



Urea mixed zeolite: A new approach for reducing nitrogen loss from soil

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Abstract

Ammonia volatilization from nitrogenous fertilizers, such as urea, presents a significant challenge in agricultural systems. The use of zeolites in agricultural practices offers numerous benefits that could enhance these systems. A field experiment was conducted using a lysimeter to examine the effects of zeolite on reducing nitrogen loss from soil, particularly under clay soil conditions. This research compared the impacts of urea combined with zeolite (UMZ) against varying application rates of urea on the agronomic parameters of wheat and maize, along with the soil's exchangeable NH_4 and available NO_3 levels in an alkaline soil context. Additionally, the presence of heavy metals in the soil was evaluated. The results showed that the morphological traits (such as plant height, crop yield, and grain weight) and physiological features (including chlorophyll content and protein concentrations) of wheat and maize were largely unaffected by the reduction of urea to 50% when supplemented with zeolite. Moreover, the application of zeolite improved the exchangeable ammonia content in the soil while simultaneously lowering the soluble NO_3 levels within the soil solution. The findings suggest that zeolites effectively mitigate nitrogen loss from soil and also aid in retaining heavy metals. Zeolites' high surface area and cation exchange capacity make them efficient in adsorbing caution. The combination of urea and zeolite significantly enhances the growth, productivity, and quality of cereal crops, while minimizing nitrogen loss from the soil.

Keywords: Urea; Zeolite; Ammonia and Nitrate leaching; Heavy metals; Wheat; Maize.

Introduction

The growth of the global population is contributing to a heightened demand for food, which underscores the necessity for a 50% increase in food production by the year 2050 in order to satisfy the requirements of the worldwide populace. This situation becomes particularly pressing given the limited potential for horizontal land expansion (Alexandratos and Bruinsma, 2012; Alexandratos, N.; Bruinsma et al., 2021). As a consequence, there has been an escalation in intensive agricultural methods, leading to an overreliance on chemical inputs, increased water usage, and dependence on heavy machinery. Over time, these methods have resulted in a decline in the productivity of arable land and a reduction in its soil retention capacity.

Nitrogen, a critical element in agriculture, is extensively utilized in various applications. However, its efficiency in nitrogenous fertilizers typically falls below 50%, largely due to losses incurred through processes such as denitrification, leaching, and volatilization (Ming and Mumpton, 1989). Moreover, the improper use of nitrogenous fertilizers contributes to the leaching of nitrate (NO_3) from soil into groundwater, leading to detrimental anthropogenic effects on groundwater quality and posing public health risks, including methemoglobinemia, cancers of the digestive system, eutrophication of aquatic ecosystems, and the generation of greenhouse gases such as nitrous oxide (N_2O) through denitrification (Peña-Haro et al., 2010; Aschebrook-Kilfoy et al., 2013; Hosono et al., 2013; Mondal et al., 2020). Phosphate (PO_4), another vital nutrient present in fertilizers, is also implicated in the eutrophication of water bodies (Delkash et al., 2014). Consequently, the retention of soil nutrients is a significant concern in contemporary agriculture, aimed at optimizing nutrient use efficiency, enhancing soil nutrient status, and preventing groundwater contamination (Bakhshayesh et al., 2014; Nakhli et al., 2014; Leggo 2015). When nutrients are applied in quantities lower than required by crops, yields are adversely

affected, leading to a decline in the long-term productivity of the land. Conversely, excessive nutrient application beyond crop requirements increases the likelihood of agronomic and environmental challenges, including nitrate leaching into groundwater and the emission of greenhouse gases. The principal dilemma in nutrient management within crop production systems is to supply adequate nutrients for optimal plant growth while mitigating environmental risks. Successfully addressing this challenge necessitates that nutrient management planners comprehend the factors governing nutrient availability to crops and their environmental implications, and implement suitable management strategies accordingly. The physical and chemical characteristics of soil play a pivotal role in determining nutrient use efficiency and facilitating plant growth. This study proposes the utilization of zeolite as an amendment for the long-term reclamation of soil physicochemical properties (Mahabadi et al., 2007; Al-Busaidi et al., 2008; Sarkar and Naidu, 2015). Zeolites are naturally occurring, alkaline-hydrated alumina-silicates, encompassing over fifty distinct forms (Vital 2002; Jha and Singh, 2016), with a broad spectrum of applications including as soil-binding agents and nutrient supplements for both terrestrial and aquatic organisms. Furthermore, zeolites serve multiple roles as materials for heat storage and solar refrigeration, as ion-exchanging agents, molecular sieving agents, and catalyzers in diverse chemical reactions (Elliot and Zhang, 2005). Their significance in agriculture has been increasingly recognized due to their varied applications (Elliot and Zhang, 2005). Natural zeolites are regarded as effective soil ameliorants, noted for their superior water and nutrient holding capacities. They enhance infiltration rates, saturated hydraulic conductivity, cation exchange capacities, while also mitigating water losses via deep percolation (Inglezakis et al., 2012; Talebnezhad and Sepaskhah, 2013; Chmielewska 2014; Ebrazzi and Banihabib, 2015; Enamorado-Horrutiner et al., 2016). Additionally, zeolites can be

employed as fertilizers and chelating agents (Perez-Caballero et al., 2008). They significantly reduce the rate of nutrient release from both organic and inorganic fertilizers, thereby promoting enhanced nutrient availability throughout the growth stages of crops (Perez-Caballero et al., 2008). Zeolites also exhibit efficacy in absorbing heavy metals such as cadmium (Cd), lead (Pb), and nickel (Ni), as well as anions like chromate (CrO_4) and arsenate (AsO_4), and organic pollutants such as volatile organic compounds (VOCs), including benzene, toluene, ethylbenzene, and xylene (BTEX) from soil and water environments (Kazemian and Mallah, 2006; 2008; Youssefi and Waring, 2015). This study aims to elucidate the applicability of zeolite in combination with urea concerning soil properties, nutrient retention capacity, crop yield, and the mitigation of heavy metal toxicity.

Materials and methods

Location

The soil used in the experiment was clay soil. Soil samples were taken from EL-Gemmieza Agriculture Research Station, of the Agricultural Research Center (ARC), El Gharbiya Governorate.

Experimental design

Lysimeter experiments were carried out at the EL-Gemmieza Agriculture Research Station, located within the Agricultural Research Center (ARC) in El Gharbiya Governorate, Egypt, during the successive winter growing season of 2019 and summer season of 2020. The purpose of these experiments was to evaluate the effects of a urea-zeolite composite fertilizer on the growth of wheat (*Triticum aestivum* L) and maize (*Zea mays* L), aimed at enhancing effective agricultural production. Furthermore, the study assessed the impact of this fertilizer on soil exchangeable ammonium (NH_4), available nitrates (NO_3), and heavy metal concentrations (cadmium, nickel, and lead). The research utilized nine lysimeters, each measuring two meters in length, one meter in width, and two meters in depth. These lysimeters were subjected to three different treatments: (T1) the

application of urea at the recommended rate (100%) for wheat (179 kg N/ha) and maize (286 kg N/ha); (T2) the use of uncoated urea at a recommended rate (50%) for wheat (89.5 kg N/ha) and maize (143 kg N/ha); and (T3) urea mixed with zeolite at a recommended rate (50%) for wheat (89.5 kg N/ha) and maize (143 kg N/ha).

The study commenced in the winter growing season of 2020, utilizing wheat variety Giza 168 (*Triticum aestivum* L) with a seeding rate of 120 kg/ha, planted on November 20, 2020. A single application of super phosphate (15.5% P_2O_5) was administered at a rate of 230 kg/ha prior to planting, mixed with the surface layer of nitrogen fertilizer (urea), which was applied in three equal portions at the heading stage and again 30 and 60 days after sowing. Potassium fertilizer in the form of potassium sulfate (K_2SO_4) (48% K_2O) was added at a rate of 238 kg/ha, applied at 60 and 90 days post-sowing. The wheat was harvested on May 15, 2021, with grains separated from the straw and weighed individually.

The second growing season involved the planting of maize seeds (*Zea mays* L., SC 168 hybrid) on May 28, 2021, using a seeding rate of 33 kg/ha, followed by thinning at 21 days post-sowing to ensure one healthy plant per hill. Urea was applied in three equal doses after 20, 40, and 60 days of sowing. Potassium sulfate was applied at a rate of 115 kg/ha (48% K_2O) during the second irrigation. At the conclusion of the growing season, maize plants from each plot were harvested on September 22, 2021, when the grains reached maturity, marking a growth period of approximately 120 days. The maize yield was subsequently separated into grains and straw and air-dried. Samples of both wheat and maize grains and straw were then oven-dried at 70°C until a constant weight was achieved for chemical analysis. Additionally, soil samples were collected from each plot following the harvest of both wheat and maize. Surface soil samples (0-30 cm) were air-dried, crushed, and passed through a 2-mm sieve for subsequent analysis of soil chemical and physical properties, as delineated in

Tables (1). A weighted sample of urea (0.70 g) was digested using H_2SO_4 (40 ml) in the presence of 2 g of salicylic acid and 5 g of sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$), in accordance with AOAC methods, as illustrated in Table (2). Soil samples were digested utilizing a combination of H_2SO_4 and HClO_4 , following the methodology outlined by Chapman and Partt (1961).

Experimental design

The subsequent three treatments were implemented under both soil conditions: T1 – urea applied at the recommended rate (100%), T2 – uncoated urea administered at the recommended rate (50%), and T3 – urea combined with zeolite at the recommended rate (50%).

Table1. Analysis of the soil type used in the experiment

| Properties | Unit | Values |
|-----------------|------------|--------|
| Clay | (%) | 50.45 |
| Silt | (%) | 29.18 |
| Fine sand | (%) | 12.32 |
| Coarse sand | (%) | 8.05 |
| Textural class | Clay Soil | |
| pH (1:2.5) | | 7.93 |
| EC | (dS/m) | 1.7 |
| CEC | (cmol /kg) | 65.65 |
| Bulk Density | (g/cm) | 1.24 |
| Total porosity | | 53.21 |
| Organic matter | (%) | 1.15 |
| CaCO_3 | (%) | 2.88 |
| N available | mg/kg soil | 49.05 |
| P available | mg/kg soil | 6.19 |
| K available | mg/kg soil | 286 |

Soil samples were meticulously examined for various chemical characteristics in accordance with the standards set forth by the Land and Development Department (2010). The soil pH was assessed utilizing a

1:2.5 soil-to-water ratio. The total soluble salts, expressed as electrical conductivity (EC), were measured with an electrical conductivity meter at a temperature of 25°C , using a soil paste extract, recorded in dS/m.

Table (2): Chemical composition of urea coated fertilizers samples

| Material | Total N | Cd | Ni | Pb |
|---------------------|---------|-----|--------|------|
| | % | | mg /kg | |
| Urea | 46.4 | 0.5 | 3.9 | 2.7 |
| Urea Coated Zeolite | 46.4 | 0.8 | 3.8 | 13.5 |

The cation exchange capacity (CEC) was evaluated through the application of ammonium acetate. The organic matter (OM) content was quantified employing the

Walkley and Black method. Furthermore, the available concentrations of nitrogen (N), phosphorus (P), and potassium (K) were extracted through KCl (2M), NaHCO_3 (0.5

M), and $\text{CH}_3\text{COONH}_4$ (1M), respectively. The determination of available N, P, and K adhered to the methodology established by AOAC (1995). Additionally, the soil samples were analyzed for nitrate nitrogen ($\text{NO}_3\text{-N}$) and ammonium nitrogen ($\text{NH}_4\text{-N}$) following the harvest of wheat and maize, collected from two soil depth ranges: 0-20 cm and 20-40 cm.

Plant sampling analysis

Plant samples, specifically grain and straw from maize, were subjected to oven drying at 70 °C and subsequently ground. A total of 0.5 g of the oven-dried plant sample underwent digestion utilizing a mixture of H_2SO_4 and HClO_4 to quantify nitrogen, phosphorus, potassium (NPK), and micronutrients, in accordance with the methodology outlined by Cottenie et al. (1982). The total nitrogen content was ascertained employing the micro-Kjeldahl technique, and the crude protein content was calculated using the following equation: $\text{Crude protein} = \text{Nitrogen} \times 6.25$. Total phosphorus was determined via the ascorbic acid method, while total potassium was measured using a flame photometer. The chlorophyll content was assessed following the procedure established by Gavrilenko and Zigalova (2003).

Statistical analysis

Statistical analysis was conducted utilizing the Statistical Analysis Software System for Windows (SAS, 2010). The significant differences between the mean values were evaluated through the application of analysis of variance (ANOVA), while Duncan's multiple range test was performed at a significance level of $p < 0.05$. All samples were analyzed in triplicate.

Results and discussion

Effect of UMZ onto morphological, physiological plant properties and crop yield of Maize and Wheat

A field experiment was undertaken to examine the effects of UMZ and urea application rates on the morphological and physiological characteristics of wheat and maize during the winter season of 2020 and the summer season of 2021. Measurements of

plant height and various crop yield parameters were conducted, and the findings are presented in Table 3. The results indicated that the morphological attributes of the plants were not significantly affected by the reduction of the recommended urea rate to 50% when combined with zeolite, as plant height exhibited non-significant differences in comparison to the recommended 100% urea rate. This observation can be attributed to the properties of zeolite, which has a high affinity for ammonium ions (Ferguson and Pepper, 1987). The substantial capacity of zeolite to retain ammonium ions suggests that these ions are shielded from excessive nitrification by microbial activity, thus minimizing ammonia loss through this pathway. Furthermore, zeolites possess the capability to sequester crystallized urea within their pores (Ahmed et al., 2010). Additionally, the zeolite's high adsorption rate for ammonium ions that are available for plant uptake facilitates enhanced plant growth. Optimal plant growth achieved with UMZ positively influenced crop yield, as various yield parameters for wheat and maize were not significantly different from those observed with the 100% recommended urea application. Notably, maize grain yield exhibited significantly higher values when utilizing UMZ compared to the 100% recommended urea rate. This finding may be elucidated by the zeolite's elevated adsorption capacity, which maintains various nutrients in a readily available form for plant uptake throughout the growth period. The role of potassium (K^+), which is crucial for carbohydrate storage in grains and is highly conducive to adsorption on zeolite surfaces, should not be overlooked. Moreover, the enhancement in plant growth may also be linked to the essential nutrients inherent in zeolite. Ayan et al. (2005) documented improvements in cation exchange capacity, water retention, and plant nutrients following the application of zeolite.

Chlorophyll A, B and percentage of protein were measured to state the influence of UMZ on physiological plant properties (Table 4).

Table 3. Influence of UMZ on morphological plant properties and crop yield of wheat and maize

| Treatment | T1 | T2 | T3 | LSD _{0.05} |
|-------------------------|---------|---------|---------|---------------------|
| Wheat | | | | |
| grain yield (Mg /ha) | 4.35a | 4.25a | 4.73a | Ns |
| straw yield (Mg/ ha) | 6.38a | 6.43a | 6.86a | Ns |
| 1000 weight (gm) | 47.14a | 47.05a | 47.41a | ns |
| plant height | 86.15a | 85.55a | 86.97a | Ns |
| Maize | | | | |
| grain yield (Mg /ha) | 6.07b | 6.14b | 6.77a | 0.34 |
| straw yield (Mg /ha) | 7.62a | 7.50a | 7.91a | ns |
| 100 kernels weight (gm) | 41.24a | 41.18a | 42.12a | ns |
| plant height | 291.67a | 290.47a | 292.33a | Ns |

The findings indicated that chlorophyll A and protein percentages in wheat exhibited negligible variations across the different treatments employed. Conversely, chlorophyll B demonstrated significantly elevated values when treated with UMZ compared to the other treatments. Furthermore, maize displayed a favorable response to the incorporation of zeolite with urea, as UMZ exhibited superior values in various physiological parameters measured (chlorophyll A, B, protein percentages) relative to the alternative treatments. These findings underscore the foundation of morphological parameters and crop yields, affirming that the amalgamation of zeolite with urea enhances nutrient availability

during the growth phase, thereby exerting a positive influence on the morphological and physiological characteristics of the plant. The concentrations of macronutrients (nitrogen, phosphorus, and potassium) in distinct plant parts were assessed post-harvest, with the results presented in Table 5. The data highlighted that the application of UMZ significantly improved the concentration of phosphorus in wheat grains and nitrogen in maize grains compared to the other treatments. In contrast, the concentrations of other nutrients within plant straw and grains were found to be insignificant across the three treatment groups, a phenomenon attributed to the equal distribution of these nutrients among all treatments.

Table 4. Influence of UMZ on physiological plant properties of wheat and maize

| Treatment | T1 | T2 | T3 | LSD _{0.05} |
|----------------|-------|--------|--------|---------------------|
| Wheat | | | | |
| Ch a (mg/g FW) | 2.61a | 2.61a | 2.67a | ns |
| Ch b (mg/g FW) | 1.11b | 1.12b | 1.19a | 0.029 |
| Protein (%) | 9.98a | 10.10a | 10.25a | Ns |
| Maize | | | | |
| Ch a (mg/g FW) | 1.63b | 1.65ab | 1.72a | ns |
| Ch b (mg/g FW) | 0.65b | 0.68ab | 0.80a | 0.11 |
| Protein (%) | 9.71b | 9.60b | 10.08a | 0.29 |

It is well-established that zeolite minerals possess a substantial surface area along with significant exchange capacity, which

facilitates elevated adsorption rates for positive ions, particularly ammonium (NH_4^+).

Table 5. N.P.K content in different plant parts influenced by UMZ

| Treatment | T1 | T2 | T3 | LSD _{0.05} |
|-----------------------|--------|-------|-------|---------------------|
| Wheat grain, % | | | | |
| N | 1.60a | 1.62a | 1.64a | Ns |
| P | 0.20ab | 0.18b | 0.25a | ns |
| K | 0.55a | 0.58a | 0.62a | ns |
| Wheat straw, % | | | | |
| N | 0.48a | 0.46a | 0.51a | ns |
| P | 0.10a | 0.10a | 0.11a | ns |
| K | 1.50a | 1.43a | 1.53a | ns |
| Maize grain, % | | | | |
| N | 1.55b | 1.54b | 1.61a | 0.047 |
| P | 0.28a | 0.27a | 0.31a | ns |
| K | 0.92a | 0.90a | 0.98a | ns |
| Maize straw, % | | | | |
| N | 0.49a | 0.48a | 0.52a | ns |
| P | 0.12a | 0.2a | 0.14a | ns |
| K | 1.43ab | 1.35b | 1.55a | 0.13 |

As a slow-release material, zeolite enables crops to effectively and consistently absorb nutrients throughout their growth phase, thereby maintaining constant osmotic pressure within the plants. The integration of zeolite with urea is a commendable practice for the gradual release of nutrients into the soil, which proves advantageous for plant absorption during the growth period. Notably, no significant values were observed in the straw of wheat or maize, as the nutrients had already been metabolized and stored within the grains.

Effect of UMZ onto available NH_4 and NO_3 in soil

The impact of UMZ on the availability of NH_4 and NO_3 in soil is presented in Figure 1. The findings demonstrated that the exchangeable NH_4 associated with soil particles increased significantly with the application of UMZ, particularly in the deeper soil layer (20-40 cm). These observations

align with the conclusions drawn by Mondal et al. (2021), who determined that the incorporation of zeolite minerals as soil amendments enhances both the physical and chemical properties of the soil, while also mitigating heavy metal toxicity. Furthermore, both natural and surface-modified zeolites exhibit selectivity for key essential nutrients, including ammonium (NH_4^+), phosphate (PO_4^{2-}), nitrate (NO_3^-), potassium (K^+), and sulfate (SO_4^{2-}), within their distinctive porous structures that aid in reducing nutrient leaching. The slow-release capability of zeolites is additionally advantageous for optimizing nutrient availability during crop growth. These distinctive characteristics of zeolites enhance both fertilizer and water use efficiency, thereby minimizing environmental pollution through the reduction of nitrate leaching and the emission of nitrous oxides and ammonia. Zeolitic minerals possess a high cation exchange capacity (CEC), which

contributes to a heightened sorption selectivity for NH_4^+ due to the electrostatic attraction between positively charged NH_4^+ ions and negatively charged sites within the zeolite structure (Aiyuk et al., 2004; Englert and Rubio, 2005). Moreover, the results indicated that plots treated with UMZ displayed lower concentrations of NO_3^- in the soil solution in comparison to those treated exclusively with urea. This outcome was elucidated by the soil application of zeolites in conjunction with chemical fertilizers, which reduces nitrogen leaching (Aghaalikhani et al., 2012; Vilcek et al., 2013; Moar et al., 2015) and volatilization (Haruna

et al., 2008; Nore et al., 2013; Rech et al., 2017), consequently slowing the mineralization process and resulting in a decrease in greenhouse gas (GHG) emissions (Zaman et al., 2012), as well as delaying the release of nutrients into the soil solution (Li et al., 2013; Behzadfar et al., 2017).

In the incubation studies, researchers have unequivocally documented the variability in ammonia loss associated with the application of chemical fertilizers, both alone and in conjunction with zeolite. The application of fertilizers combined with zeolite resulted in lower ammonia losses (Ahmed et al., 2006; Palanivell et al., 2016).

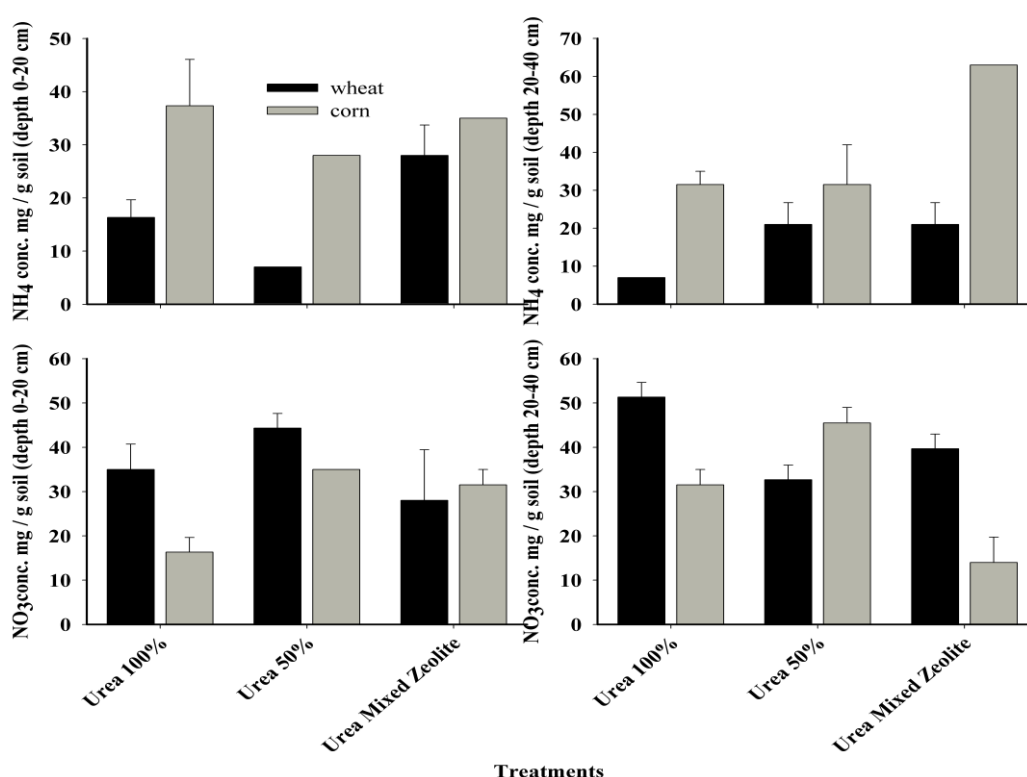


Figure (1). Influence of UMZ onto available NH_4 and NO_3 in soil

Omar et al. (2010) demonstrated a notable enhancement in the retention of exchangeable ammonium in soil treated with zeolite, achieving an improvement of 40–50%. The effectiveness of zeolite is ascribed to the minute pore structure within its crystal lattice, measuring 4–5 Å, which facilitates the adsorption of cations such as ammonium while restricting access to nitrifying microorganisms. Consequently, nitrification

processes are less readily facilitated in soils treated with zeolite (Baerlocher et al., 2007).

Effect of UMZ onto heavy metals concentrations in soil

Available heavy metals (Cd, Ni and Pb) were extracted from soil, measured and illustrated in Figure 2. In general, heavy metals were reduced using UMZ.

The observed results are ascribed to the solubility of heavy metals within the soil, which is influenced by complex chemical

degradation processes and a multitude of contributing factors. Among these factors, the soil's sorption capacity plays a significant role in the immobilization of various metals present in the soil. Shia et al. (2009) reported that the incorporation of zeolite leads to a substantial increase in soil pH, thereby enhancing the adsorption of heavy metals

onto the zeolite's surface; consequently, this results in a reduction of both the solubility and bioavailability of heavy metals. Chen et al. (2000) noted that the application of zeolite to the soil significantly diminishes the accumulation of cadmium and lead in wheat crops.

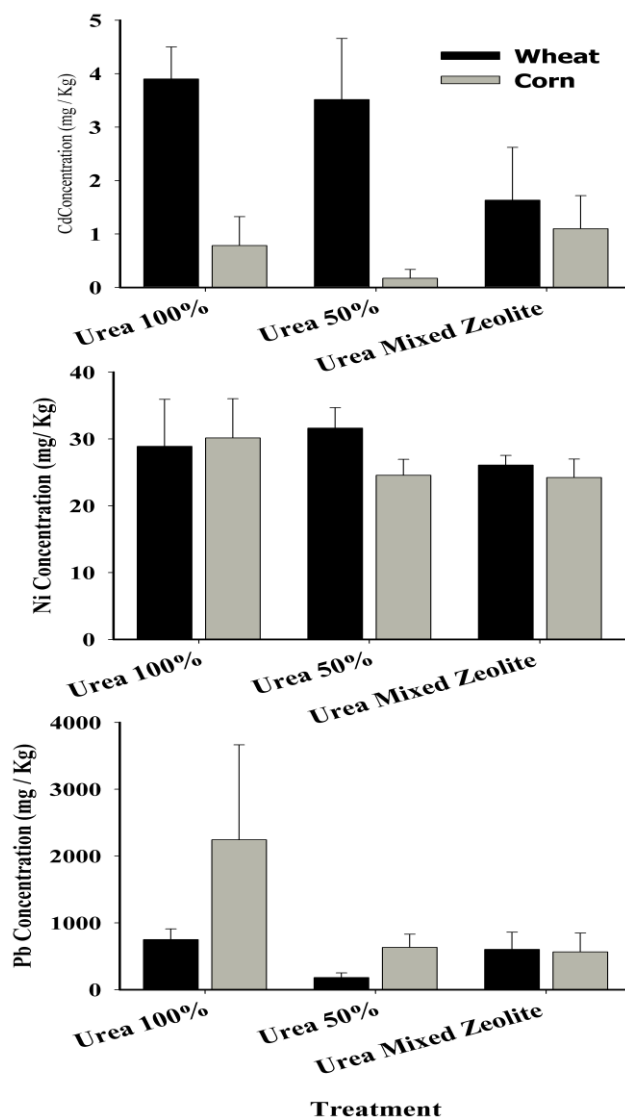


Figure (2). Influence of UMZ onto Heavy metals concentration leached from soil

Furthermore, it has been well documented that clinoptilolite zeolite effectively regulates the solubility of heavy metals, achieving reductions of up to 72% for cadmium and 81% for lead (Chlopecka and Adriano, 1997; Ghuman et al., 1999). The substantial surface area, in conjunction with a high cation exchange capacity, renders zeolite

an effective adsorbent for cations (Ghuman et al., 2011).

Conclusion

According to our research, zeolite's amelioration of the inflammatory-apoptotic axis may be able to reduce nitrogen loss and soil improvement. Our study suggests the potential of zeolite, a bioflavonoid, as a

prophylactic and therapeutic agent for mitigating methomyl-induced testicular dysfunction. These findings represent a promising first step towards developing strategies to maintain fertility in the context of exposure to pesticides like methomyl. Even though zeolite's medicinal uses seem promising, thorough clinical research should be conducted before any future clinical applications are made.

Conflicts of interest

There are no conflicts of interest.

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