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RESEARCH ARTICLE

APPLICATION OF EBURRU ROCKS FROM KENYA AS UREA CARRIER AGENTS

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ABSTRACT

Application of Eburru rock samples as urea fertilizer carrier agents was conducted using sorption studies. Characterization by EDS, FT-IR and XRD was done on the samples to determine their zeolite comparativeness. Urea loading and release studies were done through simple aqueous immersion techniques or wet chemistry techniques. The results from these studies indicated that close to 33% of urea could be loaded into the Eburru rock samples within 24 hours equilibration duration, of which 74% net loaded urea could be released in aqueous medium within the 18 experimental days.

INTRODUCTION

Urea (Figure 1) is an organic compound that is mainly applied in agricultural production as a nitrogenous fertilizer. It also finds applicationin many industrial sectors for functions like binders and analytical reagents (www.worldcat.org. novacat.nova.edu/identities/lccn-n97900852/ (Accessed 2nd Nov. 2016 at 2.31pm)). It is a colorless, odorless and highly soluble in both aqueous and organic media with its solubility in the two media being 1080 g/L at 20^{0}C and 500 g/L in glycerol respectively. Urea is mainly synthesized industrially using ammonia and carbon dioxide precursors and this supplies almost 90% of all the urea consumed in the agricultural sector (Friedrich, 1828; Meessen, 2005). In living organisms, urea is synthesized as part of the urea cycle, mainly as an oxidant of amino acids or from ammonia (Sakami, 1963). As a chemical compound, urea undergoes a number of degradation processes which includes hydrolysis and thermal decomposition. In soil, in the presence of the urease enzyme, urea hydrolysis to ammonium carbonate. Further protonation of this carbonate yields ammonium ions, that could further react with hydroxide ions with consequential release of ammonia gas (http://www.soils.wisc.edu/extension/materials/ManagingUrea.pdf (Accessed 2nd Nov. 2016 at 4.48pm).) (Scheme 1 below).

$$(NH_2)_2CO + 2H_2O \rightarrow (NH_4)_2CO_3$$
$$(NH_4)_2CO_3 + 2H^+ \rightarrow 2NH_4^+ + CO_2 + H_2O$$
$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$$

Scheme 1: Release of ammonia from urea

Thermolysis studies on urea indicate its initial vaporization occurs between 133 ^{0}C – 250 ^{0}C, followed by decomposition as shown by the equation below:

$$(NH_2)_2CO \rightarrow NH_3 + HNCO$$

Much higher temperatures could cause production of biuret, isocyanic acid or formation of ammelide or melanine (Koebel *et al.*, 2000; Schaber*et al.*, 2004). The HNCO formed could still decompose further in presence of water as shown below (Martyn, 2006).

$$HNCO + H_2O \rightarrow CO_2 + NH_3$$

The ammonia formed when NH_4^+ reacts with OH^- ions in soil could be lost by volatilization process, whose rate is increased by high temperature, high pH and low cation exchange capacity value of soil, as illustrated by the nitrogen cycle below (Figure 2) (Clain *et al.*, 2019). The major concern about urea is that, owing to its high water solubility like all nitrogeneous fertilizers, urea tends to cause great ground water pollution, fertilization and eutrophication of water bodies (Howarth, 1988; Boynton *et al.*, 1982).

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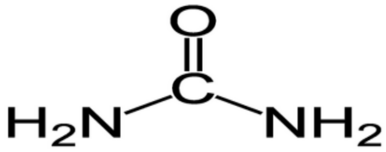

Figure 1. Structure of Urea

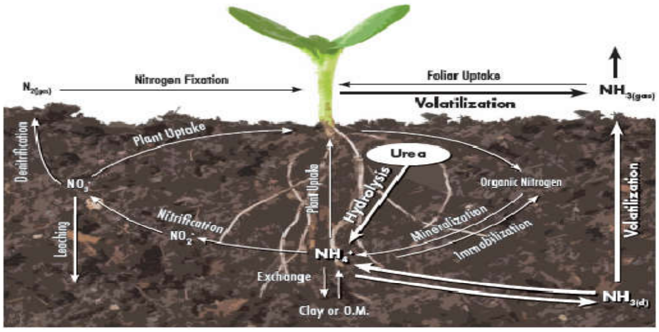

Figure 2: Illustration of the nitrogen cycle (Clain et al., 2013)

Therefore, the main objective of this work was to study and characterize Eburru rock samples as possible urea carrier materials that could be applied as smart delivery system as a way of mitigating urea environmental pollution effects.

MATERIALS AND METHODS

The following instruments, materials and reagents were used: UV-Visible spectrometer, X-ray diffractometer(XRD, D2 Phaser 2nd Gen. from Bruker), Fourier Transform Infrared (FTIR, IR Tracer-100 from Shimadzu), Energy dispersive spectrophotometer (EDS, Shimadzu EDX-720),Analytical balance (Fischer A-160), Orbital shaker (Ratek OM6), Atomic absorbance spectrophotometer (AAS, Perkin Elmer 2100), X-Ray fluorescence spectrometer (XRF Oxford Instruments MDX 1080), Flame photometer (Sherwood scientific 410), Calcinator (N3A Simon Muller 220V Berlin), Commercial Purchased zeolites (CPZ, from Sigma-Aldrich in South Africa,P-Code: 101554254, Lot # BCBM 9330V and CAS: 1318-02-1.), Urea (analytical standard 99% pure from IOBA Chemie), distilled water, rock samples from Eburru crater, Rift valley, Kenya (0.63S, 36.23E) and soil from Kikuyu area(Kiambu County, Kenya), applied as the normal for comparative purposes.

The rock samples were prepared for analysis by air drying in natural sunlight for four days to prevent nutrient transformation, crashed, calcined, sieved using 0.85mm sieve size and stored in plastic sampling bags labeled as Eburru Rock Samples (ERS). The soil from Kikuyu area was also air dried in natural sunlight for four days, sieved using 0.85mm and stored in plastic sampling bags labeled as Kikuyu Soil Sample (KSS). Elemental composition ofERS and CPZ was done using EDS,XRD was used to verify the crystallinity of the samples, FTIR was used in identification of functional groups, while all the Urea quantitation and calibration studies were done on UV-Vis spectrophotometer. A flame photometer was used to monitor levels of Na, Ca and K in the ERS and KSS samples, while at the same time P, Mg and Mncontent were determined calorimetrically. Other trace elements like Fe, Zn, and Cu and exchangeable Ca and Mg were determined by AAS. The total organic carbons were analyzed calorimetrically, based on the Mehlich Double Acid Method (Mehlich, 1953; Tran, 1993; Yang, 2005; Gislason, 2005). Total nitrogen was determined by Kjeldahl method (Jan-Åke, 2008). Soil pH was determined using a pH meter on a 1:1 (w/v) soil-water suspension. Exchangeable Na and K were determined by flame photometer after leaching with 1M KCl. Cation Exchange Capacity (CEC) was determined on the leachate at pH 7.0 by distillation followed by titration with 0.01 M HCl (Carrolland Dorothy, 1959; Turner, 1966). Other instruments used in the study were similar to those found in an ordinary laboratory set-up, including Orbital shaker (fitted with timer). To carry out sorption studies, standard concentrations of urea were prepared by varying concentrations from 1:2, 1:4, 1:10, 1:20, 1:40, 1:60, 1:80, 1:100 ad 1:200 w/v in aqueous medium. They were scanned between 200-900nm wavelengths on the UV-Visible Spectrophotometer to determine the maximum absorption wavelength of urea, which was obtained at 203 nm. Calibration curves at 203 nm were used to determine concentrations of other urea solutions.

Studies on variation of concentrations were done by treating 5.0036g of ERS with 10ml aqueous solutions each containing 1:2, 1:4, 1:6, 1:8, 1:10, 1:20, 1:40, 1:60, 1:80 and 1:100 w/v concentrations of urea. The media were shaken at room temperature for 24 hours each, and then centrifuged at 10,000 rpm for 10 minutes. The supernatants were then filtered using 0.22µm what-man papers and equilibrium concentration determined. Varying shaking time was conducted using 1.0 g of ERS suspended in 10ml urea solution of concentration 1:100 w/v, shaken for 15, 30, 45, 60, 75, 90, 100, 120, 140 and 160 minutes each and equilibrium concentration determined. Procedures modified from Manikandan andSubramanian (2014) (Manikandan, 2014). To load urea into the pores, 20 g of ERS were spiked with 35ml of 1:60w/v urea solution, shaken at room temperature for 24 hours, then equilibrium concentration of the remaining urea determined .The difference between initial concentration and equilibrium concentration gave the amount of fertilizer loaded in the samples. The resulting samples were dried at 100 ^{0}C for 24 hours and stored in air tight plastic bags labeled as Urea loaded Eburru Rock Samples (UBRS).

Controlled release behavior of fertilizer in water was conducted by placing 20 g of UBRS in 250 ml separating funnels and 50 ml distilled water infiltrated through at an approximate flow rate of 0.1667 ml/min. 50 ml distilled water was refilled every 24 hours to infiltrate the same samples for 18 days. This was repeated using a homogenized mixture of 20 g UBRS and 20 g Kikuyu Soil (KS). Modified from Bansiwal*et. al.*, (2006)).The filtrates/elutes were collected on a daily basis prior to refilling, filtered using 0.22 µm what- man papers and equilibrium concentration determined.

The amount of urea loaded (mg/g) was calculated using the equation shown below, as reported by Vanderborght and van Greikenm (Vanderborght, 1997).

$$q_e = \frac{\upsilon(C_i - C_e)}{W} \tag{1}$$

Where $q_e$is the amount of solute adsorbed from the solution, υ is the volume of the adsorbate, $C_i$is the concentration before adsorption, C_e is the concentration after adsorption, and w is the weight in grams of the adsorbent.

RESULTS AND DISCUSSION

Soil analysis

The nature of the soil greatly influences its sorption characteristics. Figure 3 below shows aERS. Both ERS andKSS wereanalysedfor their properties.

Figure 3. Rock samples from Eburru crater, Rift valley, Kenya (Sample ERS)

According to table 2 below, elemental composition comparison of these samples indicates higher mineral content in KSS. Calcination of ERS lowered its contents of volatile components.

Table 2. Soil analysis

Property	Value	
Soil depth cm	ERS	KSS
Soil pH-H_2O (1:2.5)	8.38	6.50
Elect. Cond. mS/cm	0.23	0.3
Carbon %	0.94	2.7
Sand %	-	40
Silt %	-	40
Clay %	-	20
Zinc ppm	10.22	62.9
Copper ppm	1.36	1.22
Calcium milliequivalent(me)%	4.7	44.4
Magnesium me%	0.59	3.1
Potassium me%	0.62	1.5
Sodium me%	0.84	3.6
Total nitrogen %	0.25	0.25
Phosphorus ppm	3.4	44
Iron ppm	13.34	96.2

Further characterization of ERS was donein comparison to CPZ due to their common application as carrier molecules in development of smart delivery systems (Chinnamuthu, 2009), enabled by their high porosity (Mumpton, 1984). Energy Dispersive Spectroscopy (EDS) of ERS indicates 18.8% Al_2O_3 and 37.4% SiO_2 compared to 56.4% and 43.6%respectively of the commercially purchased zeolites (tables 3 and 4). Besides, ERS had other mineral compositions like 21% Fe_2O_3 and similar amount for K_2O, implying that purification of the raw rocks could increase zeolite mineral composition. Their respective spectrums as illustrated by figures 4 and 5 indicate common peaks near the regions of 20 keV and 1-4 keV, indicating some similarity in mineral composition. Fourier Transform Infra-Red (FTIR) Spectroscopy analysis of ERS (figure 6) and CPZ (Figure 7) indicate some common peaks corresponding to their transmittance spectrums.

Table 3. EDS quantitative results of ERS

Analyte	Result %	Standard Deviation	Line	Intensity (cps/ uA)
SiO_2	37.410	0.433	SiKa	0.7178
Fe_2O_3	21.389	0.069	FeKa	116.996
K_2O	20.671	0.149	K Ka	1.8806
Al_2O_3	18.764	1.649	AlKa	0.0294
ZrO_2	0.609	0.004	ZrKa	29.8216
MnO	0.585	0.014	MnKa	2.8732
CaO	0.194	0.033	CaKa	0.2792
NbO	0.100	0.002	NbKa	5.9555
SO_3	0.075	0.004	S Ka	0.0746
Y_2O_3	0.074	0.002	Y Ka	3.6852
ZnO	0.074	0.003	ZnKa	1.6514
Rb_2O	0.057	0.002	RbKa	2.8905

Peaks in the region of 3400-3700cm^{-1} could correspond to the stretching of the –OH bridging groups such as –Al(OH)Si-. In addition, peaks between 600-800cm^{-1} are associated with asymmetrical stretching of the zeolites, while those of 300-450cm^{-1} could be of ring vibrations, which are commonly affected by the type of structure due to overlap of internal and external tetrahedral vibrations of the secondary building units, alongside the effects of dehydration cation movements (Perego *et al.*, 1984).

X-Ray Diffraction (XRD) characterization of ERS gives distinct peaks in the region of 2θ (20^0-40^0) as indicated by figure 8 below, with the highest peak at 22^0. Impurities in the sample could have contributed to peak masking, since the XRD spectrum CPZ (figure 9) gave additional peaks to the distinct in the region of 2θ (20^0-40^0).

Absorbance curves

Urea absorbance curves at 203 nm obeyed Beer's law at lower concentrations as shown in figure 10.

Kinetics of fertilizer adsorption ERS

Generally, the amount of urea adsorbed by ERS increased with increase in spiking levels (Figure 11), a factor largely attributed to the presence of high number of vacant adsorption sites, resulting to high sorption gradient between adsorbate in solution and the adsorbent surface or nano pore spaces. Equilibrium sorption rate was highly dependent on the spiking concentration of urea. Initial lower concentration recorded rapid increase in percentage of urea adsorbed, highest amount being 80% of amount spiked (as shown by figure 12 below) at 1:10w/v corresponding to 1.67moldm^{-3}. Highest adsorption amounts were recorded at higher concentrations of fertilizer. From figure 13 below, increasing amounts adsorbed (qe) varies more with solution retained amount (Ce) as concentration increases. Sorption studies of urea on variation of shaking time with constant concentration and amount of ERS used indicated slight proportional increase in amount adsorbed, of which on equilibration almost attained constant amounts of urea (figure 14). Better equilibration could be attained by increased shaking time, in which solute sorbate contact is enhanced. The low organic content (less than 1%) ERS could be attributed for the lower overall percentage amounts adsorbed, as indicated by figure 15 below. Similarly, sorption rates tend to equilibrate at around 33% for the amount adsorbed, giving near zero gradient, at higher shaking minutes.

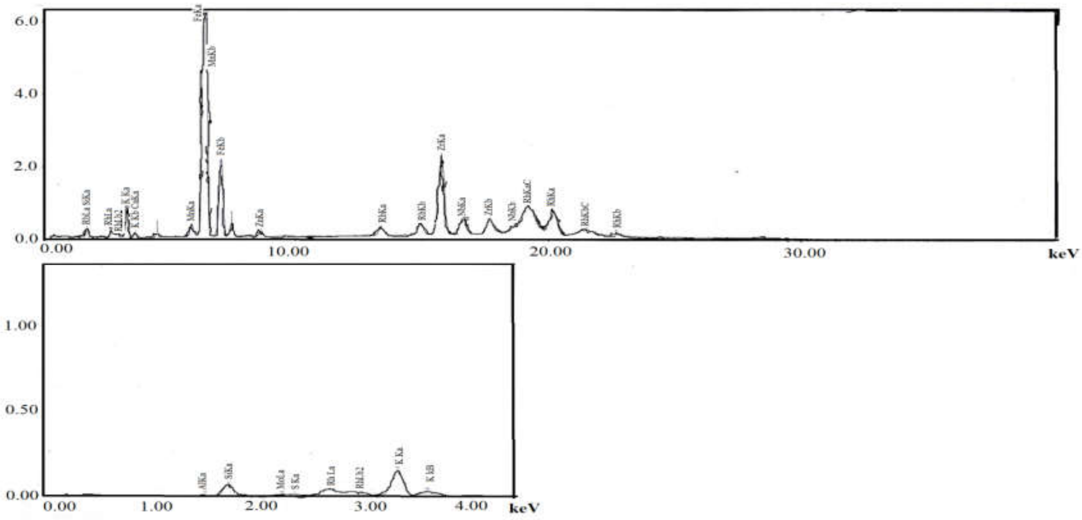

Figure 4. EDS Spectra of ERS

Table 4. EDS quantitative results CPZ

Analyte	Result %	Standard Deviation	Line	Intensity(cps/uA)
Al_2O_3	56.368	1.335	AlKa	0.0721
SiO_2	43.632	0.398	SiKa	0.4315

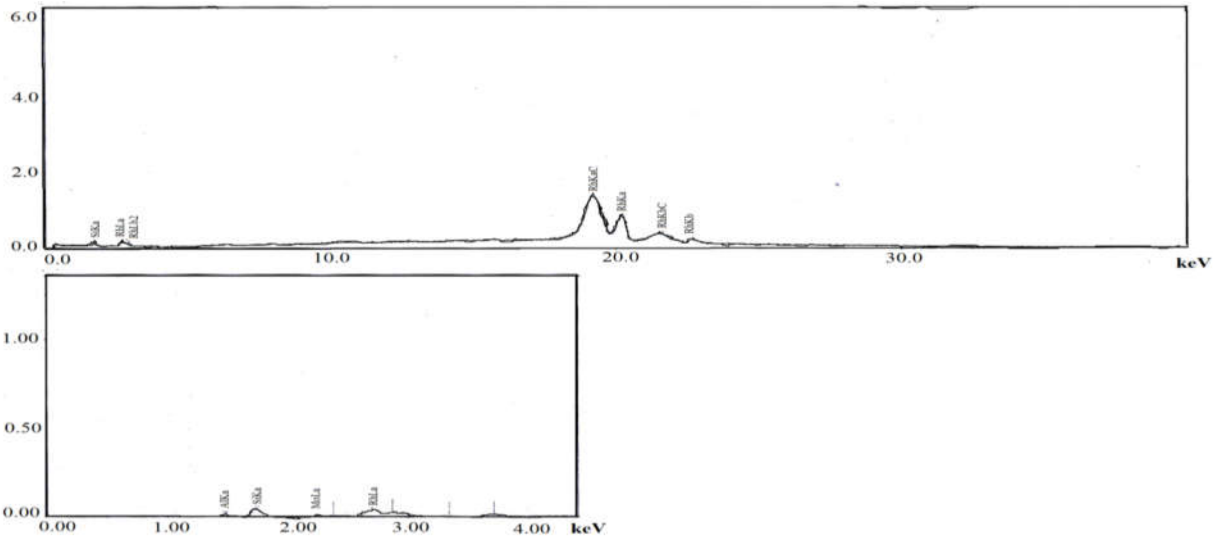

Figure 5. EDS Spectra of CPZ

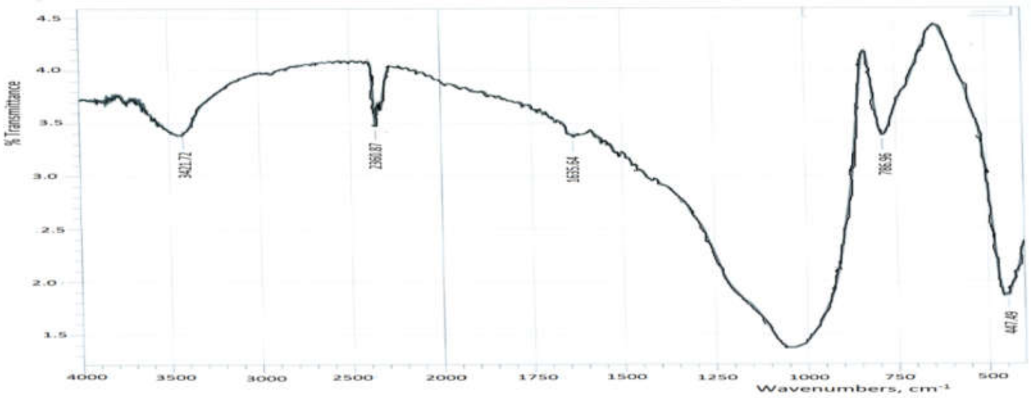

Figure 6. FT-IR spectra of ERS

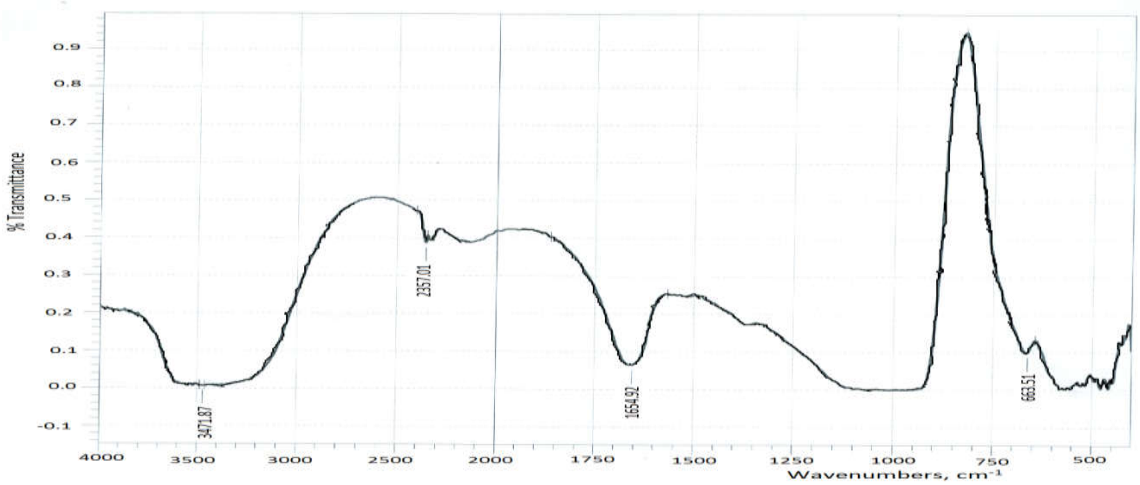

Figure 7. FT-IR spectra of CPZ

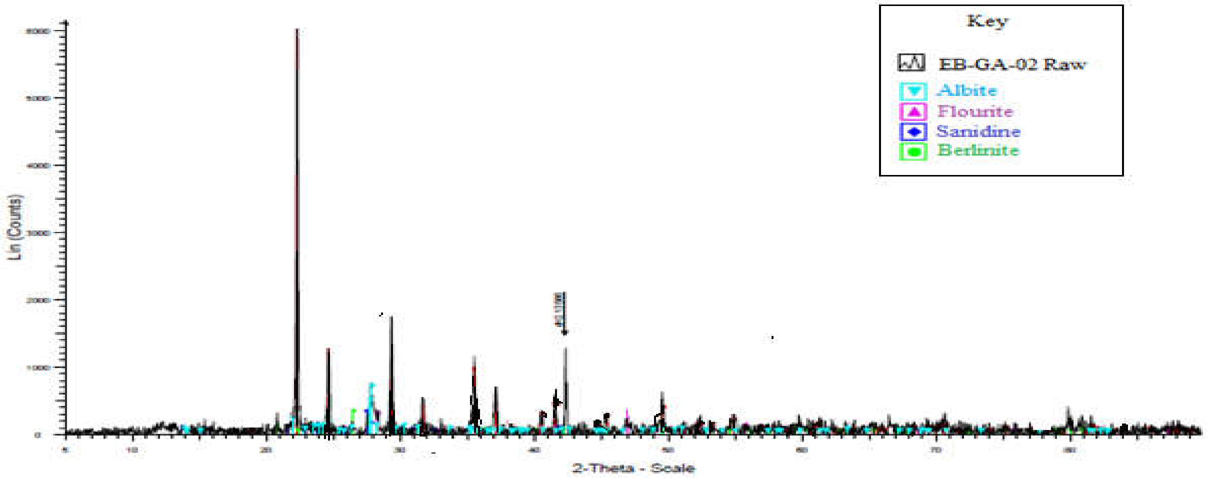

Figure 8. XRD spectra of ERS

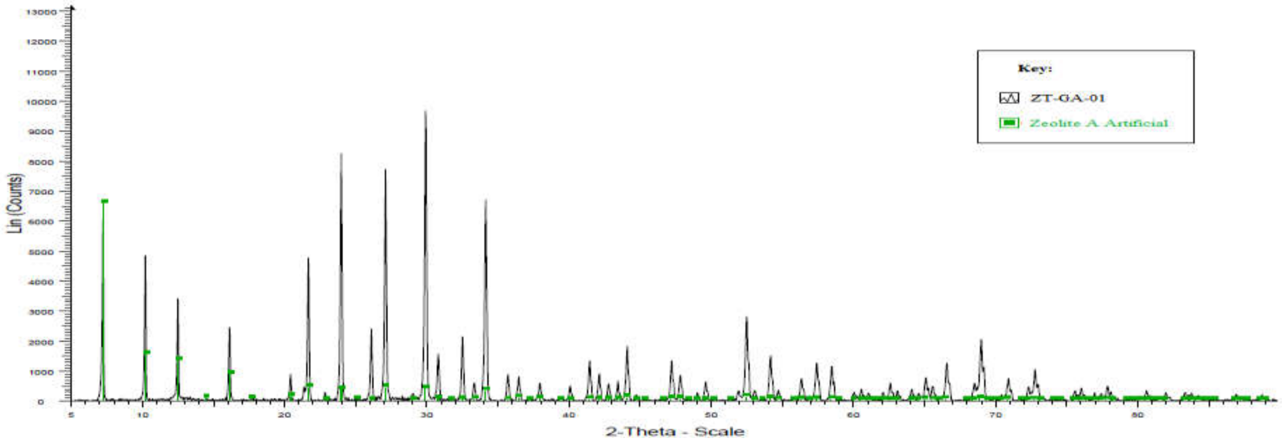

Figure 9. XRD spectra CPZ

Quantitative determination of adsorbed fertilizer

Relatively higher concentration with longer shaking durations were applied for quantitative determination of adsorbed urea. Higher concentration of sorption solutes exposed to sorption sites for longer durations, generates better equilibrations, as indicated by figure 16 below, of which the highest column represents maximum sorbed amounts shaken at 24 hours, starting with a solution of concentration 0.278 moldm^{-3} corresponding to 1:60m/v.The plot of percentage amount of urea adsorbed with longer shaking time as indicated by figure 17 below, shows that with an equilibration time of 24 hours, almost 35% of urea could be adsorbed by ERS.Hence, loading of the fertilizer into ERS as carrier material was based on the highest percentage determined above.Confirmation of the loaded urea molecules in the ERS nanopores was done using

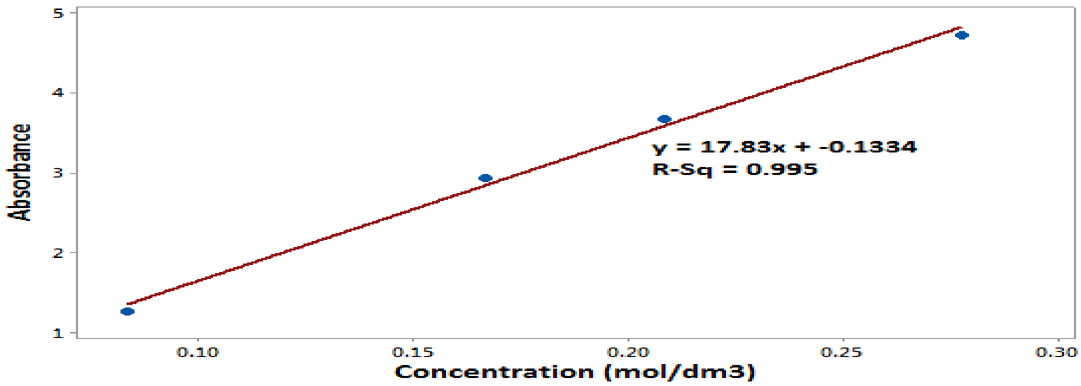

Figure 10: Calibration plot for urea between 0-0.28 M measured at λmax 203nm

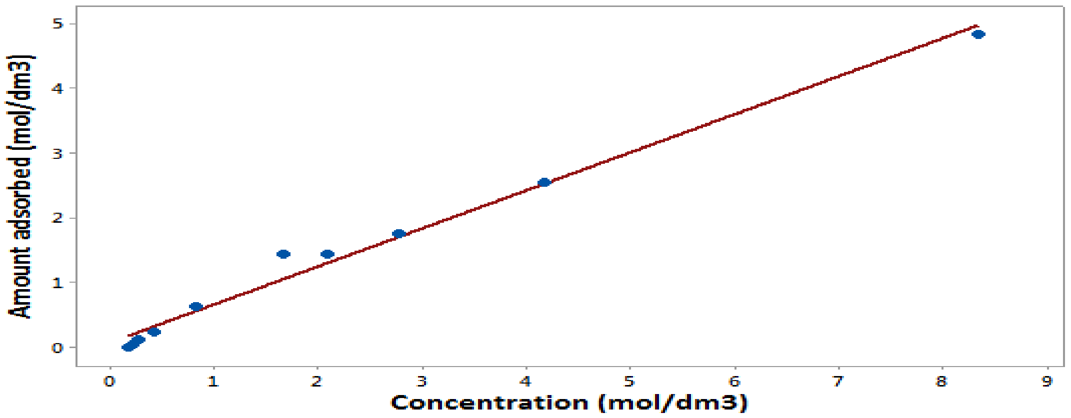

Figure 11. Changes in urea adsorption with varying spiking levels of ERS

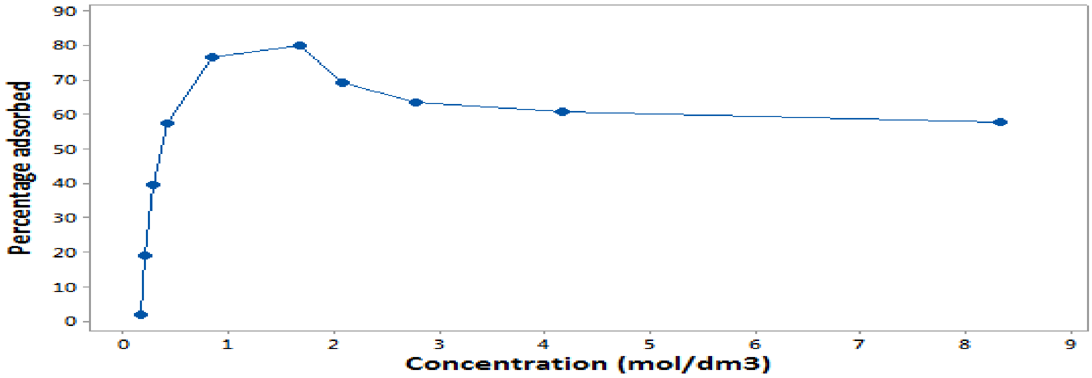

Figure 12: Percentage of urea adsorbed with varying concentration.

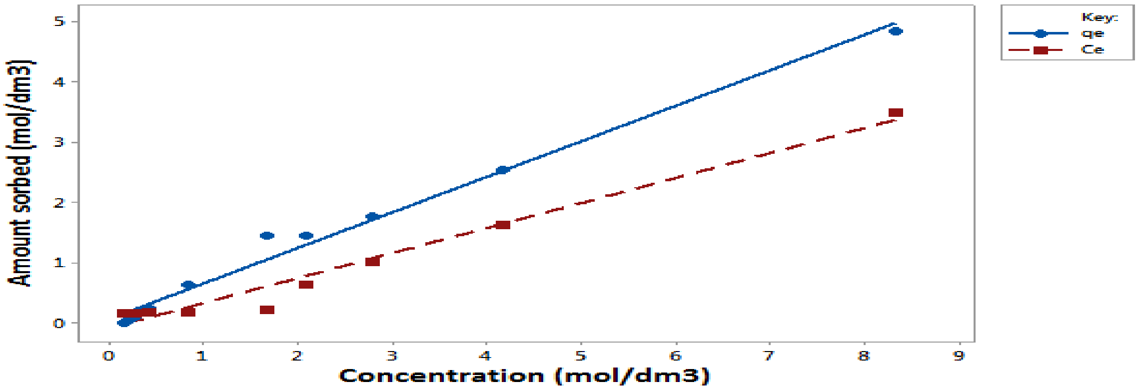

Figure 13: Variation of urea amount adsorbed (qe) with that remaining in solution (Ce) at equilibrium

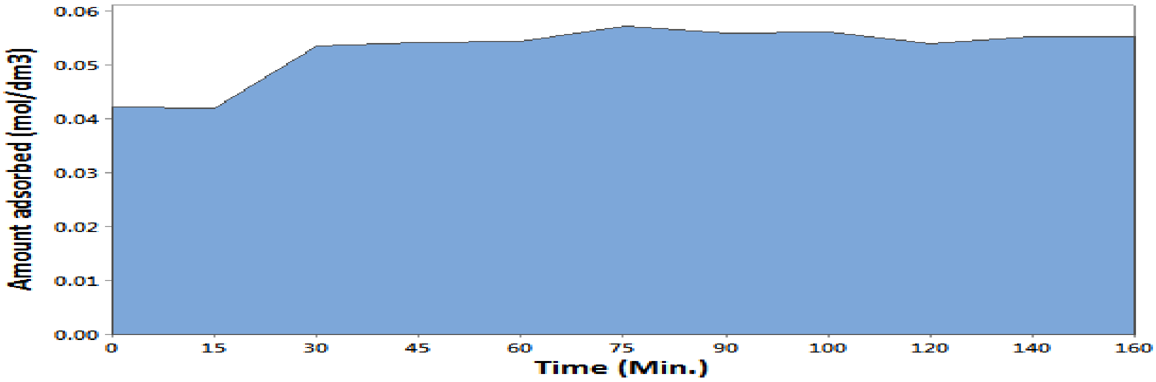

Figure 14. Proportion area on amount adsorbed with varying time

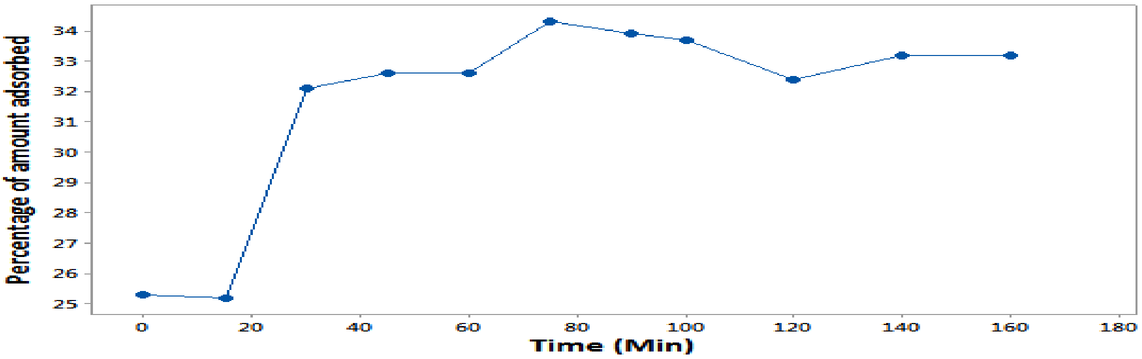

Figure15. Percentage of urea adsorbed with time

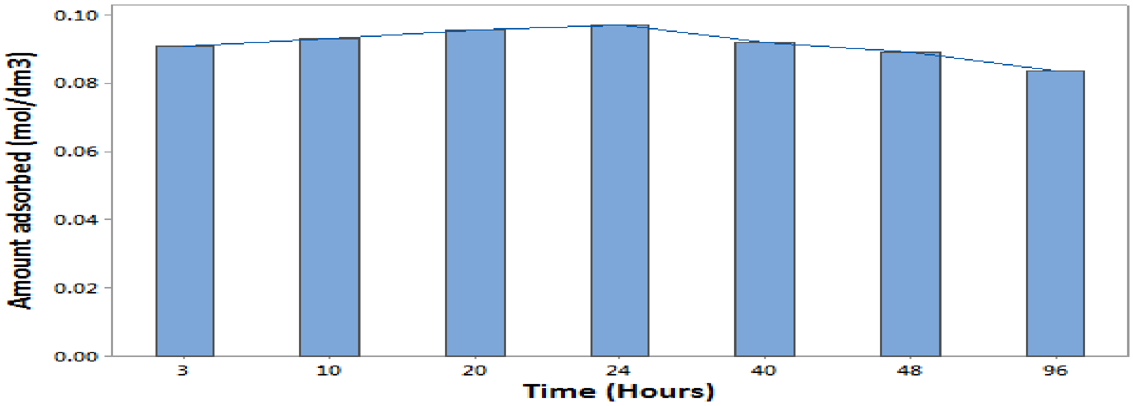

Figure16. Comparison of urea amount adsorbed on ERS with time

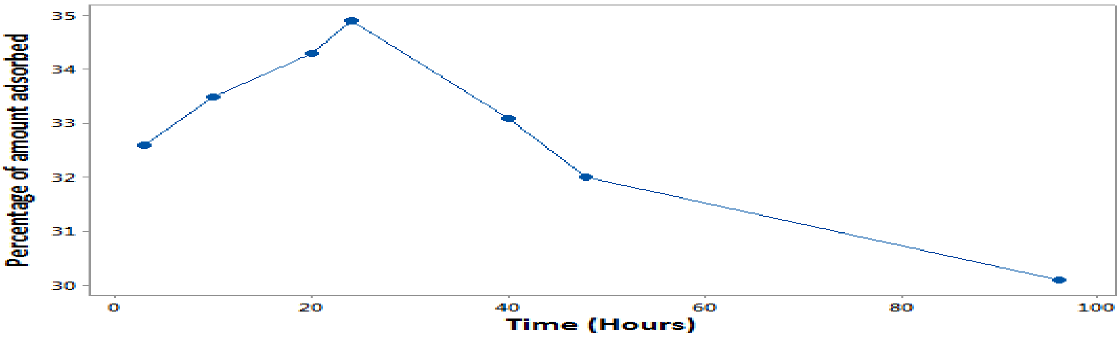

Figure 17. Variation of percentage absorption of urea with time

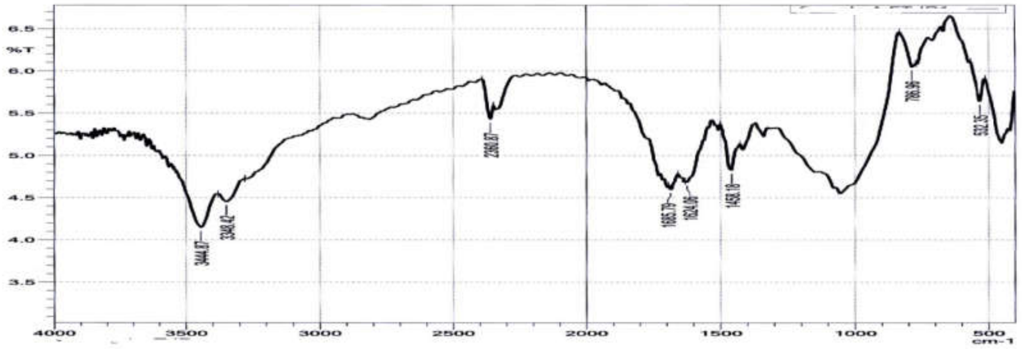

Figure 18: FTIR spectrum of UERS

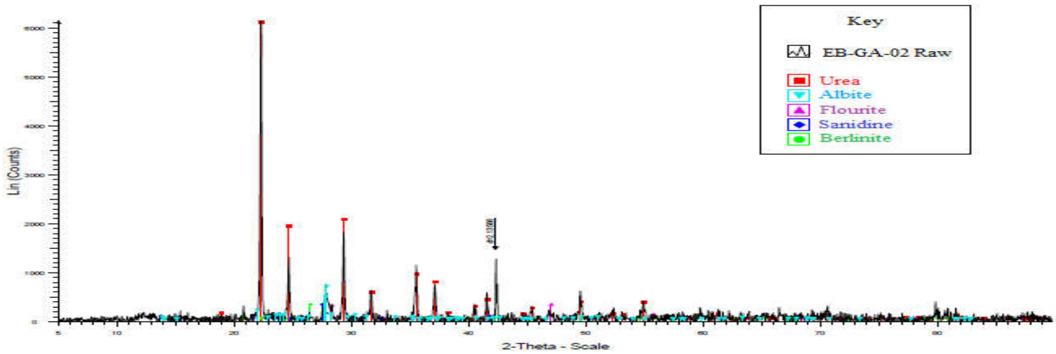

Figure 19. XRD patterns of UERS

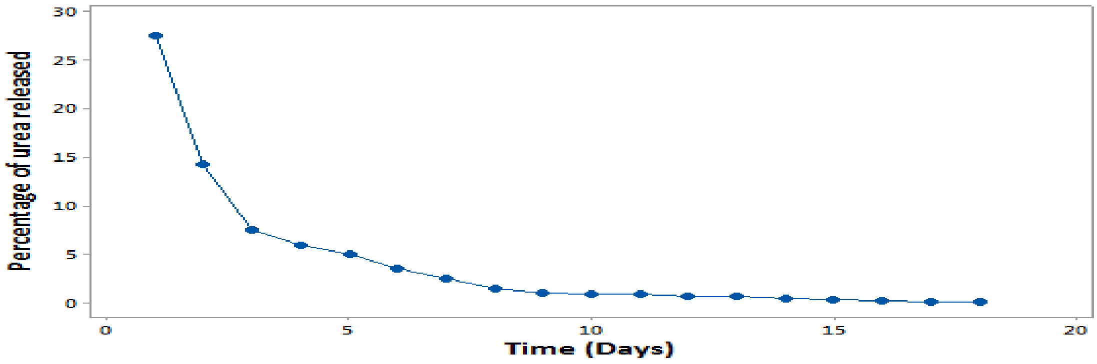

Figure 20. Variation of amount of urea released by UERS with time in water

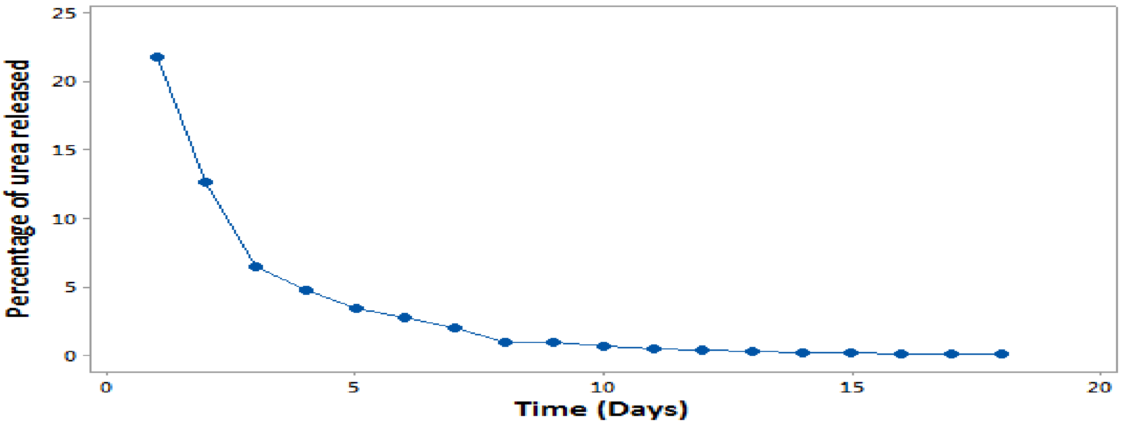

Figure 21. Variation of amount of urea released with timeby UERS mixed with KS

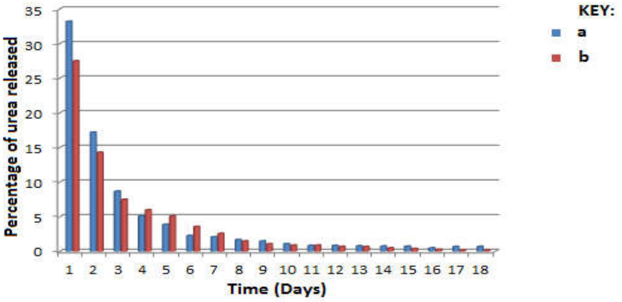

Figure 22: Comparative release of urea by UERS in water (a) and UERS mixed with KS (b)

FTIR and XRD. The mid-IR-Spectrum of UERS (Figure 18) indicates distinct peaks associated with various functional groups vibrations. The peak at 1458.18 cm^{-1} is characteristic of C-N stretching vibration, C=O stretching vibration is associated with the peak at 1685.79cm-1, while the two peaks at 3348.42 and 3444.87 are characteristic of N-H stretching vibrations (Stuart, 2004). X-ray diffraction patterns (figure 19) of UERS indicates urea composition at well-defined peaks of 2θ (22^0, 25^0, 29^0, 33^0, 36^0, 38^0).

Controlled release behavior of UERS

Nearly 74% of net loaded urea fertilizer was discharged in water within 18 days of the experimental duration. Release rate decreased with time as illustrated by figure 20 below, sustainably for the first 9 day and near zero rate for the last 5 days. Higher sorption gradient for the partitioned medium and weaker physicochemical attraction effects could be attributed for the gradual release of the urea molecules. Mixing of UERS with KS gave a percentage urea release of around 60% within the 18 experimental days (figure 21).Higher soil organic content could be attributed to the increased retention of urea in the soil, though the sustained release rate within the first 9 days was still observed. Comparatively, urea release process was better in aqueous medium than in the homogenized samples as illustrated by figure 22 below.

Conclusion

This study has shown that Eburru rock samples compares favourably to the zeolitic material, though purification processes are needed for improved properties. Kinetics of fertilizer adsorption on these samples gave good equilibration rates, with about 33% attained in 24 hours, which also corresponded to the proportion of fertilizer loaded in the samples. This was depended on spiking concentration, contact time and sample composition. From thecontrolled release determinations, it was found that 74% of the net loaded fertilizer was discharged in aqueous medium by the rock samples, having a sustained rate over the first 9 days of the total 18 days of experimental duration. This implies that UERS could potentially extend urea availability duration to plants due to this slowed release aspect. Homogenizing of UERS with typical farming soil such as KS gave 60%urea released over the total experimental duration. An aspect that could further extend duration of urea availability to plants, since the soil organic matter serves to increase urea retention, which could minimize leaching due to its high solubility. Subsequently, these findings indicate that Eburru rock samples could be positively applied in an attempt to develop urea fertilizer carrier agent from local materials for smart delivery systems.

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