Engineered Silica Nanoparticles and silica nanoparticles containing Controlled Release Fertilizer for drought and saline areas.

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Abstract. Silicon supplementation was explored to increase salinity tolerance in plants, in the beginning of this century, therefore silica nanoparticles (SiO₂ Nps) can also be used as a trial to improve salinity tolerance in plants. In this study SiO₂ Nps have been synthesized by some modification in the conventional method of Stober by thermal hydrolysis of Tetraethylorthosilicate. A compound Controlled Release Fertilizer (CRF) was synthesized that carried NPK and SiO₂ Nps inside the core and Chitosan as the first semi-permeable coating and Sodium Alginate and Kaolin as an outer most superabsorbent coating. The synthesized SiO₂ Nps were characterized by TEM and XRD. The water absorbency of CRF beads showed that they can absorb large amounts of water and double their weight. The Nutrient released rate from CRF beads was very slow and sustained for six months at room temperature. The SiO₂ Nps containing superabsorbent CRF was capable of releasing the nutrients slowly, withhold large amounts of water therefore can help plants control salinity and survive better in drought and saline conditions without harming the environment. The synthesized compound fertilizer is biocompatible, biodegradable and nontoxic so ideal for growing plants in drought and salt effected areas.

Keywords: Silica nanoparticles, saline, drought, Sol-Gel, controlled release fertilizer

1. Introduction
Silica nanoporous materials occupy analytical interest due to their extreme use in agriculture, drug delivery, enzyme encapsulation, cell markers, chromatography, chemical sensors and biological images [1]. Due to broad applications of silica nanoparticles in multidiscipline their synthesis by various methods is getting researcher’s utmost attention. Silica nanoparticles can be used in agriculture, as a source of silicon to alleviate salinity stress in plants growing in drought and saline environments. Silica nanoparticles (SiO₂ Nps) have been effectively prepared by both inorganic and organic colloids [2, 3]. SiO₂ Nps can be prepared up to 10 nm by the sol–gel method using TEOS by controlling the conditions in the Stober reaction [4]. The latest ongoing research activities have established and emphasized the capability of ultrasonication techniques for the synthesis of many nanoparticles [5]. Ultrasound-based synthesis of SiO₂ Nps resulted in tiny particles of about 13 nm [6]. Due to advantages of ultrasonication, this study has been carried out by ultrasonication based synthesis of SiO₂ Np by modified Stober process (Sol-Gel). These SiO₂ Nps were further encapsulated in a compound-controlled release fertilizer to be used for improving agriculture in drought and saline areas.

Excessive use of pesticides and chemical fertilizers for increasing agricultural yield has polluted the environment and water resources [7]. Nanoparticles like Zinc Oxide & Zinc stannite has been used for photocatalytic degradation for purification of polluted water [8-10]. The application of CRF is getting popularity over the conventional fertilizer, as the conventional fertilizer releases excessive
residues randomly that persist in the soil and can leach down to the water reservoirs. CRF can release the nutrients slowly, at the required amount and time needed by the plant, and reduces the toxic wastes and remains.

Application of Controlled Release Fertilizers is a highly beneficial technology that encapsulates or coat the conventional fertilizers in the form of granules, of incorporated polymer matrix, which have slow-release properties, allowing controlled flow of nutrients at the time and amounts needed for plant [11]. Chitosan is one of few natural polymer that is the biocompatible, biodegradable, non-toxic towards plant tissue, which offers excellent opportunity to improve controlled release fertilizer behavior and with the combination of kaolin superabsorbent polymer, it can broaden its application especially in drought and marginal areas [12]. Therefore, a compound Controlled Release Fertilizer can be synthesized that can carry NPK fertilizer and SiO\textsubscript{2} Nps inside the core and it can be coated with chitosan as the first semi-permeable coating and Sodium Alginate and Kaolin as an outer most superabsorbent coating. These beads will be capable of releasing the nutrients slowly that can withhold large amounts of water, help plants control salinity and survive better in drought conditions.

2. Materials and Methods
2.1 Synthesis of Silica Nanoparticles
TEOS (1.8 ml) was added slowly to the co-solvent (water & ethanol) and mixed by ultrasonication for 1 hour. Equal amount (1.4 ml) of NH\textsubscript{4}OH and DI water were mixed, separately on stirrer for 30 minutes and added dropwise and carefully to the TEOS solution during sonication by a micro-pipette. The mixture was sonicated for two hours until it turned milky and gel like. It was centrifuged at 4000 rpm for 20 minutes and SiO\textsubscript{2} Nps were collected and dried in the oven.

2.2 Synthesis of Controlled Release Fertilizer
2.2.1. Preparation of CS-NPK-SiO\textsubscript{2} Nps beads for controlled release fertilizer
Chitosan (3 %) solution was used as dope while TPP (5 %) solution as a cross-linker. Dissolved granules of NPK (20 %) and SiO\textsubscript{2} Nps (0.1 g) were added to chitosan solution as dope. Under continuous stirring, slowly the dope was dropwise added with the help of a syringe, into the TPP solution. After cross-linking, the formed CS-SiO\textsubscript{2} Nps -NPK beads were collected & washed with DI water to remove the remaining TPP on the beads surface.

2.2.2. Double coating of CS -NPK-SiO\textsubscript{2} -NPs beads with SA-Kaolin superabsorbent
Superabsorbent polymer coating of Sodium Alginate (SA) was made by its continuous stirring at 65 °C, for two hours. This solution was divided into two parts, one part remained with SA to provide a second absorbent coating on CS-SiO\textsubscript{2} Nps -NPK beads to make SA-CS-SiO\textsubscript{2} Nps -NPK beads that can withhold more water.

Another part contained SA and 5 % kaolin (w/v) to coat beads with Kaolin (K) superabsorbent as the outermost coat (K-SA-CS- SiO\textsubscript{2} Nps -NPK). CS-SiO\textsubscript{2} Nps -NPK beads (a) were then placed inside each treatment for 20 minutes, under continuous stirring. Coated beads were then dried in the oven at 70 °C for 24 hours for further use.

2.3 Methods for characterization of SiO\textsubscript{2} Nps & CRF beads
The particle size of SiO\textsubscript{2} Nps were determined by Transmission Electron Microscope (JEM-2100 plus) with operating voltage of 200 KV to determine the images. X-Ray diffraction spectrum was taken by Bruker, 2\textsuperscript{nd} Gen, D2, Phaser. The X-Ray Diffaraction spectrum of precipitated SiO\textsubscript{2} Nps was recorded with an intensity of 30 KV.

2.4 Water Absorbency of CRF beads
Absorbency of synthesized beads (CRF) was measured by putting small number of dried beads (0.1 g) in 100 ml water for 90 minutes. Beads were filtered and dried for calculating absorbency. Absorbency was calculated by the formula;
\[ W = \frac{M - M^*}{M^*} \] (where \( M \)= weight of wet beads, \( M^* \)= weight of dried beads)

2.5 Nutrient Release Rate of CRF beads

Release of nutrients from different types of coatings (Chitosan, Sodium alginate, Kaolin) was checked by measuring the TDS daily, of different types of beads by placing them (0.1 g) in 100 ml water for six months at room temperature.

3. Results and Discussion

3.1 Synthesis and characterization of silica nanoparticles

Although various methods have been reported for the synthesis of silica nanoparticles including microemulsions, stober and sonochemical [13-15], but the Stober method is the pioneer and the most promising simplest method that has been extensively used and also modified by many researchers. Ultrasound assisted synthesis of silica nanoparticles by modified Sol-gel (Stober method) has been carried out in some recent research [6, 16]. Ultrasonication is recommended to an agglomeration phenomenon that effects the shape of suspended nanoparticles therefore it can be used to control the shape and the size of the nanoparticles. The ultrasonication process is proved to eradicate the primary structure of the silica gel and modifies the size and the shape of the formed clusters with particle re-agglomeration [5]. The particle size of silica nanoparticles synthesized by the conventional method was 200 nm, while the particle size reduced from 100 nm to 50 nm by ultrasonication method. Therefore it can be concluded that increasing the duration or time of ultrasonication has a significant decrease in the particle size of the nanoparticles. There is no particular technique which can characterize the physiochemical properties (size and composition) of nanoparticles [17]. Therefore in this study various techniques like TEM and XRD, have been used to characterize the physiochemical properties like size, morphology and composition of Silica nanoparticles.

Figure 1. TEM image of SiNps of 200nm

Figure 2. TEM images of SiNps of 50nm

TEM images (Figure 1 & 2) illustrated that silica nanoparticles prepared by conventional Stober method were spherical and larger in size about 200 nm (Figure 1), while the silica nanoparticles by ultrasonication method reduced to size of 50 nm (Figure 2). Our synthesized \( \text{SiO}_2 \) Nps looked same like colloidal \( \text{SiO}_2 \) Nps arranged into clustures that could also be a result of drying mechanism in the sample preparation stage [5]. The diffraction patterns of precipitated \( \text{SiO}_2 \) Nps were obtained in \( 2\theta \) range from 10-70°. The characteristic peak of \( \text{SiO}_2 \) Nps prepared is presented as Figure 3. The spectrum appeared as a broad halo peak centered at \( 2\theta \) angle of 22°, that confirm amorphous nature of silica
nanoparticles. These results are similar to the spectrum obtained as a broad band with the equivalent Bragg angle at 2\(\theta = 22^\circ\) [18-20]. The broad diffraction band centered at 2\(\theta\) angle of about 22.5\(^\circ\) is a known typical characteristic of silica [5, 21].

![Figure 3. XRD pattern of SiNps](image)

### 3.2 Water Absorbency & Nutrient Release Rate of CRF beads

Water absorbency is the capability of dried beads to absorb water at room temperature without any cycling and incubation in water bath [22]. It is useful for the determination of water holding capacity of the prepared beads. The absorbency of synthesized CRF beads with different coatings and incorporation of SiO\(_2\) Nps in water was recorded. Water absorbency of chitosan coated beads < sodium alginate < Kaolin-SA which proved that Kaolin-SA polymer has unique superabsorbent properties and its application can be useful in drought, prune and marginal areas with less rainfall or water stress conditions. Sodium alginate is naturally able to absorb 200-300 times its own weight, once it was attached on the beads surface, it improved the swelling and absorbance of beads. Kaolin effected the surface of dried beads by lowering the content of hydrophilic group and decreased the osmotic pressure differences [22]. The synthesized beads (K-SA-CS-SiO\(_2\) Nps -NPK) in the present study are capable of withholding large amounts of water and can double their original weight after absorption of water.

The nutrient release rate (Figure 4 & 5) of dried beads (K-SA-CS-NPK, SA-CS-NPK, CS-NPK), with SiO\(_2\) Nps (red lines) and without SiO\(_2\) Nps (black lines) has been recorded for six months in summer (Average temperature ranged 18\(^\circ\)C - 24\(^\circ\)C) and six months in winter (Average temperature ranged 4\(^\circ\)C - 15\(^\circ\)C). The rate of nutrient released was measured as TDS (Total Dissolved Solids) which was higher in summer, as compared to the winter, certainly due to high temperature. It took about three months (90 days) in summer, to reach peak nutrient released which gradually slowed down and completed in six months. Whereas nutrient released rate reached to maximum after six months (about 180 days) as it was very slow due to low temperature in winter and it decreased gradually when the nutrients released completed. This experiment has also shown release rate of nutrients in different types of coatings. The first coating of Chitosan coated beads (CS-SiO\(_2\) Nps -NPK) released higher amounts of nutrients which decreased by second coating of sodium alginate (SA-CS-SiO\(_2\) Nps -NPK) and become lowest with the application of kaolin coating (K-SA-CS-SiO\(_2\) Nps -NPK). This result has proved the effect of superabsorbent (sodium Alginate + Kaolin) that can slow down the release of nutrient.

The synthesized SiO\(_2\) Nps containing controlled released fertilizer (K-SA-CS-SiO\(_2\) Nps -NPK) is capable of releasing the nutrients slowly and has higher water absorbing capacity. Therefore, the synthesized CRF can be highly useful for drought and marginal areas due to its absorbency and slow release properties. Moreover SiO\(_2\) Nps , can help plants to survive better in the saline environment. SiO\(_2\) Nps priming have been found effective in improving growth of wheat under salt stressed [23].
In conventional fertilizers most of the nutrients are lost in the environment. About 40% to 70% Nitrogen, 50 to 70% Potassium and 80 to 90% Phosphorous get leached and hence lost and becomes unavailable to plants within few days. Whereas this synthesized CRF is capable of releasing N, P, and K for plants from 3 to 6 months that can be very helpful for healthy growth of plants. Secondly in drought and rain-fed areas less water is available for plants. This novel CRF can withhold large amounts of water, prevent leaching of excess water and keep the roots moist and water available for plants survival.

The novelty of this synthesized controlled release fertilizer is its coating by natural, non-toxic materials like Chitosan, Sodium alginate and Kaolin, that are biodegradable and non-toxic therefore the problem of toxic wastes in the soil has been reduced. Moreover, in this study, the combination of sodium alginate and kaolin, the superabsorbent polymer has improved the absorbency & controlled release fertilizers behavior and broaden its application especially for drought and marginal areas. Although conventional polymers like, polyethylene, polyvinyl and polyacrylic acid has been used for CRF synthesis but they remained in the environment for many years and produced toxicological effects on the environment.

The introduction of clays in CRF has improved the polymer performance, due to the ability of clay particles to absorb water or lose water in response to simple-humidity-content changes in the surrounding environment. Most of the clay mineral is hydrophilic, that swells with the absorption of water and greatly increase its volume. Kaolin as a mixture with polystyrene-starch has been used for coating the fertilizer [24]. Our findings are in agreement for using kaolin clay, as the polymer (sodium alginate and kaolin) increased the water withholding capacity by many folds. Together with sodium alginate, kaolin served to inhibit too much water diffuse inside the chitosan matrix, thus maintaining low release rate of nutrients. Besides improving the release rate, the outer layer also functions to protect the CRF from physical damage. Our synthesized CRF used chitosan, sodium alginate and kaolin all of which are completely degradable which makes this CRF novel, biocompatible and environment friendly along with its excellent controlled release properties.

4. Conclusion
The results of this study indicated that ultrasonication is very helpful tool in reducing particle size in the synthesis of SiO\textsubscript{2} Nps. SiO\textsubscript{2} Nps can be incorporated in a controlled release fertilizer for growing plants in drought and saline areas. SiO\textsubscript{2} Nps and NPK were coated by Chitosan as inner layer and
superabsorbent Sodium alginate & Kaolin polymer as outer coating. This CRF was capable of withholding large amounts of water and releasing the nutrients very slowly that is very useful for plants grown in drought and saline areas. The novel CRF is biocompatible, biodegradable and non-toxic especially aimed to prevent negative effect on the environment as compared to the conventional fertilizer that releases nutrients abruptly, that remain in the soil and probably leach down to the water reservoirs.

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