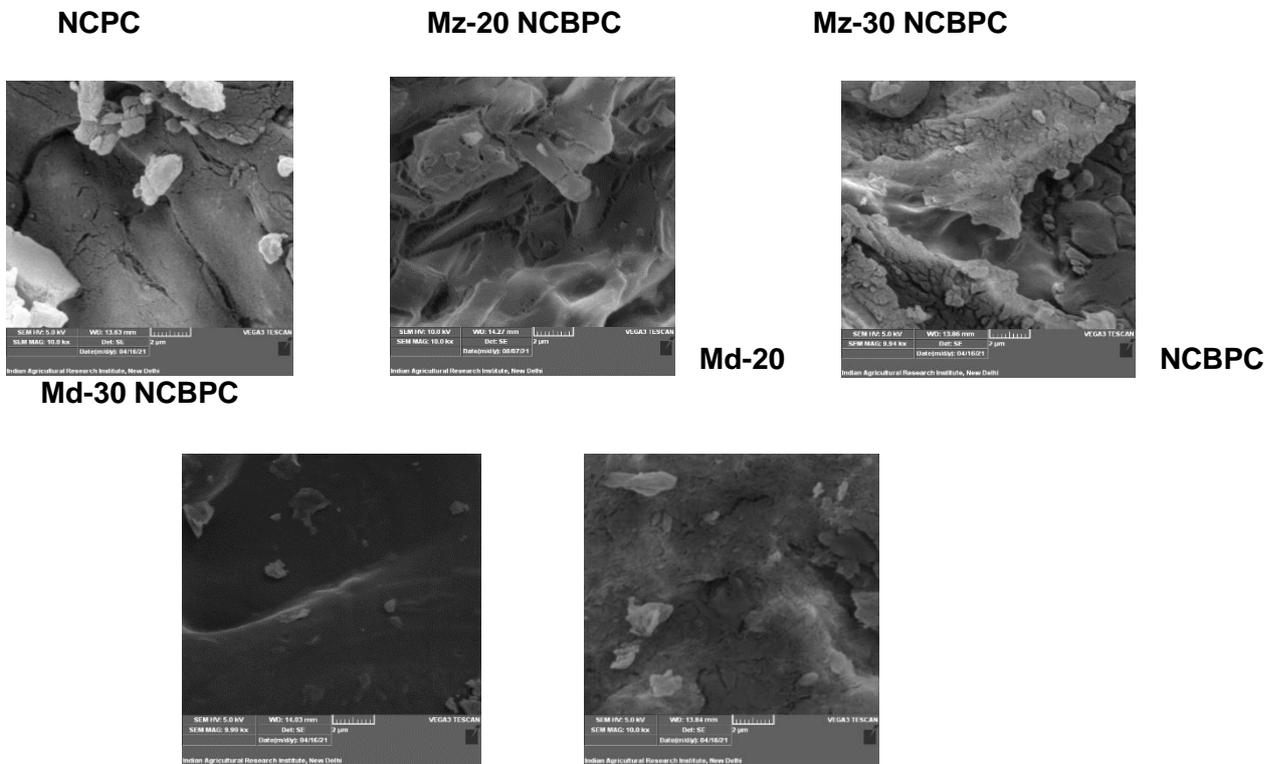


Figure 2: SEM images of N loaded polymer composites

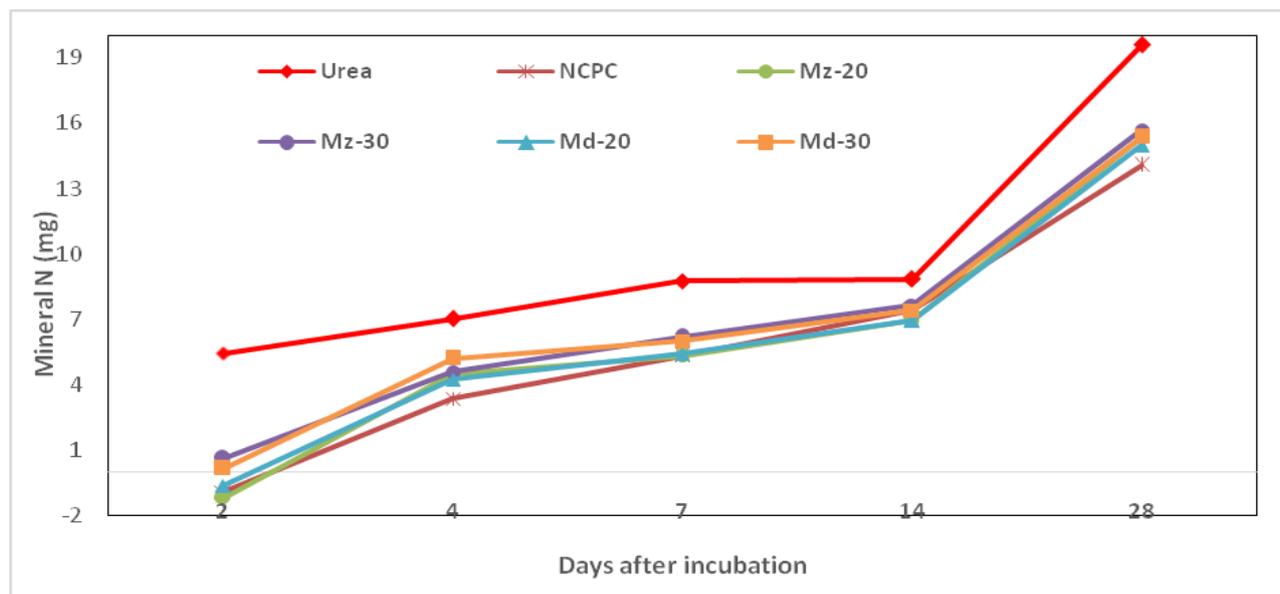


Figure 3: Release pattern of N from polymer composites in an Inceptisol

The SEM images of polymer composites were given in figure 2. The SEM analysis was carried out to study the surface morphology of polymer composites. Both N loaded NCPC and NCBPC materials showed rough and fractured surface morphology. Liang and Liu, 2007 also reported the coarser surface morphology of these materials whereas Mandal *et al.*, 2018 observed the fractured surface morphology of polymer composites. The SEM images further confirmed dispersion of bentonite clay in the polymer matrix. Highly coarse porous microstructure of these materials supported the higher absorbency by these materials.

The N release pattern of polymer composites is given in figure 3. All the N loaded nano composite materials found to be having significantly lower N release than that of normal urea in soil throughout the study. Among the NCPC materials, it was observed that the rate of replacement was more influential than that of the starch source used in case of N release property. Interestingly, NCPC and biopolymer composites with 20% replacement showed absorption of native mineral N during the initial phase of incubation but this character was

absent in case of products with 30% replacement. When urea was added to soil, it quickly dissolves in soil solution and further it would be hydrolysed and converted to ammoniacal form. So, this faster dissolution and hydrolysis might be the reason for higher mineral N content recorded during the study. But in case of N loaded polymer composites, N was gradually released to soil with exchange of free water which indirectly slows down the hydrolysis of urea. Sahoo *et al.* (2016) also reported the slow release of N from the polymer composites.

Thus, starch derived from grain flour can be used as a partial replacement of synthetic polymer for preparing nano clay bio-polymer composites. Also, FTIR and SEM revealed that bentonite clay and starch were completely dispersed in polymer matrix. The replacement level had greater impact on the nitrogen release from the biopolymer composite. The incubation study in soil disclosed the slow-release N property of these materials. Therefore, nano bentonite clay with grain flour may be used for synthesis of nano biopolymer composites with slow-release N property.

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