

KINETICS OF CARBON MINERALIZATION IN MOLLISOLS UNDER BENTONITE AND NON BENTONITE SYSTEMS UNDER VARYING MOISTURE REGIMES

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ABSTRACT

An incubation study was conducted to evaluate kinetics of carbon mineralization in bentonite and non bentonite systems under varying moisture regimes in Mollisols of Tarai region of Uttarakhand with eight treatments viz. control (soil), nitrogen, wheat straw, FYM, wheat straw + nitrogen, FYM + nitrogen, rice straw and rice straw + nitrogen. Rice and wheat straw were applied @ 6 t ha⁻¹, while FYM was applied @ 10 t ha⁻¹. Nitrogen @ 120 kg ha⁻¹ was used as starter dose. All these treatments were incubated at 30^o centigrade in BOD incubator for 90 days in triplicate using two bentonite (0% and 10%) levels and two moisture (field capacity and saturation) regimes. Decomposition rates of rice straw, wheat straw and FYM under varying moisture regimes in bentonite and non bentonite systems have been monitored periodically for 90 days on the basis of carbon dioxide evolution. The first order kinetics models gave good fit over the zero order models in describing organic matter decomposition. Both half-lives (18.38%) and turnover times (22.28%) were increased in 10% bentonite compared to 0% bentonite concentration. Similarly, longer half-lives (143.06%) and turnover times (139.14%) were recorded at saturation compared to field capacity. To, get immediate effect of added bentonite, (within 90 days of incubation) a higher amount of clay (10%) was used in this study. Though application of 10% clay under field conditions (224000 kg/ha) seems to be impractical, data generated from this lab incubation study gives a scope for further field research using different possible lower concentrations of bentonite in eroded soils alone or with other potential amendments like biochar which may give a better result for carbon sequestration.

Key words: Bentonite clay, moisture regime, half life, turnover time, Mollisols

INTRODUCTION

The mineralization of soil organic C is one of the important processes regulating the functioning of natural and managed eco-systems (Johnson 1995). The quality of detrital inputs and soil texture are hypothesized to control soil C mineralization rates (Schimel et al. 1994), but relative to the decomposition of fresh liter, little is known about how these variables alter C mineralization rates in mineral soils (Bauhus et al. 1998). Soil moisture content has a strong effect on C mineralization (Summerell and Burgess 1989). In dry soil mineralization is low because soil microbes' activity is limited in dry condition. Conversely, in saturated soil lack of oxygen limits mineralization because only anaerobic microbes can operate in such condition. The amount and type of clay in soil also affects C mineralization reactions. Mineralization tends to be greater in coarse textured soils and less as the soil clay content increases. Fine textured soils high in clay are abundant in micropores in which organic matter can find physical protection from microbial decomposition (Six et al. 1999). Clay minerals present in soil also influence the mineralization as different clay minerals form varying clay complexes. The stability of these complexes would influence the carbon mineralization. Although, compared to soil texture, the effect of soil type (mineralogy) on C and

N mineralization is less clear (Deenik 2006). Generally, 2:1 type clays with high CEC possesses higher binding potential and form various organic complexes (Mortland 1970). As per National Inventory published by Indian Bureau of Mines (IBM), a subordinate office under department of mines the quantity of recoverable reserve of bentonite in India as assessed on April 1, 2000 are about 380991132 tonnes. The state wise reserve position is: Rajasthan 274933771 tonnes, Gujrat 96590688 tonnes and Tamil Nadu 8589647 tonnes. (PIB 2002). Bentonite is also available in some pockets of Bihar and Jammu and Kashmir too. (IMYB 1971). The major mineral in bentonite is montmorillonite, having hydrated sodium, calcium, and magnesium and aluminium silicate. Sodium and calcium are interchangeable ions giving montmorillonite a high ion exchange capacity (Grim and Guven 1978). Many workers have studied the effect of bentonite on mineralization and immobilization reactions (Ambles et al. 1989; Appel et al. 1995). But, study had yet been conducted to find out the effect of bentonite clay on C mineralization under varying moisture regimes from different organic amendments. Considering all these in view, a laboratory experiment was set up to find out the kinetics of carbon mineralization in bentonite and non bentonite systems from different organic materials added under varying moisture

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regimes on Mollisols of *Tarai* region of Uttarakhand so as to generate some basic data of its effect on carbon mineralization in Mollisols. Data generated from this lab incubation study on carbon mineralization gives a scope for further long term field trials using different possible concentrations of bentonites in eroded soils to find out a conclusion on its possible effect on soil carbon sequestration. Conversely, high concentration of exchangeable Na⁺ in natural bentonites deposits of India may be a problem for researches for its large scale soil application. Consequently, it also creates a scope of doing research for using Na⁺ free bentonites for further field studies.

MATERIALS AND METHODS

Selection of soil, bentonite clay and their characterization: Composite surface (0-15 cm) sample of cultivated Mollisol (Aquic Hapludoll) was collected from Crop Research Centre of the G. B. Pant University of Agriculture and Technology, Pantnagar, Uttarakhand, India (29° 01' 13.28 " N, 79° 28' 38.86 " E, 233 m above MSL). It was a clay loam containing 32% clay, 42% silt and 26% sand. The samples were air dried and ground to pass through a 2-mm sieve. Wheat straw, rice straw and FYM collected from Crop Research Center, G.B. Pant University of Agriculture and Technology and were ground and sieved with a 2-mm sieve. Air dried soil samples and purified bentonite clay were analyzed for general physio-chemical properties using standard chemical methods. The chemical composition of organic materials was estimated by the procedures of Jackson (1973). Lignin, cellulose and hemicelluloses in the organic materials were determined following the procedure outlined by Van Soest and Goering (1970). Purification of bentonite clay was done following the procedure mentioned by Patel *et al.* (2007). Swelling volume of raw and purified clay was determined by adding 2g of bentonite in 100 mL of deionized water allowing standing for 24 hrs and noting the swelling volume. Selective dissolution analysis (SDA) of Hashimoto and Jackson (1960) was followed to determine the allophane content. The determination of percentage of smectite and vermiculite were based on the cation exchange capacity with and without potassium fixation as described by Alexiades and Jackson (1965).

Incubation Experiment: The effect of bentonite clay and moisture regimes on carbon mineralization from different organic materials in Mollisol was investigated in an incubation experiment under laboratory condition with eight treatments *viz.* T₁: control (soil), T₂: nitrogen, T₃: wheat straw, T₄:

FYM, T₅: wheat straw + nitrogen, T₆: FYM + nitrogen, T₇: rice straw and T₈: rice straw + nitrogen. Rice and wheat straw were applied @ 6 t ha⁻¹, while FYM was applied @ 10 t ha⁻¹. Nitrogen @ 120 kg ha⁻¹ was used as starter dose. Treatments were distributed thrice in a 2 factorial CRD. For each treatment two bentonite levels (0% and 10%) and two moisture levels (field capacity and saturation) were maintained. Decomposition rates of rice straw, wheat straw and FYM and the carbon dioxide evolution was monitored by the method given by Ohlinger (1996). The CO₂ evolved was calculated as follows:

$$\text{CO}_2 \text{ mg g}^{-1} \text{ soil} =$$

$$\frac{(\text{mL of NaOH Normality of NaOH} - \text{mL of HCl Normality of HCl}) \times 22}{\text{Initial weight (g)}}$$

...a

$$\text{CO}_2 (\text{mg kg}^{-1} \text{ soil}) = a \times 1000$$

Kinetics of organic matter decomposition: To describe the decomposition of organic materials, two mathematical models *viz.* zero order kinetics (Howard and Howard, 1974) and first order kinetics (Swift *et al.* 1979) have been tested as follows.

Reaction orders	Differential rate law	Integrated rate law	Characteristic kinetic plot	Slope of kinetic plot	Units of rate constant
Zero	$-\frac{d[A]}{dt} = k$	$[A] = [A]_0 - kt$	[A] vs t	-k	mole L ⁻¹ sec ⁻¹
First order	$-\frac{d[A]}{dt} = k[A]$	$[A] = [A]_0 e^{-kt}$	ln [A] vs t	-k	Sec ⁻¹

[A] = Final concentration, [A]₀ = Initial Concentration, t = Time in days

Half life (t_{1/2}) and turn over time (t₀) were calculated mathematically from the first order kinetics model due to its observed good fit over zero order kinetic models. Turnover time was calculated assuming that 95 per cent loss of carbon from organic materials represented complete decomposition.

$$t_{1/2} = \frac{0.693}{k}$$

$$t_0 = \frac{2.996}{k}$$

Performance of models: Performance of the models were judged on the basis of Root Mean Square Error (RMSE), Mean relative error (MAE), Standard deviation of MAE (STD_A), Percentage of relative mean square error (%MRE), standard deviation of % MRE (STD_R) and linear regression R² between

observed and predicted values (Kerdpiroon *et al.*, 2006).

$$\text{MAE} = \frac{1}{N} \sum_{i=1}^N \Delta P_A$$

$$\text{STD}_A = \sqrt{\frac{\sum_{i=1}^N (\Delta P_A - \overline{\Delta P_A})^2}{N-1}}$$

$$\% \text{ MRE} = \left(\frac{1}{N} \sum_{i=1}^N \Delta P_R \right) \times 100$$

$$\text{STD}_R = \sqrt{\frac{\sum_{i=1}^N (\Delta P_R - \overline{\Delta P_R})^2}{N-1}}$$

Where

$$\Delta P_A = |P_p - P_e|$$

$$\Delta P_R = |(P_p - P_e) P_e|$$

Where

P_p = Predicated output

P_e = Experimentally measured output

$$\text{RMSE} = \sqrt{\sum_{i=1}^{n_d} \left[\frac{1}{n_d} \left(\frac{d_{ci} - d_{mi}}{d_{mi}} \right)^2 \right]}$$

n_d = No. of observations (days)

d_{ci} = predicted or calculated value

d_{mi} = measured or experimental values

RESULTS AND DISCUSSION

Properties of bentonite clay: The data on chemical analysis clearly demonstrate that the bentonite clay,

used in this study, was a swelling type sodium bentonite with swelling volume 22.4 cc mL⁻¹ (Table 1). Sodium bentonite had high swelling capacity and forms gel-like masses when added to water compared to calcium bentonite (Patel *et al.* 2007). Excellent rheological and adsorption properties of Na-bentonite have been well documented by Colin and Murry (1997). The exchange complex of the bentonite samples was dominated by exchangeable Na⁺ followed by Mg⁺⁺, Ca⁺⁺ and K⁺. Rollins (1969) also reported similar distribution pattern of exchangeable cations in the bentonite clay samples. ESP of the sample was recorded to be 62.07 and 52.45 for raw and purified clay samples, respectively. The relative distribution of Na⁺ and Ca⁺⁺ ions on the clay exchange complex is a function of exchangeable sodium percentage. The two cations were randomly distributed for ESP values greater than approximately 50% (Fink *et al.* 1971). Recoded ESP values of the clays were also found to be sufficient for this type of demixing of cations. A first suggestion for cation demixing that may influence the properties of clay mineral was presented by Glaeser and Mering (1954). Washing and purification of clay removed considerable amount of basic cations from the exchange sites that to decrease in pH, base saturation, ESP and EC. Fe and Al contents (Fe_d, Fe_o, and Al_o) were also decreased after washing but slightly increase in Al_d was recorded (Table 1). This is due to more extraction of crystalline form of aluminium by

Table 1: Some properties of soil and bentonite clay

Physico-chemical properties of soil		Chemical properties of bentonite clay		
pH (1:2.5)	7.0		Raw	Purified
OC %	1.12	pH (2% w/v)	9.1	7.4
CEC (Ammonium Acetate) cmol(p+) kg ⁻¹	23.2	Ca ⁺⁺ cmol(p+) kg ⁻¹	4.5	3.9
Ca ⁺⁺ cmol(p+) kg ⁻¹	8.0	Mg ⁺⁺ cmol(p+) kg ⁻¹	10.87	6.1
Mg ⁺⁺ cmol(p+) kg ⁻¹	4.0	Na ⁺ cmol(p+) kg ⁻¹	55.87	43.01
Na ⁺ cmol(p+) kg ⁻¹	0.101	K ⁺ cmol(p+) kg ⁻¹	1.95	0.98
K ⁺ cmol(p+) kg ⁻¹	0.267	CEC (Ca/Mg) cmol(p+) kg ⁻¹	–	90
Fe _d %	0.44%	CEC (K/NH ₄) cmol(p+) kg ⁻¹	–	82
Al _d %	0.22%	Fe _d (%)	1.60	0.97
Fe _o %	0.13%	Al _d (%)	5.65	7.27
Al _o %	0.04%	Fe _o (%)	0.62	0.39
Base saturation%	55.15	Al _o (%)	1.78	1.27
		Swelling volume (ccmL ⁻¹)	22.4	29.2
		Base saturation %	81.32	58.98
		ESP	62.07	52.45
		Mineralogical properties of purified bentonite clay		
		Amorphous Al ₂ O ₃ + SiO ₂ (%)	9.70	
		Allophane (%)	10.77	
		Vermiculite (%)	5.19	
		Smectite (%)	70.18	

Al_o and Fe_o = Ammonium oxalate extractable Fe and Al; Al_d and Fe_d = Citrate-bicarbonate-dithionite extractable Fe and Al,

CBD after removal of bases in considerable amount from the exchange complex of clay. Patel *et al.* (2007), have also reported similar results. Values of CEC of the bentonite sample were quite high *i.e.* 90 and 82 cmol (p+) kg⁻¹ for (Ca/Mg) and (K/NH₄) methods, respectively. High CEC of bentonite clay in our study was one of the main causes of its adverse effect on mineralization by adsorption and complex formation. Reduction of CEC in (K/NH₄) method was due to fixation of potassium in vermiculite materials. Mixed mineralogy was seen in the clay sample and the dominant fraction was recorded to be smectite (70.18%). Dominance of montmorillonite in natural bentonite is well documented (Patel *et al.* 2007).

Properties of organic materials: It is observed from the data (Table 2) that the highest C to N ratio was found in wheat straw (91.8) followed by rice straw (70.5) and the lowest in FYM (15). C to N ratio plays an important role in mineralization of C and N from organic materials. Amongst the organic materials, maximum amount of cellulose, hemicelluloses and lignin contents were found in wheat straw followed by rice straw and the lowest in FYM (Table 2). The trend of decomposition and subsequent release of nutrients: rice straw > wheat straw followed the order of lowest to highest lignin and C to N ratio in rice straw and wheat straw, respectively (Fig 1,3,5 & 7). This can also be evidenced by longer half life and turnover time of wheat straw containing treatments compared to rice straw (Table 6). These observations are in close agreement with that of Hopkins *et al.* (1988). In contrast, in spite of having narrow C to N ratio and less lignin content, FYM decomposed slowly (Fig 1,3,5 & 7) as this had already undergone through a process of decomposition and already a humified material (Sharma and Bordoloi 1994).

Table 2: Composition of organic materials used

Characteristics	Composition		
	Wheat Straw	Rice Straw	FYM
Carbon%	45.9	42.3	28.5
Nitrogen%	0.5	0.6	1.9
Phosphorus %	0.16	0.14	0.7
Potassium %	1.5	1.4	0.9
C:N	91.8	70.5	15
C:P	286.3	302.1	40.7
Cellulose	37.5	35.8	18.1
Hemicellulose	28.4	25.4	11.6
Lignin	17.2	14.5	8.3

Carbon mineralization trend: At field capacity and 0% bentonite, higher amount of carbon mineralized during the initial periods of incubation. Then it

decreased gradually towards the end of the incubation period (Fig.1).

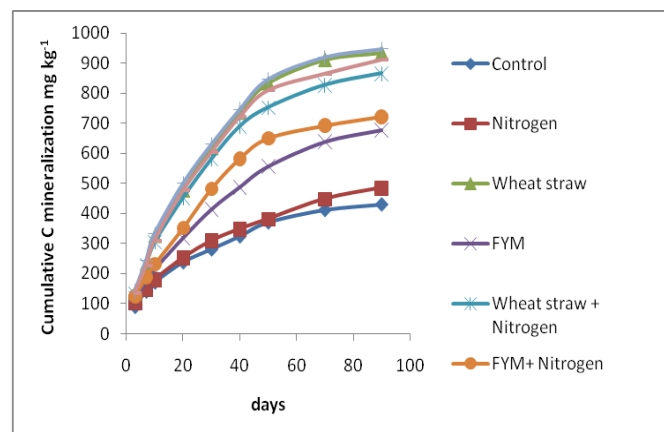


Fig 1: Cumulative carbon mineralization (gross) at field capacity and 0% bentonite

This trend was common observation when soils were incubated at a given temperature (Saggar *et al.* 1996). By the end of the incubation period (90days), carbon mineralized, by all the treatments, was greater than the control. The highest mineralized carbon was recorded in rice straw (945.9 mg kg⁻¹) followed by wheat straw (934.0 mg kg⁻¹), rice straw+ nitrogen (912.3 mg kg⁻¹), wheat straw + nitrogen (865.7 mg kg⁻¹), FYM+ nitrogen (720.4 mg kg⁻¹), FYM (678.3 mg kg⁻¹), starter nitrogen (485.0 mg kg⁻¹) and control (430.6 mg kg⁻¹). Nitrogen addition resulted decrease in carbon mineralization in case of rice and wheat straw.

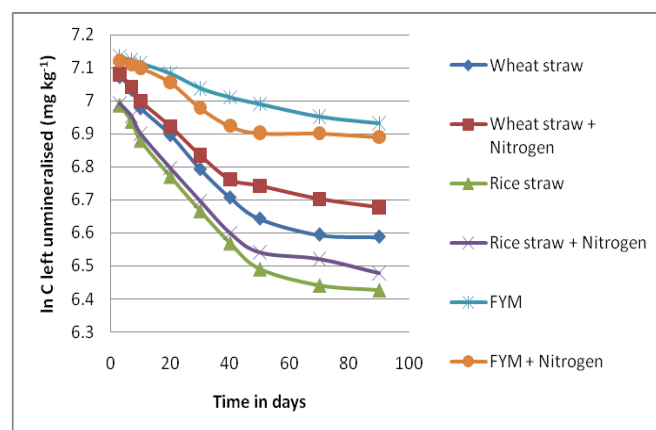


Fig 2: Amount of C (mg kg⁻¹) left unmineralised with time at field capacity and 0% bentonite

This is due to the negative effect of N on C mineralization found with recalcitrant organic matter with a high C/N ratio (straw, wood, etc.), whereas a positive effect of N is common for easily degradable organic material with low C/N ratio. The negative

Kinetics of organic matter decomposition: Two mathematical models *viz.* zero order kinetics (Howard and Howard, 1974) and first order kinetics (Swift *et al.*, 1979) have been tested for studying the kinetics of organic matter decomposition. At first, net mineralization of organic carbon from different materials has been calculated by difference method (deducing the values of control from each treatment), assuming no “priming effect”. Model fitting was done on the amount of carbon left in materials in organic form in each day (Total carbon input-Net carbon mineralized). Graphical representations of $\ln C$ left un-mineralized vs time is made in Fig 2, 4, 6 & 8.

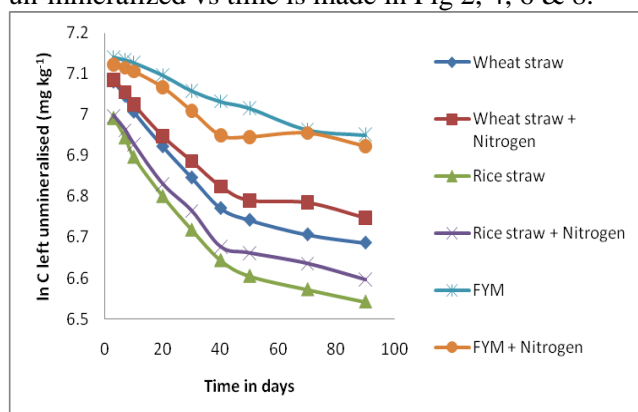


Fig 4: Amount of C (mg kg^{-1}) left unmineralised with time at field capacity and 10% bentonite

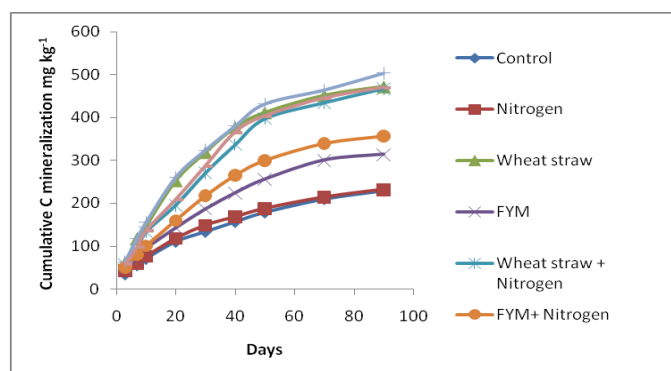


Fig 5: Cumulative carbon mineralization (gross) at saturation and 0% bentonite

The values of RMSE, MAE, STD_A , per cent MRE and STD_R were calculated to be less with higher R^2 values in first order kinetics models compared to the zero order models (Table 4). This indicates the good fit of first order kinetics models in describing organic matter decomposition from different organic materials over zero order models. These observations are in line with those of Mishra *et al.* (2001). Therefore, half-lives and turnover times have been calculated using the data of first order equations (Table 5). Both half-lives and turnover times (Table 5) were increased in 10% bentonite compared to 0% bentonite concentration.

Table 5: Half life and turnover time of different organic materials

Wheat Straw	Wheat Straw + Nitrogen	Rice Straw	Rice Straw + Nitrogen	FYM	FYM + Nitrogen
Half life (days)					
Field Capacity and 0% bentonite					
116	144	102	112	277	231
Field Capacity and 10% bentonite					
147	173	131	147	289	277
Saturation and 0% bentonite					
301	277	239	257	866	577
Saturation and 10% bentonite					
330	330	277	289	1155	630
Turnover time (days)					
Field Capacity and 0% bentonite					
499	624	441	483	1198	999
Field Capacity and 10% bentonite					
637	749	565	637	1248	1197
Saturation and 0% bentonite					
1303	1198	792	1110	3745	2497
Saturation and 10 % bentonite					
1427	1427	1198	1248	4993	2724

This is because of reduction in mineralization in presence of sufficient clay. Similarly, we found longer half-lives and turnover times at saturation compared to field capacity. This is because of the

reduction of organic matter turnover at saturation as highlighted by several workers (Summerell and Burgess (1989)). In all cases except wheat straw + nitrogen at saturation, nitrogen fertilization resulted

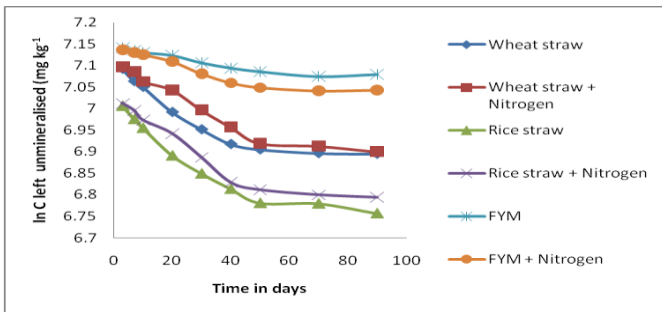


Fig 6: Amount of C (mg kg^{-1}) left unmineralised with time at saturation and 0 % bentonite

increase in half-lives and turnover times of rice and wheat straw due to the negative effect of N on C mineralization found with recalcitrant organic matter with a high C/N ratio as discussed above. Whilst, at saturation, the half life of wheat straw was calculated to be 7.97% more than wheat straw + nitrogen at 0% bentonite and but equal at 10% bentonite (Table 5).

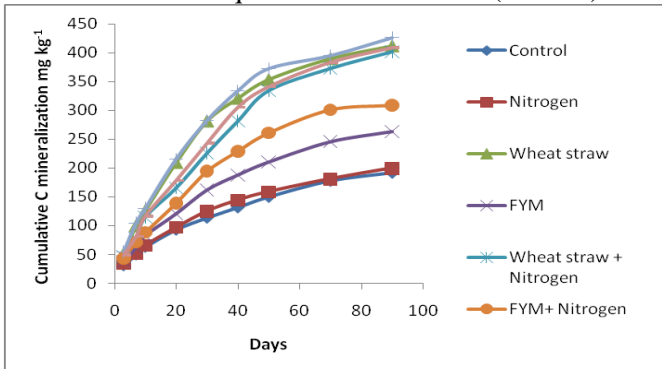


Fig 7: Cumulative carbon mineralization (gross) at saturation and 10% bentonite

This exceptional result may be due the limitations of mathematical models resulting higher slope at 0% bentonite (Equation for wheat $y = -0.0023x + 7.0573$ & equation for Wheat straw +N $y = -0.0025x + 7.0845$) and equal slope at 10% bentonite (Equation for wheat $y = -0.0021x + 7.068$ & equation for Wheat straw +N $y = -0.0021x + 7.0921$). Nitrogen fertilization resulted

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decrease half-lives and turn over times for FYM at different moisture and bentonite levels. Agrawal and Agnihotri (2007) also reported that after nitrogen fertilization immobilization of carbon occurred in wheat straw and rice straw, while increase in mineralization was seen in FYM. Farmyard manure in this study had less C to N ratio, less lignin and carbon compared to straw (Table 2). Therefore, nitrogen fertilization in FYM, unlike straw helped in carbon mineralization.

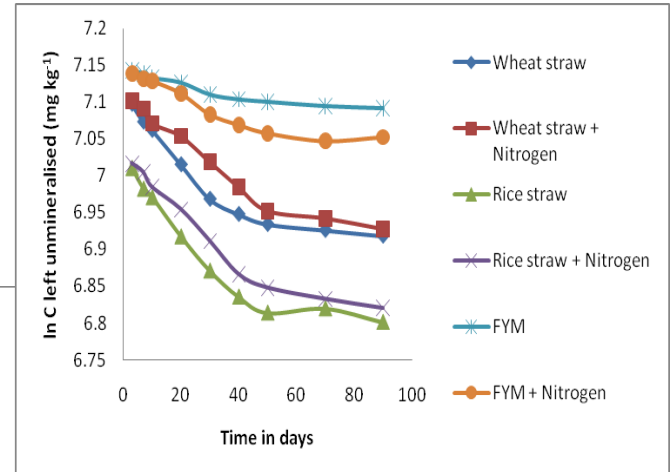


Fig 8: Amount of C (mg kg^{-1}) left unmineralised with time at saturation and 10 % bentonite

From this study, it can be concluded that use bentonite clay can reduce carbon evolution from different organic amendments applied in Mollisols under varying moisture regimes. Therefore, data generated from this incubation study will be helpful for further field research using bentonite for soil carbon sequestration in eroded soils. As India has a good reserve of natural bentonite, there is definitely a possibility of exploring this reserve in this new dimension of research for the greater interest of reducing GHG emissions more particularly from eroded soils of India.

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