Synthesis of Novel Nanocomposite Based on *Carboxymethylcellulose (CMC)*, *Kaolin* and *Urea* Fertilizer for Controlled Release

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ABSTRACT

Controlled Release fertilizers (CRFs) are new generation agrochemicals which aid in decreasing environmental pollution. In the present study, novel CRF beads are synthesized by the technique of sol-gel polymerization. CMC polymer at various concentrations was used as a matrix and kaolin was used as a binder to enhance mechanical properties of the beads. The study also reveals the incorporation of Kaolin at different concentrations and optimization of the same. Fe^{3+} was used as a cross-linker to obtain spherical beads. Also, a study was done to optimize the cross linking time and concentration of cross linking solution. The usage of polymers brings forth the issue of their degradation. But all the materials used in the current study are biodegradable. The incorporation of urea in the prepared fertilizer nanocomposite for controlled release of nutrients was confirmed by FT-IR, XRD and scanning electron microscopy (SEM) techniques. Formed nanocomposite showed diameter as small as 8.1nm as seen by SEM. The release study of fertilizer was done by incubating the sample in water and released urea content was determined using UV-Vis Spectroscopy at the wavelength of 525 nm by Diacetylmonoxime method at every alternate day. The samples showed optimum release of 66.7, 76.4 and 55.4% for 0.8, 0.9 and 1wt% CMC concentration.

KEYWORDS: *CMC, Controlled Release, Cross linking, Kaolin, Fertilizer, Urea, Nanocomposites.*

INTRODUCTION

Fertilizers are the nodal centre of agronomics. Nitrogen fertilizer, Urea with 46% N content, is the most abundantly used one round the globe. But one drawback with urea application is that the plant uptake of applied Nitrogen is only

30-40% [1] because of several factors like leaching, volatilization and surface run-off while irrigation. Even phosphorous fertilizers suffer the same fate with plant uptake of about 15-25% [2]. So, overall there is a lot of nutrient loss depending upon the concentration of available nutrients in the soil. Nitrogen loss occurs when plant utilization of the same is less and excess phosphorous gets converted into water-insoluble P after reaction with soil minerals; thereby ceasing any chances of its further utilization by the plant [3]. Henceforth, an unchecked and huge incorporation of these agrochemicals in the soil to meet the global food supply poses severe consequences of economic loss, resources loss as well as environmental degradation [4]. This existing issue in the regime of fertilizers can be tackled by the use of fertilizer formulations which could release the nutrients gradually to the soil in accordance with the plant needs.

Ever-growing concern for environmental safety has leaded the researchers to greener formulations. There are no qualms that polymers are the class of materials which are ever-lasting and so much fulfilling in each and every sphere like pharmaceuticals, agronomics, food, textile and personal care [5]. But their non-biodegradability has again deflected the researchers towards some alternates for them like biopolymers, mostly based on starch and cellulose owing to their low-cost availability, non-toxicity and biodegradability. Usage of these biopolymers in the form of blends and composites with fertilizers aided with nanotechnology in the field of agriculture has boosted up the research in an all new direction. In the recent years, polymer-clay nanocomposites with fertilizers

for controlled release of nutrients have gained major attention. These formulations reduce the labour of application of fertilisers in comparison to the traditional ones as they need not to be added again and again in single growth cycle. Subsequently, they reduce the chemical loss to environment while irrigation as well as materials like cellulose and starch can be used to prepare water reservoir systems in addition with controlled release properties which can be a boon to draught prone areas [6, 7]. Also, the total nutrient uptake by the plant depends wholly upon the amount of nutrient applied to the roots rather the amount present in the soil which depends on the rate of release of nutrients to the roots wherein, controlled release nanocomposites play the key role [8].

Carboxymethylcellulose (CMC), derived from cellulose is an efficient polymer for the same due to benefits like high viscosity and low toxicity. It is soluble in water and insoluble in organic solvents like ethanol. It is anionic polysaccharide and is derived by introducing $-CH_2COOH$ groups into cellulose framework with acetic acid in presence of alkali catalyst. Its molecular weight ranges from 90,000-7, 00,000 and its structure is based on β-(1-4)-D-glycopyranose polymer of cellulose [9]. CMC is biocompatible, biodegradable, cost effective, non-toxic and shows excellent hydrophilicity due to the presence of numerous carboxylic and hydroxyl groups present in it. One property of CMC which has attracted major attention is its easy workability as it forms gel beads in presence of polycationic molecules like Fe^{+3} and Al^{+3} [10]. But another issue with biopolymers is their poor mechanical properties due to which they are

blended with several clays and used as a matrix to hold the fertilizer particles. Several clays have been reported for the purpose like Attapulgite [11], Eudragit [12], Kaolin [13] and Montmorillonite [14] amongst other natural clays and organo-modified clays. Natural clay minerals can be classified into three types: 2:1 type, 1:1 type and layered silicic acids. Kaolin used in this study is 1:1 type with one aluminium octahedron sheet and one silicon tetrahedron sheet having the formula $Al_2Si_2O_5(OH)_4$ with neutral layer charge [15].

Biodegradable fertilizer-polymeric formulation of nanocomposites with clays is really promising in the field of agriculture in the long run as addition of fertilizers already increases the amount of chemicals in the environment and in such cases if synthetic polymers are used then we end up adding more chemicals to the ecosystem which is not acceptable. Also, polymer-clay nanocomposites present forth the dual benefits of organic materials like light weight, enhanced moldability and flexibility as well as those of inorganic materials like heat stability, increase chemical resistance and better strength [16]. Though achieving controlled release of fertilizers using only biodegradable polymers, green solvents and non-hazardous chemicals is a bit tricky but actually a saviour for the already degrading environment, as a whole. Taking this background into account the following study was conducted to check the workability of polymer, clay and fertilizer nanocomposite via *sol-gel* polymerization technique, using totally biodegradable materials like CMC as polymer matrix, Kaolin natural clay and urea with green solvents to reduce any hazardous chemical addition to the soil and overcome the above

stated problems encountered with the formulations based on synthetic polymers. The study presented here would be contributory in the agronomic sector which is suffering a major setback because of global food demand, increasing soil pollution and less availability of controlled release fertilizers which can be applied on field level.

EXPERIMENTAL

2.1. Materials

Carboxymethyl cellulose (CMC), with degree of substitution (DS) greater than 0.4 and viscosity of 1% aqueous solution at 20°C was procured from Central Drug House (CDH), India. Kaolin with molecular weight 258.20 g and molecular formula $H_2Al_2Si_2O_8H_2O$ was also purchased from CDH, India. Urea was obtained from Hi-Media Lab, India. $FeCl_3$ and NaOH used were also purchased from Hi-Media Lab, India. All the chemicals were used as such in the study without further purification or any other treatment. Distilled water was used throughout the study.

2.2. Preparation of Kaolin suspension

Kaolin was added in distilled water and stirred for 24 h at room temperature to obtain a homogenous suspension. Further, the obtained suspension was sonicated on a sonication bath for 1 h at 60°C to reduce the particle size of Kaolin.

2.3. Preparation of CMC-Urea solution

CMC was gradually added in a mixture of NaOH and Urea in the ratio of 1:2 in 50 ml distilled water, to get the final CMC concentration of 1wt%. The solution was then heated to 70°C and stirred for 2 h for proper incorporation of Urea in CMC.

2.4. Preparation of CMC-Kaolin-Urea Nanocomposite

The temperature of CMC-Urea solution was reduced to 60°C and Kaolin suspension was added to it drop wise within 30 min. The reaction mixture was then stirred for 4 h to obtain a homogenous solution and for proper intercalation of clay in polymer matrix. Further, the

reaction mass was cooled to room temperature.

2.5. Preparation of CMC-Kaolin-Urea beads

The above viscous reaction mass was taken as such for bead formation. 100 ml 2M $FeCl_3$ solution was prepared for the same and bead formation was done using a syringe and needle. The reaction mass was dropped in 2M $FeCl_3$ solution to give homogenous beads which got formed as soon as the reaction mass was dropped in the cross linker drop by drop. Beads were left undisturbed in $FeCl_3$ solution for 2 h for proper cross linking and were then filtered followed by thorough washing with distilled water to remove un-reacted $FeCl_3$. The beads were then dried in oven for 6 h at 65°C.

2.6. Urea release determination by UV-vis spectroscopy

For the estimation of controlled release behaviour of the prepared formulation, 0.5 g of sample beads were put in a beaker containing 100 ml water covered with parafilm at room temperature. 0.1 ml of sample was taken for the study of Urea content by UV-vis spectroscopy at every alternate day starting from first day. Urea content was determined by diacetylmonoxime (DAMO) method (calorimetric determination of microgram quantities of urea) based on Urea reaction with diacetylmonoxime[17, 18]. Urea-DAMO complex is formed after reaction under acidic conditions provided by the reagents. The complex gets reduced by light and losses its colour. The colour absorbency of the complex is measured by UV-vis spectrophotometer at a maximum absorbance of 525 nm. Calibration curve of absorption versus concentration (ppm) was plotted for urea. For 0.1 ml of sample, the absorption related to urea content was measured by UV-vis spectrophotometer. Urea concentration was calculated using the equation provided by calibration curve. The release of urea was calculated as percentage based on the basis of primary concentration of urea in the sample. A range of experiments were done and release by varying the concentration of CMC, Kaolin, Cross linking solution and cross linking time to study the release patterns and optimize the study.
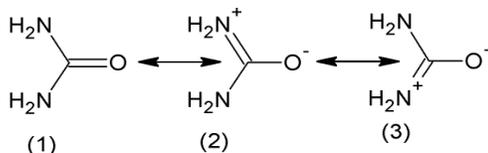
2.7. Characterizations

FTIR spectra were recorded on Nicolet, Nexus spectrometer in the range of 500-4000 cm^{-1} using samples prepared as KBr pellets. XRD analysis was done using X-ray power diffractometer (Bruker ADX D8 Advance) using graphite monochromatized with Cu k_α radiation source in 2θ range of 5-100° running at 40kV. The surface morphologies of prepared formulation were studied using Zeiss Gemini FE-SEM analyzer scanning electron microscopy at EHT of 5 kV.

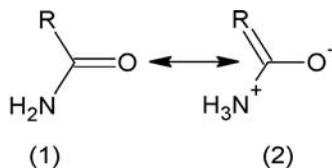## 3. RESULTS AND DISCUSSION

3.1. FTIR spectra

As shown in (Fig. 1a), the broad band in the range of 3200-3500 cm^{-1} is the characteristic peak for hydroxyl group stretching vibration for CMC. The same range also corresponds to the hydrogen interactions, both, intermolecular and intramolecular. The absorption band at 2929 cm^{-1} is attributed to C-H stretching mode; the one at 1450 cm^{-1} shows symmetrical stretching of carboxylate group and a band at 1630 cm^{-1} shows asymmetrical stretching of the same[19]. Bonds due to –C-O- stretching in CMC were observed in the range of 1000-1200 cm^{-1}. The C-H stretching band at 2920 cm^{-1}, symmetrical and asymmetrical stretching bands at 1450 cm^{-1} and 1630 cm^{-1} show a decrease in intensity after the reaction which implies that Kaolin incorporation decreased the hydrogel interactions in the polymer chains (Fig.1d). The carboxylate band shows a decrease in intensity after cross linking of CMC with Fe^{+3} ions during bead formation. This is attributed to the ionic bond formed between ferric chains and CMC carboxylate ions [20, 21, and 22]. Also the electrostataic interactions between oxygen atoms and ferric ions cause a decrease in intensity of –C-O- stretching band (Fig. 1d).

It is evident that C=O band in urea is longer than that usually found in carbonyl groups and C-N bond is relatively shorter than that in amides or amines. This is due to the existence of resonance structures (scheme 1).
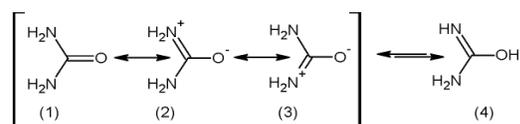

Scheme 1

In accordance with the (Fig.1b) the band observed around 3420 cm^{-1} corresponds to N-H out of the phase stretching vibrations and that at 3360 cm^{-1} and 3225 cm^{-1} corresponds to N-H in phase stretching vibrations. The stretching of C=O and bending of NH$_2$ are attributed to a band at 1687 cm^{-1}[23]. In amides the C=O stretching vibrations is lowered to 1690 cm^{-1} in comparison to aldehydes, ketones and acids at 1740-1700 cm^{-1} because of existence of (1) and (2) as in scheme 2.

Scheme 2

N-H deformation bands appear in the range of 1650-1600 cm^{-1} which gets lowered in intensity after nanocomposite formulation indicating urea interactions within the polymer-clay matrix (Fig.1d). The higher frequency shift for C-N stretching at 1465 cm^{-1} in urea is attributed to existence of resonance structures. A band in the range of 1700-1650 cm^{-1} which appears in the nanocomposite formulation (Fig. 1d) is

typical of urea inclusion in the compound. The stability of inclusion is directly proportional to the prominence of band. Also the lowering intensity of C-N band in the range of 1200-1000 cm^{-1} again shows the existence of zwitterionic resonance structures as in scheme 3 and hence, urea inclusion in the polymeric matrix[24]. The band in the range of 1160-1150 cm^{-1} (Fig. 2b) are attributed to NH$_2$ rocking vibrations, those at 1060-1050 cm^{-1} for NH$_2$ wagging vibrations and at 790 cm^{-1} for C=O wagging vibration all show a decrement in intensity after the reaction.

Scheme 3

OH stretching band of Kaolin appears at 3700 cm^{-1} as in (Fig. 1c) which disappears after reaction indicating its incorporation in the polymer. Bands in the range of 3600-3500 cm^{-1} are attributed to Al-OH stretching (Fig. 1c) which lower in intensity due to interaction of clay with –OH of polymer (Fig. 1d). Si-O stretching band of clay at 1035-1030 cm^{-1} weakens after the reaction (Fig. 1d). The OH deformation bands (Fig. 1c) at around 918 cm^{-1}; Fe-O, Fe$_2$O$_3$ and Si-O-Al stretching at 542 cm^{-1} and Si-O-Si bending at 475 cm^{-1} all get weakened in intensity showing the interactions of Kaolin with CMC and Urea [25, 26]. Hence, the formation of nanocomposite was confirmed by FTIR and the results were also in accordance with the available literature.

3.2. XRD Analysis

XRD patterns were recorded in order to study the structure of prepared formulation. A single

peak with 2θ value of 19° (Fig. 2a) is characteristic peak of CMC[27]. The reflections at 2θ values of 12° and 25° corresponding to 7.1 Å (Fig. 2c) are characteristic peaks for Kaolin [28, 29, 30]. It is evident by the existence of these patterns that the structure of Kaolin does not gets distorted after the reaction and also the intercalation of polymer chains into the silicate galleries was disrupted because of the absence of negative charges on the silicate galleries. Pure urea gives a set of characteristic peaks with 2θ values 23°, 25°, 29°, 32°, 36° and 37° (Fig. 2b)[31]. The presence of these peaks in the XRD spectrum of the formulation (Fig. 2d) clearly shows urea incorporation into the polymeric matrix. Absence of peak at 23° in (Fig. 2d) indicates the reaction of urea with CMC carboxylate group. Also the shifting of peak at 2θ value of 36° to 37.2° shows the Urea interaction with polymer-clay matrix (Fig. 2d). XRD pattern of the formulation (Fig. 2d) shows the presence of characteristic planes of CMC, Urea and Kaolin which reveal that urea got incorporated in clay-polymer matrix without damaging their basic structure. In accordance with the study of available literature, the formation of nanocomposite was confirmed. The results were also supported by FE-SEM data.
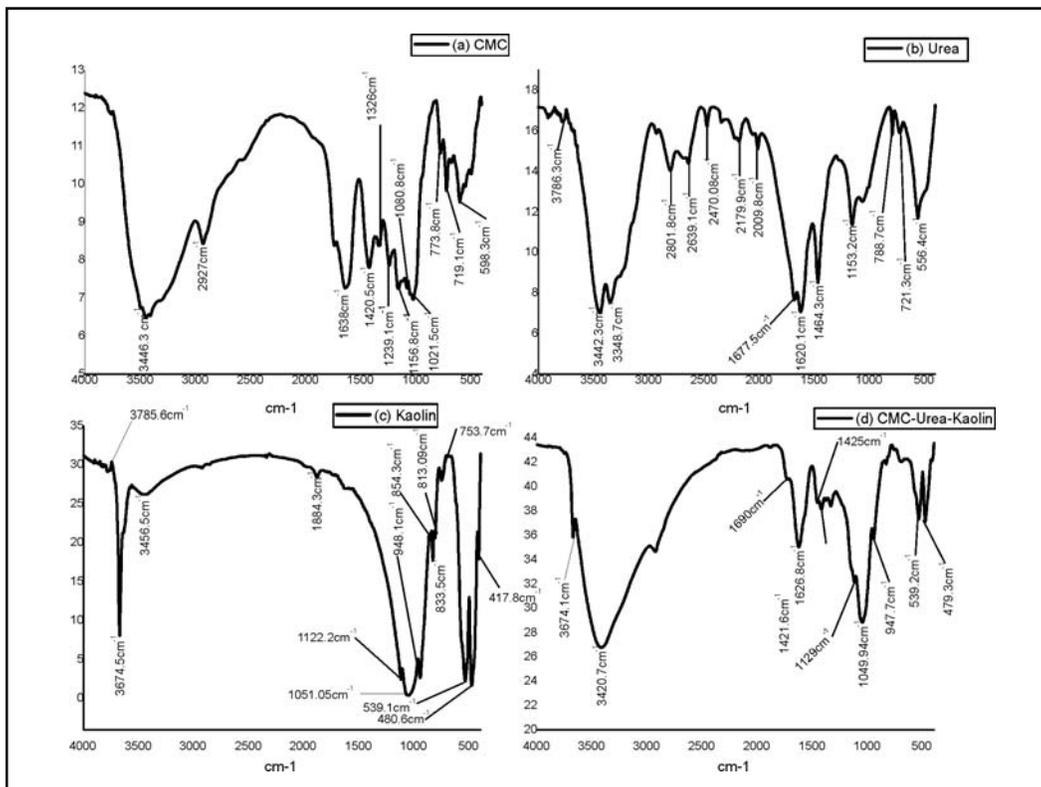

Fig. 1 FTIR spectrum of (a) Pure CMC (b) Pure Urea (c) Pure Kaolin (d) CMC-Urea-Kaolin.
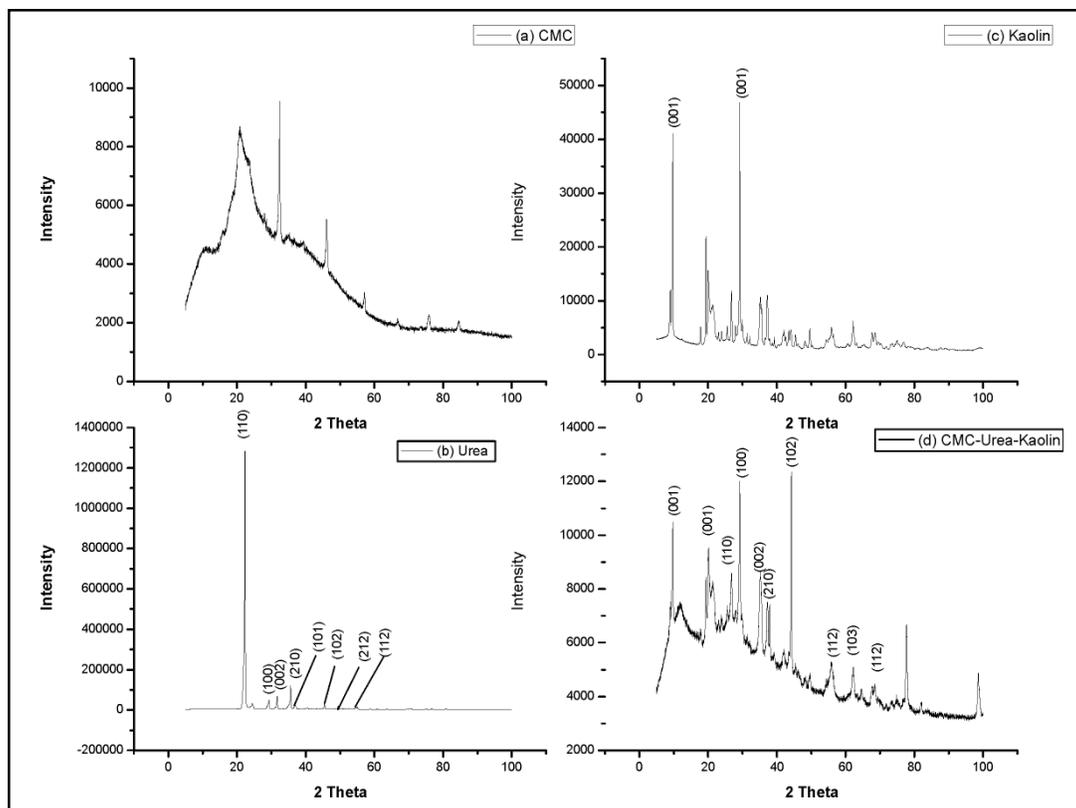
Fig. 2. XRD Graphs of (a) Pure CMC (b) Pure Urea (c) Pure Kaolin (d) CMC-Urea-Kaolin.

3.3. FE-SEM Analysis

Scanning electron microscopy (SEM) technique was used to investigate the structure and surface morphologies of the prepared formulation. As it is evident from Fig. 3, the CMC-Urea-Kaolin formulation shows spherical morphologies within the nanometre range of diameter comprising in the range of 8-14nm, which confirms the formation of nanocomposite. It also depicts that urea got incorporated into the polymeric matrix of completely cross linked CMC to form beads after binding with clay in order to achieve substantial mechanical properties. Nanocomposite formed also reveals a uniform structure in SEM analysis without any voids which shows that both clay and polymer got processed smoothly giving uniformity to the surface of material and is also related to greater chemical interaction of fertilizer with polymer.

3.4. Release study of Urea

Release of urea from nanocomposites is affected by various factors like concentration of polymer, concentration of clay, concentration of cross linker and also on cross linking time, that is, the time for which beads were kept in the cross linking solution to get properly cross

linked. In the present study, the effects of the aforesaid parameters on the release of urea were investigated. For the same urea concentration was kept constant in all the batches and one parameter was changed at one time to observe its impact on release rate and to optimize the ratio of polymer, fertilizer and clay for effective controlled release.
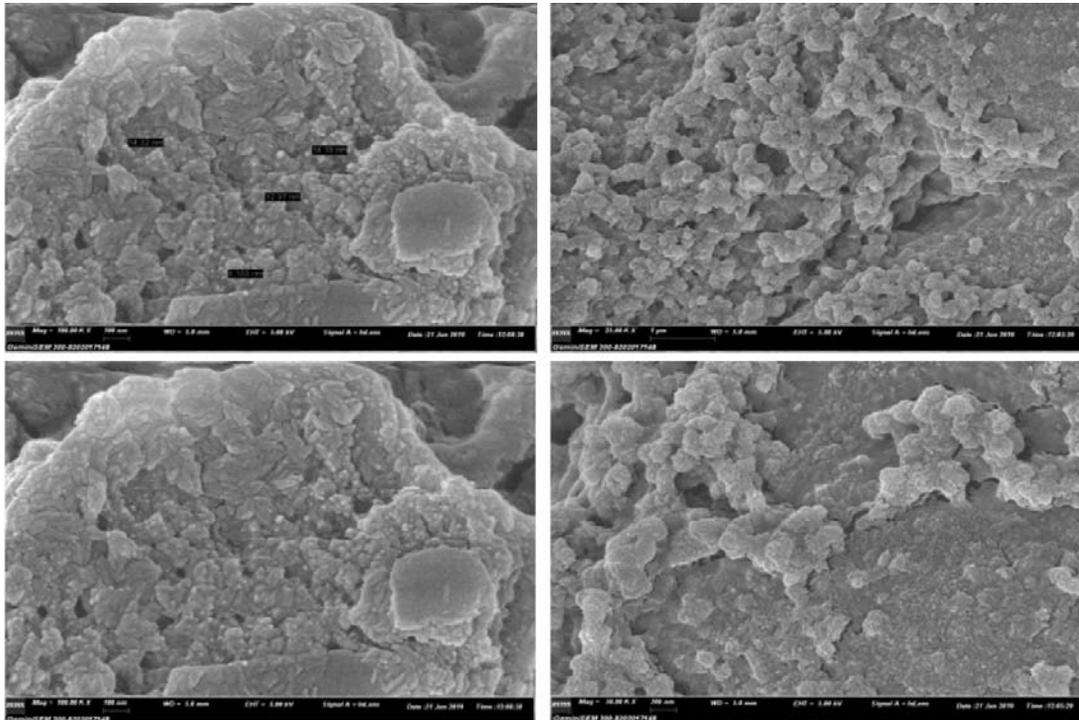

Fig. 3. SEM Images of CMC-Urea-Kaolin formulation.

3.4.1. Effect of CMC concentration on bead formation

Varying the amount of polymer in the beads can change their overall morphology which can affect the amount of Urea incorporation in the beads. A range of experiments were done in order to optimize the concentration of CMC in the beads. If lesser amount of Urea gets incorporated in the polymeric matrix, then it will lead to lesser supply of nutrients to the plant. Also, if beads lose their spherical morphology then their holding capacity for clay and fertilizer both gets reduced which leads to the burst release of Urea from the matrix. The study reveals that a CMC solution of 1wt% gives promising results in terms of proper bead formation and also controlled release of urea. The other experimental conditions were kept same. The results are as shown in Fig. 4. For more precise understanding of the release trends of urea, the kinetic data of release obtained from all the combinations prepared

after varying the concentration of CMC were fitted in the following equation:

$$M_t/M_0 = Kt^n$$

Where, M_t/M_0 is the urea release fraction at time, t. K is a constant symbolizing the properties of urea release system and n is the exponent of release which is characteristic of fertilizer release mechanism. The value of n<0.5 shows that the release pattern follows Fickian diffusion mechanism whereas, value of n>0.5 shows that the release follows anomalous mechanism of

diffusion. The values of n calculated for CUK(0.3:1:1), CUK(0.4:1:1), CUK(0.4:1:1), CUK(0.5:1:1), CUK(0.6:1:1), CUK(0.7:1:1), CUK(0.8:1:1), CUK(0.9:1:1) and CUK(1:1:1) were 0.85, 0.76, 0.58, 0.63, 0.62, 0.69, 0.67 and 0.31. Hence, the nanocomposites which were prepared follow anomalous diffusion behaviour except in the case when the ratio of all the reactants was kept same that is, in CUK (1:1:1). Thus, the amount of polymer affects the release mechanism kinetics significantly.
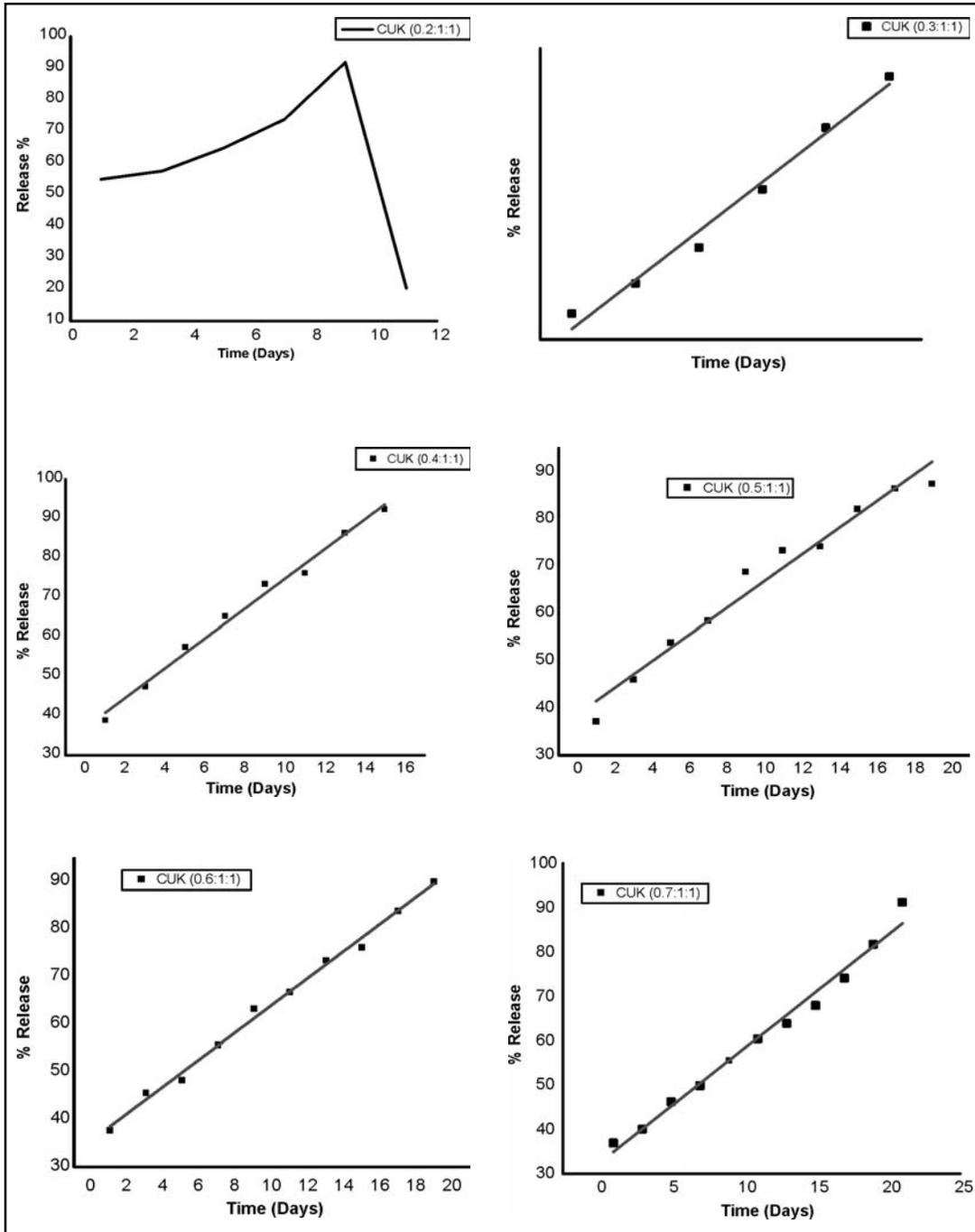
Table 1. Effect of CMC concentration on beads

CMC (wt %)	Observations	Observations from release study
0.2	No beads formed with proper morphology.	About 92% release of urea occurred by 10th day of incubation in deionised water and there after the release of urea showed a sharp decrease.
0.3	No beads formed with proper morphology.	Sample showed 85% release up to 12th day and then the release rate decreased.
0.4	Uneven beads formed in terms of size.	Complete release of urea occurred within 15 days.
0.5	Beads ruptured while filtration giving an uneven appearance.	Rate of urea release was consistent for around 20 days and reduced thereafter.
0.6	Beads ruptured while filtration thereby giving uneven morphology.	Complete release occurred within 20 days.
0.7	Beads formed.	Complete release occurred up to 20th day.
0.8	Proper beads formed.	Complete release occurred up to 20th day.
0.9	Proper beads formed.	Complete release occurred up to 25th day.
10	Proper beads formed.	Sample showed about 92% release up to 45th day.

3.4.2. Effect of Kaolin Clay

Kaolin used for the formulation is chemically less reactive with pore water and also has a very limited surface activity which makes it a good binder[32]. Though clay incorporation within the polymeric networks does pose a decrement

in the water absorbency and consequently alters the fertilizer nutrient release rates when studied in distilled water. This may be attributed to the fact that due to clay particles the overall density of the already dense polymer increases which subsequently lessens the
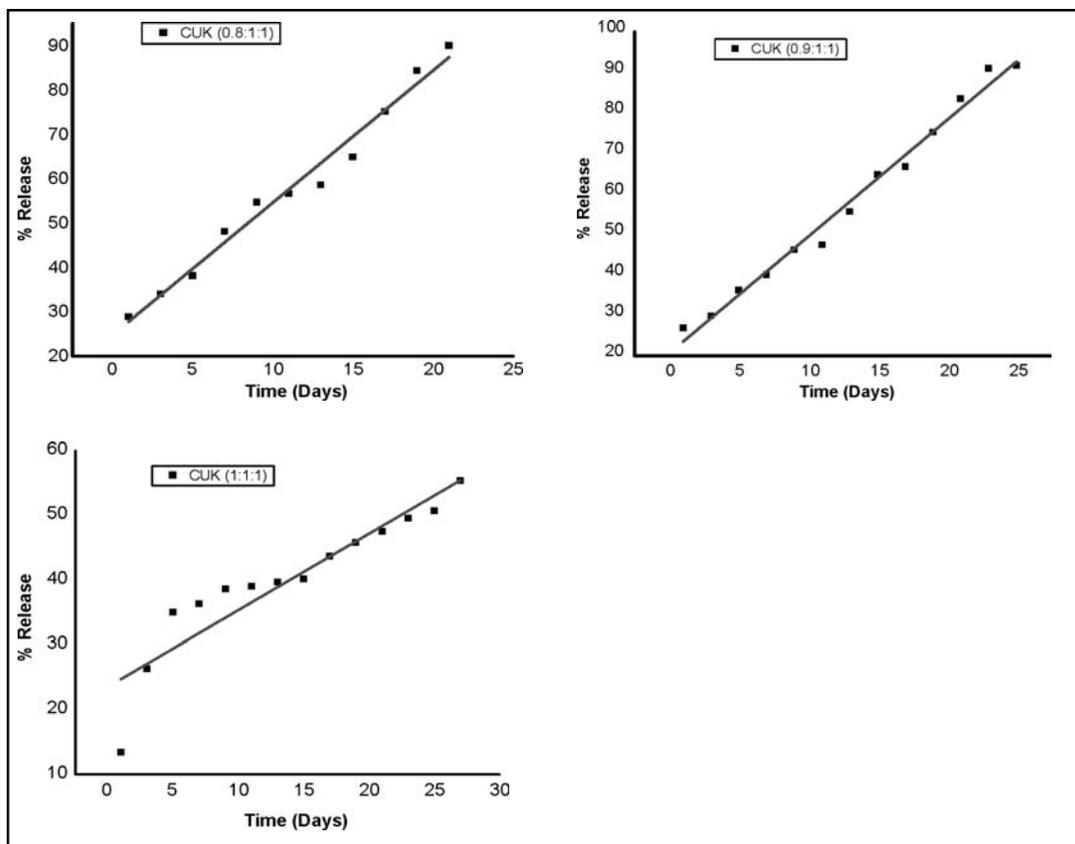
Fig. 4. Release trends of Urea after varying the concentration of CMC.

elasticity of polymeric chains. Higher density of cross linking leads to a decrease in space for the water molecules to get accommodated in the cross linked network of polymer and hence the equilibrium water absorbency decreases. This also affects the release of urea which shows a decreasing trend with increasing amount of clay. The same effect is seen with the cross linkers. When increased in concentration, they reduce the water holding capacity of polymer [33]. The above stated observations were in well synchronization with the studies done on the prepared formulation.

Kaolin was used at various concentrations in the study ranging from 0.2%, 0.5%, 1% and 2% (Fig. 5) in order to optimize the same for the formulation. Beads were formed in all the cases. The sample with 0.2% Kaolin showed around 92% release in 20 days depicting Fickian diffusion (n=0.2) in comparison to 0.5% Kaolin formulation which showed the same release within 25 days depicting anomalous mechanism (n=0.81). Whereas the formulations with 1% (n=0.41) and 2% (n=0.88) Kaolin showed much delayed release of urea depicting Fickian and anomalous mechanism respectively. The

experiments done revealed that 0.5% concentration of Kaolin worked best for the

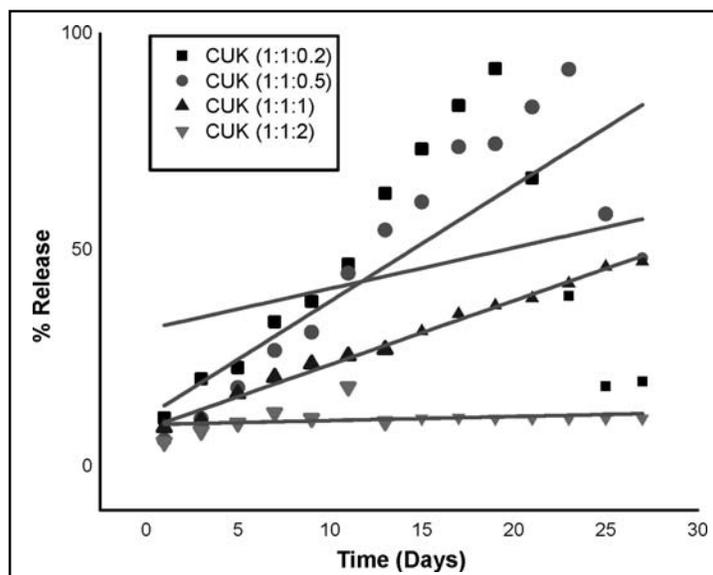formulation of the beads taking into consideration the release of urea.

Fig. 5.   Dependence of Release time of urea on the concentration of Kaolin.

3.4.3. Effect of cross linking time and cross linker strength

Cross linker strength and cross linking time, both play a pivotal role in formation of CMC beads. Formation of beads was done in 2M $FeCl_3$ solution which was optimized by studying bead formation taking CUK (1:1:0.5) as standard batch. Cross linking was done in 0.5M and 1M, 2M and 3M $FeCl_3$ solutions and the trend of release of urea was studied from them for 15 days which revealed that 2M $FeCl_3$ solution gives promising results during release of urea. Beads formation was unsuccessful in 0.5M $FeCl_3$ solution. Cross linking time was optimized as 2h less than which the beads ruptured immediately while filtration. A study

was also done with the same composition that is, CUK (1:1:0.5) for urea release in which the effect of time of cross linking of the beads was observed. The reaction mass was divided in four equal parts and bead formation was done separately in 2M $FeCl_3$ solution. In one part beads were left to cross link for 20 minutes, in second 2h, in third 12h and lastly 24h, after which they were filtered and dried. Same amounts of beads were taken from four parts and the release of urea was studied from them for 15 days which showed that 2h cross linking time is the optimum time of cross linking for the prepared formulation as it gave a better trend of urea release when compared to beads formed after 20 minutes, 12h and 24h cross linking time. The details are given in Fig. 6.
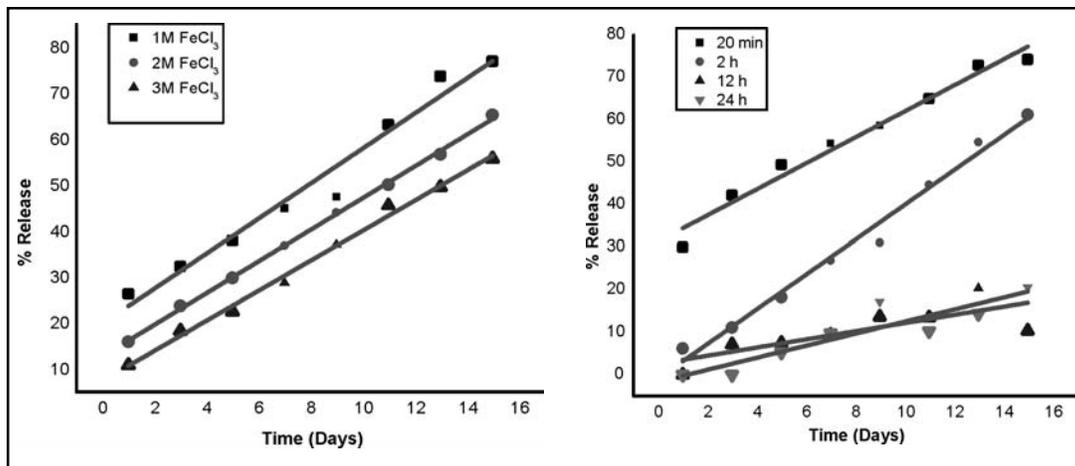
Fig. 6. Dependence of Release time of urea on the concentration of cross linker and time of cross linking

4. CONCLUSION

The findings of the study presented herewith coincide with the available literature related to nanocomposites of polymer and clay with fertilizers. By this work, nanocomposites of urea with clay and polymer have been successfully prepared. Also, the formulation contributes majorly in the arena of nanocomposites prepared from only biodegradable materials. The study gives good results in context of controlled release of urea and can be helpful in other field studies without posing any harm to the soil. It is inferred from the study that 0.8-1.0 wt% CMC concentration is must for the formation of a proper bead with better release kinetics. Formulations with CMC 0.8%, 0.9% and 1% CMC showed 66.7, 76.4 and 55.1% release within 27 days of incubation. 0.5-1wt% Kaolin concentration works out best with CMC for controlled release and sample with 0.5wt% Kaolin showed 91.8% release within 25 days whereas that with 1 wt% Kaolin showed

47.4% release in 27 days of incubation. Best results for controlled release were shown by the formulation CUK (1:1:1) in which showed 91.9% release till 45th day of incubation. Also, cross linking the beads in 2M FeCl$_3$ solution for 2 h gives good results in terms of release giving 65.3% release on 15th day whereas with 3M FeCl$_3$ release of urea was observed to be delayed with 55% in 15 days. In most of the combinations prepared, the release follows non-fickian or anomalous mechanism typical of nanocomposites of polymers as the areas for molecular movement is very low in them owing to the highly complex matrix provided by the polymers.

Improvisations can be done to enhance the water holding capacities of the nanocomposites and also to improve the release rates of fertilizers by the usage of other cross linking agents. The formulation is prepared using biodegradable components in order to make it usable for agricultural applications in order to avoid soil pollution from

any of the used materials. The beads prepared are easy to handle and can be scaled up considerably. The objective of study to synthesize an eco-friendly fertilizer nanocomposite is met and can be helpful for further studies in the same domain.

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