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Dissipation and Sorption of Urea on Eburru Soils in Kenya

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Abstract

Dissipation and sorption of urea on Eburru soils in Kenya was done using kinetic studies which indicated that 35.00% of urea was adsorbed in the Eburru soil matrix nanopores within an equilibration of 24 hours. The presence of urea molecules in the loaded soil samples was further confirmed by XRD, FTIR and SEM characterization. Controlled urea release behavior of Eburru loaded soil samples was also determined to be 82.8% in water and 74.2% in Kikuyu soil.
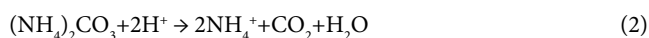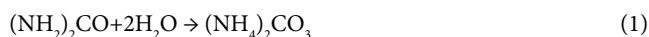
Keywords: Dissipation; Degradation; Sorption

Introduction

Urea (Figure 1) is an organic compound that is mainly applied in agricultural production as a nitrogenous fertilizer. Beside, urea which is also called carbamide, is applied in many industrial sectors for functions like binders and analytical reagents. Manufacture of urea from inorganic starting materials (ammonia and carbon dioxide) was discovered as early as 1828 [1], processes which were modified subsequently leading to industrial production, with almost 90% of the produce meant for agricultural consumption [2]. In living organisms, urea is synthesized as part of the urea cycle, mainly as an oxidant of amino acids or from ammonia [3-5]. Urea is usually a colorless, odorless and highly soluble organic compound.

Urea degradation processes

Hydrolysis is soil: On studying reactions of urea in soil (IRPTC data profile) [6]. Bund [7] from University of Wisconsin indicates that when applied to soil, urea decomposes in the presence of water and urease to ammonium carbonate that further forms ammonium ions. Presence of hydroxide ions in the soil could lead to ammonia being discharged through reactions (volatization), as shown by the equations below:

$$(NH_2)_2CO + 2H_2O \rightarrow (NH_4)_2CO_3 \qquad (1)$$

$$(NH_4)_2CO_3 + 2H^+ \rightarrow 2NH_4^+ + CO_2 + H_2O \qquad (2)$$

$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O \qquad (3)$$

He argues that the rate of ammonia loss in this process is favored by high temperature, high pH and low soil CEC.

Volatization of ammonia from soil: Ammonia formed when NH_4^+ reacts with OH^- ions in soil could be lost by volatization process, as illustrated by the nitrogen cycled below Figure 2. As already mentioned, high temperature, high pH and low CEC value of soil favors this process, which in turn accelerates the nitrogen cycle [4].

Materials and Methods

The following instruments, materials and reagents were used: UV-Visible spectrometer (UV-1700 model, Shimadzu Corporation, Kyoto, Japan), Analytical balance (Fischer A-160), Orbital shaker (fitted with timer), Urea, distilled water and soil samples from Eburru crater, Rift valley, Kenya (0.63 S, 36.23 E). The soil samples were prepared for analysis by air drying in natural sunlight at room temperature for four days to prevent nutrient transformation, crashed, sieved using 0.85

mm sieve size and stored in plastic sampling bags. The soil analysis method and results were as recorded in our previous work done by Waswa et al. [5]. Kinetics of fertilizer adsorption on zeolitic materials was done by preparing Standard concentrations of urea fertilizer from 1:2, 1:4, 1:10, 1:20, 1:40, 1:60, 1:80, 1:100 and 1:200 w/v in aqueous medium. The varying concentrations were scanned between 200-900 nm wavelength on the UV-Visible Spectrophotometer to determine the maximum wavelength of urea and subsequently generate the calibration curves at obtained wavelength of 203 nm which was subsequently used to determine concentrations of urea in the current studies. Sorption studies on effect of concentration variation was done by treating 5.0036 g of the zeolitic materials with 10 ml 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 solutions. The mediums were shaken at room temperature for 24 hours each, then centrifuged at 10,000 rpm for 10 minutes. The supernatants were then filtered using

Figure 1: Structure of Urea.
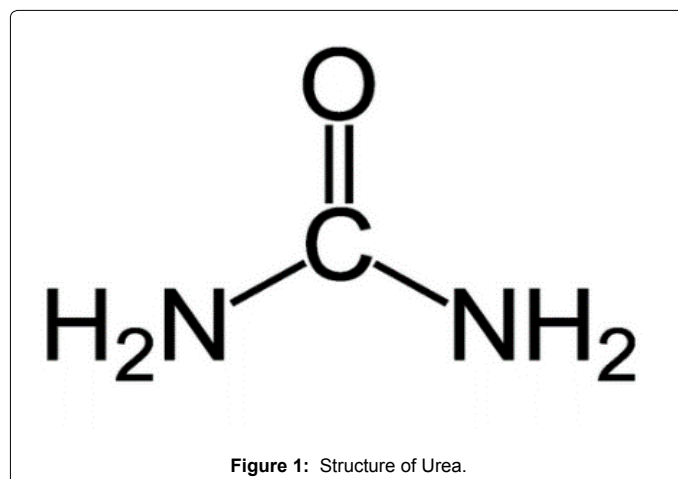
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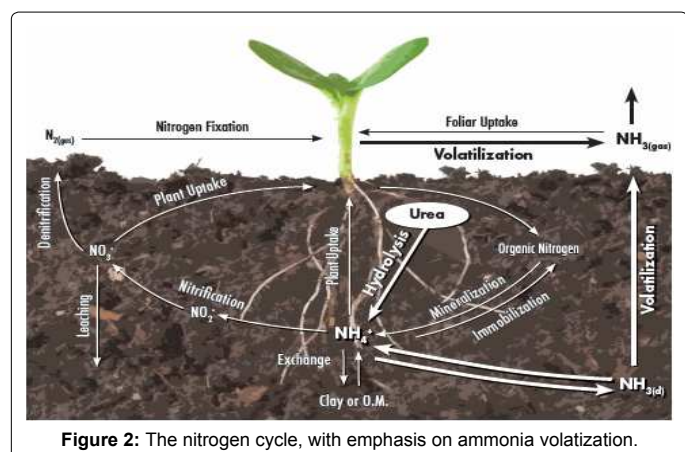
Figure 2: The nitrogen cycle, with emphasis on ammonia volatization.

0.22 um whatman papers and equilibrium concentration determined by UV-Visible Spectrophotometer at 203 nm. Sorption studies on varying shaking times were conducted using 1.00 g of zeolitic material suspended in 10 ml urea solution of concentration 1:100 w/v. The mediums were shaken at room temperature for 15, 30, 45, 60, 75, 90, 100, 120, 140 and 160 minutes each, then centrifuged at 10,000 rpm for 10 minutes. The supernatants were then filtered using 0.22 um whatman papers and equilibrium concentration determined by UV-Visible Spectrophotometer at 203 nm. Quantitative determination of equilibrium amount of loaded urea was done by spiking 1.00 g of zeolitic materials with 10 ml of 1:60 w/v urea solutions. The mediums was shaken at room temperature for varied timings of 3, 10, 20, 24, 40, 48 and 96 hours, and then centrifuged at 10,000 rpm for 10 minutes. The supernatant was then filtered using 0.22 um whatman papers and equilibrium concentration of the remaining urea determined by UV-Visible Spectrophotometer at 203 nm. The difference between initial concentration and equilibrium concentration gave the amount loaded in the samples used in determination of equilibration time. Loading of fertilizer into zeolitic materials was done by spiking 20.00 g of zeolitic material with 35 ml of 1:60 w/v urea solution. The mediums was shaken at room temperature for 24 hours, then centrifuged at 10,000 rpm for 10 minutes. The supernatant was then filtered using 0.22 um Whatman papers and equilibrium concentration of the remaining urea determined by UV-Visible Spectrophotometer at 203 nm. The difference between initial concentration and equilibrium concentration gave the amount loaded in the samples. The resulting urea loaded samples were dried at 100°C for 24 hours. Similar procedures were repeated for soils samples obtained from Kikuyu area, applied as control experiment. Controlled release behavior of fertilizer loaded zeolitic materials in water was done by placing 20.00 g of urea loaded zeolitic materials 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. The filtrates/elutes were collected on a daily basis prior to refilling, filtered using 0.22 um Whatman papers and equilibrium concentration determined by UV-Visible Spectrophotometer at 203 nm. Blank experiment was conducted using 20.00 g of zeolitic material following similar procedures. Controlled release behavior of fertilizer loaded zeolitic materials in soil was done by homogenizing 20.00 g of urea loaded zeolitic materials with 20.00 g of soil samples from Kikuyu, placed 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. The filtrates/elutes were collected on a daily basis prior to refilling,

filtered using 0.22 um Whatman papers and equilibrium concentration determined by UV-Visible Spectrophotometer at 203 nm. Control experiment was done using 20.00 g of urea loaded Kikuyu soil placed in 250 ml separating funnel, followed by similar procedures above.

Results and Discussion
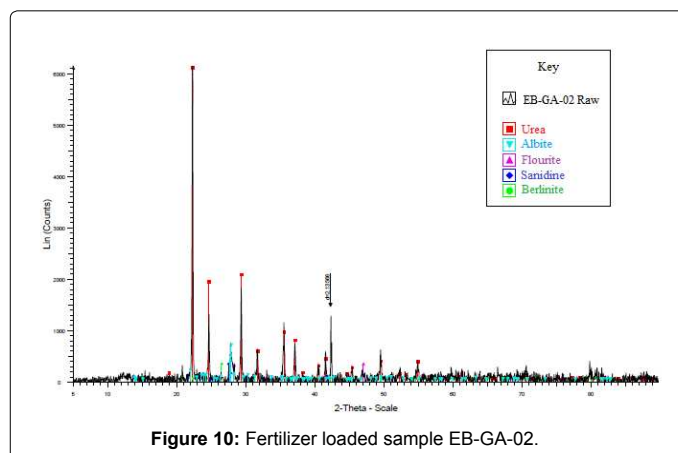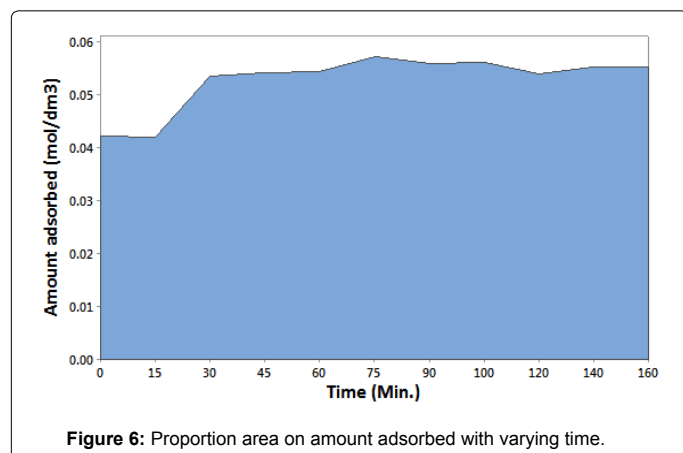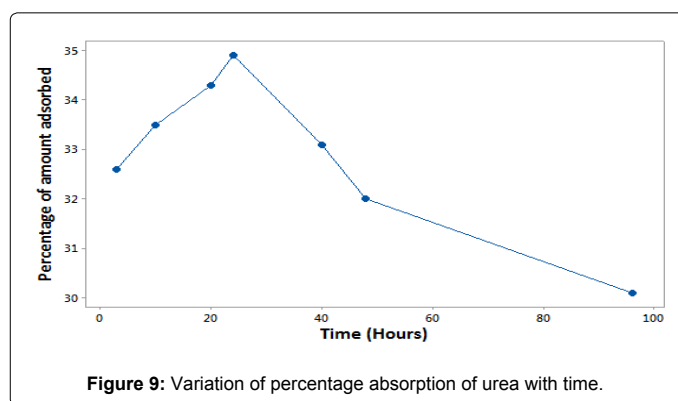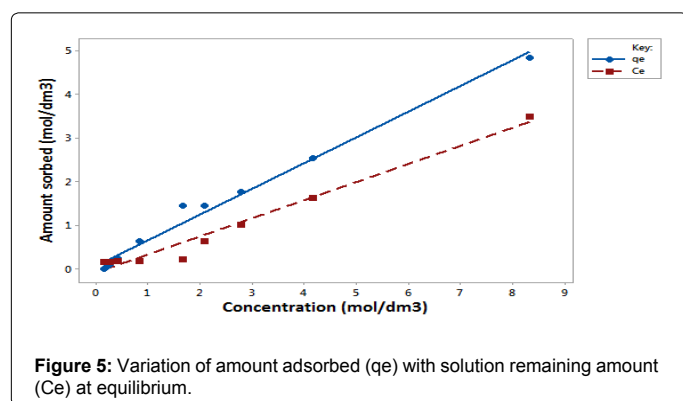
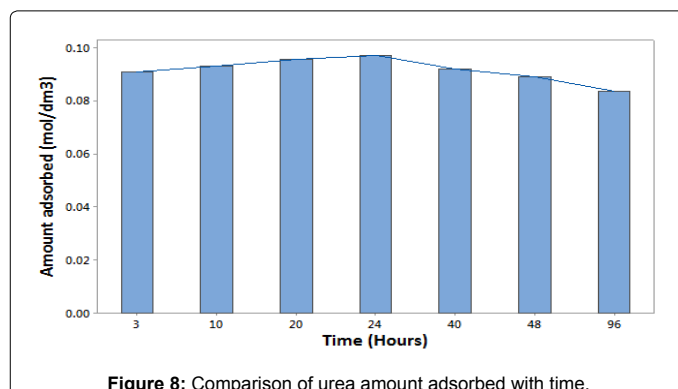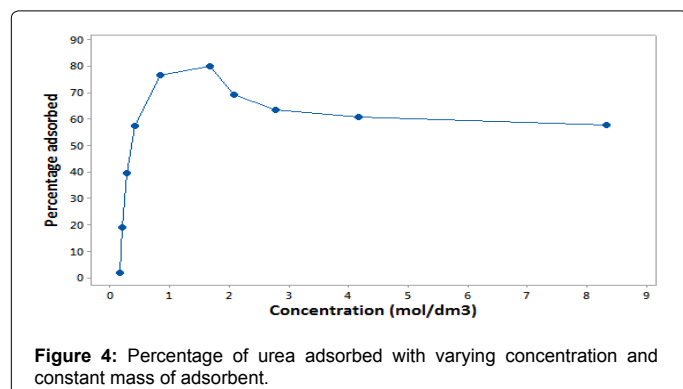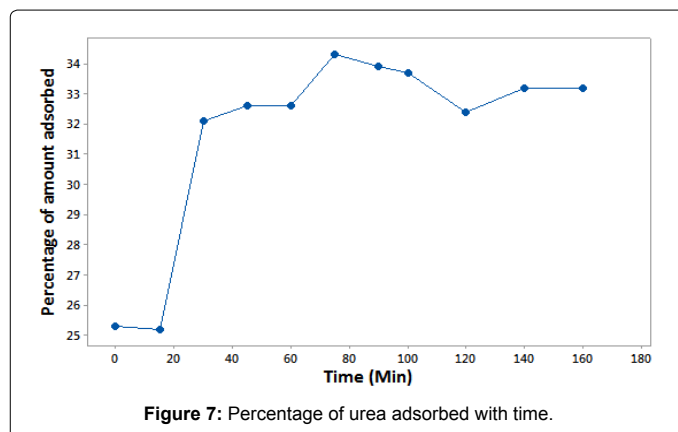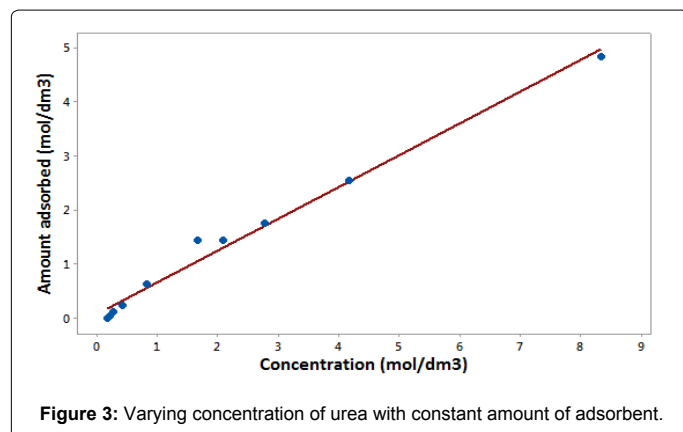### Kinetics of fertilizer adsorption on zeolitic materials

Generally, there is an increase in amount of urea adsorbed as the spiking concentration increases as illustrated by Figure 3. This may be attributed to gradual increase in adsorbate molecules in solution as compared to higher initial adsorption active sites of the adsorbent surface. The highest percentage de-sorbed was determined to be 80.0%, preceded by an initial rapid adsorption from 1.90% and then proceeded by final gradual adsorption to 58.00% as represented by Figure 4. The initial rapid phase could be due to a high initial sorption gradient between adsorbate in solution and the adsorbent surface of sample EB-GA-02, resultant of initial high number of vacant adsorption sites. Equilibrium sorption rate was attained at the recorded highest percentage above, beyond which desorption also started occurring. Significantly, more amount of urea was adsorbed from the solution initially till equilibration, after which more of the urea molecules could be desorbed back in the solution as illustrated by Figure 5. Keeping the spiking concentration constant while increasing the shaking time enhances solute sorbate contact that represents more stable equilibration timing with dismal change in amount adsorbed beyond the 30-60 minutes as represented by Figure 6. Better equilibration was recorded at a slightly higher shaking time, though once the most of the sorption active sites were used up, further increase in contact time between the urea molecules and sample EB-GA-02 had no significant change of rate of adsorption. Determination of the percentage of amount of urea adsorbed with increasing shaking time indicated that adsorption rate tend to equilibrate at approximately 33% for the amount adsorbed, giving near zero gradient at higher shaking time as demonstrated by Figure 7 below.

Quantitative determination of adsorbed fertilizer

Relatively, a higher concentration and longer shaking intervals were used in this study for quantitative determination of adsorbed urea. Higher concentration of sorption solutes exposed to sorption sites for longer durations generated better equilibrations as indicated by Figure 8, of which the highest column represented maximum desorbed amounts shaken at 24 hours duration starting with a solution of concentration 0.278 moldm^{-3} corresponding to 1:60 m/v. Similarly, at maximum equilibration, there is an almost equivalent sorption rate on amount of urea molecules binding the sample EB-GA-2 sorption active site as to those released in the aqueous medium. The positive gradient to the maximum could be attributed to more sorption sites and gradual increase in physicochemical binding, while the subsequent decline could be a factor of reverse process of desorption. Further analysis of variation of percentage of urea adsorption with time as represented by Figures 9 and 10 below gives the highest index at approximately 35% when contact shaking time is done for 24 hours. Hence, this experimental finding gave the optimum parameters for loading urea fertilizer in the nanopores of sample EB-GA-02, as will be was done in the subsequent procedure.

Loading of fertilizer into zeolitic materials

Confirmation of the loaded urea into the samples was determined by characterization of the urea loaded samples using X-ray diffraction spectroscopy and Fourier transform infra-red spectroscopy. X-Ray

Figure 3: Varying concentration of urea with constant amount of adsorbent.

Figure 4: Percentage of urea adsorbed with varying concentration and constant mass of adsorbent.

Figure 5: Variation of amount adsorbed (qe) with solution remaining amount (Ce) at equilibrium.

Figure 6: Proportion area on amount adsorbed with varying time.

Figure 7: Percentage of urea adsorbed with time.

Figure 8: Comparison of urea amount adsorbed with time.

Figure 9: Variation of percentage absorption of urea with time.

Figure 10: Fertilizer loaded sample EB-GA-02.

diffraction analysis (Figure 10) indicated 2θ peaks values of 22, 24.5, 29.5, 32, 35.5, 37, 38.5, 40.5, 41.5, 45.5 and 55 corresponding to urea peaks. Fourier Transform Infrared analysis of urea fertilizer (Figure 11) showed major peaks at 3348.42-3444.87 cm^{-3}, 1624.06-1681.93 cm^{-3} and 1465.90 cm^{-3} corresponding to N-H, C=O and C-N functional groups respectively [8]. On the other hand, the spectrum of Urea loaded sample EB-GA-02 below (Figure 12) contained distinct peaks appearing on the urea spectrum at 3348.42-3444.87 cm^{-3}, 1624.06-1681.93 cm^{-3} and 1465.90 cm^{-3}, corresponding to N-H, C=O and C-N stretching vibrations for the urea fertilizer functional groups respectively, as appeared in the previous. The SEM images obtained for the urea loaded sample EB-GA-02 were as recorded in Figure 13. Comparative studies were also conducted on Kikuyu soil (sample KIKI-GA-01) for urea loading procedures. The urea loaded soil was also analyzed to confirm the presence urea molecules in their matrix as represented below. For the X-Ray diffraction analysis of urea loaded Kikuyu soil, indications of urea fertilizer peaks at 2θ values of 22.5, 24.5, 26.5, 29.5, 35.5, 37.0, 41.5, 45.4 and 49.5 degrees were noted as shown in Figures 14 and 15 below. Furthermore, the corresponding Infra-red analysis (Figure 14) of the urea loaded kikuyu soil showed conspicuous peaks of N-H stretching at 3444.87 cm^{-1}, with tiny shoulders at 3618.46 cm^{-1} and 3699.47 cm^{-1}. The C=O stretching peak appears at 1624.06 cm^{-1}, while the C-N stretching peak shifted to 1458.18 cm^{-1}. The obtained SEM images were also recorded in Figure 16.

Controlled release behavior of fertilizer loaded zeolitic materials in water

The total amount of desorbed fertilizer was determined to be 0.100254919 mol/dm^3. From this study, it was found that a total of 82.8% of loaded urea fertilizer was released in water from the carrier material sample EB-GA-02. The rate of discharge was rapid initially, but gradually declined beyond the fifth day till the end of the monitoring period, with steady sustainable release of the fertilizer as represented by Figure 17.

Controlled release behavior of fertilizer loaded zeolitic materials in soil

The total amount of desorbed fertilizer was determined to be 0.089776702 mol/dm^3, giving a percentage desorption of 74.2% on the initial amount loaded. Graphical representation on the rate of percentage of urea released in Kikuyu soil medium was represented by Figure 18. Comparatively, a higher percentage was determined for the discharge of urea loaded sample EB-GA-02 in aqueous medium as compared to discharge on Kikuyu soil medium. As already discussed, natural rock samples of EB-GA-02 had a lower organic carbon content compared to the Kikuyu soil sample KIK-GA-01, a factor that could contribute to low attraction of urea molecules to the sample matrix. The total amount of desorbed fertilizer from urea loaded sample KIK-GA-01 was 0.071309 moldm^{-3} giving a 58.9% percentage desorption. Previous discussions on this sample KIK-GA-01 which essentially was soil from Kikuyu area indicated a higher organic matter content and proportion of clay. The lower release of loaded urea could then be alluded to stronger binding forces between the urea molecules and the soil matrix, which could be of physicochemical aspect. Graphical representation of the release process indicates lower percentage changes with a relatively much lower desorption percentage rates as represented by Figure 19. Comparative analysis studies on the urea release for the loaded carrier materials was also conducted for urea loaded sample EB-GA-02 in aqueous medium, urea loaded sample EB-GA-02 in Kikuyu soil and urea loaded sample KIK-GA-01 in
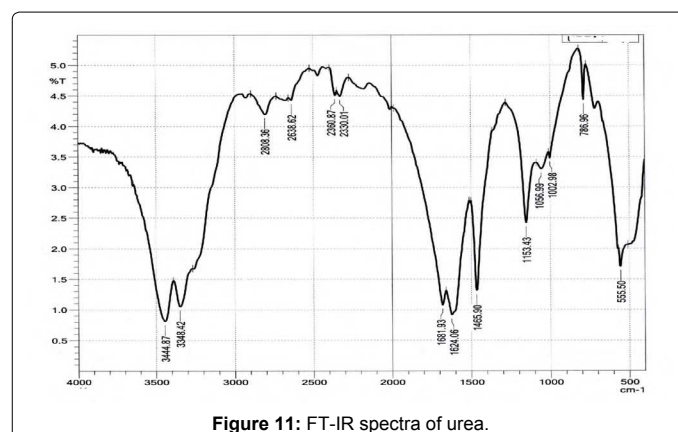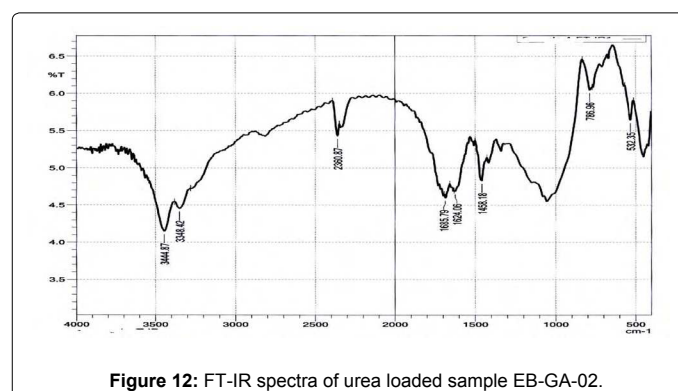

Figure 11: FT-IR spectra of urea.

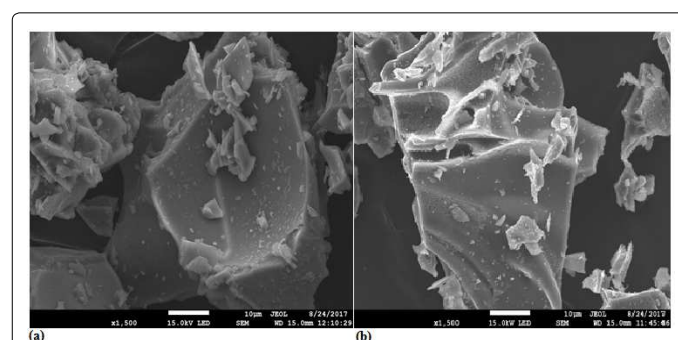**Figure 12:** FT-IR spectra of urea loaded sample EB-GA-02.

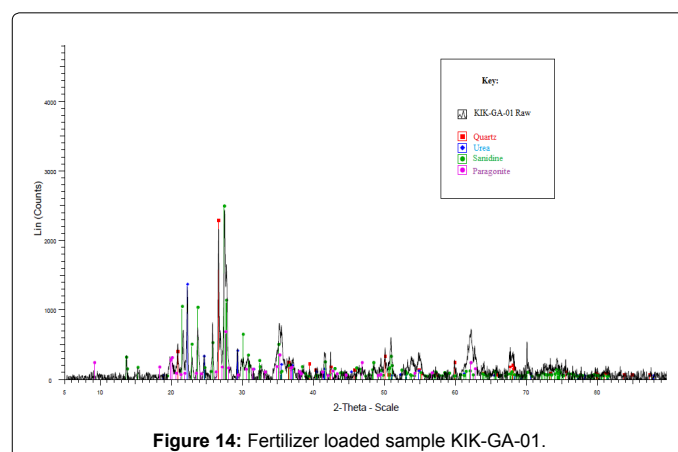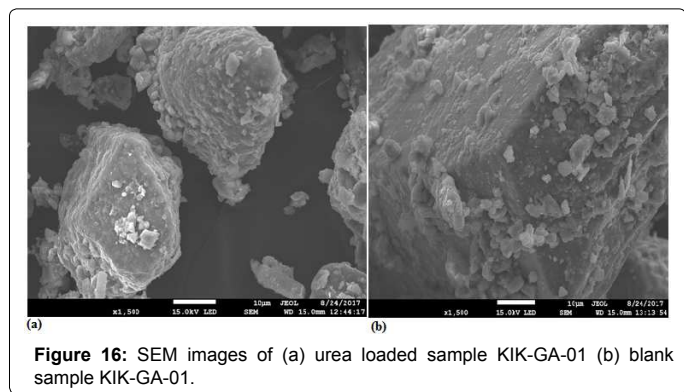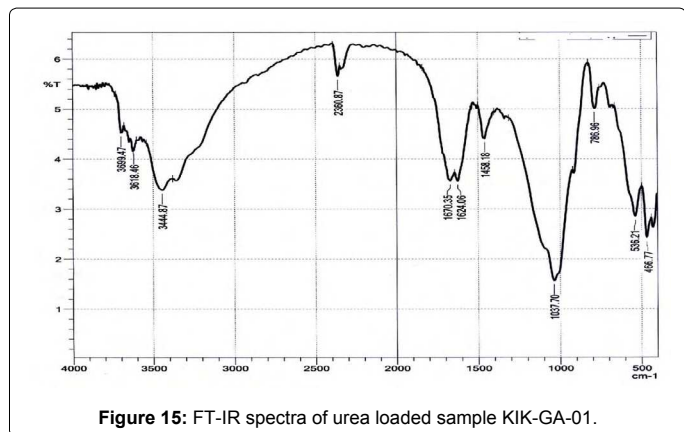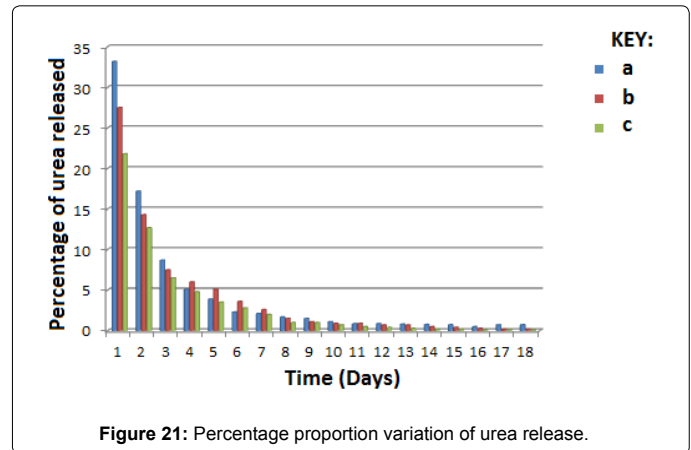**Figure 13:** SEM images of (a) urea loaded sample EB-GA-02 (b) blank sample EB-GA-02.

Figure 14: Fertilizer loaded sample KIK-GA-01.

Figure 15: FT-IR spectra of urea loaded sample KIK-GA-01.

Figure 16: SEM images of (a) urea loaded sample KIK-GA-01 (b) blank sample KIK-GA-01.

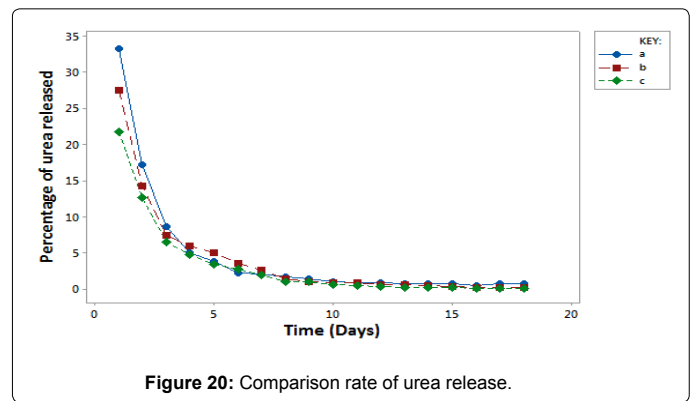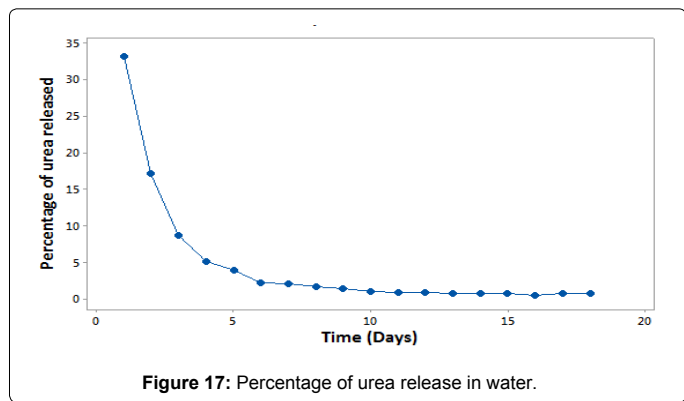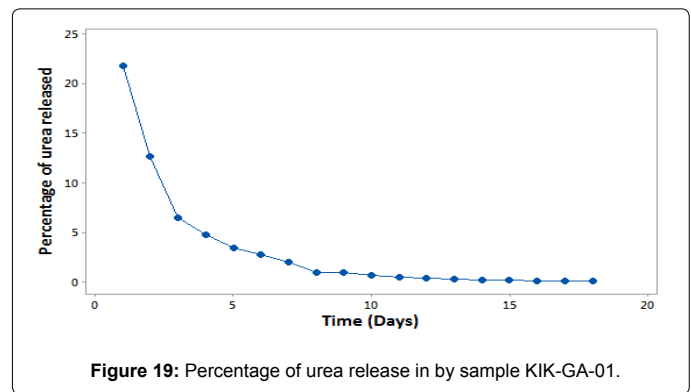**Figure 17:** Percentage of urea release in water.

Figure 18: Percentage of urea release in soil.

aqueous medium represented by 'a', 'b' and 'c' respectively in the 'key' for Figures 20 and 21. Significantly, a higher percentage of urea was discharged in the aqueous medium by the urea loaded sample EB-GA-02 at slower rate on evaluation of the starting point and initial gradient of the three curves in the figure above. Furthermore, this is clearly illustrated by Figure 4. 62 that represents relative heights of the bars in the graph. Evidently, urea loaded sample KIK-GA-01 had the least discharge amount of urea in aqueous medium as shown by both figures. Beyond the 12 days, it can be seen again from Figure 21 below that the curve and bars respectively of discharge of urea loaded sample EB-GA-02 in aqueous medium was higher proportionally than the others. This implies that loading urea fertilizer into sample EB-GA-02 and applying the same as carrier agents had a better sustained release rate, which could still avail the minimum remaining fertilizer to the crops for slightly longer duration than the direct application.

Figure 19: Percentage of urea release in by sample KIK-GA-01.

Figure 20: Comparison rate of urea release.

Figure 21: Percentage proportion variation of urea release.
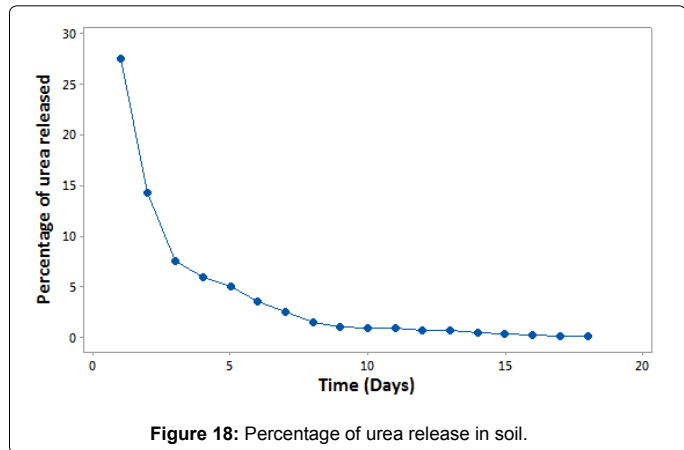
The study shows that Eburru soil samples can effectively adsorb urea fertilizer molecules, a method that can be applied on loading urea into the nanopores of these soil samples. Rate and amount of urea adsorbed was depended on the equilibration time and initial concentrations of the solutions. Desorption studies carried out indicated that most of the adsorbed urea molecules could be released into the water or soil medium. In conclusion, the study found that urea molecules can be loaded and released from Eburru soil materials, an aspect that can be applied as fertilizer carrier agent.

Acknowledgements

References

1. Friedrich W (1828) On the artificial formation of urea. Annals of Physics and Chemistry 88: 253-256.

2. Meessen JH, Petersen H (2000) Urea ullmann's encyclopedia of industrial chemistry.

3. Sakami W, Harrington H (1963) Amino acid metabolism. Annual Review of Biochemistry 32: 355-398.

4. Clain J, Brad DB, Rick E (2013) Factors affecting nitrogen fertilizer volatilization.

5. Waswa GA, Andalab D, Aluochc AO (2017) Kinetics and isothermal studies of lambda cyhalothrin sorption on eburru soil in Kenya. Journal of the Kenya Chemical Society 10: 24-34.

6. Larry GB (2016) Managing urea-containing fertilizers.

7. IRPTC Data Profile (2016) International register of potential toxic chemicals.

8. Stuart B (2004) Infrared Spectroscopy: Fundamentals and Applications.